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D. Stolten and B. Emonts (Editors)

Technical Session:
Fuel Cell Systems
of the World Renewable Energy Congress VII

Proceedings

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HYDROGEN, FUEL CELLS, AND INFRASTRUCTURE TECHNOLOGIES

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The U.S. Department of Energy (DOE) is supporting the development of hydrogen and fuel cell technologies that will enhance power production and energy supply in the future. DOE's transportation fuel cell R&D is focused on fuels and fuel processing, stack subsystems, and system issues, while hydrogen R&D is targeting cost-effective hydrogen production, storage, and utilization. The United States' National Energy Policy and DOE's FreedomCAR program are discussed specifically with regards to fuel cells and hydrogen. Also presented are DOE's preliminary findings for Congress concerning the need for public and private cooperative partnerships to demonstrate the use of fuel cells in commercial scale applications in order to accelerate marketability.

1 National Energy Policy

In May 2001, the Bush Administration released the National Energy Policy for the United States, which proposes new technology investments in appropriate renewable energy and alternative energy research and development. This Policy gives special attention to fuel cells and hydrogen in several areas. For example, it calls for development of the next generation hydrogen technology for a variety of applications, including hydrogen-fueled fuel cell vehicles. The Policy also calls for the integration of current programs regarding hydrogen, fuel cells, and distributed energy. In response to the recommendations of the National Energy Policy, DOE has recently combined into one program its efforts in fuel cells for transportation and buildings, and hydrogen technologies. The DOE Office of Hydrogen, Fuel Cells, and Infrastructure Technologies will incorporate all R&D for low-temperature fuel cells, specifically polymer electrolyte membrane (PEM) fuel cell technology, as well as hydrogen production, storage, and utilization R&D. Integration of these programs will leverage the synergies that exist between the various fuel cell applications. DOE maintains another fuel cell program, under the Office of Fossil Energy, which focuses on high-temperature fuel cells (specifically solid oxide and molten carbonate) for large stationary applications and grid-connected distributed generation.

2 Freedom CAR

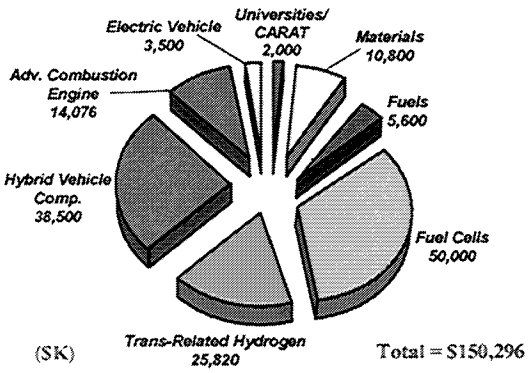

Figure 1. FreedomCAR FY03 budget

In January 2002, the U.S. Department of Energy unveiled its vision of the future of personal mobility. A new cooperative automotive research initiative, known as FreedomCAR (Cooperative Automotive Research) has the long-term strategic goal of developing technologies for hydrogen-powered fuel cell vehicles requiring no dependence on foreign oil and emitting no harmful pollutants or greenhouse gases. The revolutionary goal of the FreedomCAR program is to achieve this technology shift, which has obvious and dramatic benefits to society, without sacrificing mobility or freedom of choice for American consumers. In addition, FreedomCAR will continue to provide support to other conventional automotive technologies designed to reduce oil consumption and environmental impacts, and will target technologies that are applicable across a wide range of passenger vehicles. In recognition of the importance of FreedomCAR, fuel cells and hydrogen R&D were carefully considered during preparation of DOE's fiscal year (FY) 2003 budget request (Figure 1). This budget contains $76 million to develop transportation related fuel cells and supporting hydrogen technologies.

3 U.S. Department of Energy's Fuel Cell R&D Activities

Under FreedomCAR, the Department of Energy is leading an ambitious, cost-shared, government-industry R&D program to develop automotive fuel cell power system technologies. Fuel cell technology is being targeted for transportation applications because of its potential for high efficiency, near-zero emissions, and fuel flexibility. Fuel cells are likely to be the long-term replacement for internal combustion engines in automobiles and other transportation systems, but many important technical issues, including cost, remain to be solved before fuel cells can become a viable alternative. DOE is supporting a broad range of R&D projects for PEM fuel cell technology focusing on materials, components, and enabling technologies to improve performance and lower costs.

3.1 Transportation Fuels and Fuel processing

DOE is pursuing a dual pathway approach to evaluating and developing fuels for fuel cell vehicles (Figure 2). The focus of the near-term R&D pathway is the evaluation of gasoline, in particular EPA Tier 2 gasoline, as a suitable fuel for fuel cell power systems. Other fuels, including reformulated diesel, methanol, ethanol, and natural gas-derived fuels such

as Fischer-Tropsch liquids, will also be evaluated as neat fuels for the fuel-flexible fuel processor. The long-term R&D pathway is focused on developing and demonstrating the technologies needed for using hydrogen directly as a fuel, i.e., hydrogen refueling of vehicles. Initially, the focus will be on generating hydrogen from fuels such as natural gas. This work will parallel efforts to develop technologies for producing hydrogen from renewable sources.

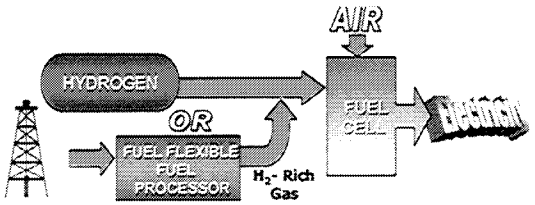

Figure 2. DOE's dual pathway approach to fuels for PEM fuel cells

In recent years, DOE has increased its emphasis on fuel processing, recognizing that fuel flexibility and compatibility with the existing fuel infrastructure are key requirements. Historically, the development of fuel processing technologies has lagged behind fuel cell stack development. This is especially true for PEM fuel cells because of the difficulties involved in purifying the reformate gas (sulfur in the fuel and carbon monoxide resulting from fuel processing are major contributors to failures). In terms of transient response and start-up capabilities, fuel processing technologies have not yet achieved performance levels acceptable for automobiles mainly as a result of the large thermal mass and high operating temperatures of these systems. Start-up times are currently between 10 and 20 minutes, which results in a major fuel efficiency penalty. DOE is exploring the use of more active and durable catalysts for the water-gas shift reactor to reduce size and to eliminate one stage of the shift reactor or preferential oxidizer. The program is also developing microchannel fuel processing technology to achieve dramatic size reduction (1/10 conventional systems) and improve start-up. DOE has established a major go/no-go decision point for FY 2004, where fuel flexible fuel processing must demonstrate start-up in less than 60 seconds or DOE-sponsored fuel processor R&D will be terminated.

3.2 Transportation Fuel Cell Stack Subsystems

The primary challenge in the area of stack subsystems is to reduce the estimated cost of their components, and subsequently of integrated PEM fuel cell power systems, from today's greater than $300/kW (at high production volumes) to the program target of $45/kW (Figure 3). Membrane electrode assemblies (MEAs), the core of the fuel cell stack, require very high quality and production yields to achieve automotive cost and performance targets. DOE is working with industry to develop low-platinum MEAs in parallel with high-volume manufacturing

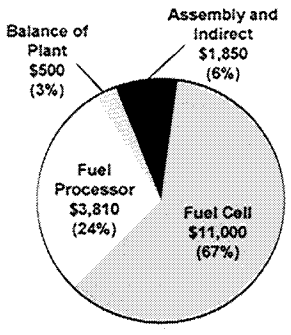

Figure 3. Estimated costs for year 2001 50kW$_e$ PEM fuel cell power system

processes to meet cost targets. The program is also developing low-cost compression-molded, carbon composite bipolar separator plates and design concepts for mass production.

With regard to performance, the power density of today's PEM fuel cell systems is too low when the stack is operating at high voltages. However, operation at high voltage is necessary to achieve high system efficiency. The cathode is the limiting component, and DOE is exploring new cathode catalysts and optimized electrode structures to improve performance. Another major technology breakthrough being pursued is the development of novel, lower cost membrane materials that operate at temperatures of up to 150° C. Not only would operation at higher temperatures help mitigate the challenge of rejecting heat from the fuel cell stack, but it would also increase the system's tolerance to carbon monoxide, possibly eliminating the need for the preferential oxidizer as part of the fuel processing system.

3.3 Transportation System Issues

For several years DOE has placed emphasis on developing tools that simulate fuel cell systems. Models of PEM fuel cell systems and components help identify key design parameters and operating efficiencies to simulate start-up and dynamic performance, and provide information to support fuel cell developers. Models and analyses are used to better understand the trade-offs between ambient and pressurized fuel cell systems, as well as to identify critical cost barriers and assess the impact and progress of technology advances on overall system costs. DOE is also continuing to work with industrial suppliers to overcome the technical and cost barriers facing the unique air management requirements for PEM fuel cells.

3.4 Distributed Generation

Fuel cell research for stand-alone distributed generation applications is targeting higher temperature PEM fuel cell technologies primarily powered by natural gas. This effort includes cooling, heating, and power (CHP) principles for recoverable heat and is focus-ing on natural gas reforming technology, critical components, and codes and standards.

4 U.S. Department of Energy's Hydrogen R&D Activities

In the area of hydrogen research, DOE is focusing its efforts on enabling cost-effective hydrogen production, storage, and utilization for utility, buildings, and transportation applications (Figure 4). DOE efforts are aimed at reducing the cost of producing hydrogen, which currently runs about $3.50 per gasoline gallon equivalent, down to a cost of $1.25 per gasoline gallon equivalent with a well-to-pump efficiency of 70 percent. Advanced reformer technologies with higher efficiency are being developed and designed for ease of manufacture and reduced capital costs. The program is also performing long-term R&D on

electrolytic, photoelectrochemical, and photobiological processes in order to produce hydrogen from renewable sunlight and water. Improved electrolyzers (including those operating at high temperature) are being developed with a cost goal of about $300/kW.

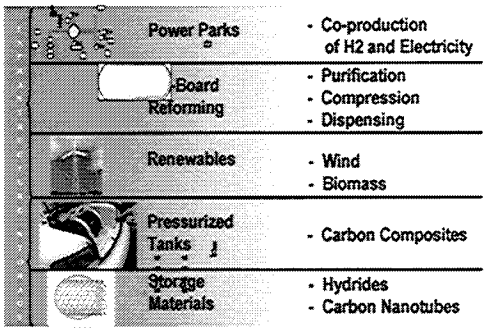

Figure 4. DOE's hydrogen R&D activities

In Las Vegas, Nevada and in Palm Desert, California, facilities are being developed for the commercial demonstration of hydrogen as a safe and clean alternative for vehicle refueling. These efforts involve the development and demonstration of small-scale, on-site hydrogen production technologies, and the design and installation of hydrogen and hydrogen/compressed natural gas (CNG) blend refueling facilities.

Hydrogen storage research projects are focused on physical (tank) storage for the near term, metal hydrides for the medium term, and carbon structures for the long term. Composite tank research is focusing on denser (up to 10,000 psi), and lighter-weight hydrogen storage for vehicles. Prototype high pressure tanks have demonstrated up to 11-weight percent storage with the goal being to achieve greater than 6-weight percent hydrogen for the entire storage system. More efficient composite utilization and advances in thin liners impermeable to hydrogen, as well as process and material research to establish the feasibility of blow-molded liners, are expected to result in lower costs for hydrogen storage. Significant progress has been achieved in recent years; however, hydrogen tank storage is subject to volume and energy density limitations.

Metal hydride research and development is focusing on several areas including sodium aluminum hydride ($NaAlH_4$) and other alanates. Titanium catalyzed sodium aluminum hydrides can store 4-5 percent hydrogen at ambient pressure and 125°C. However, desorption at less than 100°C is still slow and the material cost is high. Research into carbon structures is focusing on carbon nanotubes. Carbon single-wall nanotubes (SWNTs) have the capability to store reversibly 6-7 weight percent hydrogen safely at ambient pressure. Here, efforts are focusing on the production of nanotubes with optimized physical, kinetic, and thermodynamic properties and on introducing hydrogen-bonding dopants to facilitate adsorption and desorption of hydrogen.

5 Partnerships for Success

The United States Congress has asked the Department of Energy to report on the technical and economic barriers to the use of fuel cells in transportation, portable power, stationary, and distributed generation applications. This full report is due in November 2002 and is to include recommendations on program adjustments based on an assessment of the technical,

economic, and infrastructure requirements needed for the commercial use of fuel cells by the year 2012 in stationary and transportation applications. DOE is also to provide an interim assessment that describes preliminary findings about the need for public and private cooperative programs to demonstrate the use of fuel cells in commercial scale applications. After extensive consultation with stakeholders, DOE is recommending three government-industry partnerships to address the diversity of fuel cell markets and technologies.

5.1 Stationary and Distributed Generation Partnerships

These include early, high-value markets where customers are likely to pay for premium benefits that fuel cell systems can provide, such as emergency back-up power, consumer electronics, and remote off-grid applications. The need for public involvement is limited, but continued public support for R&D is required to develop technology and regulations for fuel supply and fuel storage, including codes and standards.

5.2 Transportation Partnerships

Without a significant public role, the widespread use of fuel-cell powered vehicles may not occur for a long time. Conventional, internal combustion engine vehicles are readily available and refueling is convenient and inexpensive. However, the volume associated with the transportation sector will help establish a strong fuel cell component supplier base and significantly drive down costs. Supplier R&D, being sponsored by DOE, is leading to improvements in materials performance and in high volume manufacturing processes, which is reducing technology costs in areas such as membranes and electrodes. Figure 5 illustrates the timeline for DOE's proposed fuel cell demonstration program for vehicles.

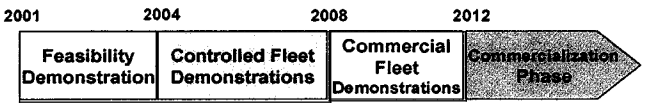

Figure 5. Potential fuel cell demonstration program for vehicles

5.3 *Infrastructure Partnerships*

Transitioning the current fuel supply infrastructure to the production and delivery of hydrogen will be a major undertaking. The public role in transitioning to a hydrogen economy requires leadership in resolving regulatory and standard-setting issues. Important anti-trust concerns of the energy industry must also be addressed as new infrastructure is developed in a collaborative manner.Each of the three partnerships envisioned is to consist of a strong R&D program coupled with a demonstration program carried out over several phases leading to initial commercialization by the private sector. The technology R&D component within each of the partnerships comprises the activities necessary to advance the technology to a lower cost through improvements in performance, materials, and manufacturing. The demonstration component provides the means to validate the results of the R&D program in terms of performance, reliability, etc. It also provides the opportunity

to practice codes and standards, evaluate fuel infrastructure technologies, and gauge acceptance by public and local officials. Demonstrations will also define the requirements for remaining technology development. The envisioned relationship between the phased R&D and demonstration program within each partnership is shown generically in Figure 6. This figure illustrates the use of independent reviews between each phase of the partnerships with the provision to terminate the program at various stages.

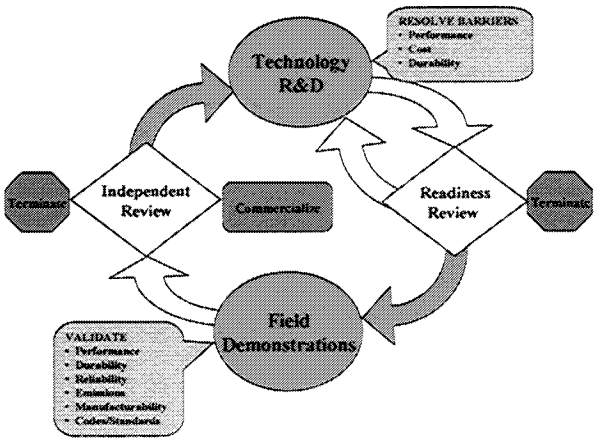

Figure 6. Partnership demonstration and R&D cycle

Indian Strategy for Fuel Cell Development

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ABSTRACT

Due to environmentally cleaner and more efficient technology, fuel cells are considered to be a future option for domestic, industrial, transport and agriculture sectors and also for power supply in remote areas. Fuel cell program in India has included technology development for the components as well as various types and sizes of fuel cells in various power ranges.

The program is essentially government sponsored involving R&D institutions and the industry. A Public Ltd. Company, Bharat Heavy Electrical Ltd has developed Phosphoric acid fuel cell (PAFC) stacks of 5 kW, 10 kW and 25 kW. The R&D division of this company has also developed 50 kW PAFC power plant. A Canadian PAFC fuel cell of 200 kW has been tested for an automobile in the Indian conditions using propane rich liquefied petroleum gas as the fuel. Work is also in progress on Molten Carbon fuel Cells (MCFC), Polymer electrolyte membrane fuel cell (PEMFC), Solid Oxide Fuel Cells (SOFC) in different power ranges.

1. Introduction

Considering the fact that fuel cell technology can provide power in a cleaner way by utilizing a conventional or a non-conventional fuel, the Government of India has aimed to developed fuel cell technology with the potential user listed in Table 1 [1]:

The fuel cell program in India has included technology development as well as demonstration, largely supported by Government – the Ministry of Non-conventional Energy Sources, Department of Science and Technology, Ministry of Coal and few other divisions.

2. Types of fuel cells

The development of fuel cells is more than 150 years old. The classification of fuel cells can be done on the basis of configurations, fuel and oxidant, direct or indirect fuelling, type of electrolyte and temperature of operation. Various parameters of classification are given in Table 2. Temperature – electrolyte relationship is given in Table 3.

Table 1 Power Range and Potential User of Fuel Cells in India

Size	Potential Users
1.5 MW	• Luxury hotels • Hospitals/Banks • Information technology • Chlor-alkali industry • Petro-chemical industry • Dairies • Off shore oil rigs
0.2 MW – 1 MW	• Small Commercial Complexes • Restaurants • Residential buildings
1 – 25 kW	• Decentralized power packs • Military applications • Remote and disaster site applications

Table 2: Parameters for classification of fuel cells

Direct	Indirect	Oxidant	Temperature °C	Electrolyte
Hydrogen	Hydride	Oxygen	Low < 260	Aqueous Acid
Hydrazine	Ammonia	Air	High (600 – 700)	Sulphuric Acid
Ammonia	Hydrocarbon	Hydrogen peroxide	High (> 750°C)	Phosphoric acid
Hydrocarbon	Methanol			Sodium; or Potassium Hydro oxide
Methanol	Ethanol			- do -
Coal	Coal			Solid oxide, Molten carbonate, Solid polymer electrolyte

Table 3: Temperature range, Electrolyte and type of fuel cell

Low temperature (<260°C)	Alkaline fuel cell (65°C – 160°C) Solid Polymer Electrolyte Fuel cell (<120°C) Phosphoric acid fuel cell (175°C – 200°C
High temperature (600 – 700°C)	Molten carbonate fuel cell
Very high temperature (>750°C)	Solid oxide fuel cell

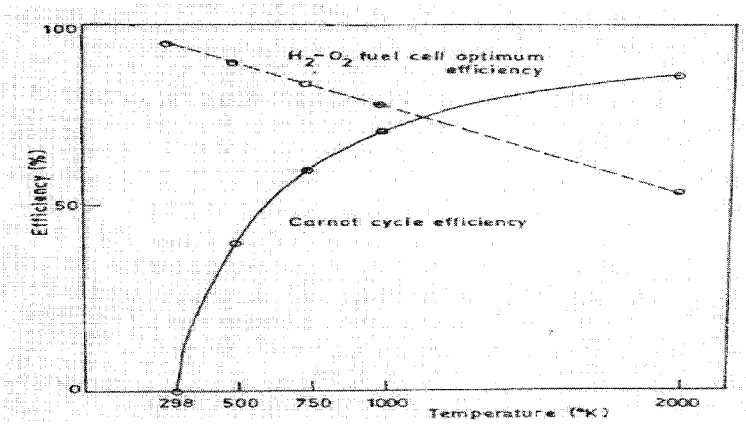

Fig 1: Cell voltage as a function of the operating temperature for various types of fuel cells.

Fig.1 gives the achieved cell voltage, a measure of efficiency, as a function of cell operating temperature. Even though, phosphoric acid fuel cell has the lowest efficiency, it is technologically most advanced. It is considered to be the first generation fuel cell but it has proven cell life, tolerance to impurities in the fuel and oxidant and it is low cost. Molten carbonate fuel cell is considered to be the next generation fuel cell, while solid oxide fuel cells are in the development stage. Alkaline and solid polymer electrolyte fuel cells are being developed for vehicular applications.

3. Global Overview of the technology

A number of leading industries, namely, Ballard Power Systems, Plug Power, Fuel Cell Energy, International Fuel Cells Corporation (IFC), Energy Partners, H-Power, Honeywell, Northwest Power Systems, Toyota, Siemens and others have been targeting fuel cell markets for transportation stationary and portable applications.

OEMFC fuel cells are being used for decentralized as well as for decentralized power generation. Ballard is the leading manufacturer of PEMFC Power Systems. This company has signed an agreement for the supply of 30 public buses in 10 cities in Europe. Daimler – Chrysler (D-C) and Ford Motor Company committed $ 750 million for research in PEMFC. Plug Power and North West Power Systems are developing PEMFC Systems in 5-50 kW and 7-10 kW for home applications. A 50 kW system is being developed for the DOE. IFC has demonstrated an unpressurized fuel cell for automobile engine.

PAFC units of 200 kW are commercially offered by IFC. About 200 PAFC Systems had been put up for demonstration and field-testing in Japan, Germany, Italy, and USA etc. Based on methane, a fuel cell system runs at the wastewater treatment plant in Oregon. PAFC developers are targeting cogeneration market where the heat produced by fuel cell power plants can be utilized.
Developers of MCFCs in USA target commercial fuel cell sizes of 250 kW to 3 MW for power generation and cogeneration applications. Some of the manufacturers of MCFC's are Fuel Cell Energy, Hitachi Ltd. Mitsubishi and some other companies. During these developments, however, one needs to address the following issues:

- High power density of 0.18 - 0.22 Watts/cm^2
- Increasing cell life up to 40,000 hours
- Electrolyte management
- Corrosion problems
- System integration
- Reliability and Durability of MCFC stacks
- Cost reduction

Siemens Westinghouse, Ze-Tek, Honeywell, Global Thermoelectric and Ceramic Fuel Cells Ltd are working on SOFCs. Siemens had developed tubular SOFC units of 1 kW, 25 kW, 100 kW and 250 kW. It plans to commercialize SOFC plants of 1-5 MW shortly. Siemens AG and Shell Hydrogen jointly plan to develop fuel cell commercial power systems of 250 kW to 10 MW capacities. Ceramic Fuel Cells Limited of Australia has tested a 1 kW SOFC stack on liquefied propane gas. Honeywell is targeting portable power packs of 500 kW SOFCs.
The niche applications of different type of fuel cells are summarized in the Table 4.

Table 4: Type of fuel cells and niche applications

Fuel Cell Type	Applications
PEMFC	Commercial, domestic, back up power systems, automotive
PAFC	Commercial power generation, Co-generation
DMFC	Portable stationary and automotive application
MCFC/SOFC	Distributed power, centralized power, industrial cogeneration.

4. Indian Program

The fuel cell program in India has included technology development as well as demonstration, largely supported by Government – the Ministry of Nonconventional Energy Sources (MNES), Ministry of Coal and recently by Council of Scientific and Industrial Research (CSIR).

The various projects taken up by the Ministry lay emphasis on the development and application of suitable materials, catalysts, processes, components and systems. Phosphoric acid fuel cell (PAFC) stacks of 5 kW, 10 kW and 25 kW have been developed and tested. The application of PAFC fuel cells for demonstrated in laboratory conditions. A 50 kW PAFC power plant, based on hydrogen, has been developed by a government owned company (BHEL) . After initial performance tests, the plant will be commissioned at a chemical industry for performance monitoring in actual working conditions. A commercial module of 200 kW size of PAFC was also tested under Indian conditions for an automobile. The demonstration of commercial model used propone rich liquefied petroleum gas as the fuel.

Under a program for the development of MCFC, indigenous procedures have been developed for making electrodes, matrix and electrolyte tapes of size 512 cm^2 . A MCFC was tested on pure hydrogen. The stack delivered an out put of 250 W against the rated output of 350 W.

A scientific foundation has developed components and stacks of proton exchange membrane fuel cell (PEMFC). The cell sizes upto 450 cm^2 have been developed yielding 300 mA/cm^2 of current density at operating voltage of 0.65 V. Several stacks of 5 kW size have been developed and tested under different climatic conditions including the including the harsh Antarctica region. Using compressed hydrogen in metal cylinders, two 5 kW size fuel cells have also been used in an electric vehicle. Hydrogen on board the vehicle is stored as compressed gas in metal cylinders.

The work on solid oxide fuel cells (SOFC) HAS BEEN GOING ON AT central Glass and ceramic Research Institute (CGCRI), Kolkata for past several years and achievements include development of fabrication process for electrodes and matrix. Kilowatt range fuel cell stack is being developed presently.

The Indian Institute of Science, Bangalore has been working component development for SOFC and direct methanol fuel cell (DMFC). In direct methanol fuel cells, a proton conducting polymeric membrane is used and methanol is reformed with in the cell.

Under a UNDP/GEF project, a 'Fuel cell Bus" project is being executed through the R&D unit of Bharat Heavy Electrical Ltd., a public limited company. A fuel cell vehicle has been in operation with two PEMEC stacks in combination within a 120 volt battery bank. The electricity drawn from a fuel cell battery bank hybrid system

drives a 13 kW series wound DC traction motor. The vehicle is in operation for demonstration, awareness creation and for evaluation of its performance.

5. Government Policy

The government policy on fuel cell development so far has been towards R&D and demonstration projects. The efforts on commercialization are hazy, though plans are underway to define the policies and fiscal incentives that can lead to large scale investments in fuel cells from private sectors and corporate giants.

As a result of various workshops a consortium of institutions has been created to develop various technologies. Organizations involved in fuel cell development are given in Table 5.

Table 5: Organizations involved in fuel cell related activities

Organization	Fuel Cell Type
Bharat Heavy Electrical Limited (BHEL), Hyderabad	Phosphoric acid fuel cell
Spic Science Foundation (SSF), Chennai	Polymer electrotype membrane fuel cell
Central Glass and Ceramic Research Institute (CGRI), Calcutta	Solid oxide fuel cell
Indian Institute of Science Ban galore	Solid oxide fuel cell

6. Industrial base

The industrial base in the country is yet to break the ground. Though several companies including battery and generator manufactures have shown interest in setting up manufacturing basis in India by way of technology transfer from leading manufacturers in USA and Europe, the industrial base is still a distant dream. The steps to address the major concerns of the prospective manufactures include lack of government policy on incentives for setting up industrial base, regulations on facilitating market development for fuel cells and demonstration of fuel cell technology.

7. Conclusions

Fuel cell development in India is taken up as an R&D and demonstration program involving research institutions and R&D division of an industry. The government, for developing efficient and cost effective fuel cell systems, components like reformers/processors, electrodes, bipolar plates, membranes, power electronics etc, is supporting research. Though there are niche applications for fuel cells in India but

the cost and identification of fuel or lack of adequate hydrogen production technology are the basic barriers for fuel cell development for commercial purposes.

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National Strategies

INNOVATIVE FUELS FOR FUEL CELLS TO PROVIDE ELECTRICTIY; HEAT AND MOBILITY RESP. TRANSPORTATION

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The present demand of electricity, heat and liquid fuels for driving power of vehicles is mainly satisfied by converting fossil fuels into the secondary energy carriers requested, this linked to the threat of climate change. The future demand of electricity, heat and liquid fuels for driving power of vehicles - most likely appreciably higher than at present - has to be satisfied ensuring stainability of environment and of development. Towards this goal innovative technologies like fuel cells fed by proper innovative fuels like - among others - hydrogen, synthetic hydrocarbons and bio-hydrocarbons, these provided in sufficient amounts, with proper quality and at tolerable costs are major challenges.

1 Introduction

The present annual demand of electricity, heat and liquid fuels for driving power of vehicles is mainly satisfied by converting about 310 EJ of fossil fuels, coal, oil and natural gas into the secondary energy carriers requested, see fig. 1. This amount of fossil fuels adds up to nearly 80 percent of the total demand on primary energy of about 400 EJ at present.

On the one hand the future demand on all secondary energy carriers as well as on primary energy will be most likely appreciably higher than at present, this mainly due to the expected economic development of many of the developing countries, see fig. 2.

On the other hand the consumption of fossil fuels in total should be reduced to less than 50 percent of the consumption at present, this for keeping climate changes within tolerable dimensions[1,2].

Such an aggravating change of the use and consumption of energy could be realised by increasing the proper use of renewable and nuclear energy together with proper innovative technologies[3] to provide all secondary energies requested, see fig. 3.

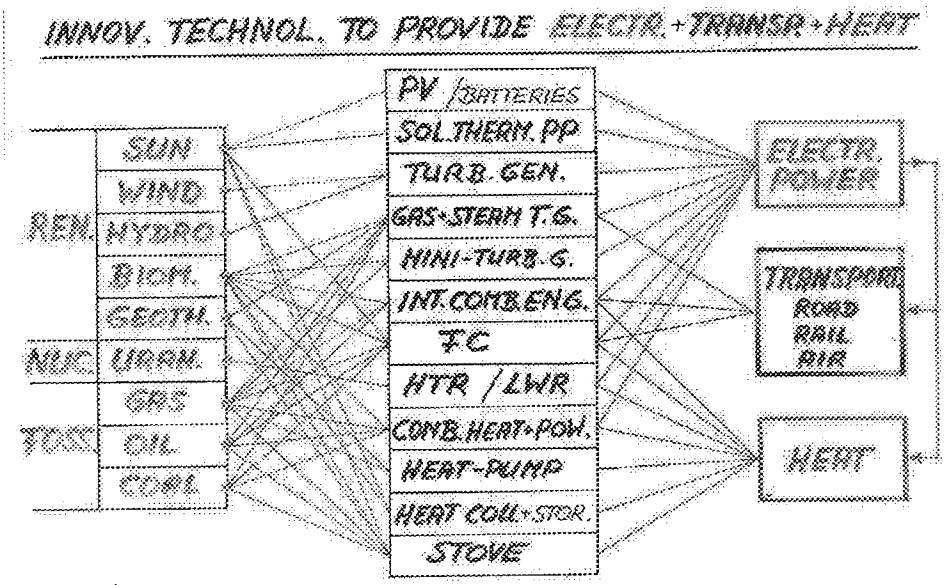

Figure 3: Innovative technologies for transforming primary energy into secondary energy.

Fuel cells are certainly one of the innovative technologies, in strong competition with other technologies already highly developed and will be established on the market.

Fuel cells may gain advantages by making proper use of innovative fuels provided from sustainable sources of primary energy, see fig. 4.

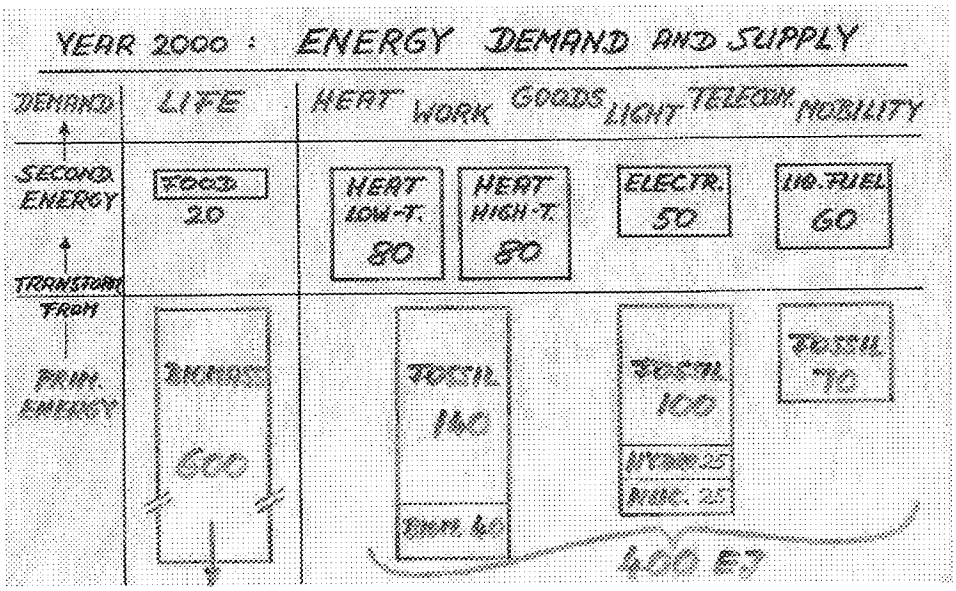

Figure 1: Demand and supply of energy at present.

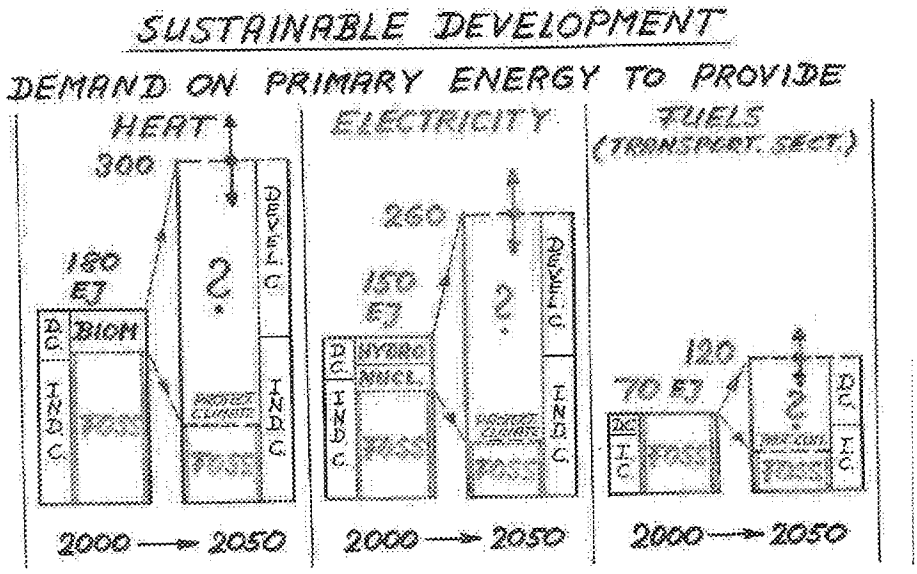

Figure 2: Development of demand of energy till 2050

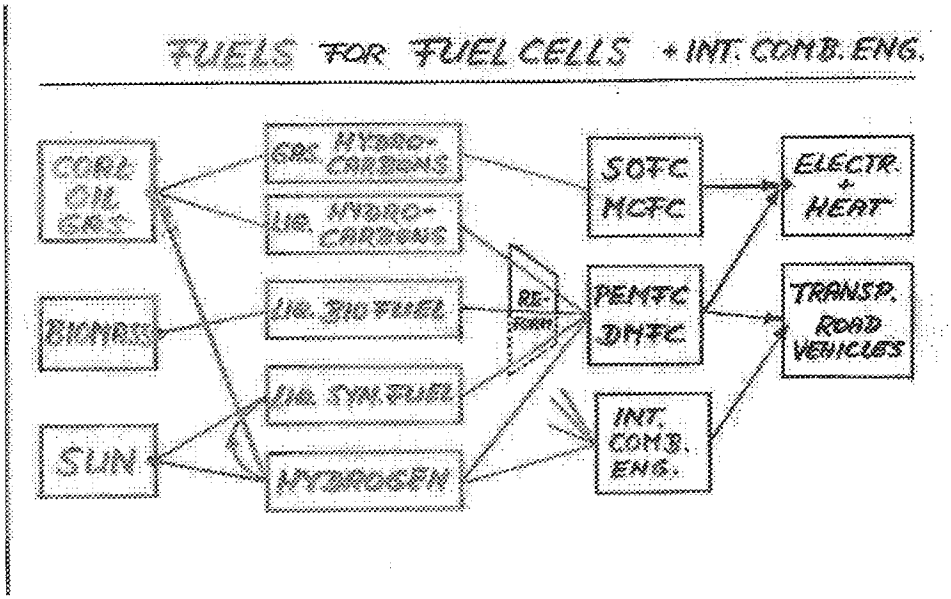

Figure 4: Fuels for fuel cells

2 Innovative Fuels

2.1 Bio-Methanol (see fig. 5)

Bio-fuels like e. g. methanol can be readily produced from biomass of any kind. An annual provision of an amount of methanol of e. g. 60 EJ (equal to the total worldwide demand of liquid fuels for driving power of vehicles at present) would call for harvesting biomass from 450 million ha agricultural land, an area the size of 1/3 of all agricultural land worldwide at present. So how can we provide sufficient food for a still rising world population as well as large amounts of bio-fuels, both from biomass? This can be achieved only if further loss of agricultural land due to unsustainable agricultural practices is avoided and if additional agricultural land for energy crops is provided by recultivation of proper large areas of land. The resulting costs for producing methanol from biomass partially arising from the costs of recultivation have to be expected to be about 2 to 4 US $ per gallon gasoline equivalent. Such an amount of costs for gasoline from crude oil would arise at costs of 50 to 100 US$ per barrel of crude oil.

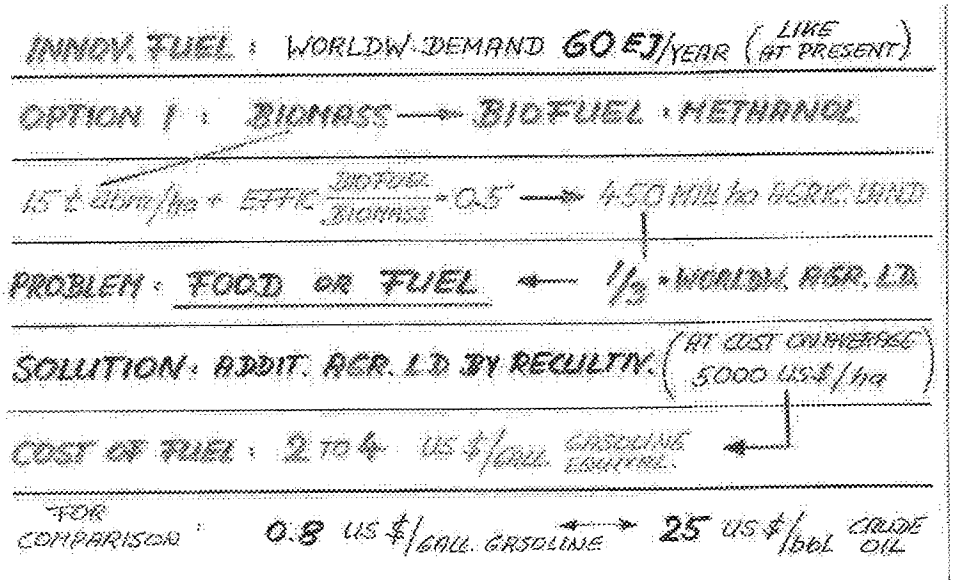

Figure 5: Innovative fuels: methanol from biomass

2.2 Hydrogen (see fig. 6)

The only comparatively cheap way to produce hydrogen is from catalytic steam reforming of natural gas. The provision with an amount of hydrogen of 60 EJ (equal to the total worldwide demand of liquid fuels for driving power of vehicles at present would more than double the present consumption of natural gas worldwide. The resulting costs for producing hydrogen from electrolysis of water - a technology well developed - is closely linked to the corresponding costs of electricity: about 4 US$ per gallon of gasoline equivalent at costs of a few cents per kWh from conventional power plants, about 10 US$ per gallon of gasoline equivalent at costs of about 10 cents per kWh from future „low cost" photovoltaic plants. Furthermore the provision of 60 EJ of hydrogen would require 120 EJ of electric energy, about twice as much as the present worldwide consumption of electric energy. For all other options to provide hydrogen, investigated a present, like solar-thermal or photochemical or photo-biological water splitting, the resulting production costs can be roughly estimated to be at least about 10 US$ per gallon of gasoline equivalent. The final costs of hydrogen are further enhanced due to the required rather expensive infrastructure for storage, transportation and distribution of hydrogen.

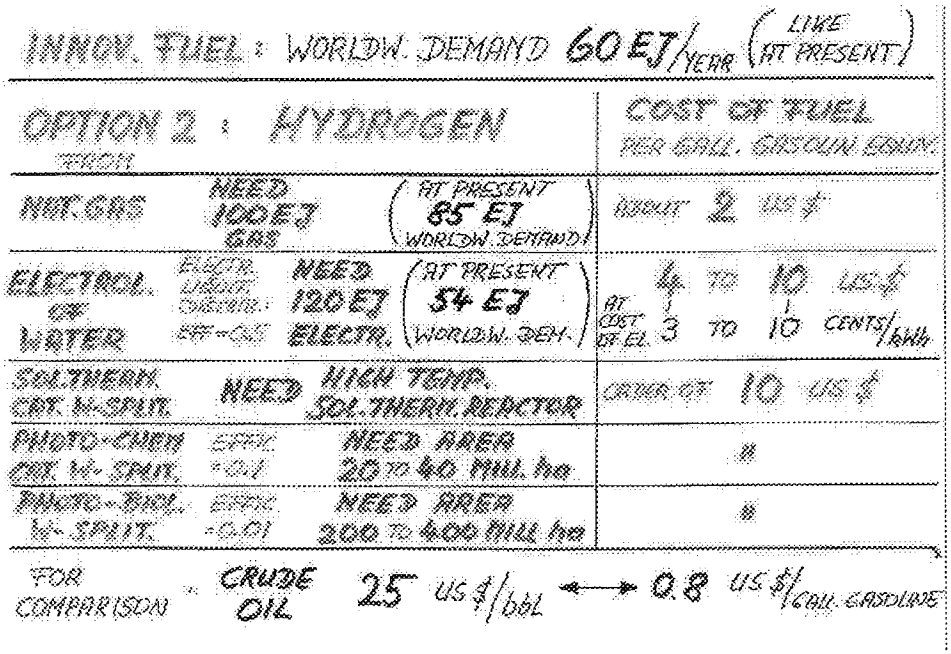

Figure 6: Innovative fuels: hydrogen

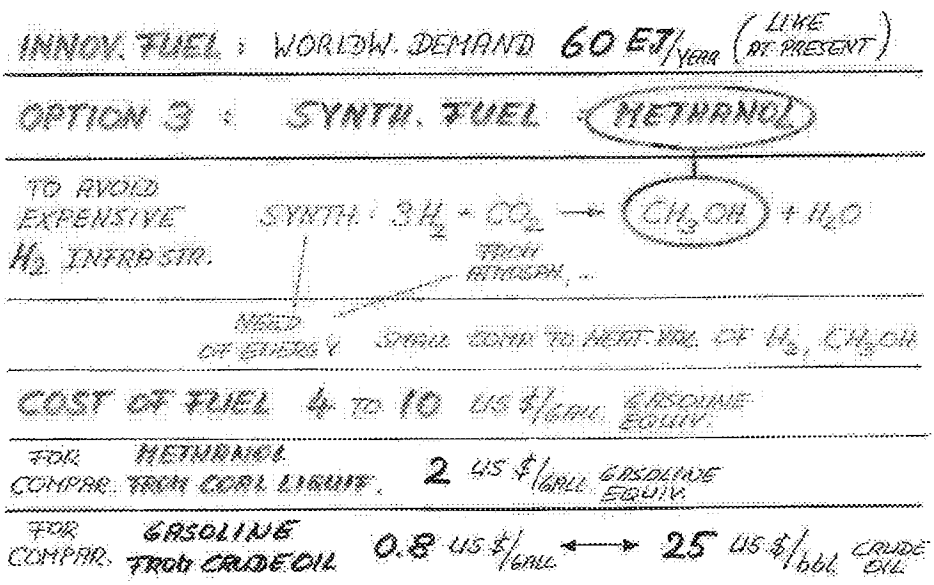

Figure 7: Synthetic fuel: methanol from hydrogen

2.3 Synthetic fuel: Methanol (see fig. 7)

In order to avoid an expensive infrastructure for handling hydrogen it could be synthesised with CO_2 (either from combustion plants or from the atmosphere) to methanol. The energy required for this syntheses of methanol including the provision of CO_2 is small compared to the heating values of both hydrogen and methanol. Thus the resulting costs for the synthesis should not increase the costs of methanol appreciably above the costs of the production of hydrogen.

3 Comparison of the different options of innovative fuels (see fig. 8)

Comparing the production costs of methanol from biomass, of hydrogen in different ways and of methanol from synthesis of hydrogen and CO_2 the option methanol from biomass is clearly favoured. This option could be realised within some decades. And bio-methanol could compete on the world market with fuels derived from crude oil if the costs of crude oil would reach a level of about 50 to 100 US$ (either by future shortage of crude oil or by political decisions to increase the price of fossil fuels to fight further global warming).

Hydrogen is certainly the ideal fuel for fuel cells operating at low to medium temperatures. Unluckily all options for hydrogen production (excluding hydrogen from natural gas) with technologies already existing or to be at least envisaged at present can be estimated to lead to production costs prohibitively high. A further barrier is caused by the necessity of an expensive infrastructure for handling hydrogen as a fuel by large.

The latter barrier could be avoided for methanol from synthesis of hydrogen and CO_2.

At this stage I want to express my sincere hope that some new revolutionary ideas together with proper further research and development of technologies will finally lead both to produce as well as to handle hydrogen in a much less expensive way as can be foreseen at present.

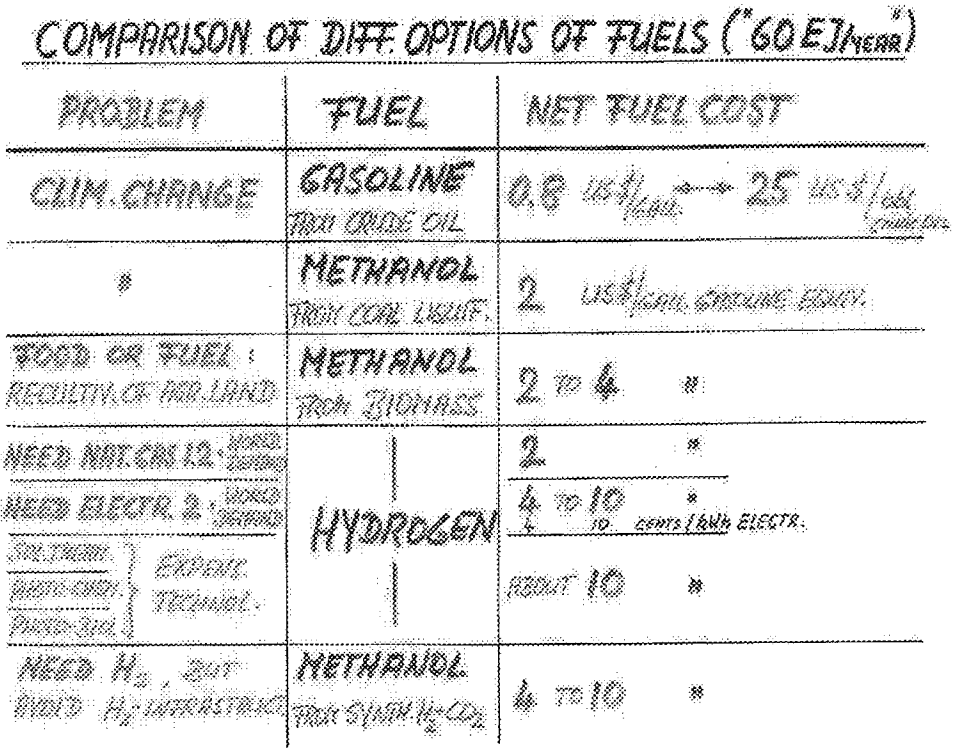

Figure 8: Comparison of different options of innovative fuels

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[2] Ministerial Declaration of the 2nd Conference of Parties of the Framework Convention of Climate Change, Geneva,1996

[3] K. Heinloth (Ed.), Energy Technologies, Landolt-Börnstein VIII, 3A (Fossil), 3B (Nuclear: Fission and Fusion), 3C (Renewable), Springer Publ. Co., Berlin 2002/2003

Report on DaimlerChrysler Fuel Cell and Energy Strategy

Dr. Ing. Gerhard Isenberg, DaimlerChrysler AG
Research Center Ulm

VISION

Ecologically friendly driving without emissions, with clean and renewable fuels like hydrogen or methanol, with cars and buses, and at the same time as affordable, comfortable, fast and secure as usual – all this could be realized with fuel cell drive concepts.
Fuel cells (FC) are considered to be the most promising alternative to conventional internal combustion engines (ICE) offering the greatest developing potential in terms of emission and consumption reduction.

STATUS

At present, almost all automotive companies worldwide are engaged in developing, testing and preparing the market introduction of FC powered cars and buses.

At the beginning of the 90ies DC started to develop FC drive concepts and presented Necar I in 1994.
Necar I was powered by a hydrogen-fuelled PEM-FC.

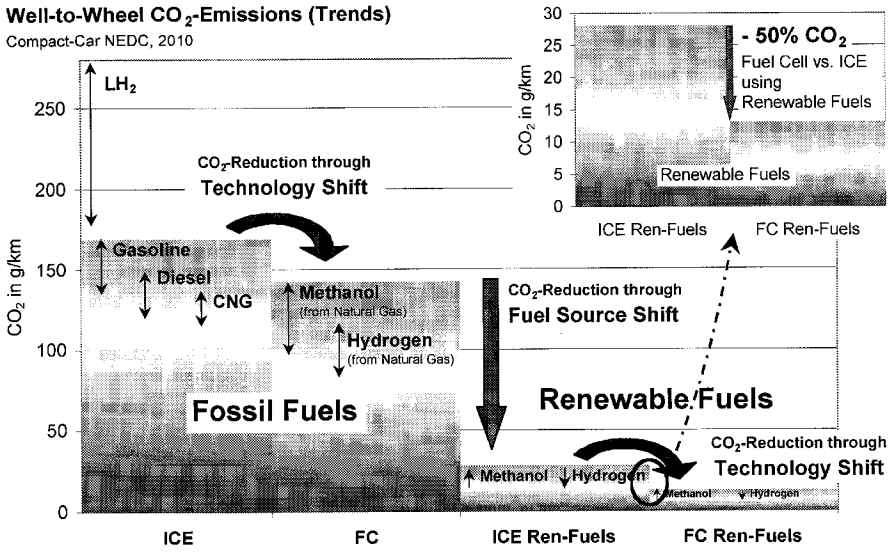
The driving forces of this development are:
- Increasing fuel demand, currently completely covered by crude oil (increasing demand for mobility of persons and goods)
- Increasing local and global emissions such as CO_2, particles, and noise

The dependence on oil and the increasing local and global environmental impacts of mobility will cause politics and industry:
- To improve air quality by reducing local transportation emissions
- To mitigate global warning by reducing green-house-gases-emissions
- To diversify fuel supply to lower the dependence on oil.

Possible solution approaches are:
- Enhancing efficiencies of drive train concepts by
  - improving conventional ICE technologies
  - developing new propulsion systems such as FC
- Introduction of CO_2-free and CO_2-reduced fuels on the basis of renewable energies under long-term aspects

Most promising benefits of FC drive systems are:
- high efficiency (up to 50% lower fuel consumption)
- emission-free/-reduced operation (depending on fuel)
- low noise
- highly efficient use of alternative fuels

Renewable fuels powering FC vehicles enable emission-free or low-emission driving and could become an option of sustainable mobility.



Quelle: Isenberg FT1/E, Edinger FT1/E, Kraftstoffwende März 2001. Daten nach VES und DaimlerChrysler.

DC-FC-PROGRAMME

In the beginning of the 90ies, DC started the development of FC-powered vehicles. Since the presentation of Necar I in 1994, the FC-drive-concept has made great advances toward production maturity (reduction of volume and weight by a factor approx. 4, increasing efficiency and reliability, etc.)

Main highlights:

1996 Necar II (CGH_2)
1997 Nebus (CGH_2, City-bus)
1997 Necar III (on-board H_2-production by steam reforming of methanol)
1998 P3 buses (CGH_2)
1999 Necar IV (LH_2, first ZEV with range of more than 400 km)
2000 Necar V and Jeep Commander (Methanol)
Cart with DMFC-drive-system
2002 Necar V adv., crossing USA from West to East

The DC-FC-philosophy is following a multi-fuel strategy:

- hydrogen for central fuelled vehicles (fleets of buses or delivery vans)
- methanol for area-covered refuelling
- gasoline reforming

Market preparation projects are planned for attractive target markets in order to receive public acceptance and technical experiences:

- California Fuel Cell Partnership
- Iceland Hydrogen Programme
- Driving tests in Japan
- CUTE (Clean Urban Transport for Europe, European bus project with H_2-powered buses and different refuelling options)
- CEP (Clean Energy Partnership
- The DC-Energy-Strategy relies on conventional fuels and engines as the main line in the next two decades. To promote and support the market introduction of alternative and renewable fuels, DC is participating in projects for producing and testing alternative fuels, e.g. in Freiberg/Saxony: production of methanol and Fischer-Tropsch-fuels on the basis of wood-residues in order to classify the environmental advantages of these fuels.

FCs can become the link between fossil and renewable energy and have the potential to guarantee sustainable mobility.

The Role of High Efficiency Solid Oxide Fuel Cells in the Transition to a Sustainable Energy Supply

K. J. Li, Shell Global Solutions International
Joep Huijsmans, Shell Hydrogen
Knut Bakke, Shell Technology Norway
Wolfgang Heidug, Shell Global Solutions International

Renewable energy will ultimately replace fossil fuel although the time scale for this replacement is highly uncertain. World fossil fuel reserves are adequate for centuries to come but climate change and pollution effects are already accelerating the inevitable transition. Hydrogen is one of the energy carriers of choice for renewable energy sources. Fuel cells have features that give them a unique position in the transition from a hydrocarbon based fuel system to a renewable energy system. They can be used both with hydrocarbon fuels, where they beat conventional power generation technology in terms of efficiency and pollutant emissions, or with hydrogen from renewable sources.

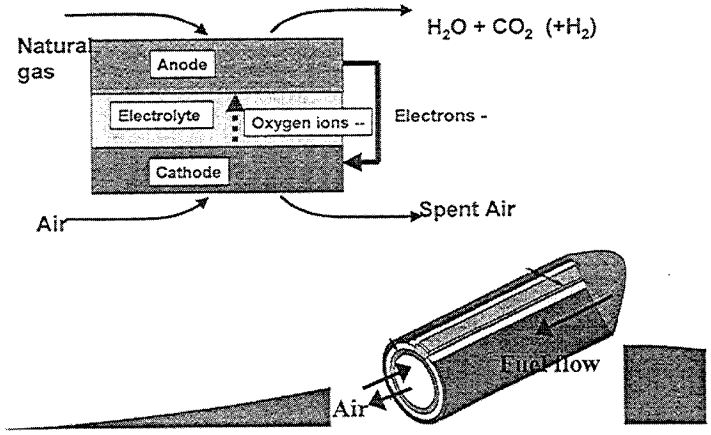
Shell in conjunction with Siemens Westinghouse is developing a new type of solid oxide fuel cell (SOFC) that can capture CO2 from the exhaust stream with the intention to inject the CO2 into the subsurface for sequestration. This paper gives an update of these plans and on the status of this technology, which is currently entering the demonstration stage.

1 Introduction

Since the signing of Kyoto Protocol, several oil and engineering companies have been developing CO2 capture technologies. These CO2 removal technologies can be categorized as pre-combustion, oxy-combustion and post-combustion. However, essentially all these technologies will reduce thermal efficiency in order to capture CO2 from the power plants.

Shell in conjunction with Siemens Westinghouse is developing a new type of solid oxide fuel cell that can capture CO2 from the exhaust stream with the intention to inject the CO2 into subsurface for sequestration. In this type of fuel cell the electrolyte used selectively transports oxygen from cathode to anode to provide oxygen for chemical reaction with fuel. The Ni coated anode is a reforming catalyst to convert methane and water into carbon monoxide and hydrogen under elevated temperature (figure 1).

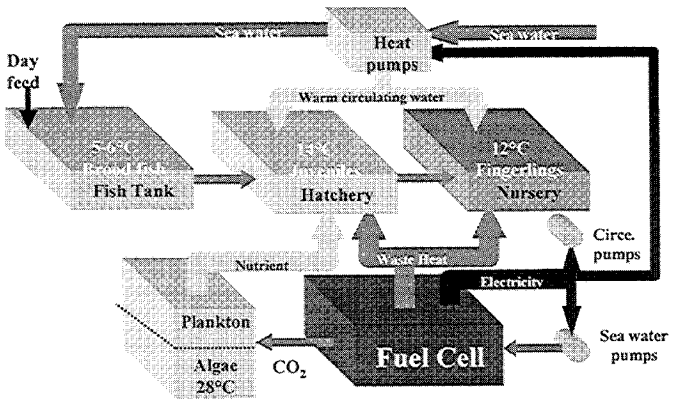
Figure 1 Oxygen transport in SOFC



2. Pilot Plant in Norway

To demonstrate the concept, an order was placed in April 2000 to Siemens Westinghouse Power Corporation for the development and manufacture of a 250 kW zero emission SOFC unit to be installed at Kollsnes Industrial Park near Bergen, Norway. While the main application of this technology is for the offshore oil and gas industry, the pilot plant will be integrated with a fish farm project located at the same industrial park. Electrical power generated from the fuel cell will be supplied to the fish farm to run seawater pumps and heat pump. Hot water from the pilot plant will be used to heat the fish tanks to minimize the growing period of the fish fingerlings. And, the CO2 produced by the solid oxide fuel cell will be used in the production of algae upon which plankton feed which in turn are feed for the fish juveniles (figure 2).

Figure 2 Fuel cell integration with fish farm



For the project to be successful, two technical challenges need to be overcome. One is to develop a dynamic seal system to separate the carbon dioxide and steam effluents from the spent air and the other is to develop a new fuel cell (afterburner) to convert the remaining fuel from the main fuel cell unit to near completion of 98% (Figure 3) None of these are easy. SWPC has successful tested the new concept and is in the process of designing and manufacture a small test unit of one-sixteen scale of the pilot plant. The pilot is scheduled for delivery to Norway in late 2003.

3 Applications of the zero emission SOFC units

The prime objective of the SOFC development is to provide clean power for the offshore oil and gas industry. In Norway approximately 30% of CO2 emission comes from offshore oil and gas production activities. To meet the challenge of the Kyoto Protocol, the offshore emission from Norway must be reduced by 16% within 6 to 10 years. SOFC could provide clean power without losing efficiency. In the application shown as figure 4 prime separation of oil from associated gas and produced water takes place at the seabed. Oil and some gas are brought to the second stage separator located on a platform or a floating tanker for further degassing. The low-pressure gas from the second stage separator is used to fuel the SOFC unit, which in turn generates power to run the injection pumps. CO2 from the SOFC is also injected into a subsurface structure. In this application only the stabilized oil is produced. Produced water, excess gas and CO2 production from the fuel cell are all reinjected into subsurface structure.

Figure 3 Zero Emission concept

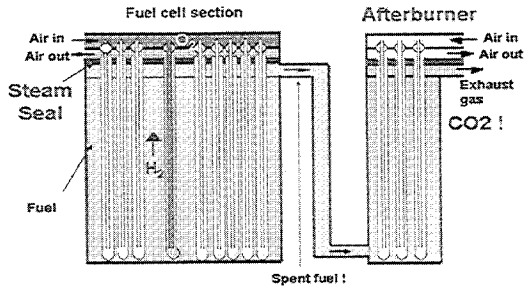
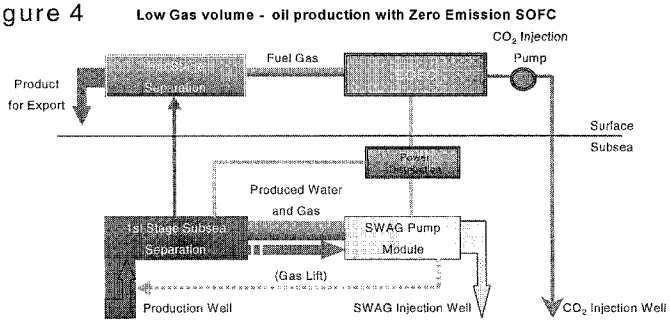


Figure 4 **Low Gas volume - oil production with Zero Emission SOFC**



The oil industry has many other potential applications where SOFC's in the power range of 20 MW could be an excellent fit. Applications in which the water, the heat and/or the CO2 can be utilised in conjunction with the electricity make the SOFC a unique fit as a solution. Water for drinking, heat for process utility and CO2 for enhanced oil recovery. If all the needs of the oil and gas applications are addressed, SOFC could be an economical and technically superior solution.

If SOFC is accepted by the industry and sufficient CO2 is produced. The CO2 stream can be collected and injected into oil reservoir to enhance oil recovery when the reservoir is toward the end of the field life. For gas fields near depletion when the reservoir pressure is too low to justify the cost of gas compression, SOFC can be used to extend the field life by generating electricity with the low-pressure gas instead of supplying the gas. In this application abandonment of the offshore platforms or onshore facilities can be deferred into the future.

4 Next Steps

For a typical process development a full-scale plant is normally considered after sufficient data are collected from the pilot plant. However, greenhouse gas emission must be curbed by both the oil industry and other industries in general. There is an urgency to develop a zero (or low) emission power generation concept. Among the challenges for this phase of the development is to reduce the size of the SOFC unit. There are options to improve the power density of the unit by running the fuel cell at a moderated higher pressure and to use the hot exhaust in a turbine to generate additional electricity. A study has been commissioned at Forschungszentrum Jűlich to investigate means to increase power density of the SOFC unit.

To speed up this development Shell has also signed a co-operation agreement with the Norwegian state power company Statkraft and an engineering firm Aker-Kvaerner to study the feasibility of developing a larger size SOFC unit in the range of 5 to 20 MW. In this partnership, Shell will continue to coordinate the fuel cell projects and develop the technology, Aker Kvaerner will provide engineering and construction expertise in building the power plant and Statkraft shall develop the market and may also operate the power plant.

The partnership will study the feasibility of building a small-scale unit initially suitable for local power demand and with an aim to relocate the unit to an offshore platform. The unit will be designed with high efficiency and the capability to capture CO2 for potential application in enhanced oil recovery scheme.

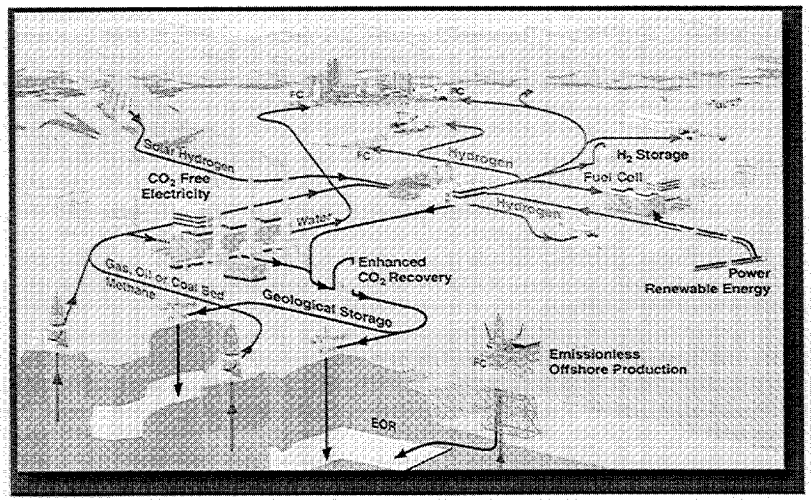
5 Conclusions and the Vision

The zero emission SOFC will demonstrate that CO2 can be captured effectively while maintaining high efficiency in power generation.

From a long term prospective SOFC is one of the promising technologies that could help create a sustainable development in the offshore, onshore and transportation sectors. This could be viewed as an intermediate step toward a sustainable energy supply.

In the long run Shell aspires to introduce SOFC's to power part of its operation to reap advantages in efficiency and greenhouse gas emission reduction. The first CO2 sequestration projects are expected to tap CO2 from large concentrated sources and in doing so they will establish a pipeline network into which smaller quantities of CO2 captured, for example using the new SOFC cell technology, can be added. This network enabling CO2 sequestration opens many opportunities for emission-less hydrogen production from a variety of fossil fuels and thus enables an environmentally sound and cost effective route to establishing a hydrogen infrastructure (figure 5). Availability of high efficiency devices in the form of fuel cells for converting hydrogen to power and a cheap way to produce hydrogen without accompany CO2 emission will greatly accelerate the viability of renewable technologies.

Figure 5



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J. Blake Moore, K. J. Li, Mike Haines and Wolfgang Heidug, Solid oxide fuel cell developments for CO2 recovery at Kollnes, Shell in-house Gas Technology Conference, 11-14 June 2001.

Figure 5 was modified from a viewgraph originally prepared by Olav Kaastad of Statoil.

Possibilities of the Market Introduction of Mobile Fuel Cells and Effects on Industry- Component Analysis and Scenarios for Market Introduction

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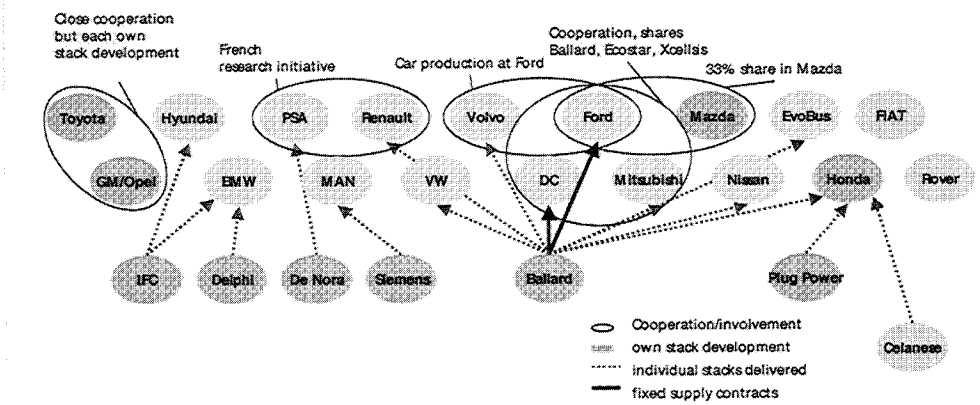
Introduction

The research activities in the field of fuel cell technology have been greatly intensified over the last few years and months. Alongside the basic research of public institutes and the research activities of a few large concerns which have already been dealing with this topic for many years, there is a growing interest of small and medium-sized enterprises in this technology (see Figure 1). However, companies and organisations are often confronted by the question for which components it would be worth starting research activities and the risk assessment of such development activities is problematic.

Figure 1: Fuel cell strategies of automobile manufacturers (Date 2001)



Within the scope of a project sponsored by the North Rhine-Westphalian Ministry of Economics and Small Businesses, Technology and Transport, different system variants with individual components were elaborated and described in detail in order to make it possible for the enterprises to identify company-specific potentials. The project was carried out by the Fraunhofer Institute for Systems and Innovation Research, the Forschungszentrum Jülich and agiplan ProjectManage-

ment. Supplementing the systems, scenarios for market introduction with the necessary frame conditions and impacts are presented to allow a risk analysis (Schirrmeister et al., 2002).

System variants

Four system variants were examined (see Figure 2). The fuel variants hydrogen, methanol and petrol are represented. Numerous components occur in several system variants with only minor adjustments having to be made. The development risk for the company involved decreases for these particular components. Based on the lists of components, it can also be depicted which structural changes are to be expected in the supplier industry if the classical transmission is replaced by fuel cell technology.

Figure 2: System variants analysed

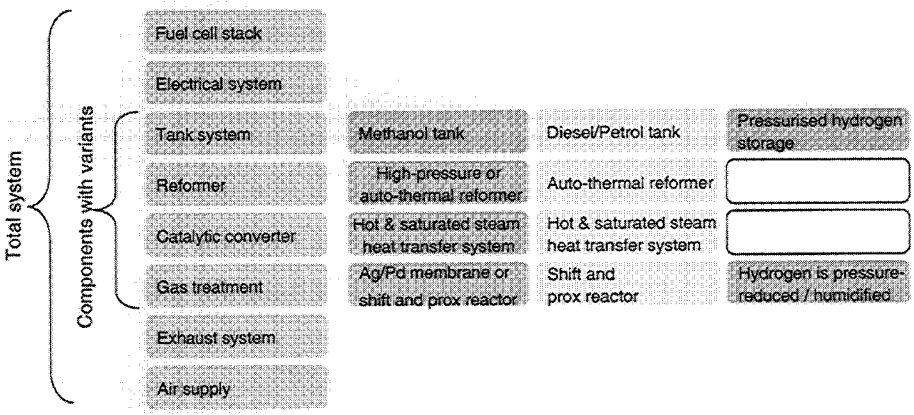
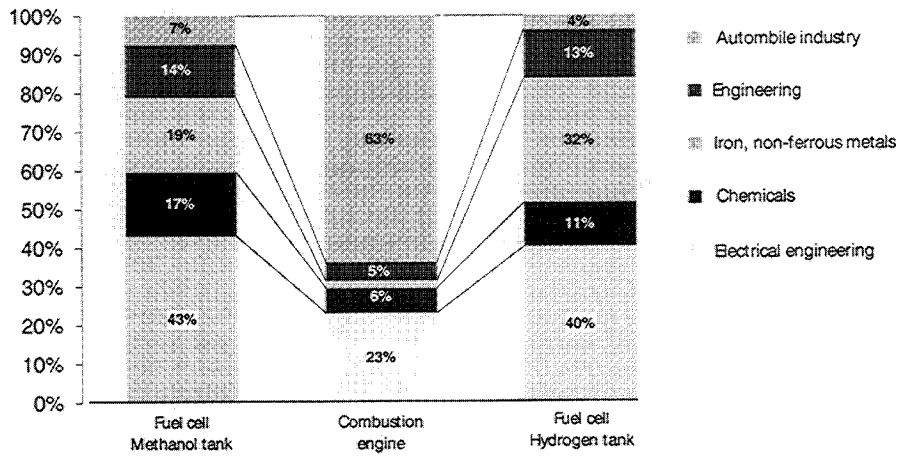


Figure 3: Potential changes in supplier structure



As can be seen in Figure 3, there are major shifts in the supplier industry involved in the production of one transmission system. Whereas for conventional combustion engines, 63 % of the value added is generated in the automobile industry, this figure drops to only 4 % (7 %) for fuel cell vehicles. In contrast, the sectors electrical engineering, chemicals and non-ferrous metals stand to gain from the shift to fuel cell technology.

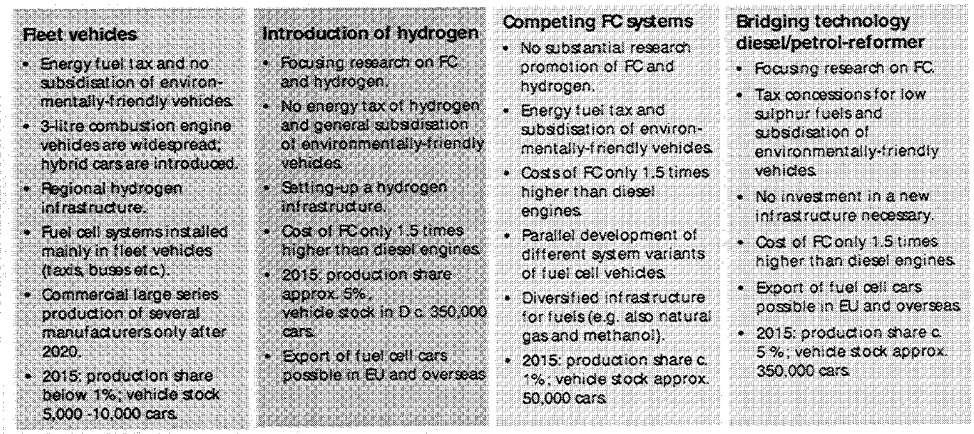
Scenarios

When assessing the risks it must also be taken into account which introductory scenarios are possible. A list of factors of influence was compiled and their possible development examined (see Table 1). Based on compatible factors, four introductory scenarios were derived. These scenarios each establish a link to the different fuel variants and estimate potential production volumes for 2015 in Germany (see Figure 4).

Table 1: Factors of influence

- Economic frame conditions.
- Transport infrastructure.
- Research promotion.
- Prices of natural gas and oil.
- Customer acceptance.
- Mobility requirements and behaviour.
- Fuel taxation.
- Vehicle taxation / subsidies for new vehicles.
- Emission limits for new and used vehicles.
- Strategy of automobile manufacturers.
- Technical alternatives (several combinations possible).
- Production costs of fuel cells.
- System variants.
- Setting-up a fuel supply structure.
- Oil price.
- Global market for fuel cells.

Figure 4: Overview of the scenarios



Fleet vehicles: In this scenario, not only test fleets are realised but also fleets with greater numbers such as taxis, buses and delivery vehicles. Strong competition exists with (less than) 3 litre combustion engines.

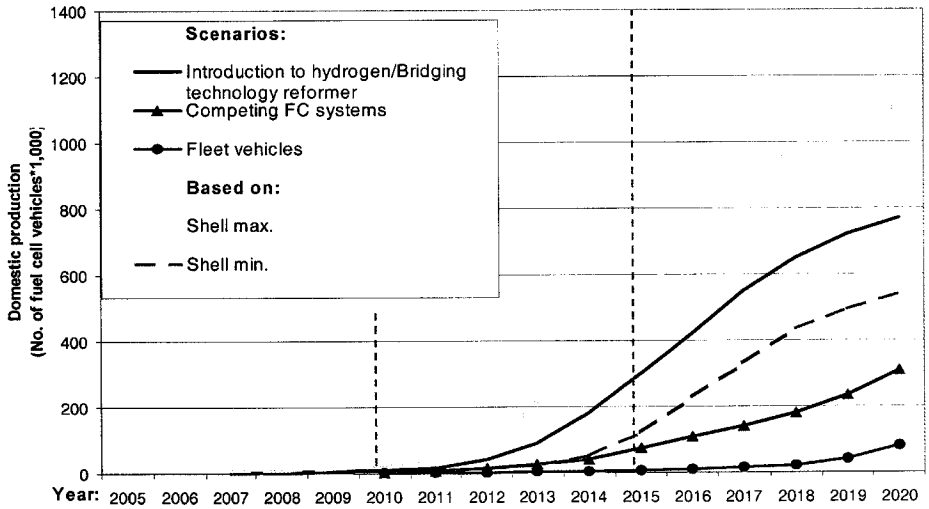
Introduction of hydrogen: In this scenario, it is estimated that Germany becomes a hydrogen society. R&D focuses on fuel cells and hydrogen technology and the government supports fuel cells by offering subsidies for consumers purchasing fuel cell vehicles.

Competing fuel cell systems: This scenario is based on today's situation: there are several competing fuel cell systems which continue to be developed independently up to 2015. A diversified fuel infrastructure (e.g. methanol, pressurised hydrogen) is necessary.

Bridging technology diesel/petrol reformer: This scenarios assumes a breakthrough in the reformer technology for diesel/petrol. If it is possible to produce these reformers economically, this technology could be a bridge to the hydrogen society.

Whereas the fleet vehicle scenario with the lowest production and stock level for fuel cell vehicles can be seen as a bottom estimate, the scenarios "Introduction of hydrogen" and "Bridging technology diesel/petrol" represent the prospects under the supposition of a very positive development of the frame conditions (Figure 5). Nevertheless the fleet vehicle scenario can be seen as a possible step towards a (later) hydrogen society.

Figure 5: Domestic production in Germany



Conclusions

At present, it is impossible to predict which system and which fuel will predominate in fuel cells in the long term (therefore the derived scenarios). Organisations and SMEs with limited R&D

budgets should concentrate on fixed components which are independent of the fuel cell technique involved (SOFC or PEM). These might also be components with synergies to other technologies (e.g. electronics, pumps).

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FUEL CELL TECHNOLOGIES - FURTHER EDUCATION AND TRAINING CONCEPT FOR STATIONARY AND MOBILE FUEL CELL APPLICATIONS

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In the Federal Republic of Germany are a lot of activities and efforts to support the fuel cell technology. There are several programs of different ministries, some german countries and organisations. Some of them are introduced in this performance.

Programs to support research and development

Support for Forschungszentrum Jülich (Research and Testing of different fuel cells)
Zentrum für Sonnenenergie und Wasserstoffforschung
(Research, Demonstration and Testing of PEM-Fuel Cells)
Deutsches Zentrum für Luft- und Raumfahrt (Research and Testing on SOFC's)
Fraunhofer Institutes
.....

Programs to gain practical experience

Project "Negev" (Virtual Power Plants)

55 mini block heating systems of Sulzer Hexis and
50 mini block heating systems of Vaillant will be installed in the next years in different locations and build a virtual power plant under the leadership of EnBW.

Project "CUTE"

30 Public Fuel Cell Busses in 9 European cities,
(Amsterdam, Barcelona, Hamburg, London, Luxemburg, Madrid,
Porto, Stockholm and Stuttgart) and perhaps in one city in Australia

Project "Mega SOFC"

1 Megawatt fuel cell demonstration plant in Marbach/Neckar
Cooperation of EnBW, Gaz de France, Tiroler Wasserkraftwerke AG (TIWAG), Siemens KWU and Siemens Westinghouse Power Corporation / USA. The project ist supported financially by the European Commission and the US-Department of Energy.

250 KW Molten Corbonate

Fuel Cell for generating electrical power and process heat for
producing tires. Michelin in cooperation with EnBW and MTU Friedrichshafen.

Project "EDISON"

250 KW PEM Fuel Cell Power Plant in the thermal bath in Mingolsheim. Supported by the federal ministry of economy.

Programs to improve fuel cell technology

Berta: Brennstoffzellen "Entwicklung und Erprobung für stationäre und mobile Anwendungen.
Fuel Cells: "Development and Testing for stationary and mobile applications"
BMWi, Federal Ministry of Economy
Working groups are active in 4 different fields
- Industrializing fuel cells
- Improving a supplier industry
- Norming and licensing of fuel cell plants
- Training and information of the public

Challenges to the handicrafts companies based on the innovation fuel cells.
Feasability study of Heinz Piest Institute Hannover, Ludwig Bölkow Systemtechnik Munich and Fraunhofer Institut ISI

Training and Demonstration Center Fuel Cell (see figure 1)
– Placed in North Rhine Westphalia at the Research Center Jülich
– Placed in Baden-Württemberg at the ZSW Ulm (Center for Solar Energy & –Hydrogen Research)

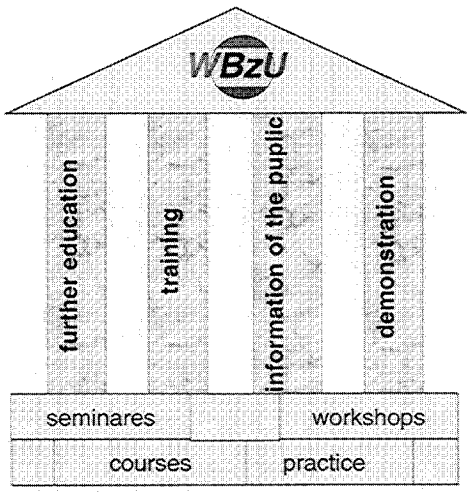

Figure 1: Tasks of the Training and Demonstration Centers

Program to develop a training concept

Further education and Training concept for stationary and mobile fuel cell applications

EAZ Aalen is taking a lead in the development of a dynamic training concept for professional education in the fields of fuel cell technology. In a preliminary study in the research field of fuel cell technology the Electrical-Training-Center Aalen (EAZ) has together with the Fraunhofer Institute for Industrial Engineering (FhG IAO) determined the educational and educational requirements which will be needed for future fuel cell plants and equipment.

A detailed questionnaire sent out to members of the regional vehicle repair, electrical and building installation guilds showed proof of the considerable interest in the subject of fuel cells. Nearly 2/3 of the firms which responded expressed interest in taking part in courses to prepare them for "fuel cell technology" (Figure 2).

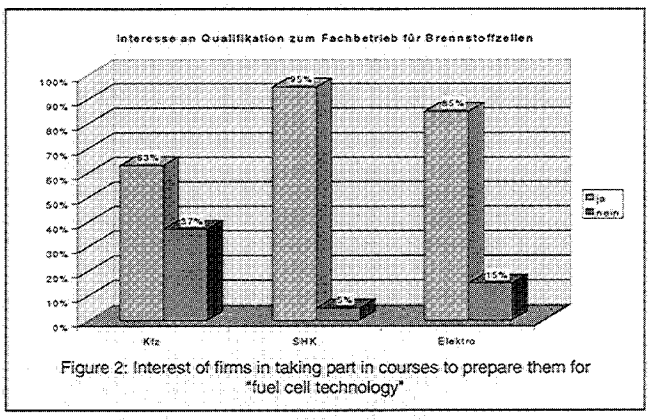

Figure 2: Interest of firms in taking part in courses to prepare them for "fuel cell technology"

The skilled tradesmen thus indicated clearly their wish to participate in the chances offered by this exciting new technology. However, to ensure a successful launch of the new fuel cell products coming on stream, it is essential to improve public awareness of the possibilities offered by this technology. This is best done through direct contact between the potential customer and a well qualified and competent practitioner. This is why it is necessary to start early with training the relevant craftsmen and other interested persons, to provide them with the knowledge and skills they will need.

A further important aspect of the preliminary study was to tap into the experience of manufacturers, operators and research institutes involved in the development and testing of fuel cell applications. Here, everyone agreed on the need for foresight in the development of further education and training concepts. Otherwise, wide market acceptance and introduction of this innovative technology in Baden-Württemberg will be put in jeopardy or at least delayed. The keen interest of the group questioned was also demonstrated by the fact that manufacturers, operators and research institutes all expressed their willingness to contribute their knowledge and experience to the training module to be developed.

Which trades / professions could be concerned ?

- Boat builder
- Electrical plant fitter
- Electrician
- Electrical / mechanical engineer
- Electrical machine fitter
- Electro -mechanic
- Water utilities technician
- Heating and chimney fitter
- Gas and water fitter
- Industrial electronics technician
- Information / communicationssystems electrronics technician
- Information electronics technician
- Refrigeration technician
- Plumber
- Communications electronics technician
- Vehicle maintenance electrician
- Vehicle maintenance mechanic
- Engineering mechanic
- Mechatronic technician
- Micro -technologist
- Pipe fitter
- Chimney sweep
- Central heating and air conditioning fitter
- Motorcycle mechanic

Effects on the professional training in the fields of plumbing , heating , air conditioning , electrical installation , vehicle repair and chimney sweeping

Figure 3: (Selection of) Professions concerned by the introduction of fuel cell technology

This is the basis on which we propose to develop future-orientated training modules for fuel cell technology. In contrast to more traditional approaches, these modules will be developed dynamically, taking account of experience gained in practice and in long term trials. With this in mind, the empirical results, gained by operators and supervisors of fuel cell systems, based on seven categories, will continuously be updated during the course of the project and integrated into the training modules, such that at the end of the project all the modules reflect the latest state-of-the-art. Particularly the practical experience of the skilled and manual workers directly involved with fuel cell equipment should be included in the modules, so that those taking the training courses become familiar with the practical situations with which they will later be confronted.

In developing the training modules we are concentrating primarily on the needs of the electrical, building installation and vehicle repair professions, even though many other professions will also be concerned with the changes associated with the introduction of fuel cells. A selection of some of these is shown in Figure 3.

Another aim is to reduce the fear of a gas explosion, which many people remember about hydrogen in chemistry lessons at school. Of course, depending on how it is handled, hydrogen is just as dangerous or as harmless as petrol, natural gas, propane, butane, etc. The desire is to present hydrogen in the "right light" in the public mind.

These profoundly affects the overall reliability and safety of the application. We take account of this in its training concept by concentrating not only on the fuel cells but also on the whole application and the interrelationships with the components which surround the fuel cell. This is also reflected in the approach to content mentioned earlier, whereby the skilled or manual craftsman is trained on the basis of practical examples which he is likely to meet in practice.
In order to gain the necessary practical feedback, We have built up a wide network of contacts to manufacturers, operators and institutes, all of whom have promised their support (see table 1)
With good feedback, this close cooperation should guarantee that technical innovations are rap
idly incorporated into the training modules and implemented speedily in novel ways in the practical training sessions. Through this dynamic concept, the information on fuel cell technology – which certainly will continue to undergo rapid change – can be kept continually up to date.

We think the most important factors which will affect successful introduction into a wide market are: the availability of trained practitioners, a well informed public and technically suitable products at reasonable prices. Even the latter will be helped by the proposed training concept, since experience gained by the practical application of the existing fuel cell technology should help manufacturers to further develop and streamline their products.

It is likely to be difficult for many educational institutes for the foreseeable future to set up an appropriate infrastructure as far as the technical equipment is concerned. The main reason being the high price of the equipment at present. For this reason, the EAZ has adopted a two track approach:
On the one hand, a new building is being planned, specifically for training in fuel cell power generation plants but also equipped with a fuel cell vehicle and fuel cell experimental models. Other educational institutions which are not too far from Aalen will be able to share these facilities. In a similar way, the Center for Solar Energy & Hydrogen Research (Zentrum für Sonnenenergie und Wasserstoffforschung - ZSW) in Ulm is planning a demonstration center which will be open to others.
On the other hand, in co-operation with a manufacturer of fuel cell models for teaching purposes in Berlin, the EAZ is helping to develop models with which not only "normal" conditions can be demonstrated but also typical practical faults simulated, allowing trainees to learn how to find them and put them right.

TABLE 1:Network of manufacturers, operators and institutes of research

	Emphasis in the field of fuel cell technology
Company:	
Daimler-Chrysler AG	R&D of fuel cell vehicles
EnBW Energie Baden- Württemberg AG	Operation of fuel cell block heating power stations: 1 MW SOFC plant in Marbach 250 kW PEM plant in thermal baths at Mingolsheim 250 kW MCFC plant at Michelin in Karlsruhe Fifty 1 kW units in single family houses
Sulzer-Hexis AG	Manufacturer of SOFC block heating power stations
Vaillant	Manufacturer of PEM block heating power stations
Heliocentris	Manufacturer of models and teaching aids for teaching the basics of mobile and stationary fuel cell applications.
Klärwerk Rodenkirchen	Operator of a 250 kW PAFC power plant operating on sewage gas
Institute:	
ZSW - Zentrum für Son- nenenergie und Wasser- stoffforschung	Research in various areas of fuel cell technology. Setting up and testing of fuel cell systems
DLR - Deutsches Zentrum für Luft- und Raumfahrt	Research and testing primarily in the field of high temperature fuel cell (SOFC, MCFC) and development of a fuel cell driven vehicle
FZ Jülich - Competence Network NRW	Research in various areas of fuel cell technology and operation of a network of companies and institutes, mainly in North Rhine Westphalia.
DWV - Deutscher Wasser- stoffverband	Association for the advancement of fuel cell technology. Members are mainly institutes, operators, manufacturers and private individuals
HPI - Heinz-Piest-Inst.	Cooperation in the field of educational concepts
FhG IAO	Active project partners and scientific supervision

To facilitate the transfer of knowledge, EAZ plans to use multimedia elements, such as project-based practical instruction and help in the form of teaching albums. The latter are well suited both for use under supervision of an instructor and for reference by the trainee on his own.

Our objective is, to make a valuable contribution to ensuring that
fuel cell technology, which holds such promise, is successfully introduced into the market place. In this, we not only had the support of the firms, manufacturers and institutes already mentioned but also the backing of the European Union and the State of Baden-Württemberg. Thus the preliminary study was jointly supported with funds from the European Social Fund and from the Landesgewerbeamt Baden-Württemberg. We also see good chances of receiving additional funding for the development of the training concept itself.

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Fuel Cell Applications

FUEL CELLS FOR MOBILE AND STATIONARY APPLICATIONS -ANALYSIS OF OPTIONS AND CHALLENGES

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Abstract

Highly efficient energy conversion systems with fuel cells for vehicles and stationary applications are currently being discussed all over the world as a technology which will be able to reduce primary energy demand and emissions of limited and climate-relevant pollutants. The high flexibility of fuel cell systems with respect to energy carriers opens up possibilities of modifying the energy market in the long term. New environmental legislation, above all in the USA, stipulating the introduction of emission-free cars from 2003, has led in the transport sector to an intensified search for alternatives to conventional drive concepts. In stationary applications, numerous demonstration plants and some field tests already implemented reflect the developmental stage of fuel cell systems.

A major milestone on the road to market success for all the above-mentioned systems – in order to compete with conventional technologies – is the reduction of costs. The definition of the "appropriate" fuel represents a serious obstacle to the market introduction of fuel-cell-powered vehicles.

1 Energy carriers for fuel-cell systems

At present, significantly growing energy requirements are assumed especially in the transport sector, which will continue to be chiefly covered by crude oil originating predominantly from the Middle East and which will exhibit a production peak in the next decade (for economic oil production only). Expanding natural gas markets will in future primarily have to make use of the great reserves in the Middle East (Iran, Qatar, Saudi Arabia) and the Russian Federation projected to last worldwide for 62 years (reserves/current annual production – as of early 2001) [SCHMITZ 2002]. This situation of future fuel supply is likely to produce instabilities from an ecological, economic and political point of view [ISENBERG 2001]. Higher fuel prices and a reduction of climatically relevant and local emissions and of the associated secondary pollutants dictated by environmental policy intensify the pressure on increasing the efficiency of "clean" energy conversion systems and by introducing "clean "fuels into the market.

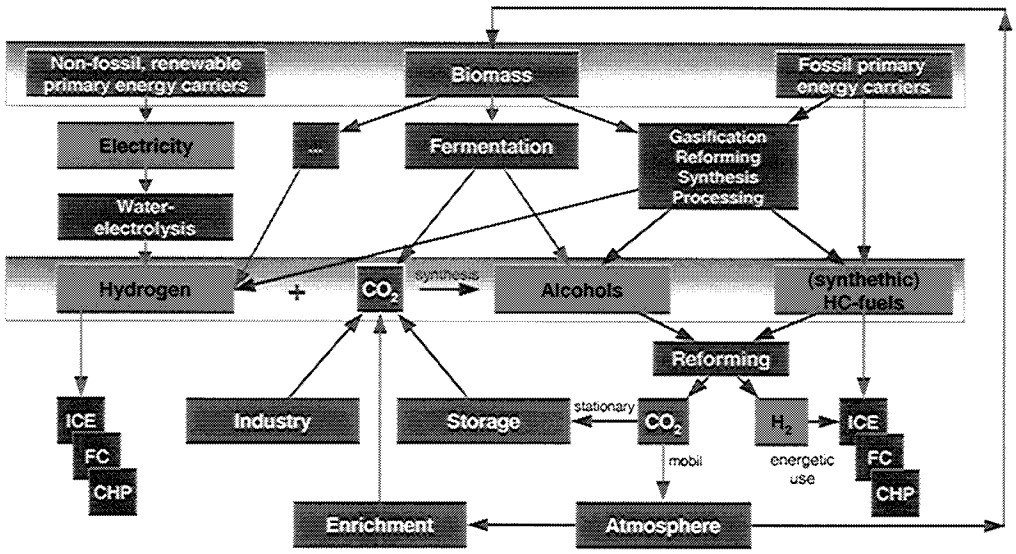

Figure 1: Energy Carriers for the Future

Many experts expect hydrogen from non-fossil, renewable energy sources to become technically, economically and ecologically important in the next 20 years, although from the present point of view hydrogen still does not play a major part in the energy supply. Wherever hydrogen can be produced in an economically sound and ecologically acceptable manner and supplied to the consumer, it should also be used directly for high-efficiency fuel cells (fleets of motor vehicles, stationary applications). Hydrogen will not be a suitable or economically

feasible energy carrier for all markets and countries, and other alternative sources of energy must remain under discussion (Figure 1). This includes, for example, the use of methanol, synthetic liquid hydrocarbons in fuel-cell vehicles or natural gas for stationary fuel-cell applications with the respective reformer technology for on-site hydrogen generation.

Final energy carriers will have good prospects for future use if they can be used simultaneously for both conventional and new fuel-cell energy conversion systems in the long term and cumulatively also with the application of regenerative primary energy carriers. A future enhanced incorporation of regeneratively produced energy carriers requires sufficiently large potentials, adequate availability along with a competitive cost situation and the creation of new infrastructures, which applies to:

- hydrogen production by electrolysis with non-fossil-generated electricity,
- hydrogen and/or liquid energy carrier production from biomass,
- CO_2 use by synthesizing CO_2 + non-fossil-produced H_2 to obtain CH_3OH.

On these paths (Figure 1) towards a supply of energy carriers for internal combustion engines (ICE), fuel cell systems (FC) and combined heat power stations (CHP) with a preferably increasing significance of the energy carriers produced on a renewable basis, petroleum (decreasing) and natural gas (increasing) will be the dominant hydrocarbon primary energy carriers for at least the next three decades. In this period, however, final energy carriers other than gasoline and diesel will also be discussed and introduced onto the fuel market: liquefied natural gas, alcohols, as well as synthetic HC fuels (Fischer-Tropsch).

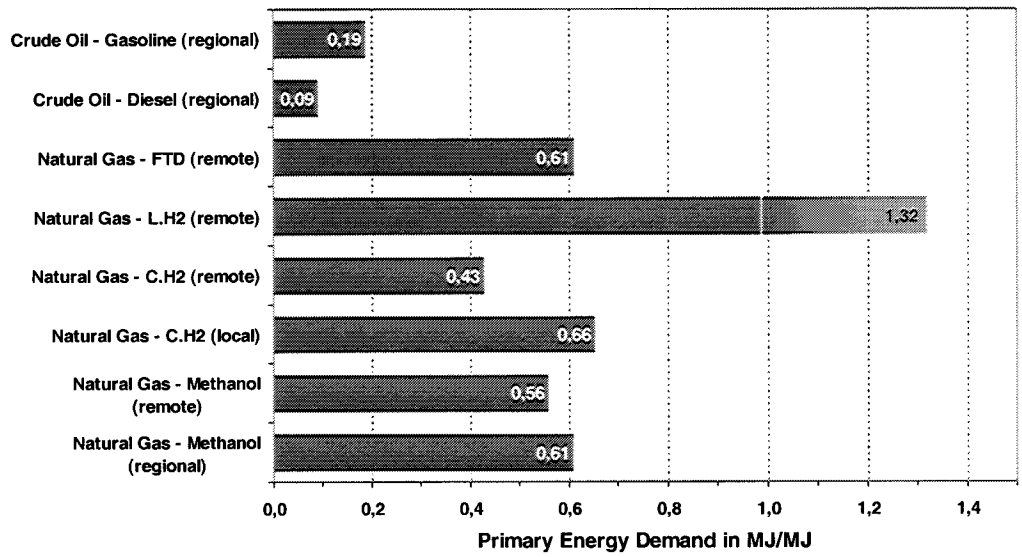

Figure 2: Energy demand of fuel supply

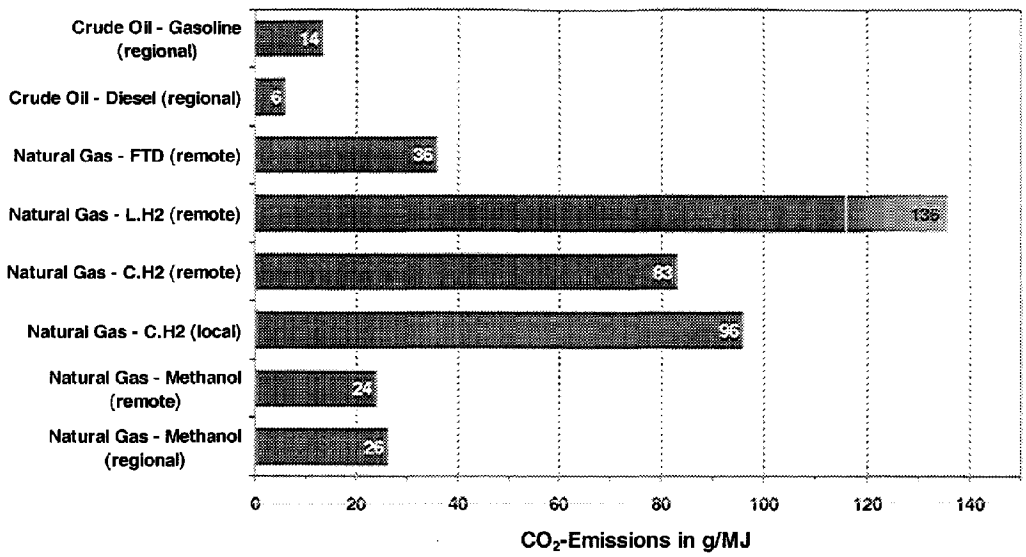

Figure 3: CO_2 emissions from fuel supply

In order to assess the options of future energy supply systems, it will be necessary to determine primary energy demand (Figure 2), CO_2-emission (Figure 3) and cost balances from the primary energy carrier at the source or well up to the final energy carrier at the filling station [GRUBE et al 2001].

In summary, it can be seen from Figure 2 showing the fossil-based fuel cycles that the lowest primary energy input for the supply of gasoline and diesel is followed by the provision of compressed hydrogen produced in large plants based on natural gas and transported in pipelines before being compressed to 300 bar at the filling station (CH_2 remote), which requires 0.43 MJ of primary energy carrier input per MJ of CH_2 (300 bar) and is thus clearly lower than for methanol (overseas remote and regional). The largest primary energy carrier input is involved in the supply of liquid hydrogen from remote natural gas. Compressed natural gas (CNG) supply in Germany, which is not shown here, would require a primary energy input of 0.24 MJ/MJ for compression to 250 bar at the filling station accordingly that of a local compressed hydrogen supply would amount to 0.66 MJ/MJ. It is ultimately shown in Figure 3 for the hydrogen cycles that due to total C separation the specific emissions are the highest and are particularly high for LH_2 due to the fossil-loaded electricity mix input for liquefaction. The CO_2 balance for CNG supply would amount to about 14 g/MJ and thus be in the upper range of conventional fuel cycles. A conclusive statement concerning the CO_2 balances, however, can only be made if the overall balance is set up including the use in different passenger car drives. For a better understanding of the overall balance, it can already been stated here that about 70 g of CO_2/MJ is released in complete oxidation for gasoline/diesel/methanol/ethanol, about 55 for natural gas and 0 g for hydrogen.

2 Comparative evaluation of fuel-cell power trains

From an evaluation of vehicle drives with fuel cells, potential advantages in comparison with internal combustion engines can be defined as follows:

- advantages in the fuel consumption of the vehicle
- no (H_2 operation) / low limited emissions (methanol, hydrocarbon operation)
- advantages in the balance of greenhouse gases (great for H_2 operation)
- mechanical simplicity, low vibration/noise
- reduced maintenance, no engine oil required
- powerful on-board energy supply
- modular design for fuel cell stack (passenger car, commercial vehicle, railway)
- new technologies: fuel cells, electric motor, transmission, gas generation, injection, catalytic converters

All the technical systems to be discussed range between performance, service life and costs with sufficient user friendliness, good operating and environmental behaviour as well as long availability of raw materials and primary energy carriers with respect to the criteria to be met.

California's regulations will require for light duty vehicle (LDV) manufacturers the marketing of zero- (ZEV) and partial-zero-emission (PZEV) vehicles beginning in 2003 (Dec. 2000) including:

10 % of LDV's marketed must be ZEV's

- 2 % pure ZEV's: (Gold standard)	Batteries FCV's (Hydrogen)
- 2 % PZEV's: (Silver standard)	Advanced Technologies, Credits > 0,4 Hybrids (Prius, Insight), CNG-ICE, ...
- 6 % PZEV's:	SULEV's or Credits > 0,2 < 0,4 FCV's with Reformer (MeOH, HC) New Fuels ...

That means, electrically operated fuel cell drives (FCVs) will have to be measured against the competing drives of conventional design with internal combustion engines (ICE) but with new energy carriers, hybrid drives with system-related higher drive weights and costs, as well as electric drives with batteries and, in total, battery-related higher costs and drive weights.

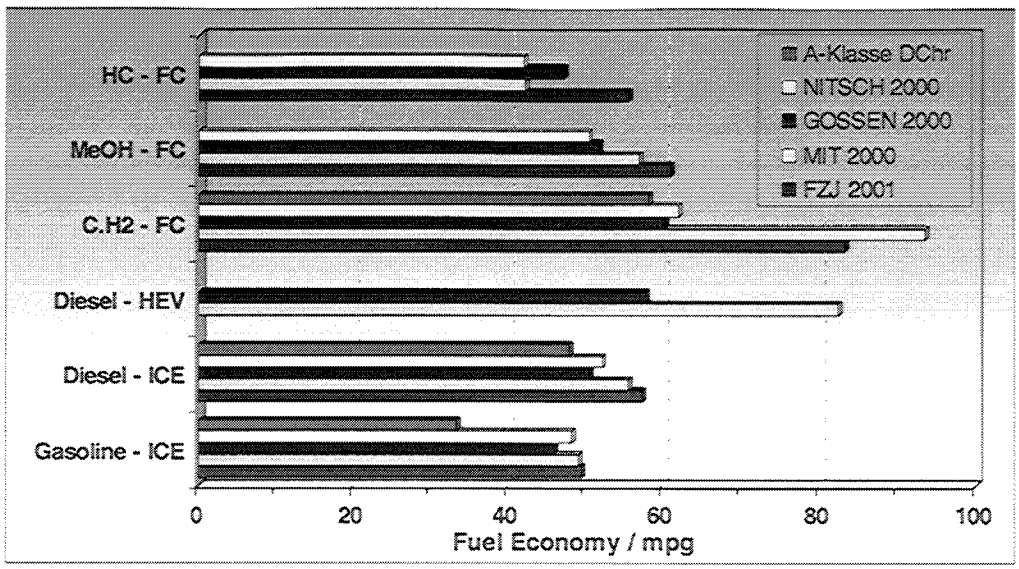

Figure 4: Fuel economy of vehicles based on different studies

In comparison to internal combustion engines (ICE), electrochemical energy converters in combination with electric drives exhibit clear efficiency advantages. The use of fuel cells permits greater ranges than battery-operated electric vehicles due to the separation of energy converter and energy storage. A significant obstacle to the introduction of fuel-cell-powered vehicles, however, is the still unclarified question of the "appropriate" fuel. The direct use of hydrogen is rather a medium- to long-term perspective due to the low storage density of currently available hydrogen stores and on account of the lack of a hydrogen infrastructure and large renewable potentials. Transition solutions available in the medium term could be methanol- or hydrocarbon-fuelled fuel cell drives, such systems must be equipped with a fuel gas generation system for the on-board production of hydrogen.

Conceptual design vehicles with fuel cells confirm worldwide activities for the development of fuel cell vehicles. Interest has been centred in the past on vehicles with hydrogen and methanol in the tank; the use of fuel cell systems based on hydrocarbons is under development but has not yet been demonstrated in vehicles.

Figure 4 shows results from different studies in terms of estimated fuel economies of compact vehicles and compared with a Mercedes-Benz A-Class vehicle for gasoline (ICE), diesel (ICE) and hydrogen (FC-NECAR 4).

3 Well-to-Wheel Analyses

For a comparative evaluation the following Table 1 shows data for future hydrogen- and methanol-fuelled fuel cell vehicles on the basis of analyses by Research Centre Jülich [GRUBE et al 2001] in the new European driving cycle comparing them with an assumed gasoline-fuelled passenger car with internal combustion engine of the future (2005/2010). The balances include the energy requirements and the emissions of the upstream fuel cycles (well-to-tank) and of the vehicles in the reference driving cycle EURO 4 (tank-to-wheel).

In the well-to-wheel evaluation after [GRUBE et al 2001] in Table 1, directly hydrogen-powered FCV have advantages compared with ICE-LDV in terms of primary energy consumption as well as greenhouse gas emissions. The reference LDV is an LDV consuming 5 litres of gasoline per 100 km in the European driving cycle. The advantages are smaller for methanol-fuelled FCVs, but these are near-zero emission vehicles (PZEV).

Table 1: *Balances: future power trains and fuel supply at filling stations (after [GRUBE et al 2001] Research Centre Jülich); electricity mix and natural gas mix in Germany; methanol and hydrogen production in Germany; CH2 = compressed hydrogen*

Oil – Gasoline – ICE	PEC MJ/100km	CO_2 kg/100 km
Gasoline at the station	29	1.7
LDV: 1064 kg EURO 4	153 (22 %)	11.1
Balance	182	12.8
Natural Gas – Methanol – PEFC	PEC MJ/100 km	CO_2 g/100 km
MeOH at the station	69	3.0
LDV: 1257 kg << EURO 4	125 (30 %)	8.8
Balance	194	11.8
Natural Gas – CH_2 – PEFC	PEC MJ/100 km	CO_2 g/100 km
Compressed hydrogen at the station	50	8.3
LDV: 1164 kg ZEV	91 (39 %)	0
Balance	141	8,3

The comparison of different studies concerning well-to-wheel analyses does not show any reference to cost structures (exception: [MIT 2000]) and provides different answers in terms of greenhouse gas emissions because of

- different driving cycles,
- different fuel supply patterns (transport and energy),
- different reference vehicles (ICE)
- different time horizon
- different development stages for FCVs.

Some of the results from different studies are presented in Table 2 (other studies see references). It can be said that:

- there is a high CO_2 reduction potential for hydrogen-powered fuel-cell vehicles in comparison to gasoline-driven vehicles with internal combustion engines (ICEs) (hydrogen on the basis of natural gas).
- the CO_2 reduction potential of methanol-powered fuel-cell vehicles is lower compared to the above comparison and disappears altogether if the comparison is made with a future diesel-driven ICE vehicle [GRUBE et al 2001, MIT 2000], nevertheless it has limited emission advantages compared with gasoline-operated ICEs (methanol on the basis of natural gas),
- major differences between the studies result from the different assumptions for the reference vehicle (gasoline-based ICE) with ~ 5 $l_{gasoline}$/100 km for 2010 after [GRUBE et al 2001], ~ 8 $l_{gasoline}$/100km (2002 baseline and non-hybrid ICE) but ~ 6 $l_{gasoline}$/100km (2002 baseline and hybrid ICE) after [GM 2002], also ~ 8 $l_{gasoline}$/100 km (base year 1996) but ~ 5 $l_{gasoline}$/100km (base year 2020) after [MIT],
- the developmental stage of the various vehicles considered in the well-to-wheel analyses is different and therefore not always comparable.

With respect to the vehicles discussed here, there are several H_2-operated FCVs worldwide but only one methanol-operated FCV driving on the road as a concept car, and although the reference vehicle (ICE) assumed by GRUBE would fulfil the requirement of the European automobile manufacturers' association, ACEA, for 140g/km and that of the EU for 120g/km CO_2 emissions, it is not yet ready for series production.

Table 2: *Balances: Greenhouse gas well-to-wheel evaluation of future power trains and fuel supply*

	2010		> 2010	2020		2010	
Sources	FZJ	PEH	DChr	MIT	MFCA	GM	THO
	GHG Advantage in %						
Oil – Gasoline – ICE							
LDV [MJ/100km] FZJ: 153, GM: 250-180[1)], MIT: 273 (1996) - 154 (2020) [2)]							
Balance Well – to – Wheel	0	0	0	0	0	0	0
Natural Gas – Methanol – PEFC							
LDV [MJ/100km] FZJ: 125, GM: 160-140[1)], MIT: 133 [2)]							
Balance Well – to – Wheel	8	10	18	10-48[3)]	42-39	28-12[1)]	20
Natural Gas – CH_2 – PEFC							
LDV [MJ/100km] FZJ: 91, GM: 115-105[1)], MIT: 81 [2)]							
Balance Well – to - Wheel	35	28	30	19-52[3)]	55-44	59-44[1)]	44

after [FZJ: GRUBE 2001], [PEH: PEHNT 2001], [MFC: MFCA 2002], [THO: THOMAS 2001], [GM 2002], [DChr 2000/2001], [MIT 2000], [IFP 2002]

[1)] *GM baseline 2002 for non-hybrid –ICE drives: 8,15 lgasoline/100 km, that means well-to-wheel balance = 22 kgCO2/100 km for non-hybrid –ICE drives or 16 kgCO2/100 km for hybrid-ICE drives; baseline for non-hybrid MeOH-FC drives: 160 MJ/100 km, that means well-to-wheel balance 16 kgCO2/100 km for non-hybrid MeOH-FC drives or 14 kgCO2/100 km for hybrid MeOH-FC drives (MeOH from remote NG); baseline for non-hybrid H2-FC drives: 115 MJ/100 km, that means well-to-wheel balance 10 kgCO2/100 km for non-hybrid H2-FC drives or 9 kgCO2/100 km for hybrid H2-FC drives (H2 from NG, electricity EU mix)*

[2)] *[IFP 2002] study assumes as vehicle fuel economy in MJ/100 km: gasoline ICE 238, diesel ICE 194, hybrid diesel ICE 165, H2 FCV 144*

3) *MIT: H2 hybrid FCV advantage 19 % (basis 2020) or 52 % (basis 1996) with 273 MJ/100 km for gasoline-powered LDV; MeOH-hybrid FCV advantage 10 % (basis 2020) or 48 % (basis 1996) with 273 MJ/100 km for gasoline-powered LDV*

4 Stationary use of fuel-cell systems

Fuel cells permit extremely environmentally friendly energy generation with comparatively high efficiencies. They are thus particularly suitable for decentralized stationary energy supply close to the end user. The end user market is characterized by a demand for electricity and heat so that is suitable for energy provided by the combined generation of heat and power (CHP).

The role fuel cells will play in the future will be defined by their economic efficiency and emission regulations. The key uncertainties which could limit the adoption of fuel cell technology for combined heat and power generation are fuel-cell life and the cost of the fuel cell system. The start of commercialisation of the technology will be facilitated if markets can be identified where fuel cell systems can be convincingly presented as having unique advantages that might justify higher investments.

5 Technical status of fuel cells

The potential mass markets for fuel cell systems are already provided with a range of technologies for the generation of electricity and heat. These technologies are based on well-established, fully developed and well-proven systems or on newer systems. The types of fuel cells addressed have attained different degrees of progress towards their commercial use [TAB 2001, BM 2002].

5.1 Low-Temperature Fuel Cells

The PAFC facility ONSI PC25 (IFC) has proved its technical maturity with 8000 operating hours per year and an availability of more than 90%, nevertheless the investment costs of the PC 25 of at present € 5000/kW_e are still not competitive (VDI nachrichten 14.6.2002, No. 24, p.22). The PAFC has successfully played a pioneering role in the introduction of fuel-cell systems.

Pilot plants with stationary PEFC plants already exist and are also planned. The electric power of these fuel-cell systems ranges from a few kW_e to 250 kW_e. PEFC facilities in the power range of 250 kW_e, suitable as combined heat and power stations for supplying electricity and heat to major housing developments and with a power of a few kW_e, are being studied in field tests for the residential sector.

5.2 High Temperature Fuel Cells

Internal reforming and electrochemical conversion of carbon monoxide is only possible with SOFCs and this essentially distinguishes them from low-temperature fuel cells. There is no need for extensive CO purification in front of the anode, as in the case of the PEFC. Utilization of the fuel cell waste heat means that there is no separate combustion of additional fuel to cover the heat requirements for reforming so that SOFCs offer the greatest potential for the highest achievable efficiency.

Of the MCFC facilities, the MTU *hot-module* concept (650°C) currently represents the most advanced MCFC technology. The greatly simplified integrated stack concept has led to the desired compacting of the system. The peripheral components of the system also have further potential for simplification and compacting. However, long-term experimental operation is still required to demonstrate that ageing of the stack is acceptable. Further development steps will have to provide evidence of cost reduction.

In connection with internal reforming, integrated air preheating, pressure operation, coupling to a gas microturbine and/or separation of pure CO_2, SOFC facilities (800-900°C) offer on the whole good opportunities for a future highly optimized energy conversion system. The SOFC is relatively insensitive to impurities in the fuel gas. No elaborate gas pretreatment is therefore necessary, which has a positive effect on the capital expenditure for the whole plant. In addition to the SWPC tubular concept, a planar concept (FZJ etc.) is also being explored. Cost cutting, temperature reduction and improvement of long-term stability are major tasks for the future. The maximum allowable costs for the fuel cell to remain competitive are dependent on the actually achievable difference in efficiencies between fuel cells and conventional plants. 250 kW_e facilities in the form of a CHP plant from SWPC and small facilities for buildings from SULZER-Hexis are being tested.

6 Present cost structures

Stationary power plants can be used for single houses (< 10 kW_e), housing estates (100-300 kW_e) or for on-site generation plants (> 1000 kW_e). Table 3 shows different types of stationary fuel cell systems of 100 -300 kW_e electrical power and their state of development and the cost target that has to be reached by fuel cell systems in order to be competitive.

Table 3: Specific costs, state of the art and cost targets for CHP plants with fuel cells

	PEFC (BPS)[1]	PAFC (ONSI)[2]	MCFC (MTU, Hot Modul)[3]	SOFC (SWPC)[4]
Electrical power	250 kW_e	200 kW_e	280 kW_e	100 kW_e
η_e (el. efficiency)	34 %	38 %	48 %	47 %
State of the art	Demonstration	Commercial	Demonstration	Demonstration
Spec. costs €/kW_e	~ 10,000	~ 5,000	~ 8,000	~ 20,000
Conventional CHP	**> 1000 to 500 €/kWe for < 100 to 1000 kWe**			

1) BPS: e.g. BEWAG Berlin: 250 kW_e PEFC, natural gas, co-generation system

2) ONSI: 200 kW_e PAFC, natural gas, co-generation system, cost basis: 36 plants/a

3) MTU: Hot Modul, e.g. Stadtwerke Bielefeld, RWE: 250 kW_e MCFC, natural gas, co-generation system

4) SWPC: 100 kW_e Siemens Westinghouse Power Corporation tubular SOFC co-generation system
see also e.g. 250 kWe RWE, E.ON (2003) Brennstoffzellen-Magazin 2/2002, p. 2

An example of a 200-kW_{th} fuel cell combined heat and power plant (CHP) is used here to show electricity generation costs for different concepts, also regarding CHP modernization (Table 4).

The necessary calculations of profitability and life cycle analyses are dependent on the supply structures, the operating and operator models as well as the local energy carrier situation (2,5 c/kWh for natural gas in the calculation). Due to the different electricity and heat shares of the different plant types, comparative calculations are oriented to electricity generating costs and not to investment costs at comparable heat capacity.

The examples show that merely for the generating costs and assuming the same annuity and also considering the new CHP modernization act and a heat credit that fuel-cell CHPs (Case C in Table 4) may involve capital expenditure roughly twice as high as that for conventional CHPs (Case A in Table 4). The reason for this is to be found in the different power-to-heat ratios for the same overall efficiency (power and heat: $\eta = 85\%$) and the same heat availability of 200 kW_{th}.

In spite of a legally provided bonus payment for fuel cell CHP packages, additional technology support for the first plant series (Case B in Table 4) is required to reduce costs by series production and plant simplification. The remuneration provided for in the CHP modernization law for feeding electricity into the public grid for FC-CHP < 2 MW, however, is not suffi-

cient according to empirical values to reduce the cost of industrial manufacturing processes to a competitive level. Technology support is thus also required for financing the necessary investment jumps. e.g. novel techniques for components and manufacturing processes, new materials as well as new solution approaches for FC peripherals and system integration. Additional investment assistance in industrial as well as state-funded research and development is therefore required with a long-term planning and funding horizon.

Table 4: *Calculation of electricity generating costs: CHP fuel-cell system and motor CHP package with identical thermal power of 200 kWth [after FZJ-IWV Annual Report 2001, Forschungszentrum Jülich GmbH, Jülich, IWV]*

A: Conventional motor CHP Plant 200 kW_e (η_e = 35%): investment cost 800 €/kW_e	
electricity generating cost	approx. 11 c/kWh
with heat credit (3 c/kWh)	approx. 6,5 c/kWh
with electricity bonus + electricity/heat credit	approx. 1,5 c/kWh
B: FC-CHP Plant: investment cost 10,000 €/kW_e (e.g. present PEFC/MCFC-CHP system (η_e = 50%)	
electricity generating cost	approx. 32 c/kWh
with heat credit (3 c/kWh)	approx. 27 c/kWh
with electricity bonus + electricity/heat credit + CO_2 Task	approx. 18 c/kWh
C: FC-CHP Plant 200 kW_e (η_e = 50%): investment cost 1600 €/kW_e	
electricity generating cost	appox. 11 c/kWh
with heat credit (3 c/kWh)	approx. 8,5 c/kWh
with electricity bonus + electricity/heat credit + CO_2 Task	- 2 c/kWh (profit)

7 Outlook

As a whole, the orientation of fuel cell development is characterized today by the discussion of the "appropriate" fuel (mobile application), the demonstration of the functionality of the technology in application, especially in long-time operation, the materials optimization required from the present perspective along with a reduction in costs, the possible contribution to an energy demand and emission reduction and the feasibility of market penetration (all fuel cell applications).

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BROAD PUBLIC DEMONSTRATION OF HIGH AND LOW TEMPERATURE FUEL CELLS

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Within the space of a few years, so the optimistic view of different fuel cell manufacturers, fuel cells – an innovative technology for decentralized energy supply - will be meeting a proportion of electrical energy and heat requirements, both in households and in commercial and industrial applications.

This paper describes RWE's today's efforts to integrate fuel cells of the state of the art into the supply of domestic energy, as well as to apply them in various commercial and industrial plants. Fuel cells will allow the additional potential of combined heat and power (CHP) to be provided on a distributed basis for small generation units. The aim is to conserve resources, reduce emissions and provide an inexpensive supply of energy.

1 Introduction

The concept of distributed generation (DG) has – since the power markets in Europe have been opened - transitioned during the past few years from a marketing movement by technology vendors into a mainstream option for energy planners and consumers. The initial advocacy commenced with the photovoltaic and wind energy technologies but soon expanded to the emerging technologies of micro gas turbines and fuel cells.

Although the electrical energy sector is a historically slow adaptor of innovative technology, fuel cells are - like a "disruptive wave" technology - rapidly embraced by all quarters of the market. The rise in the interest in fuel cell markets is noted in Europe and North America and particularly in Japan. Companies are joint venturing to cover all geographic markets with their technology.

Starting in 1991 with first activities in collaboration with mtu and other companies concerning the development of MCFC fuel cells RWE has gained already a lot of experience in testing and operating CHP-systems based on fuel cell technology. Now the former fuel cell project of the RWE Group has been transformed into a new company which is based in Essen.

2 RWE Fuel Cells GmbH

RWE as one of the biggest provider of energy and energy services in Europe developed the new RWE Plus subsidiary RWE Fuel Cells GmbH as an independent company from the fuel cell project of the Group in March this year.

The tasks of the new company are

- coordination, control, and development of the fuel cell business within the RWE Group;
- development and marketing of products, systems and services based on fuel cells;
- operational support and integration of RWE companies and/or subsidiaries regarding fuel cell activities.

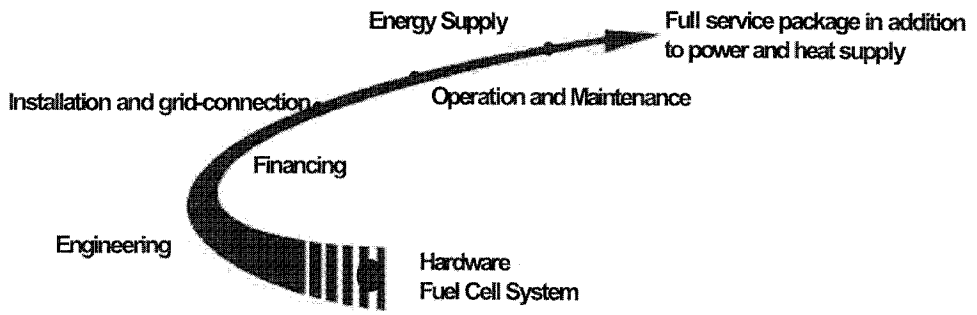

Figure 1: Fuel Cell product range

The goal is to offer expertise from a One-Stop-Shop for all possible future fuel cell products. This means that RWE and its partners will tender single source professional solutions (full service packages) on the basis of a modular service concept. This will cover the entire market – from residential units to industry and business.

To meet these targets, RWE Fuel Cells has been supplementing its own competencies through partnerships and broad demonstration of state of the art natural gas fed fuel cell technology. In different projects with fuel cell energy providing systems - based on PEMFC, SOFC, and MCFC technology– RWE Fuel Cells and its partners are preparing the market introduction for residential, commercial and industrial applications. Here industrial MCFC and SOFC applications within a power range of approximately 100 to 5000 kW_{el} are expected to supply power, heat, steam, and air cooling, whereas smaller PEM and SOFC within a range of 1 to 50 kW_{el} shall provide power, heat and air conditioning for residential and commercial applications in e.g. single homes, multiple dwellings, shops, and stores.

3 The Meteorit demonstration site

The main RWE demonstration projects can be observed by the public all day long in an glassy pavilion at the Meteorit site in Essen. The "Meteorit" demonstration pavilion was opened on August 17, 2001, after a construction time of less than 8 months. Already in June 2001 an atmosperic SOFC from SiemensWestinghouse Power Corporation (SWPC) with an electrical output of 100 kW had started its operation at this site. This plant had been operated in Arnheim, NL before and continued operation in Essen without modification. The total amount of operation hours until shutdown is about 20.000. After this experience the preparations to replace the atmosperic plant by a pressure charged 300 kW SOFC unit with downstream micro gas turbine - also from SWPC - already have begun. The exchange shall be finished until the end of 2002. This plant will be the first of its type connected to the grid and is expected to operate for 4 years.

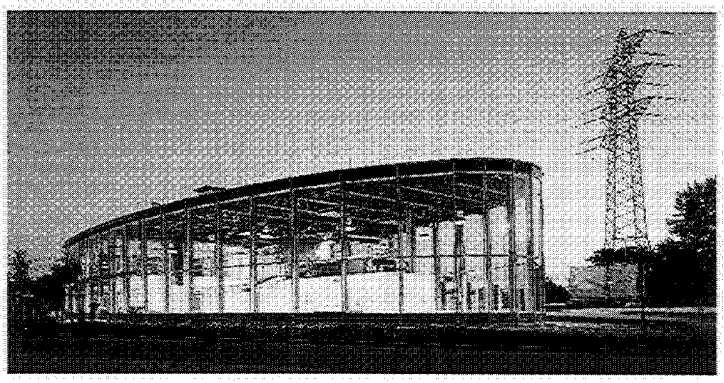

Figure 2: "Meteorit" demonstration pavilion

The pressurized SOFC plant is designed for a total electrical output of approx. 300 kW. Approx. 80 % of the power will be generated by the SOFC, the remainder by the gas turbine. The electrical net efficiency will be close to 60%. The overall efficiency value of >80 % is typical for CHP plant. Further improvements in efficiency are conceivable, for instance by improving the gas turbine efficiency.

Another fuel cell plant with 250 kW electrical output has been installed in May 2002. It is a MCFC of MTU Friedrichshafen, who, beside of FCE, Hitachi and Mitsubishi Electric is one of the leading manufacturers of MCFCs.

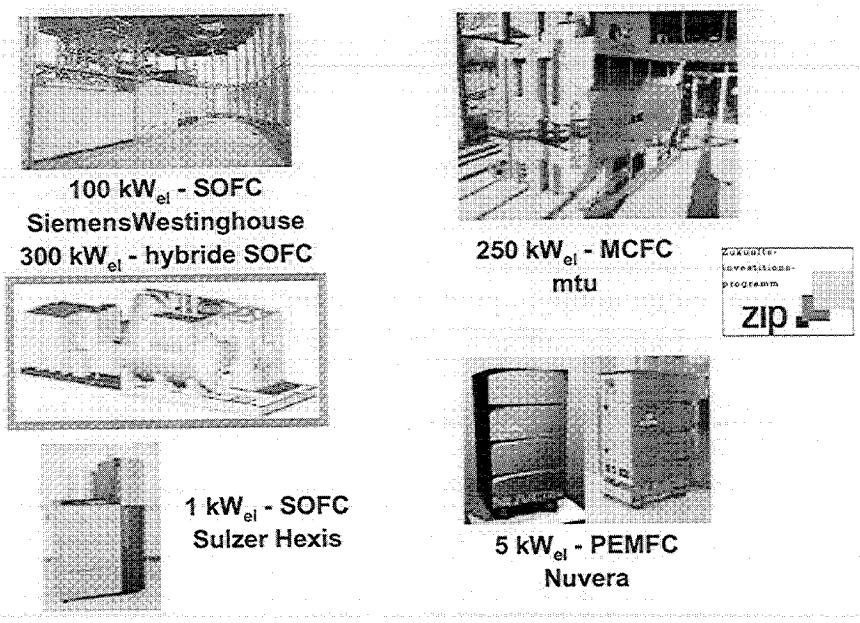

Figure 3: Fuel Cell Demonstration at the Meteorit site

RWE previously had joined forces in 1991 with MTU, Elkraft and Ruhrgas for the development of MCFCs. An electrical efficiency of 48 % has been achieved to date, a target of 50% is set for the near future and 55% in the medium term. The first field plant commenced operation in Bielefeld in October 1999. That plant benefited from experience gained in a demonstration plant in Dorsten. Another field plant has been operated in Germany at Rhön Klinikum in Bad Neustadt/Saale successfully since May 2001 before the Meteotit prototype started operation. All mentioned field test units are designed to have an electric output of 250 kW.

The Meteorit pavilion also contains smaller fuel cell installations that may be used in future decentralized energy providing concepts for single and multi-family houses. There are 2 main types of fuel cells for domestic supply: the PEM cell and the planar SOFC. The leading suppliers include Sulzer-Hexis (SOFC) and e.g. Nuvera (PEM). RWE demonstrates both types. A first Nuvera "Power stream" test unit was installed in February 2002 and is used to gain more experience in operation, grid connection and in the adaption to European standards. It will be followed by a first prototype "Avanti" unit in late 2002 that will be more powerful and more reliable even though it will have only half of the size of the Power stream unit. Avanti units are designed to supply 5 kW of electic power and about 7 kW thermal power.

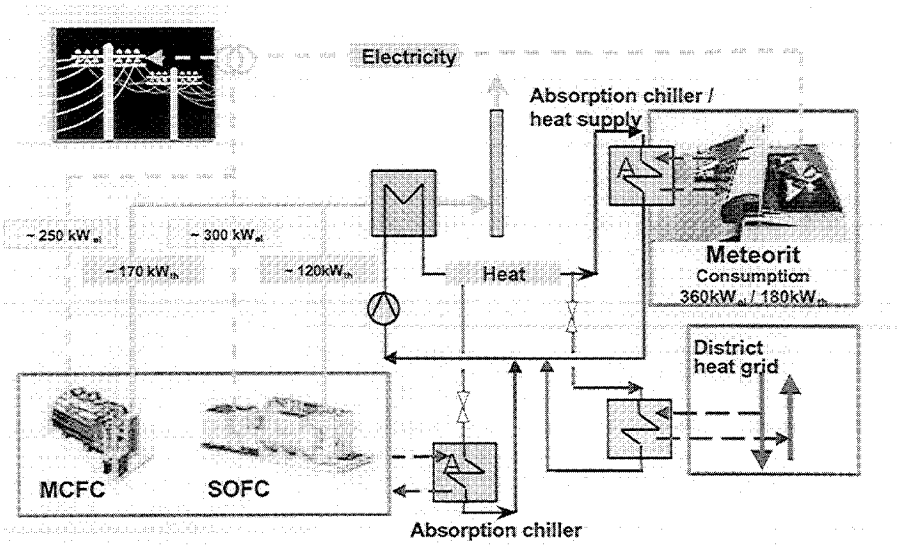

Figure 4: Heat and power used at the Meteorit site

A 1 kW electric power providing Sulzer Hexis unit has been installed in the pavilion too in May 2002. This unit is tested as part of a huge field test that Sulzer Hexis has started in 2001. It is the first fuel cell at all that probably may fulfill the energy needs of new single houses in the future.

All fuel cell demonstration plants are integrated into the Meteorit energy supply system. This means that the generated electricity is used to supply the needed 360 kW for Meteorit's electrical equipment. Excessive electricity is fed into the grid. The generated heat can be used in different alternative ways, for district heating or for heating/cooling purposes at the meteorit site.

4 Further demonstration projects

Additionally to the Meteorit demonstration units RWE and its partners and subsidiaries are gaining more experience in different special applications at different other sites all around Germany. In the residential energy supply area this are Sulzer Hexis SOFC units that are tested by Thyssengas primarily and Nuvera units at the Meteorit site and in Mechernich, another RWE location.

Bigger SOFC units are demonstrated at the Meteorit site only, whereas MCFC units are expected to take place at different sites in first customer applications. For example a 250 kW MCFC will be used for district heating of a new housing stock. Other units are planned to be built and operated in Ensdorf and Grünstadt. All MCFC units are part of the MTU field test and are promoted by the German government: Within the framework of the ZIP – (Future Investment Programme) Promotion of the German Ministry of Economics subsidies are granted.

Another demonstration site, the Delegate's Residence of North Rhine Westfalia in Berlin, is used to test the seperate installation of a micro gas turbine and a fuel cell to provide the needed heat, cold and electric power. Additionally, in summer, an absorption chiller will be operated. The micro gas turbine is expected to start operation in late 2002 and the fuel cell to follow in 2003. Both units will have an electrical output of 30 kW each. The fuel cell will supply 30 kW thermal energy too and the micro gas turbine 60 kW.

Based on this experience it is perfectly imaginable that - in a few years time - RWE will install a fuel cell in the cellar and the customer will receive electricity, heat and further services in the form of a complete package. Co-operation with regional suppliers of electricity and gas, such as municipal utilities, can offer considerable advantages as customer access is an important component when developing new markets for CHP applications. Within the framework of such co-operation activities RWE could provide the complete know-how from its ongoing fuel cell activities, especially with respect to operation and services.

5 Potential of Fuel Cells for Distributed Generation

Based on own studies RWE expects the power production from distributed generation in Germany to double for 2015. This means that a share of 30 % could be reached. Coincident assuming positive framework conditions there is a considerable market potential for fuel cells of approx. 10 % of electricity generation in Germany up to the year 2015 in the optimistic view.

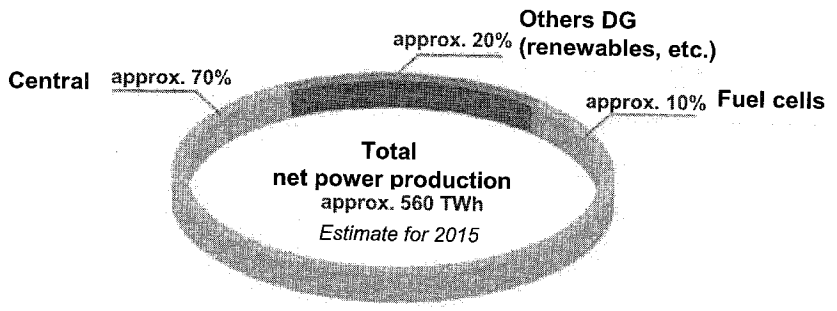

Figure 5: Power generation in Germany in 2015

In detail this means for residential systems in Germany a range of 1,000 - 3,000 MW, for commercial / industrial systems 2,000 – 8,000 MW and in total a fuel cell capacity of 3,000 – 11,000 MW effecting a total possible CO2-reduction of up to 50 Mio. t/a compared to today's coal fired power plants. Related to the European market there could be an accessible market potential for the most important EU countries of more than 40,000 MW in 2015, while the possible installed fuel cell capacity is estimated to be in the range of 10,000 – 30,000 MW. These data is explained by various underlying development scenarios.

The marketing strategy developed by RWE can be described as follows:

- Co-operation with manufacturers in demonstration projects
  - Acquisition of relevant know-how early on for the operation and maintenance of decentralized fuel cell installations and their integration into existing electricity grids
  - Product development closely tailored to customer requirements
- Use of existing marketing networks and customer access routes
- Comprehensive range of products and services
- Partnerships with communal suppliers of energy
  - Uniform image of supply company and onward distributors
  - Common products and marketing concepts to ensure autonomy and safeguard sales potential

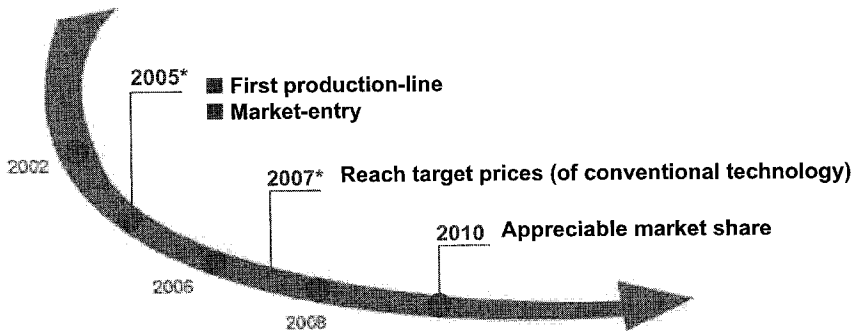

Figure 6: Development of Fuel Cells

Based on manufacturers indications the further development of fuel cells for residential, commercial and industrial applications will continue with first product-lines and market-entries in 2005 earliest. If so, we will be able to reach target prices (of conventional technology) in about 2007 and an appreciable market share in 2010. The speed of fuel cell development is high grade depending on industrial and political support. The more subsidies are granted during the market entrance period the earlier people can take advantage of fuel cell products.

6 Conclusions

Because of their very high fuel efficiencies, fuel cells can be used in small-scale decentralized CHP systems for the generation of electricity and heat with a low environmental impact which cannot be matched. They are bound to attain a market share in the future – the question is how quickly the new technology will become established.

RWE Fuel Cells as the competence and business center for innovative decentralized energy providing systems within the RWE Group already has started to develop energy solutions and services for industrial use as well as for the residential and business area.

The launch of natural gas operated fuel cells on the market, according to manufacturers indications, is expected within the next few years. RWE and it's partners are preparing the market entry by broad public demonstration of the most essential technologies. The point at which use becomes profitable will depend on the number of units produced. The creation of suitable political framework conditions, for instance in the form of initial financing, can substantially accelerate the implementation of fuel cells within various market segments.

RWE has gained considerable expertise in the testing of different types of fuel cells and the development of suitable CHP-based energy applications and services for its customers. This will allow the existing market potential for decentralized fuel cell applications to be exploited at an early date. An important aspect of market launch is the access to the existing customer base, which RWE already has because of its established supply framework.

RWE's target is to provide energy to our customers in a manner, which has a low environmental impact, but is profitable, and in particular to satisfy the needs and desires of our existing and new customers and to act in concert with our partners to improve environmental conditions.

INTEGRAL POWER CONDITIONER FOR GRID CONNECTED FUEL CELL SYSTEMS

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ABSTRACT
The paper introduces the HYDRO BOY® inverter dedicated to the connection of "Fuel Cell based Combined Heat and Power" generators (FC-CHP) for residential premises to the public grid. The technical realisation and the operational behaviour of the HYDRO BOY® are presented. The integration of several functions and components of an FC-CHP system into an Integral Power Conditioner for grid connected fuel cell systems is described as an effective approach to cost reduction.

1 INTRODUCTION

The use of "Fuel Cell based Combined Heat and Power generators" (FC-CHP) for residential premises is a very promising future market. In combination with water electrolysis and hydrogen storage the FC-CHP is an elementary component for the decentralised power supply of the future which will be characterised by a high content of renewable energy. In order to bring in the existing know-how and expertise SMA Regelsysteme GmbH has gained in the last 20 years in the area of decentralised power supply the HYDRO BOY inverter family for fuel cell applications has been developed. The suitability for practical use of the HYDRO BOY 1000 (the 1000 W inverter version) is currently being evaluated in a field test. In this field test carried out by SULZER HEXIS some hundred FC-CHPs (HXS 1000 Premier) including HYDRO BOYs are going to be put into operation [1].

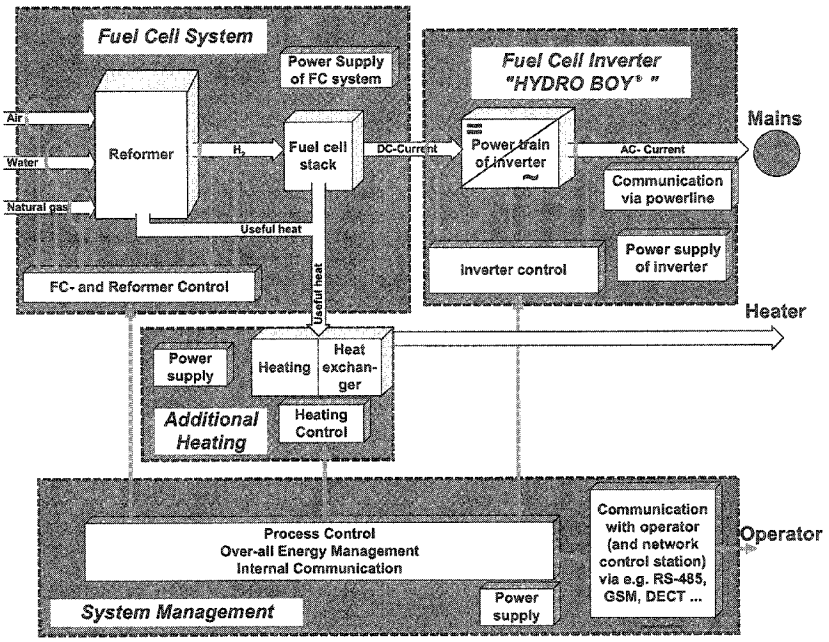

Figure 1: *General Structure of a Combined "Fuel Cell based Heat and Power" generator (FC-CHP) for residential premises using a HYDRO BOY®*

Figure 1 depicts the general structure of such a FC-CHP. Most of today's FC-CHP systems comprise many independent components including fuel cell, reformer, additional heating (for peak heat demand), grid-connected inverter and system control unit. For SOFC-CHP or FC-CHP using hydrogen as energy carrier the reformer is not necessary. The nominal DC power of the fuel cell in such an FC-CHP for typical one-family houses or apartment buildings ranges from 1 kW_{el} to about 6 kW_{el}. In the following the inverter is described in some detail.

2 REQUIREMENTS FOR FUEL CELL INVERTERS AND CORRELATIONS WITH INVERTERS FOR PHOTOVOLTAIC APPLICATIONS (E.G. SUNNY BOY®)

A systematic comparison of the requirements for inverters for grid connected FC-CHP and photovoltaic (PV) applications shows that PV and fuel cell (FC) applications are very similar. Fuel cells and solar cells are both DC power sources of a modular type with load dependent cell voltage. The nominal power of the source can be selected by serial (and / or parallel) connection of cells.

The general requirements for grid-connected inverters for FC and PV applications are:

- Grid-tied operation of inverter for optimal use of electricity
- Mains monitoring e.g. V_{AC} and f_{AC} supervision and / or monitoring according to DIN VDE 0126.
- High reliability and long lifetime (PV > 20 a)
- Very high electrical efficiency due to high costs for generation of DC power.
- Electromagnetic compatibility according to EN 50081 and EN 50082.
- Wide input DC-voltage range of at least 1 : 2 due to VI characteristic of DC-Source (FC or PV).
- Small ripple of DC-voltage for maximum electrical energy yield and lifetime of FC.
- Earth fault detection.
- Communication capability for monitoring purposes.
- Dynamic requirement for load changes and disturbances caused by the connected grid.

The specific requirements for an FC inverter are:

- Mechanical and electrical integration into the FC-CHP system.
- Controllability by a superimposed power supply network control centre ("virtual power plant").
- Heat recovery of inverter losses to be fed back into the heating circuit.
- Small size.
- Protection class IP00 is sufficient in most cases.

15 years ago at the time of introduction of grid-connected PV plants the field test components of PV plants showed a high failure rate. In the past a lot of effort has successfully been spent in order to improve the reliability of PV systems. The development of FC inverters can benefit from these lessons learned in the PV industry in recent years. This is possible due to the very good correlation between requirements for FC and PV inverters shown above. Therefore SMA Regelsysteme GmbH based the development of the FC inverter on serial PV inverters in order to bring in experience of about 15 years in which period more than 50,000 inverters were built for PV applications.

3 HYDRO BOY® - THE INVERTER FAMILY FOR GRID-CONNECTED FUEL CELL APPLICATIONS

As yet the HYDRO BOY inverter family has two members: HYDRO BOY 1000 and HYDRO BOY 2000 with a nominal power of 1 kW and 2 kW respectively. Due to the modular design the HYDRO BOY can easily be adapted to any FC-CHP power.

3.1 TOPOLOGY

In order to meet the above requirements the inverter topology shown in Figure 2 using a line frequency transformer and an H-bridge has been chosen for the inverters of the HYDRO BOY family. A systematic investigation of topologies published in [2] has shown that line frequency transformer topology will be the dominating topology for PV applications in the medium-term. This topology has advantages compared to transformerless topologies and topologies with high-frequency transformers among others in terms of robustness, cost effectiveness and high efficiency for a wide input voltage.

3.2 TECHNICAL REALISATION

Due to the high similarity of PV and FC applications the HYDRO BOY design is based on Europe's best-selling photovoltaic inverter SUNNY BOY® [3]. Therefore the HYDRO BOY fuel cell inverter benefits from many experiences gained in operating more than 50,000 photovoltaic inverters in the harsh environment of grid-connected PV plants. Additionally many components of the SUNNY BOY can be used. Due to the high efficiency and the good thermal design of the components no fan cooling is necessary. However, the design offers the opportunity of liquid cooling of the dissipative components if desired.

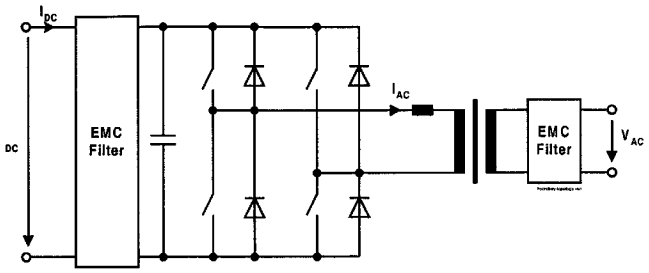

Figure 2: *Simplified topology of fuel cell inverter HYDRO BOY®*

The inverter control unit of the HYDRO BOY consists of a double µ-controller system using state-of-the-art components like Digital Signal Processors (DSP).

3.3 CONTROL

The HYDRO BOY inverter offers a wide range of control modes, which can be selected via software according to the customer's needs. The default values for all controller parameters have been calculated to guarantee stable operation with high dynamic performance. Typical control modes for fuel cell operation are:

- DC voltage control: Terminal voltage of fuel cell stack is controlled including overcurrent protection.
- DC current control: Fuel cell current is controlled.
- Power Control: Either DC-power supplied by the fuel cell or AC-power fed into the grid is controlled.

In each case the setpoint value is provided by the superimposed system management unit of the FC-CHP system. Overvoltage and undervoltage protection to prevent fuel cell and inverter from damage are included. The line current control guarantees sinusoidal line currents.

The high speed control of the inverter's state variables is realised in a DSP. Additionally any customer-defined control algorithms can be implemented. Due to the high capability of the DSP and associated µ-controller there is still enough space to perform the remaining control tasks of the FC-CHP without extra costs for hardware.

3.4 EFFICIENCY

The electrical efficiency is a very important criterion for the evaluation of FC-inverters. Therefore, Figure 3 shows the efficiency curves of the HYDRO BOY inverter for different input voltages (V_{DC}). The first generation HYDRO BOY already reaches a maximum efficiency of 93.3 %. This is slightly higher than the efficiency of an FC inverter using a high frequency transformer [4]. However, the comparison with PV inverters in the corresponding power range shows that an increase of the maximum efficiency up to about 95 % is possible. The shape of the inverter's efficiency curve is currently being optimised for fuel cell applications by shifting the maximum point of efficiency from partial load towards nominal load.

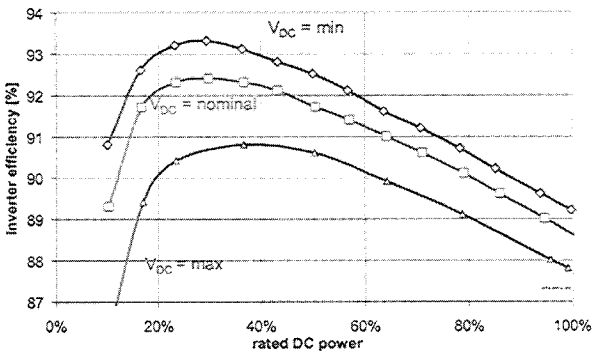

Figure 3: *Efficiency of a HYDRO BOY® inverter prototype as a function of the DC power for different input voltages*

4 INTEGRAL POWER CONDITIONER FOR FC-CHP

The general structure of a typical FC-CHP system presented in Figure 1 shows that many functions (e.g. power supply or control) are included in each of the subsystems, i. e. fuel cell, heating, inverter and system control. This situation bears a substantial potential for cost reduction of FC-CHP systems which is one of the main goals for further development.

As part of the cost reduction campaign SMA Regelsysteme GmbH introduced the Integral Power Conditioner in order to cut costs in FC-CHP system technology. The costs of an FC-CHP system can be reduced with lower material costs or shorter assembly time. Additionally, using an Integral Power Conditioner the R&D effort can be minimised and development time can be reduced due to the minimum number of interfaces.
Besides the overall system efficiency and reliability can be improved due to the reduced component count and a minimum number of power supplies operating.

FC-CHP systems are developed either by heating manufacturers and fuel cell manufacturers or dedicated FC-CHP system assembly houses. Depending on the FC-CHP manufacturer's philosophy and resources the level of integration of the proposed Integral Power Conditioner will differ.
For reasons of brevity only one of the numberless possibilities is presented. Figure 4 shows a high level Integral Power Conditioner where the following integration measures have been applied:

Power Supplies
All power supplies have been integrated into one universal power supply for all electronics, pumps and vents. This power supply has an optional UPS functionality.

Control
Comparing Figure 1 and Figure 4 one can see that the control structure of the FC-CHP has been rearranged. Due to the high capability of the DSP and associated µ-controller (see Figure 5) all these control tasks can be performed by the HYDRO BOY's controllers without extra costs for hardware. The decentralised controls have been combined into a powerful control unit divided into two parts. The "Process-oriented Control and System Management" block is responsible for all high speed control tasks and triggering of the different actuators (e. g. relays for pumps and vents). These tasks are taken over by the DSP.

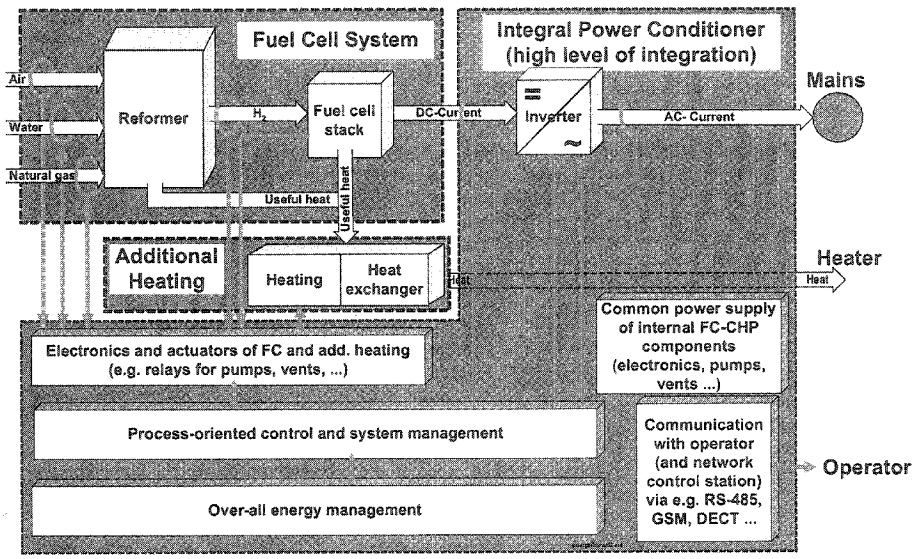

Figure 4: *Structure of a Combined Fuel Cell based Heat and Power Generator for residential premises using an Integral Power Conditioner*

The superimposed "Over-all Energy Management" is responsible for determination of the corresponding setpoints for the "Process-oriented Control" in order to achieve optimum operation of the FC-CHP in terms of over-all system efficiency and lifetime of the critical components (i. e. fuel cells). It also carries out the general monitoring and control tasks.

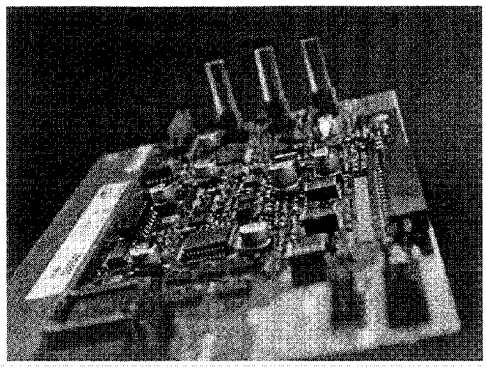

Figure 5: Controller Unit for Integral Power Conditioner using DSP and associated µ-controller

Communication

Finally the "Integral Power Conditioner" supports communication with the operator, the maintenance personnel or a central network control centre if the system is operating as part of a virtual power plant. Any communication module depending on the requirements can be included: display, serial data link (RS232, ...), modem, wireless communication (e.g. DECT, GSM) or the Internet.

Thermal integration

In order to increase the over-all system efficiency the losses generated in the power electronics are fed into the heating circuit by liquid cooling of the dissipative components of inverter and power supply.

5 CONCLUSIONS AND OUTLOOK

The paper introduces the HYDRO BOY® inverter family dedicated to the connection of "Fuel Cell based Combined Heat and Power generators" (FC-CHP) for residential premises to the public grid. The systematic evaluation of the requirements for fuel cell inverters has shown a very close relation to inverters for photovoltaic applications. Therefore, further development of fuel cell inverters can benefit from the experience and know-how gained in the field of grid-connected photovoltaics. The technical realisation and the operational behaviour of the HYDRO BOY® have been described. In the field test carried out by SULZER HEXIS in collaboration with international power supply companies a few hundred FC-CHPs "HXS 1000 Premiere" including HYDRO BOY 1000 inverters are going to be put into operation in 2002 and 2003.

Future work will deal with the integration of several functions and components of an FC-CHP system into the "Integral Power Conditioner" for grid connected fuel cell systems. This will pave the way to future cost reduction and an increase of over-all system efficiency. The development of an additional UPS functionality for the fuel cell inverters will allow the FC-CHP to supply selected electric loads in times of black-outs.

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Fuel Processing

MULTI-FUEL REFORMER FOR SOFC TECHNOLOGIES IN STATIONARY AND AUTOMOTIVE APPLICATIONS

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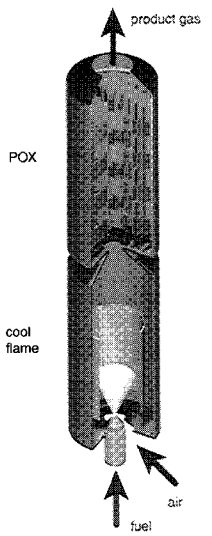
ABSTRACT

In the field of fuel cell technology different fuel cells will reach the break-even point in the next future. In consideration of the fuel infrastructure liquid hydrocarbons like gas oil, diesel, liquid gas or gasoline as well as Fatty Methyl Ester (FAME) will play an important role in the commercialisation of fuel cell systems. In many fuel cell applications the usage of liquid hydrocarbons is inevitable. Liquid fuels offer high storage densities and an already existing infrastructure. In automotive appliances like auxiliary power units (APU) fuel cell systems facilitate high engine efficencies by decoupling all electric devices from the motoric propulsion. CHPs without an available infrastructure like a natural gas pipeline have to use gas oil or liquid gas as an energy carrier. Due to the low purity demands on the feed gases the SOFC-technology offers a simple technology of fuel processing and allows the development of multi-fuel purposes.

The Oel-Wärme-Institut (OWI) has developed a fuel processor to convert liquid fuels into a hydrogen and carbon monoxide rich gas (Fig. 1). The fuel processor based on catalytic partial oxidation (CPO) is designed for feed supplies equal to a power from $P = 1$ kW up to $P = 12$ kW thermal input. To avoid high expenses the fuel processor is able to run without supply of steam. In high temperature fuel cells, the gas mixture produced by POX can be used to generate electrical current directly. Likewise carbon monoxide participates in the fuel cell reaction. This way the gas preparation is substantially simplified.



INTRODUCTION

The growing interest in the environmental and efficiency characteristics of fuel cells pushes the development to bring this new technology to the market. Various fuel cell technologies are presently under development, the most evident difference being their operating temperature and the reformer technology. Currently the most highly developed and commercially available processes for hydrogen synthesis use natural gas. In consideration of the fuel infrastructure liquid hydrocarbons like gas oil, Diesel, liquid gas or gasoline as well as fame will play an important role in the commercialisation of fuel cell systems. In many fuel cell applications the usage of liquid hydrocarbons is inevitable. Liquid fuels offer high storage densities and an already existing infrastructure. In automotive appliances like auxiliary power units (APU) fuel cell systems facilitate high engine efficencies by decoupling all electric devices from the motoric propulsion. CHPs without an available infrastructure like a natural gas pipeline have to use gas oil or liquid gas as an energy carrier. Due to the low purity demands on the feed gases the SOFC-technology offers a simple technology of fuel processing and allows the development of multi-fuel purposes.

FUEL PROCESSING OF LIQUID FUELS

Two different ways to produce hydrogen from fossil fuels can be distinguished. Current applications of fuel cell technology within the energy industry only make use of natural gas or methane to produce hydrogen by steam reforming. For hydrocarbons with boiling ranges above 220 °C this procedure is not implemented as there is an increasing tendency for soot to be formed [Pich65], in particular this is caused by an unsatisfactory air/fuel mixture of liquid fuel and air. Long chain hydrocarbons are therefore synthesised into carbon monoxide- and hydrogen-rich gases by exothermic partial oxidation (POX) by the addition of oxygen. Through supply of water vapour in the process the hydrogen yield can rise (autothermal reforming, ATR). However water vapour is included in the system the water treatment means high expense of the system and requires additional space which is especially in automotive applications well limited (Fig. 2).

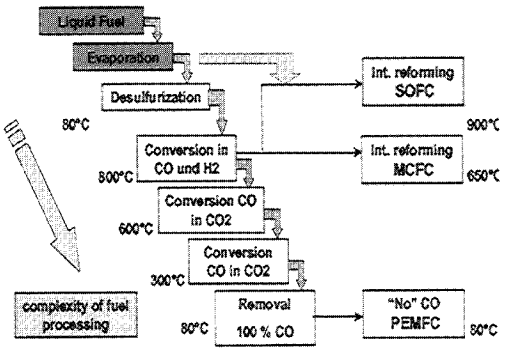


Figure 2: Complexity of fuel processing in dependence of the fuel cell system [Schu00]

Reforming catalysts are sensitive on sulfur compounds in the fuel. The sulfur tolerance given by catalyst developers lies at ξ_s = 30-50 ppm for ATR. For IGO a hot-gas desulfurisation has to be implemented anyway. For new diesel qualities related to new European legislations it seems to be possible that for high temperature fuel cells no desulfurisation has to be implemented. For PEM cell technology a desulfurisation is mandatory. Steam reforming is strongly endothermic whereas POX is exothermal. The autothermal reforming can be classified between both methods. In all described processes the hydrocarbon reforms catalytically at around 800 °C to form hydrogen and carbon monoyde.The reforming efficiency is a quantitative value which gives information about the energy content of the product gas after fuel processing. In this paper the reforming efficiency η_{Ref} is defined as the ratio of the heating value of product gas to fuel (Eqn. 1). The data for the fuel $H_{u,Fuel}$ and hydrogen H_{m,H_2} are based on the lower heating value (LHV).

$$\eta_{Ref} = \frac{\dot{n}_{H_2} \cdot H_{m,H_2} + \dot{n}_{CO} \cdot H_{m,CO}}{\dot{m}_{Fuel} \cdot H_{u,Fuel}} \tag{1}$$

The quantities for hydrogen and carbon monoxide have been calculated by thermochemical equilibrium by minimizing the Gibb´s Enthalpy using the Chemkin database. With a fixed reforming temperature of 800 °C the reforming efficiency for industrial gas oil (IGO) is given as a function of the air ratio λ and the steam to carbon ratio *SCR* in the left diagram of Fig. 3. The heat that has to be supplied or discharged of the process is given in the right diagram of Fig. 3.

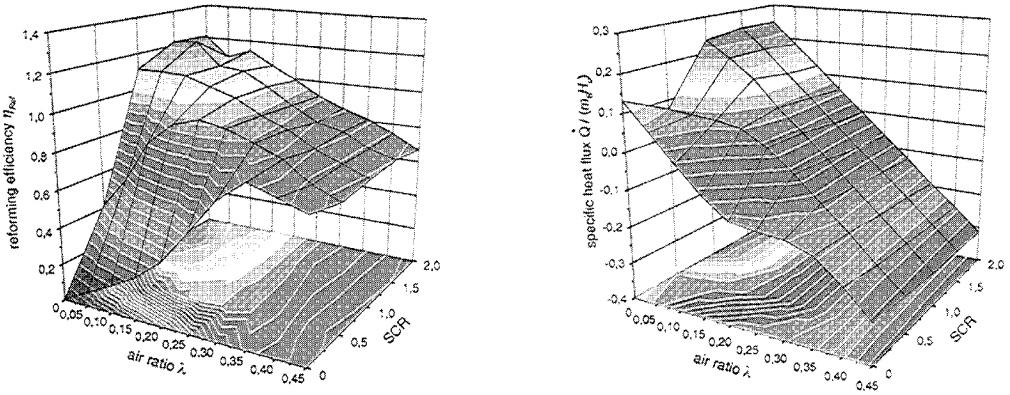


Figure 3: Reforming efficiency (left) and specific heat (right) for iso-thermal fuel oil reforming at 800 °C [Hart02]

Best reforming efficiencies are reachable for steam reforming when no air is supplied ($\lambda = 0$, $SCR = 1.5$). The heating value of the product gas is more than twenty percent higher as the feedstock. The specific heat needed for the process is fourth to the fuel heating value. Autothermal conditions are reached when the specific heat flux has negligible amounts for example for $\lambda = 0.35$ and $SCR = 0.5$. In these operation points about 85 % of the fuel heating value remains in the product gas. At pure POX conditions without water supply ($SCR = 0$) the reforming efficiency amounts to almost 78 %.

For low temperature fuel cells like PEM fuel cells steam has to be involved due to shift reactions necessary to prevent membrane poisoning by CO. For high temperature fuel cells the addition of steam is not necessary. The gas mixture produced by POX can be used to generate electrical current directly. Likewise carbon monoxide participates in the fuel cell reaction. This way the gas preparation is substantially simplified. This leads directly to a lower system complexity of the fuel processing for high temperature fuel cells (see Fig. 3).

COOL FLAMES FOR THE EVAPORATION OF LIQUID FUELS

The generation of the mixture constitutes a key factor in terms of the quality of a reaction. It is easier to produce mixtures in pre-mixing combustion systems for gaseous fuels, since two gaseous substances are being mixed. Liquid fuels, however, such as IGO, first have to be atomised and vaporised into microscopically sized droplets. At present, the pre-mixing technology for liquid fuels does not correspond to the state of the art. Temperatures above 400 °C, however, are required, since the upper boiling point of IGO lies between 380 °C and 400°C. With direct vaporisation, it is possible to atomise the fuel in a pre-heated air stream, where it can be fully vaporised by supplying additional heat. Through having to use high temperatures auto-igniting of the mixture can not strictly be avoided.

By using pre-reactions in the form of cool flames it is possible to realize a complete and residue-free evaporation of liquid hydrocarbon mixtures. Cool flames are exothermal pre-reactions which can be initialised when a liquid hydrocarbon is atomised into preheated air stream. As a result of the exothermal process the gas temperature rises (Fig. 4). The reaction mechanism of cool flames is temperature-limited. The key to the production of cool flames lies in the lack of stability of the links formed within the chain reactions as a result of oxygen being absorbed. That means that by achieving gas temperatures of approximately 480 °C further reactions of the mixture are limited. For this reason a reduction in the preheating of the air has only a very small effect on the final temperature of the cool flame.

The phenomenom of cool flames have been validated for different fuels (see Fig. 4). It was found that the initial and final temperatures of the fuels used are virtually identical. Apart from the initial temperature of FAME, which is raised due to the boiling range of 330 °C to 340 °C, all the temperatures lie within a narrow band. The dependency of the final temperature on the air ratio is negligible.

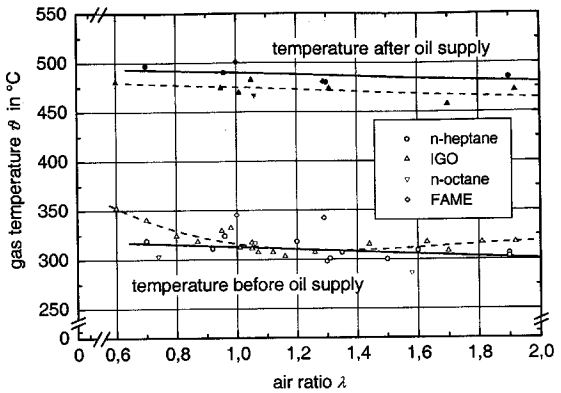


Figure 4: Influence of the air ratio on the final temperature of the cool flame for different fuels [Luck99]

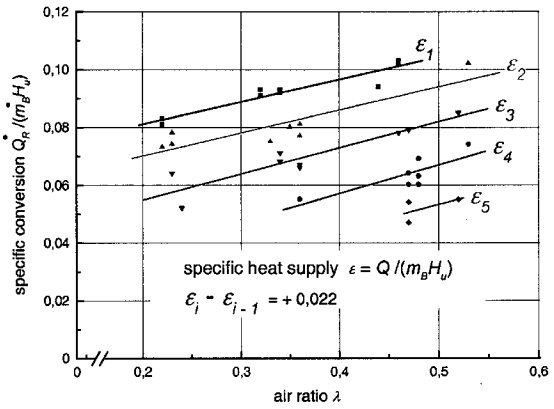


Figure 5: Reaction conversion in the cool flame as a function of the air ratio and the specific heat supply; IGO, $P = 5$ kW

After the cool flame is initialised the system runs without additional external heat. Equally the reaction conversion rises with a decrease in the heat supply (Fig. 5). Approximately eight percent of the heating value is converted in the cool flames to evaporate the hydrocarbons and to pre-heat the oil-air-mixture in sub-stoichiometric operation points when no air pre-heating is included. As a result of oxidation and decay reactions, it is mainly long hydrocarbon chains that react to form short molecules during this process. A conversion into carbon monoxide and carbon dioxide can be verified in the cool flame product.

REFORMER DESIGN

The Oel-Wärme-Institut (OWI) has developed a fuel processor to produce fuel cell suitable gases by using industrial gas oil, diesel or gasoline as well as renewable fuels. The fuel processor consists of two reaction chambers which are thermally decoupled as well as isolated to prevent flash back. The design of the fuel processor is shown in Fig. 1. In the first stage the liquid fuel is mixed and evaporated with the combustion air necessary for the process. The heat required for the evaporation is produced autothermically by pre-reactions of the fuel/air mixture in the form of a cool flame. This phenomenon features a complete and residue-free evaporation of liquid hydrocarbon mixtures. Auto-ignition does not result even after long residence times as the characteristics of the reaction kinetics inhibit this. The initialisation of the cool flame reactions takes place when the hydrocarbon is atomised in the preheated air stream with

$\vartheta \sim 310$ °C. Therefore an air pre-heater is provided in the set-up. The heat needed to actuate the pre-reaction can also be produced with a start-up burner. After initialisation air pre-heating is not mandatory since the internal heat management of the evaporator holds the reaction zone steady. By using cool flame for the evaporation the demand on the oil-spray quality is less than in conventional systems. Therefore low firing rates are achievable with commercially available atomising systems.

The produced homogeneous fuel/air mixture at a temperature of about 420 °C is transferred to the second stage of the fuel processor by catalytic partial oxidation (CPO) below 1000 °C. The mesuared temperatures are shown in Fig.6 with respect to time. The system is sensitive on variations of the air ratio. After 15 h on stream the air ratio has been reduced from $\lambda = 0.38$ to 0.36. Thus the temperatures in the catalyst are reduced by 80 K whereas the temperatures in the cool flames keep steady.

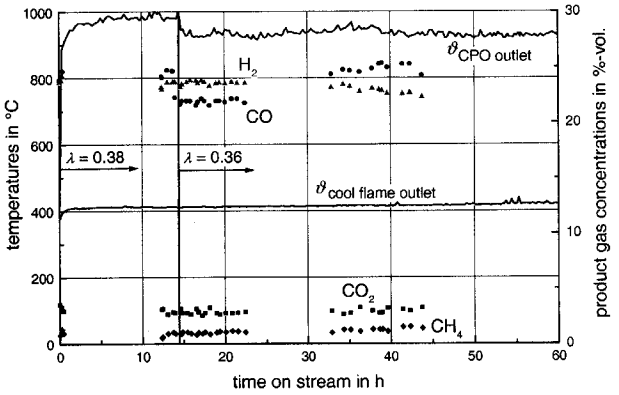


Figure 6: Measured product gas concentrations and temperatures in the fuel processor with respect to the time on stream ($\lambda = 0.38 - 0.36$, $P = 5.5$ kW, fuel sulfur content $\xi_s = 10$ ppm)

The conversion of hydrocarbons is very good. The concentrations of carbon monoxide and hydrogen reach 23 % to 24 % and are close to the equilibrium concentration. Caused by the high catalyst temperatures the overall hydrocarbon concentration is lower than 1.5 %. The formation of acetylene as a soot precursor can be neglected so that the formation of soot is avoided. Soot formation has not been detected in the evaporator or the catalyst. Carbon deposits have been found in the outlet tube which connects the fuel processor to the off gas burner. In this region where the temperature is significantly below 800 °C the conditions for the Boudouard and heterogeneous water gas reaction are favoured.

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Biofuels for Fuel Cells
- Gas Purification and Gas Processing -

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The different fuel cell types have different demands with regard to fuel gas composition and fuel gas purity. For all fuel cell types generating electricity from gasified biomass dust and tar must be removed upstream the fuel cell system. In case of liquid biofuels like bioethanol and biodiesel a reformer generates a hydrogen rich gas mixture, containing carbon monoxide, carbon dioxide, water steam and residual methane. In case of biogas, landfill gas or digester gas which mainly consists of methane and carbon dioxide and traces of different impurities, a preliminary gas purification system is necessary to protect the catalysts of the fuel processor and the fuel cell.

1 Introduction

Fuel cells are highly efficient and clean energy conversion devices that convert chemical energy directly into electrical energy. Since the beginning of the 1990s their technology is progressing rapidly in a wide range of applications in the energy sector. Fuel cell technology is under development for bulk power plants, decentralized combined heat and power production as well as for mobile applications and even battery replacement. Although the development of stationary fuel cell systems cannot keep pace with the dynamic in the transportation sector, also in this field an accelerating activity can be observed all over the globe. Main application area is the decentral power generation on the basis of natural gas. Nevertheless biofuels like gasified biomass, alcohols like methanol and bioethanol and of course biogas are very interesting and promising energy carriers for future fuel cell applications.

The different fuel cell types have different demands regarding fuel gas composition and fuel gas purity. For example for all fuel cell types generating electricity from gasified biomass dust and tar must be removed upstream the fuel cell system. In case of liquid biofuels like bioethanol a steam reformer

generates a hydrogen rich gas mixture, containing carbon monixide, carbon dioxide, water steam and residual methane. This process can be performed under elevated pressure to feed the product gas to a pressure swing adsorption unit (PSA) in order to separate pure hydrogen as fuel for the cell. The off-gas of the PSA can be used as fuel for a burner to supply the necessary heat for the reforming process. In case of biogas, which mainly consists of methane and carbon dioxide but also containing different catalyst poisoning impurities like H_2S, NH_3, chlorine and fluorine components etcetera, a preliminary biogas purification system is necessary to protect the catalysts of the fuel cell system.

2 Fuel Cells

In conventional power generation the chemical energy of the fuel is converted via thermal and mechanical energy into electrical energy. The maximum efficiency of this process, which is dependent upon the process temperature T_O and the ambient temperature T_U, is given by the Carnot efficiency:

$$\eta_C = 1 - \frac{T_U}{T_o} \ .$$

Fuel cells on the other hand are not subject to the Carnot limitation imposed on heat engines as chemical energy is converted directly into electrical energy. The principle is realized by separation of the reactants, in most cases hydrogen and oxygen, by an electrolyte. Hence, fuel cells are able to convert the fuel gas into electrical power very efficiently.

The different fuel cell types are generally classified according to their electrolyte and the respective operating temperature. Figure 1 shows the operating principle of the different systems with the respective ionic species that are responsible for the charge transport through the electrolyte, i.e. hydroxyl ions, protons, carbonate ions or oxygen ions. Also depicted is the working temperature together with the most likely field of application of each system. In the low temperature regime between 60 and 130 °C the alkaline fuel cell (AFC) and the polymer electrolyte fuel cell (PEFC) can be found. The direct methanol fuel cell (DMFC), which is not listed in the figure, also uses a polymer membrane as electrolyte. In a DMFC the liquid methanol is directly electrooxidized at the anode without the need of externally reforming methanol to hydrogen. The phosphoric acid fuel cell (PAFC) is operated in the medium temperature range between 160 and 220 °C, while the molten carbonate fuel

cell (MCFC) and the solid oxide fuel cell (SOFC) belong to the high temperature fuel cells.

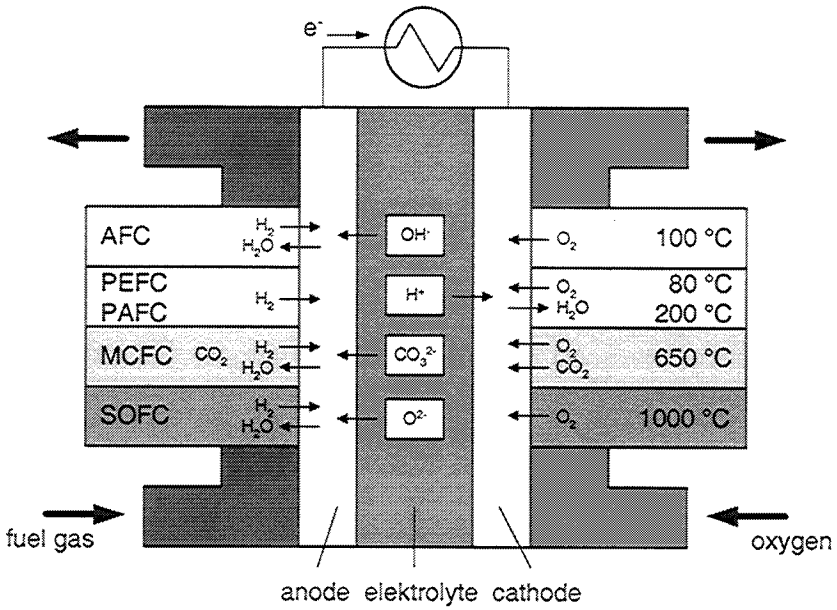

***Figure 1:** Types of fuel cells listed in order of increasing temperature*

A complete fuel cell system consists of the fuel cell stack, the gas processing unit and a power conditioning unit, as presentetd in Figure 2. Especially the gas processing unit has to be tailored for each type of fuel cell and fuels from various feedstocks as the different fuel cell systems have more or less stringent requirements with regard to the purity. The low temperature fuel cells AFC and PEFC (exception: DMFC) and also the PAFC require clean hydrogen for power generation. Traces of CO in the fuel, that stem from the reforming of fossil fuels, have to be eliminated down to about 10.000 ppm for the PAFC and about 20 ppm for the PEFC because CO acts as a strong poison for the Pt-based catalysts. For the high temperature fuel cells MCFC and SOFC any CO in the fuel gas presents no problem as it can be used as fuel at the anode of those fuel cell types.

Pure hydrogen is attractive as a fuel but due to a lacking hydrogen infrastructure, for most applications hydrogen has to be extracted from hydrocarbonaceous fuels such as natural gas, biomass, biogas, ethanol, methanol, liquid gas, gasoline or diesel. This is done by converting the carbonaceous materials by steam reforming, autothermal reforming, partial oxidation or pyrolysis into a hydrogen-rich mixture which has to be purified in several purification steps

to obtain clean hydrogen. The heat needed to drive the fuel reforming reactions can be provided by an external burner, which can use the anode exhaust gas, or internally via the waste heat of the fuel cell stack (MCFC, SOFC).

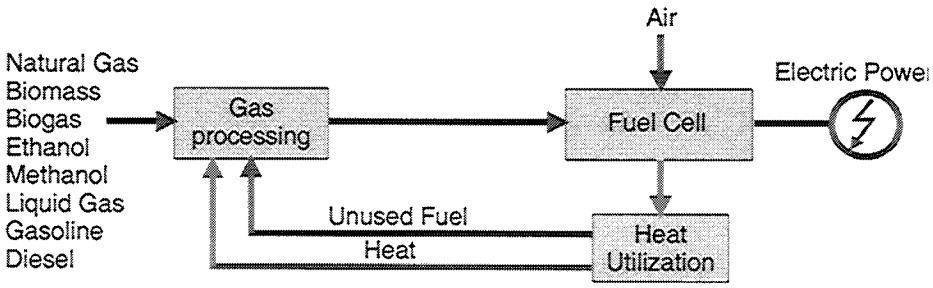

Figure 2: *Simplified scheme of a fuel cell system*

In the field of stationary fuel cell power plants most recent developments concentrate on natural gas as fuel because of the existing fuel infrastructure. Nevertheless, a very interesting option to combine regenerative energy production with fuel cells is the use of of gasified biomass, bioethanol or biogas. In any way, volatile organic compounds including sulfur and halogenated compounds as well as dust and tars have to be removed in a gas pretreatment unit from the fuel gas for all fuel cells.

Due to the relatively low operating temperature the AFC needs pure hydrogen and oxygen as fuel. A very harmful impurity to the AFC is carbon dioxide (CO_2) because it reacts with the KOH electrolyte as follows:

$$2\ KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

As the potassium carbonate (K_2CO_3) is formed inside the porous structure of the electrodes, it blocks the pores and causes malfunction of the fuel cell The tolerance level depends on the structure of the electrodes. The carbon monoxide (CO) is also harmful to the AFC as it poisons the Ni/PTFE electrodes [1]. Gultekin et al. have studied various CO contents in the hydrogen gas in the range of 0.05 - 0.95 % and have observed significant deactivation of the electrodes. They also observed that the recovery of the electrodes, when pure hydrogen was fed into the fuel cell, increased with the higher operation temperature [2]. In addition to CO_2 and CO, the AFC does not tolerate sulphur gases. SO_2 in the cathode gas and H_2S in the anode gas poison the catalysts. Quantitative tolerance levels allowed for sulphur impurities were not found in the literature.

The properties of the PEFC are mainly determined by the polymer ion exchange membrane and the catalyst used for electrode manufacturing. The catalyst for this low temperature electrochemical reaction is the noble metal platinum, according to the state of the art as a thin layer of noble metal powder, finely dispersed platinum on carbon as support is under development. Platinum is subject to poisoning by some chemical compounds, which can be present in biofuels. One of the main components is gaseous CO, which is reversibly but quite tightly adsorbed on the catalyst surface thus decreasing the performance of the fuel cell. For the PEFC, the fuel therefore should be nearly CO-free. The level which can be tolerated is reported to be < 10 to 100 ppm. Several measures are investigated to overcome this problem: for example the injection of traces of oxygen into the anode chamber, or the increase in operating temperature, or the development of CO-tolerant catalysts.

As the operation temperature is 80 °C, every substance condensing in this range of temperature must previously be removed from the fuel the same is true for particles and dust. Volatile organic compounds have been added in traces to the fuel by Belsey et. al. and Amphlet et. al. [3]. Traces of methanol, formaldehyde, formic acid and methyl format have been investigated. All compounds led to a decrease in cell voltage but only formic acid caused a significant voltage degradation and an irreversible loss of performance. Summarising the experiences, the fuel should be clean hydrogen, dilution by inert gases like nitrogen, CO_2, methane is acceptable [4]. Water vapour is a necessary component of the feed gas. Several ppm of CO can be tolerated, especially as the decrease in performance during temporary higher CO-values is reversible.

The PAFC is mainly operated in combination with a reformer for natural gas, the composition of the gas after two shift stages lies in the range of 0,5 vol.-% CO, 4 vol.-% CH_4, 20 vol.-% CO_2, balance hydrogen and nitrogen according to the quality of the natural gas (3 - 8 vol.-%). According to Kinoshita et al., the CO content must be below 1 % [5]. The sulphur gases (H_2S and COS) are also harmful to the PAFC. They adsorb to the anode and hinder H_2 adsorption. The total content of sulphur gases (H_2S + COS) must be below 50 ppm, and the H_2S content must be below 20 ppm. The ammonia (NH_3) reacts with the phosphoric acid electrolyte (H_3PO_4) as follows:

$$H_3PO_4 + NH_3 \rightarrow (NH_4)H_2PO_4$$

The salt content in the electrolyte should be below 0.2 mol-%. Furthermore, metal ions such as Fe and Cu are not allowed at all, and the limit for halogen compounds is less than 1 ppm [7]. Investigation of the PC25 of the Hessian utility have shown, that according to the nitrogen content in the feed gases,

the loss of electrolyte increases [8]. So besides tar and dust removal, the nitrogen content of the gasified biomass is maybe a major problem.

The high temperature fuel cells are in general less sensitive with respect to fuel purity. At these temperature levels, catalysis is possible with nickel containing electrodes, no noble metals are required. For the molten carbonate fuel cell, even the concept of internal reforming is performed. This means feeding natural gas and steam directly into the fuel cell, the anode gas channels being equipped with a special reforming catalyst. The MCFC is so robust, that any gaseous organic compound will be converted to hydrogen too, provided enough steam is present.

The SOFC operates at the highest temperature, therefore this type of fuel cell should cope with nearly all hydrocarbons being present in e.g. gasified biomass. In a paper, the sensitivity of the SOFC with respect to typical contaminants being present in gasified brown coal have been investigated by a consortium of companies. The results were quite promising [9]. Synthetic coal gas was used with a composition CO 45 vol.-%, H_2 34 vol.-%, CO_2 17 vol.-% and CH_4 4 vol.-%. To this feed gas, well defined amounts of contaminants have been added, and the influences have been recorded in table1.

***Table 1**: Influence of contaminants on SOFC performance*

Contaminant	**concentration in feed gas**	**Result**
Ethane	7 ppmV	no influence
Ammonia	4 800 ppmV	no influence
Toluene	550 ppmV	no influence
prussic acid (hydr. cyanide)	200 ppmV	no influence
hydrogen sulphide	4 ppmV 8,7 ppmV < 10 ppmV	3% incr. of internal resistance 8 % incr. of internal resistance < 2 % decr. in current density

2 Biomass Gasification for Fuel Cells

Gasification of biomass is a process to convert carbonaceous materials by means of partial oxidation into a combustible gas using air, oxygen, steam or a mixture of these. Air gasification produces a low heating value gas (LHV/

4-6 MJ/m³). Due to its low energy density, this is suitable for boiler and gas engine operation but not for pipeline transportation. Oxygen gasification produces a medium heating value gas (MHV/ 10 - 15 MJ/m³) suitable for limited pipeline distribution and as synthesis gas for conversion e.g. into methanol. Steam gasification also produces a MHV gas, with a slightly higher heating value (15 - 20 MJ/m³). For smaller plants, the gasification with pure oxygen is unfavourable with respect to the cost-effectiveness ratio. The main reactions of the gasification of carbonaceous material are:

1)	partial oxidation	$C + ½ O_2$	↔	CO	ΔH = - 123,1 kJ/mol
2)	combustion reaction	$C + O_2$	↔	CO_2	ΔH = - 404,7 kJ/mol
3)	Boudouard reaction	$C + CO_2$	↔	2 CO	ΔH = + 159,9 kJ/mol
4)	water gas reaction	$C + H_2O$	↔	$CO + H_2$	ΔH = + 118,5 kJ/mol
5)	hydrogenating gasification	$C + 2 H_2$	↔	CH_4	ΔH = - 87,5 kJ/mol
6)	water gas shift reaction	$CO + H_2O$	↔	$H_2 + CO_2$	ΔH = - 40,9 kJ/mol
7)	methanation reaction	$CO + 3 H_2$	↔	$CH_4 + H_2O$	ΔH = - 205,9 kJ/mol

Gasification can be carried out at atmospheric pressure or at elevated pressure. The product gas composition will vary according to the pressure, the reactor design and configuration and also to the temperature range in the reactor. A wide range of reactor configurations has been developed, as shown in table 2. In table 3 typical gas compositions of an autothermal and an allothermal gasification process are presented. Additionally there is a certain amount of dust and condensable hydrocarbons in the product gas. The amount of tar varies between 0,1 - 100 g/m³ strongly depending on the gasification process. During start up or during non steady-state operation conditions high amounts of tarry components may be produced causing additional problems.

In the purification process removal of dust and tar must be the first steps because the subsequent CO-shift conversion and fine purification will be damaged by these impurities. Condensable organic compounds and dust can cause plugging of process lines and equipment. The impurities especially can poison the catalysts as well as block the catalyst surface. The energy and carbon losses and waste disposal problems must be considered, if the simple but costly solution of cooling and water scrubbing is applied.

Table 2: Gasifier Reactor Types and Operation Conditions

Gasifier	**Fixed bed**	**Downdraft**	**Updraft**	**Co-current**
Reactor		Counter-current	Cross current	Variations
Type	Fluidized bed	Bubbling bed	Circulating bed	
	Other Types	Entrained flow	Twin reactor	Moving bed
		Rotary kiln	Molten metal bath	Cyclonic or vortex reactors
Pressure		Atmospheric p.	Elevated p.	
Oxidant		Air	Oxygen	Steam
Heat production		autothermal	allothermal	

Table 3: Product gas of autothermal and allothermal gasification process

Autothermal gasification [NOELL]				Allothermal gasification [DMT]			
composition of biomass used [wt.-%]		composition of product gas [Vol.-%]		composition of biomass used [wt.-%]		Composition of product gas [Vol.-%]	
C	28,46 %	N_2	32,24	C	50,7 %		
H	3,39 %	HCl	0,02	H	6,6 %		
O	23,75 %	H_2	22,62	O	40,6 %	H_2	40 - 55
N	0,44 %	H_2O	19,6	N	1,5 %	H_2O	
S	0,07 %	H_2S	0,02	S	<0,2 %	H_2S	
Cl	0,06 %	CO	13,3	Cl	<0,5 %	CO	15 - 25
F	0,00 %	CO_2	12,2	F	0,0 %	CO_2	15 - 25
H_2O	40,65 %			H_2O		CH_4	5 - 10
ash	3,16 %			ash (db)	5,1 %		

In literature, different processes to remove higher molecular hydrocarbons are described. It can be stated, that it is feasible to remove approximately 90 % of the tar from the product gas. This can be achieved e.g. with noble metal catalysts, selective oxidation, filtration etc. Comparative results are achieved with dolomites as catalyst. To achieve a higher tar conversion rate it seems to be necessary to combine several processes for example filtration, catalytic cracking with different catalysts and selective oxidation in one system.

3 Bioethanol Reforming

Ethanol as a liquid fuel has the advantages that it is on one hand easy to handle with respect to the storage and transportation and on the other hand it has

a relative high mass specific energy content. First bioethanol will be reformed in a steam reformer to a gas mixture containing hydrogen, water vapour, carbon monoxide and carbon dioxide. Residual amounts of ethanol and other organic compounds may also be present. The ethanol/water conversion into a hydrogen rich gas takes place in a endothermic catalytic reforming process. After the reforming step a first conversion of CO to hydrogen and CO_2 takes place in a HT-shift reactor at 400 °C, where additional steam can be fed to the reformat gas stream. According to the operation temperature of the LT-shift reactor of about 200 °C a carbon monoxide content in the range of 0,3 to 1 % is achievable. The resulting gas mixture has to be fed to a further gas purification step to reduce the CO-content to 5 - 20 ppm and to separate the organic compounds from the hydrogen gas. A PSA process (Pressure Swing Adsorption) adsorbs all components except hydrogen at an elevated pressure and generates a pure hydrogen fuel gas stream for a PEFC. In general a PSA is a very suitable gas purification system for liquid energy carriers like ethanol or methanol.

A simulation of the complete bioethanol conversion process allows to predict the behaviour of the process. The simulation uses basic engineering relationships such as mass and energy balances and phase and chemical equilibrium. With reliable thermodynamic data, realistic operation conditions and the equipment models given by the simulation program actual plant behaviour can be simulated and calculated. Necessary for the simulation of the reformer is the knowledge of the ethanol and water streams for a complete conversion of ethanol into hydrogen and carbon dioxide. The coefficients of the reaction equation are:

$$C_2H_5\text{-}OH + 3\ H_2O \Leftrightarrow 6\ H_2 + 2\ CO_2$$

The stoichiometric steam to carbon ratio (s/c) of this reaction is s/c=1,5. First it was important for the simulation to find out the optimal reforming pressure with a maximum of hydrogen production and a minimum of carbon dioxide, carbon monoxide and methane production. The results for the final simulation of the overall bioethanol conversion process are a reforming pressure of 7 bars (absolute) and a reforming temperature of 700 °C at a steam to carbon ratio of 3. To avoid carbon deposition on the reformer catalyst the s/c-ratio for the later reformer is set to 4. For the simulation of the overall bioethanol reforming process several system components are required. The ethanol and water streams are fed into two separate pumps providing the required system pressure of 7 bars absolute. Leaving the pumps ethanol and water are mixed in front of a preheater. After preheating the gas mixture reaches the reformer where the gas is converted into a typical reformat gas. Since the gas leaving

the reformer has a temperature of 700 °C it has to be cooled down in a heat exchanger before entering the HT-Shift (400 °C) and in a second heat exchanger before reaching the LT-Shift (200 °C). Behind the LT-Shift the reformat gas has to be cooled down again before the gas is fed into the PSA. To increase the overall efficiency of the bioethanol process a recycling of all possible energy streams of the process is required. Another important aspect of the recycling of energy streams is the usage of the offgas produced by the PSA as fuel for the burner of the reformer.

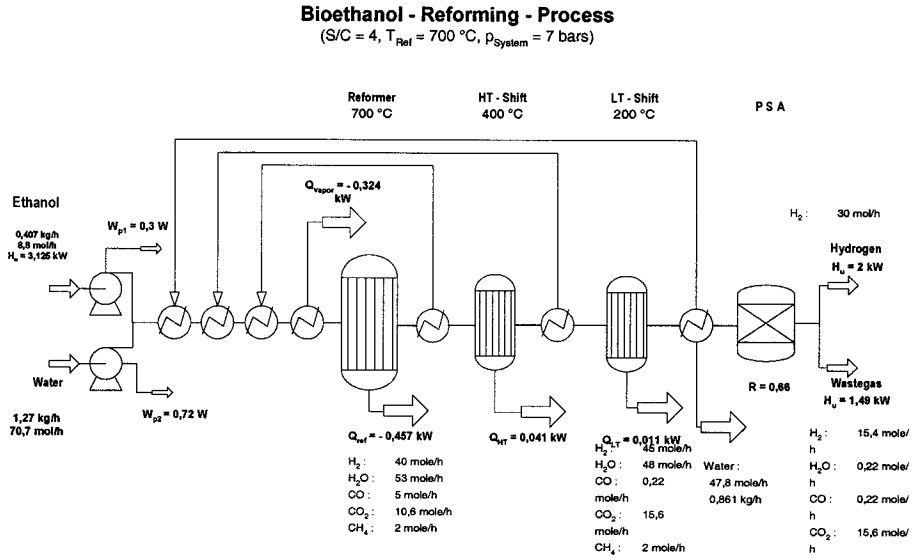

Figure 5: *Simulation diagram of the complete bioethanol process*

The calculation of the thermal efficiency of the system is in general the lower heating value of the produced hydrogen divided by the lower heating value of the used bioethanol. The highest thermal efficiency is achievable by using the offgas coming out of the PSA and can reach nearly 90 %. The offgas has a very high energy content. This energy can be used to feed the burner of the reformer and the final vaporiser in front of the reformer. Since the offgas is produced as continuos flow the reformer can be fuelled after the first production of the offgas. The complete system will be self-sufficient referring to the heat balance.

The Pressure Swing Adsorption process is a gas purification system using different adsorption capacities of solid materials, the so called adsorbents, and pressure differences between adsorption and desorption. Typical adsorbents

are activated carbon, zeolithic molecular sieves, silica gel and carbon molecular sieves. The adsorption itself takes place at high pressure where the impurities of a gas stream are forced onto the surface of the adsorbents. In the bioethanol reforming process the impurities are mainly CO, CO_2 and CH_4. The principle of the Four-Bed-PSA is illustrated in figure 6.

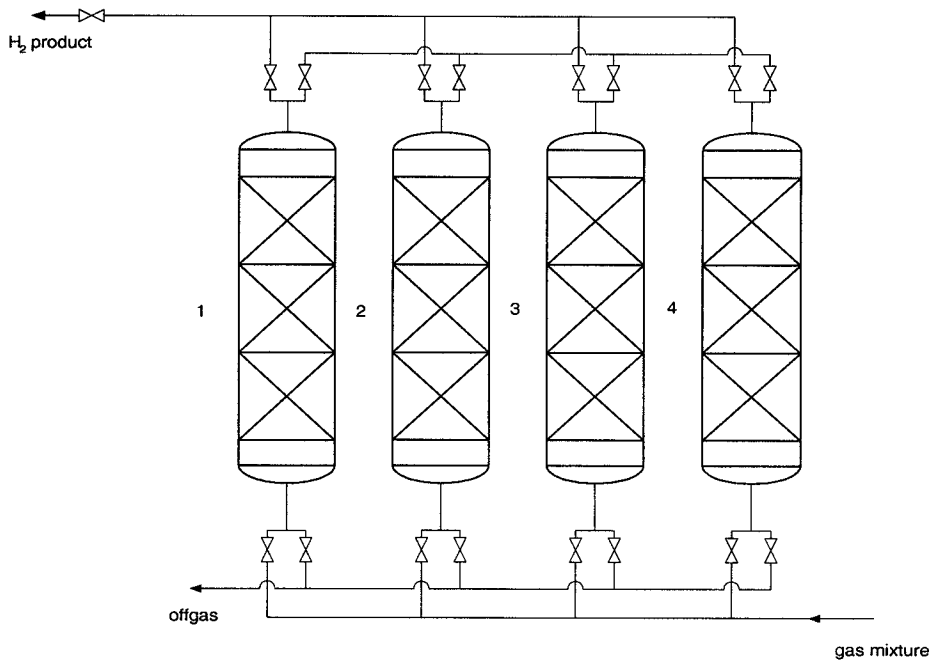

Figure 6: *Schematic of the Four-Bed-PSA*

The adsorber are connected to each other with four solenoid valves. For the feed gas inlet, the product gas and offgas outlet for all adsorber 12 further solenoid valves are needed. Such a small PSA system for 2.5 kW thermal hydrogen power was developed at the University of Duisburg (figure 7). The PSA is operated automatically using a SPC (Stored Programmable Controller or PLC = Programmable Logical Controller). For the automation of the PSA a program was developed. The connection of the beds is achieved using solenoid valves. The maximum pressure of the valves is limited to 8 bars. The valves are so called 3/2 valves, that means there are 3 possible tube junctions and 2 different switch types. The valves in the adsorber head enable a gas flow in both directions, the valves in the adsorber foot can only be operated in one flow direction.

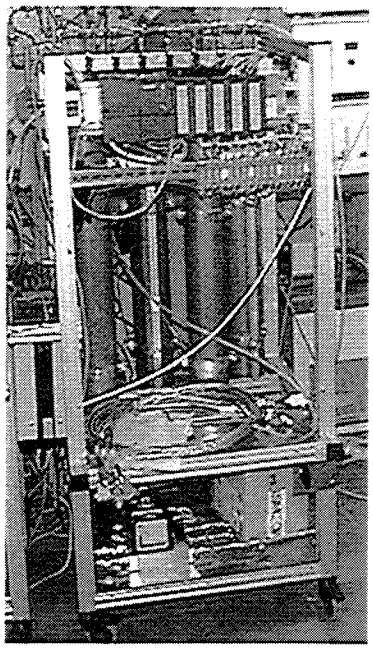

Figure 7:
Small Pressure Swing Adsorption System (PSA) for 2.5 kW thermal hydrogen power developed at the University of Duisburg

4 Biogas Reforming

Biogas is a hydrocarbon gas mixture, which consists of about 60 to 75 % of CH_4, about 30 to 40 % CO_2 and ca. 1 % of a mixture of trace components, mainly H_2S, N_2, O_2, H_2 and NH_3. Biogas is generated by the anaerobic decomposition of biomass with the aid of bacteria forming mainly methane and carbon dioxide. An alternative process to conventional internal combustion engines using biogas is a fuel cell system, while upstream the hydrogen generation process (reformer) a special preliminary purification system is necessary.

Steam reforming has been selected as gas processing technology because the endothermic reaction heat is provided by an external burner leading to high hydrogen concentrations in the dry product gas. Autothermal and partial oxidation processes generate product gas qualities containing less hydrogen. This is possible because of a high nitrogen content while the reaction heat is supplied by internal combustion of a part of the methane with air. The design of the process is explained referring to Figure 8, where the main reactions of each conversion step are described. The biogas preliminary purification consists e.g. of three steps, separation of condensate, removal of H_2S with impregnated activated carbon and and the following removal of halogenic hy-

drocarbons with another type of activated carbon. After adding liquid water to the biogas stream, the mixture reacts at a Nickel catalyst at about 800 °C. In the following water-gas-shift reactors, the CO-content can be reduced to less than 1 % before the residual catalyst-poison is removed in a preferential oxidation unit (PrOx). The refomat gas is now fed to the PEM fuel cell, where electrical power and heat are generated.

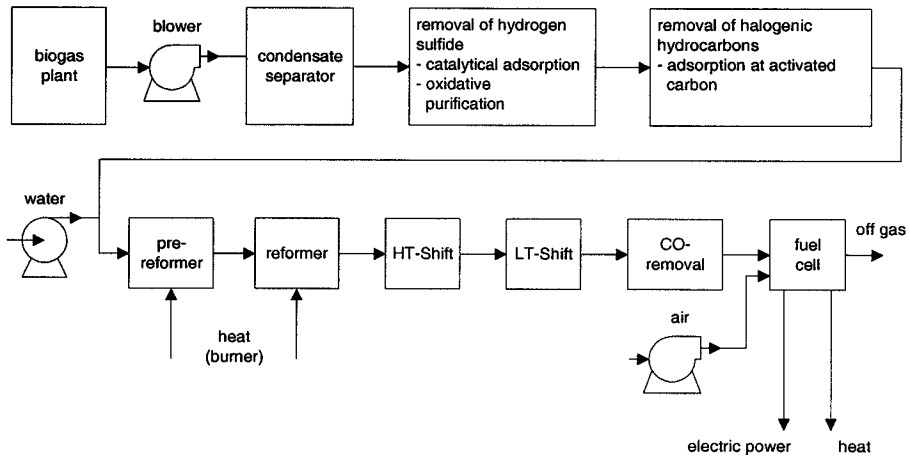

Figure 8: *Schematic of a complete fuel cell system based on biogas as fuel*

The University of Duisburg has developed a 12.5 kW_{th} fuel processor system for natural gas, LPG and biogas, which is highly modular, compact and using low-cost sub-units, which mainly incorporates standard components (figure 9). Using commercially available burner systems and catalyst pellets lead to an economically competitive gas processor. The efficiency of the reformer is about 80 % at rated power. Several of these modules can be combined to meet higher power demands.

Such a steam reformer system is principally suitable also for biogas, if the biogas has been treated in a preliminary purification. The following figure 10 demonstrates the result of a thermodynamical simulation, while a synthetic biogas consisting of 70 % methane and 30 % carbon dioxide has been used as fuel and the product gas composition is shown downstream the reformer system for each single reactor. Despite the high carbon dioxide content in the feed, it is obvious, that a hydrogen content of about 60 % in the dry product gas can be achieved. First experimental results with synthetic biogas based on the reformer system presented in figure 9 validate the thermodynamical calculations and show a good correspondence to the simulations.

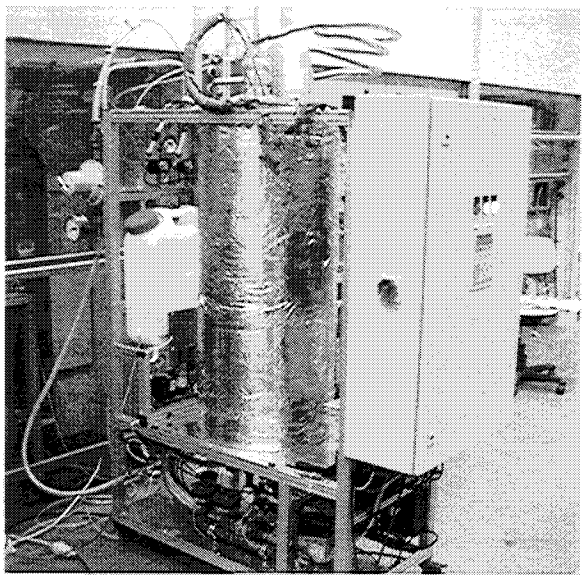

Figure 9:
12.5 kW Multifuel Steam reformer system, developed at the University of Duisburg (together with HESE Umwelt GmbH and minitec engineering GmbH) for natural gas, LPG and biogas

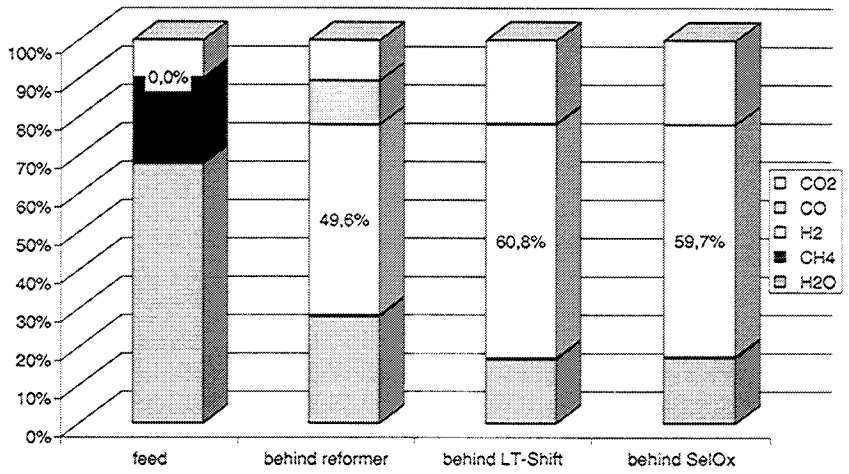

Figure 10: *Thermodynamical gas composition of steam reforming of biogas*

Biogas and biogas treatment is similar to the treatment of digester gas and landfill gas. Some projects using those gases have been performed based on a PAFC ONSI PC25. For example in 1996 Yokohama City and Toshiba jointly demonstrated for the first time ever an ADG (Anaerobic Digester Gas) fueled PAFC. ADG is produced by the anaerobic digestion of waste water treatment

sludge and contains about 60 % methane and about 40% CO_2. This system consists of an ONSI 200 kW PAFC designed to operate on natural gas and a special ADG treatment unit, which contains a desulfurizer, an absorber for absorbing ADG contaminants and a methane concentrator to concentrate methane [10]. Parametric tests were conducted for three different methane concentrations, 90 %, 75 % and 60 %. The tests confirmed that ADG fueled PAFC operate steadily given the proper methane concentration. An electrical output of 200 kW has been obtained with a methane concentration of 60 % by modifying the fuel supply system (pipes and valves) of a standard PAFC using natural gas.

In Cologne the GEW is successfully operating an ONSI PC25C with sewage gas as fuel located at the waste water treatment plant in Rodenkirchen. The electrical net power output of the fuel cell system of about 200 kW could be demonstrated and the availability of the system was in the range of 90 % due to some modifications of the preliminary biogas purification and and subsequent test phases [11].

5 Conclusions

Biomass is a very promising regenerative energy source because of the technical potential and the relatively low cost compared to other regenerative energy sources. An advantage of biomass is availability, in contrast to wind and solar energy biomass can be stored. Biomass is mainly used as heat source at the time being, but generating electricity from biomass gets more and more into the focus of development.

Fuel cells are able to achieve high efficiency even in small units and in part load operation. The modular design of fuel cells is predestinated for a wide power range and for residential power supply with low emissions of hydrocarbons and NO_x.

Using biofuels in fuel cells is a very promising issue of development, some technical problems regarding fuel gas purity have to be solved. Biofuels like gasified biomass or biogas from anaerobic fermentation have to be preliminary purified due to the necessary fuel gas qualities and fuel gas purities. Literature data of tolerable impurities in the fuel gas have to be validated with respect to their influences on system efficiency and life cycle.

6 Acknowledgments

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HYDROGEN PRODUCTION VIA THE AUTOTHERMAL REFORMING OF DIESEL FUEL

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Hydrogen for the operation of a polymer electrolyte fuel cell can be produced by means of the autothermal reforming of liquid hydrocarbons. Experiments especially with ATR Type 4, which produces a molar hydrogen stream equivalent to an electrical power in the fuel cell of 3 kW_{el}, showed that the process should be preferably run in the temperature range between at least 700 °C and 930 °C. This ensures complete hydrocarbon conversion and avoids the formation of considerable amounts of methane and organic compounds in the product water. Experiments concerning the dynamic behavior of the reformer proved that within 60 s after the addition of water and hydrocarbons the reformer reached 95 % of its maximum molar hydrogen flow. Experiments with commercial diesel showed promising results with, however, insufficient long-term stability. Future experiments will therefore focus inter alia on measures to improve the evaporation and mixing of diesel fuel with air and water.

1 Introduction

Fuel cell technology is of special interest from the present perspective due to its higher efficiency in energy conversion, less harmful emissions and a considerable noise reduction. Fuel cells are supposed to offer the potential for becoming the energy converter for future energy management. However, in the mid-term pure hydrogen generated from renewable or sustainable energy sources will not be widely available.

Since fuel cells will have to replace well-established and developed technologies like the internal combustion engine, it is most probable that in the beginning they will penetrate small niche markets. Among them, the leisure sector is one of the most suitable applications since the environmental advantages of fuel cell systems with respect to the reduction of emissions and noise play a dominant role in that sphere. They increase the individual's personal comfort and safety.

However, the most important premise for that option is to provide a technically reliable technology which ensures a steady supply of hydrogen from widely available fuels. Among them, carbonaceous energy carriers such as middle distillates are a promising candidate for conversion into hydrogen by means of chemical processes. Besides diesel, middle distillates include marine gas oil, jet fuel, low-sulfur diesel and biodiesel. In the long run, when fuel cell technology on the basis of carbonaceous materials will have become established in several

markets there will be a chance for hydrogen technology with advanced storage systems to replace fossil energy carriers.

2 Hydrogen generation from liquid fuels

2.1 Autothermal reforming (ATR)

One possible way of producing hydrogen in a so-called fuel processor from carbonaceous substances such as hydrocarbons or alcohols is autothermal reforming. Fuel is converted into a hydrogen-rich gas mixture according to the following reactions:

$$C_nH_mO_l + (n - l)\,H_2O \longrightarrow n\,CO + (m/2 + n - l)\,H_2 \qquad \Delta H^0_{298} > 0 \qquad (1)$$

$$C_nH_mO_l + (n - l)/2\,O_2 \longrightarrow n\,CO + m\,H_2 \qquad \Delta H^0_{298} < 0 \qquad (2)$$

The necessary heat for the endothermic steam reforming (eq. 1) is supplied by the partial oxidation of hydrocarbons (eq. 2). The water-gas shift reaction (eq. 3) and the methanation reaction (eq. 4) proceed simultaneously and yield a gas composition which corresponds to thermodynamic equilibrium [1,2].

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \Delta H^0_{298} < 0 \qquad (3)$$

$$CO + 3\,H_2 \longrightarrow CH_4 + H_2O \qquad \Delta H^0_{298} < 0 \qquad (4)$$

Important parameters for the ATR process are temperature, pressure, $n(O_2)/n(C)$ and $n(H_2O)/n(C)$ ratio. These parameters should be chosen with the aim of avoiding the formation of carbon and minimizing the methane content of the product gas. Criteria for carbon-free operation can be found by means of thermodynamic calculations [3,4]. Nevertheless, the formation of carbonaceous deposits can occur in the autothermal reforming of higher hydrocarbons [4]. The oxidation of the products hydrogen (eq. 5) and carbon monoxide (eq. 6) may also occur. The result of a combination of equations 2, 5 and 6 is the deep oxidation of hydrocarbons (eq. 7). The consumption of oxygen for deep oxidation will enhance the amount of hydrocarbons to be converted by steam reforming.

$$H_2 + 0.5\,O_2 \longrightarrow H_2O \qquad \Delta H^0_{298} < 0 \qquad (5)$$

$$CO + 0.5\,O_2 \longrightarrow CO_2 \qquad \Delta H^0_{298} < 0 \qquad (6)$$

$$C_nH_m + (n + m/2)\,O_2 \longrightarrow n\,CO_2 + m/2\,H_2O \qquad \Delta H^0_{298} < 0 \qquad (7)$$

Fuel processors on the basis of autothermal reforming can be utilized in a wide range of applications such as:

- auxiliary power unit for passenger cars, trucks, trains, ships and airplanes
- house heating systems based on heating oil
- fuel cell drive systems based on diesel fuel
- portable power units for the leisure sector, e.g. camping and outdoor activities

In order to be marketable they must fulfill the following requirements:

- low costs
- working on easily available fuels
- high power density, low weight and volume
- fast start-up
- good transient behavior at different loads

2.2 Choice of fuel

A serious problem to be solved in connection with hydrogen generation from liquid energy carriers by means of reforming is to identify suitable fuels. On the one hand, they must be very widespread and easily available in large amounts and at low costs. Actually, this is obviously true of refinery products from crude oil such as liquid gases (LPG), straight-run gasoline, middle distillates and heavy heating oil. However, the price of crude oil will become increasingly higher in future, since petroleum resources are becoming scarcer and their development more and more expensive. In 1999, worldwide estimated petroleum reserves amounted to approx. 138 billion t with a total consumption of approx. 3.4 billion t in 1999 [5]. In addition, there is a great demand for crude oil as the base product for numerous important chemical syntheses above all in the chemical industry inter alia in the field of polymers, fibers or solvents.

Therefore, on the other hand, suitable fuels must offer a certain potential for being partly replaced by so-called synfuels and sustainable fuels. Synfuels such as liquid hydrocarbons can be synthesized by means of the gas-to-liquid process (GTL). In the GTL process syngas ($CO + H_2$) is converted into higher liquid hydrocarbons using Fischer-Tropsch catalysts. Methanol can also be made from syngas on suitable catalysts. An example of a sustainable fuel is biodiesel on the basis of fat-acid methyl ester (FAME) or biomass.

At present, middle distillates fulfill the above demands in an excellent manner. Middle distillates consist of kerosene, sulfur-free diesel, heating oil and marine gas oil. There is a splendidly developed infrastructure for middle distillates. In future, they can be progressively displaced by biodiesel, biomass or Fischer-Tropsch diesel in correlation with the increasing capacities of these future energy carriers. Furthermore, middle distillates are simpler to reform than gasoline due to their lower amount of aromatic hydrocarbons (especially sulfur-free diesel), they are easier to handle compared to the gasoline of today and they can be used in internal combustion engines as well as in fuel cell systems.

3 Experimental results

3.1 Small-scale testing

Fig. 1 shows the results of the small-scale testing of a precious metal catalyst for the autothermal reforming of liquid hydrocarbons. Hydrocarbon conversion as a function of $n(O_2)/n(C)$ ratio at different $n(H_2O)/n(C)$ ratios is presented. The catalyst which was supplied by OMG & Co. KG consisted of coated spheres with a diameter of 2 mm. It was diluted with Al_2O_3 grains. The hydrocarbon used was a C_{13}-C_{19} mixture with a feed of 30 g/h. Fig. 1 makes obvious that hydrocarbon conversion was strongly increased with increasing $n(O_2)/n(C)$ ratio. Furthermore, higher $n(H_2O)/n(C)$ ratios clearly enhanced hydrocarbon conversion. More details about the small-scale testing including the classification of different catalysts for autothermal reforming are given by Palm et al. [6,7].

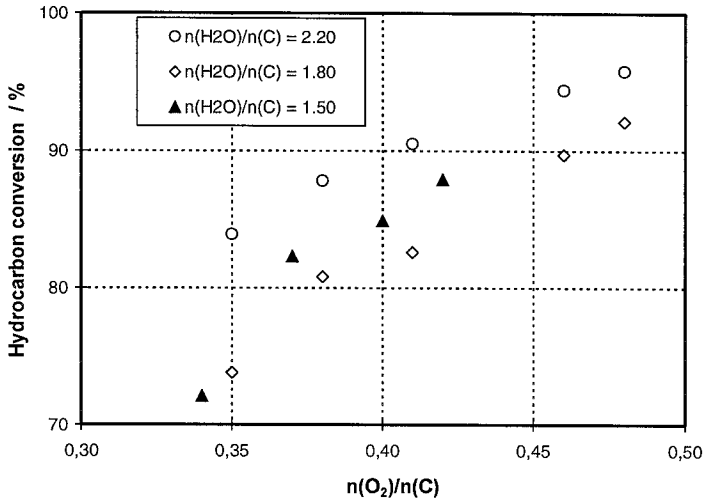

Fig. 1: Hydrocarbon conversion as a function of $n(O_2)/n(C)$ ratio with a C_{13}-C_{19} alkane mixture, $m_{Cat.}$ = 6 g, m(hydrocarbon) = 30 g/h, T(furnace) = 550 °C, p = 1.6 · 10^5 Pa.

3.2 Experiments with ATR Type 3

Fig. 2 shows the experimental results obtained with the so-called ATR Type 3 reactor (cf. Fig. 3) which was designed and constructed on the basis of results obtained within the above-described small-scale testing [6,7]. The catalyst used was a precious-metal-coated ceramic monolith with a diameter of 46 mm and a length of 60 mm. It was supplied by OMG AG & Co. KG. Experiments were performed at an $n(O_2)/n(C)$ ratio of 0.405 and a $n(H_2O)/n(C)$ ratio of 1.85. The hydrocarbon stream amounted to 340 g/h and was more than ten times higher in comparison to the small-scale testing. Two different hydrocarbon feeds were applied: A C_{13}-C_{15} alkane mixture as well as a commercial low-sulfur diesel fuel. Fig. 2 underlines that in both cases high reformer efficiencies of about 81 % were found. Due to larger amounts of

aromatic compounds in the commercial diesel fuel, the H_2 outlet concentration was slightly lower than in the case of the alkane mixture. However, the reactor outlet temperature was about 30 K higher in the case of the experiment with commercial diesel. Unfortunately, the time on stream of the experiments with commercial diesel was restricted to about 4 hours due to problems with respect to the evaporation of the fuel.

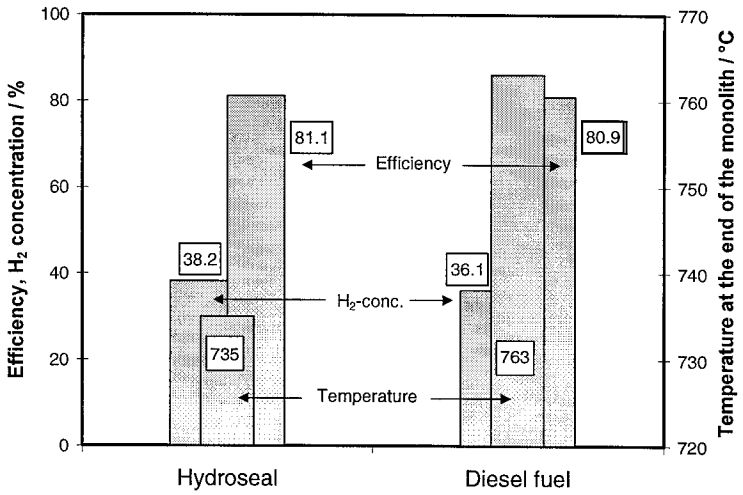

Fig. 2: *Reformer efficiency, H_2 outlet concentration and exit temperature of ATR Type 3 using a C_{13}-C_{15} alkane mixture (boiling range: 235 °C – 265 °C, 1 ppm S) and a commercial low-sulfur diesel fuel (boiling range: 186 °C – 305 °C, 5 ppm S), $n(O_2)/n(C)$ = 0.405, $n(H_2O)/n(C)$ = 1.85, precious-metal-coated monolith (d = 46 mm, l = 60 mm, 600 cpsi).*

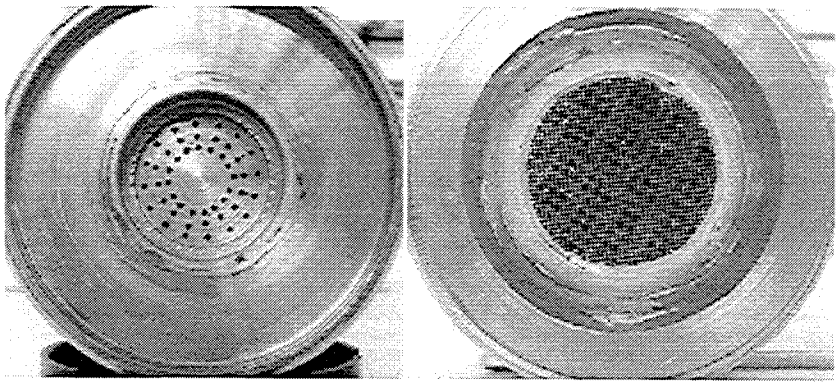

Fig. 3: *Mixing chamber (left) and pre warming zone (right) of ATR Type 3.*

3.3 Experiments with ATR Type 4

After ATR Type 3 was fully characterized a next generation of fuel processors with clearly higher molar hydrogen flow (equivalent to approx. 3 kW_{el}) was designed in Jülich. Fig. 4

shows the start-up behavior of ATR Type 4 at an $n(O_2)/n(C)$ ratio of 0.43, a $n(H_2O)/n(C)$ ratio of 1.8 and a hydrocarbon flow of 700 g/h (C_{13}-C_{15} alkane mixture). The catalyst used was again supplied by OMG AG & Co. KG with a diameter of 50.8 mm and a length of 85 mm. In the induction period of the experiment before water and liquid hydrocarbons were injected into the reactor the temperature of the catalyst in ATR Type 4 increased to about 330 °C via a constant flow of preheated air. No temperature gradient in the axial direction was observed. The temperatures at x = 10 mm and x = 75 mm were almost the same. Then within a few seconds the hydrocarbon and water flows were raised to their maximum values according to the above-given figures for the $n(O_2)/n(C)$ and $n(H_2O)/n(C)$ ratios. Immediately after the hydrocarbon flow had reached its maximum the product flow drastically increased. After approximately 60 s it reached a value which corresponded to about 96 % of the product flow at steady-state operation. The temperature at the end of the catalyst (x = 75 mm) also strongly increased to about 620 °C 30 s after the addition of hydrocarbon. At steady state the outlet temperature reached about 670 °C. However, the fastest step within the reaction is the ignition, i.e. the strongly exothermic partial oxidation of the hydrocarbons according to equation (2). The temperature at x = 10 mm in the axial direction of the monolithic catalyst increased from about 350 °C to more than 900 °C within approx. 15 seconds. This is slightly lower than the value at steady-state operation (about 930 °C). Additionally, Fig. 4 shows that the heating-up procedure of ATR Type 4 was much faster than that of ATR Type 3.

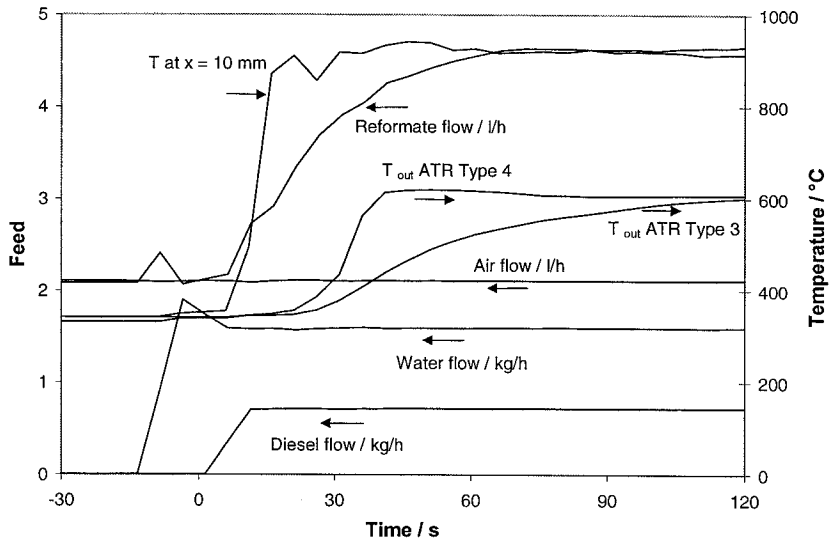

Fig. 4: Start-up behavior of ATR Type 4 using a C_{13}-C_{15} alkane mixture (boiling range: 235 °C – 265 °C, 1 ppm S), $n(O_2)/n(C)$ = 0.43, $n(H_2O)/n(C)$ = 1.80, precious-metal-coated ceramic monolith (d = 50.8 mm, l = 85 mm, 600 cpsi).

In further experiments a factorial design was chosen to characterize ATR Type 4 with respect to reformer efficiency, temperature at the end of the monolith and methane concentration in the reformate. This design requires relatively few runs per factor studied and although they

are unable to fully explore a wide region in the factor space they can indicate major trends and thus determine a promising direction for further experimentation [8]. Two levels for the three operation variables, $n(O_2)/n(C)$ ratio, $n(H_2O)/n(C)$ ratio and hydrocarbon feed, were selected on the basis of preliminary experiments (cf. Table 1). All possible combinations (2^3) of these three factors were examined. At the center of the parameter field three additional experiments were run to exclude a decline of the catalytic activity and to verify the reproducibility of the results. For each experimental run the composition of the product gas and the temperature profile in the axial direction of the monolith were recorded. Table 1 summarizes the results of these experiments.

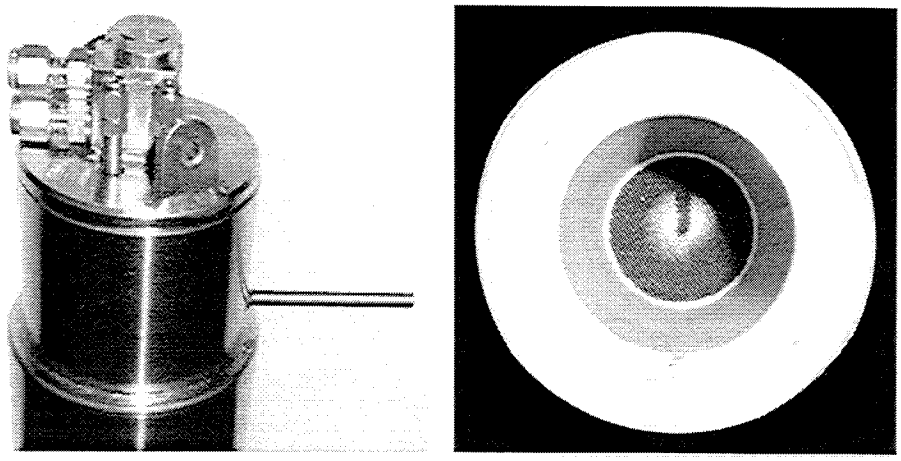

Fig. 5: ATR Type 4, external view (left) and internal view from the bottom (right).

Table 1 Results of the 2^3-factorial design using a C_{13}-C_{15} alkane mixture (boiling range: 235 °C – 265 °C, 1 ppm S) on a precious-metal-coated ceramic monolith, (d = 50.8 mm, l = 85 mm, 600 cpsi).

$n(O_2)$/ n(C)	$N(H_2O$/ n(C)	HC feed [g/h]	CH_4 conc. [%]	H_2 Conc. [%]	CO conc. [%]	ϑ_{out} [°C]	η [%]	TOC[1)] [mg/l]
0.41	1.7	600	0.61	37.32	11.21	644	76.1	96.0
0.45	1.7	600	0.13	35.31	11.46	702	70.8	24.0
0.41	1.9	600	0.61	38.11	10.03	646	76.8	73.0
0.45	1.9	600	0.10	35.78	10.90	702	75.4	16.0
0.41	1.7	800	0.85	37.87	10.88	642	79.0	120.0
0.45	1.7	800	0.25	36.09	12.27	698	80.8	17.0
0.41	1.9	800	0.82	38.45	10.40	634	80.0	44.0
0.45	1.9	800	0.21	36.63	10.38	694	76.6	16.0
0.43	1.8	700	0.32	37.16	11.22	672	78.4	44.0
0.43	1.8	700	0.38	37.08	11.20	672	74.5	53.0
0.43	1.8	700	0.37	37.21	10.91	670	77.7	42.0

1) Amount of total organic carbon in the product water (one phase)

The product gas compositions and temperatures at the end of the catalyst obtained for the three experiments at the center point (runs 9, 10, 11) indicate a very good reproducibility of the measurements. Table 1 underlines that the $n(O_2)/n(C)$ ratio of 0.45 resulted in higher temperatures at the end of the catalyst. This gave rise to lower methane concentrations of 0.1 vol.% to 0.2 vol.%. The amount of total organic carbon (TOC) in the product water was also plainly lower in the case of an $n(O_2)/n(C)$ ratio of 0.45. Since concentrations of CO, which has to be removed from the reformate in the downstream water-gas shift reactor, were only slightly enhanced by the higher $n(O_2)/n(C)$ ratio, it can be concluded that this value for the $n(O_2)/n(C)$ ratio is more applicative than 0.41. The only drawback of 0.45 is that due to the dilution of the reaction feed with air the H_2 concentration was universally lowered.
A regression equation was set up and fitted to the data in Table 1 to quantitatively describe trends of important variables such as reformer efficiency, temperature at the end of the monolith and methane concentration in the reformate. As an example, in this paper the response surface of the catalyst end temperature at a hydrocarbon flow of 800 g/h is given by the rectangular area in Fig. 6.

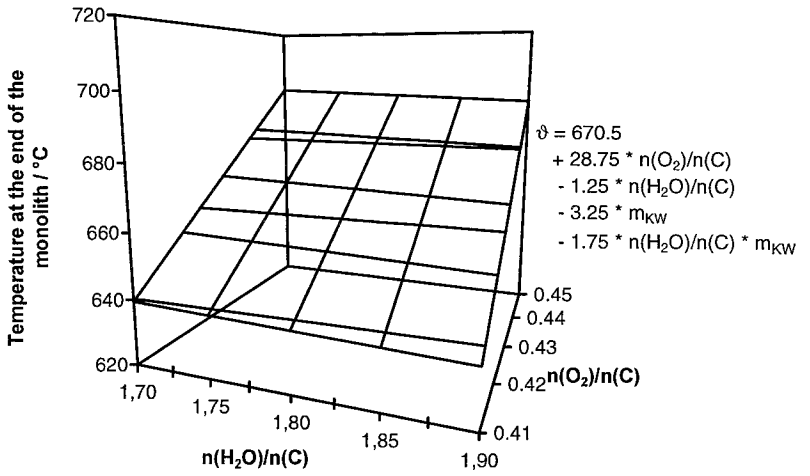

Fig. 6: Regression surface of the catalyst end temperature at a feed of 800 g/h (C_{13}-C_{15} alkane mixture) on a precious-metal-coated ceramic monolith (d=50.8 mm, l = 85 mm, 600 cpsi).

It becomes obvious from Fig. 6 that the $n(O_2)/n(C)$ ratio is the most dominant factor since the temperature at the end of the catalyst strongly increased with increasing $n(O_2)/n(C)$ ratio as mentioned before. Oxidation reactions (cf. eqs. 2, 5 and 6) were favored by higher partial pressures of oxygen in the feed. The equation for ϑ in Fig. 6 quantitatively stresses the strong influence of the $n(O_2)/n(C)$ ratio on the temperature at the end of the monolith. There was almost no influence of the $n(H_20)/n(C)$ ratio on the catalyst end temperature (cf. Fig. 6). The corresponding response surface in the case of a hydrocarbon flow of 600 g/h, which is not presented in this paper, shows very similar trends. Therefore, no influence of the hydrocarbon feed on the temperature at the end of the monolith was observed.

4 Conclusions

Hydrogen for the operation of a polymer electrolyte fuel cell can be produced by means of the autothermal reforming of liquid hydrocarbons. Experiments especially with ATR Type 4, which produces a molar hydrogen stream equivalent to an electrical power in the fuel cell of 3 kW_{el}, showed that the process should be preferably run in the temperature range between at least 700 °C and 930 °C. This ensures complete hydrocarbon conversion and avoids the formation of considerable amounts of methane and organic compounds in the product water. The latter might poison the catalysts of the downstream reactors (high- and low-temperature shift reactor) whereas methane has to be converted at relatively high temperatures (600 °C) in the catalytic burner. Experiments concerning the dynamic behavior of the reformer proved that within 60 s after the addition of water and hydrocarbons the reformer reached 95 % of its maximum molar hydrogen flow. Experiments with commercial diesel showed promising results with, however, insufficient long-term stability. Future experiments will therefore focus inter alia on measures to improve the evaporation and mixing of diesel fuel with air and water.

5 Acknowledgements

The authors thank Mr. B. Sobotta for valuable technical assistance. The authors are grateful to OMG AG & Co. KG for supplying catalysts for the autothermal reforming and for technical discussions.

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RENEWABLE FUELS – RESOURCES, SYNTHESIS AND UTILISATION

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The production and utilisation of renewable fuels are key aspects for power supply and road transport in the future. In the framework of this paper technologies for the production of renewable fuels – carbon based and hydrogen – from biomass, CO_2 and electricity are analysed. Furthermore, the renewable resource potential, the synthesis pathways and fuel utilisation with different technologies are discussed. Some concrete examples of technologies for the generation of renewable synthetic fuels are presented.

1 Introduction

Since the onset of the industrial age, the structure of the energy end-use sector has experienced a transition from solid to liquid and gaseous fuels and a shift towards more flexible, convenient and cleaner energy carriers which is motivated by easier fuel handling and rising environmental concerns at the local, regional and global level. Concerning global warming, CO_2 emissions, depletion of fossil energy resources, increasing energy demand, a sustainable energy strategy has highest priority. The production and utilisation of renewable fuels are key aspects for power supply and road transport in the future. Biomass is one of the most promising source for non-fossil fuels. Furthermore, hydrogen production from renewable electricity combined with biomass and CO_2 resources will be considered as source for renewable fuel generation. Using biomass as feedstock, there are three main ways for fuel generation:

a) extraction of bio-oil from oil plants,

b) fermentation of starch-rich and sugar-rich crops or cellulose materials to ethanol

c) the gasification of biomass and the subsequent fuel generation from synthesis gas.

The highest potential – in respect to a wide range of feedstock availability – have fuels, generated from synthesis gas. In comparison to other paths this route corresponds to an integral (whole plant) use of biomass. Among these fuels, the most promising are hydrogen, methanol and synthetic hydrocarbons such as methane and diesel/gasoline substitutes.

In the end-use sector special attention will be paid to fuel cell propulsion and combined heat and power generation technologies. In principle the use of renewable fuels is possible with all conversion technologies such as combustion engines today, or with fuel cell powered engines in the future. Especially hydrogen, but also methanol, are dedicated fuels for fuel cells but can also be used in adapted conventional engines. Liquid hydrocarbon fuels and substitute natural gas (SNG) are dedicated for propulsion systems with an internal combustion engine. Nevertheless, synthetic naphtha fractions may also be used as fuel for fuel cell systems with onboard conversion to hydrogen in the future.

Besides the synfuel routes, biofuels via extraction and fermentation as pure fuels or blendings may also be an option.

2 Resources

The main resources of renewable fuels are biomass, renewable electricity (e.g. from large hydropower, PV and wind energy) and CO_2 (both, atmospheric or concentrated). Resources and the manifold pathways of fuel generation are shown in Figure 1. The different conversion paths and techniques could be

divided in three areas according their implementation: present, short term and long term applications.

In Germany the only state-of-the-art technology for renewable transportation fuels is the plant oil extraction and subsequent esterification. The resulting product is plant oil methyl ester (PME) which is a 100 % diesel fuel substitute. In 2001 the total biodiesel production amounted to 600000 t/a in Germany, showing a rapidly growing tendency [1]. Distribution was realised at 1000 conventional petrol stations.

A world wide other established conversion path is the fermentation of plants, rich in starch and sugar, to ethanol. This is done on large scale in Brazil, North America and Canada. The world production of ethanol in 2001 was 31,4 x 10^9 l/a. The leader is Brazil with 12 x 10^9 l/a which represent about 42 % of the Brazilian transportation fuel consumption [2,3]. There are global R&D activities concerning the use of lignocellulosic feedstock for ethanol production which will increase substantially the availability of this feed. In the long term the world bioethanol production from sugar crops could be 600 x 10^9 l/a, whereas that of lignocelluosic biomass could be three times higher. With 1.65 x 10^{12} l/a the world ethanol production will make up ca. 37 % of the world petroleum consumption [4].

Another growing conversion path is the anaerobic fermentation of biomass to produce biogas. In Germany many fermentation reactors exist in combination with cattle-breeding or municipal waste water treatment plants. However more and more the anaerobic fermentation is used to treat the organic part of domestic waste.

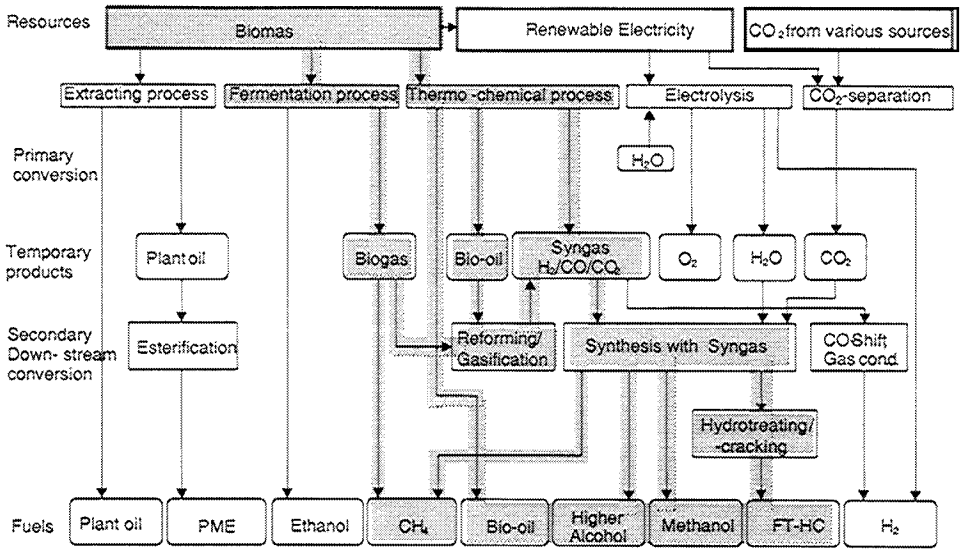

Figure 1: Conversion paths and resources of various renewable fuels

On the right side in Figure 1 is shown the hydrogen path which is expected in long term. Thereby hydrogen as fuel will be generated via electrolysis from renewable electricity or from biomass via thermo-chemical conversion. Another long term possibility is to produce synthetic fuels such as higher alcohols, methanol and Fischer-Tropsch (FT) hydrocarbons from carbon dioxide and hydrogen. But this path needs cheap electricity for hydrogen production. Carbon dioxide could be extracted from the ambient air or more efficiently from a concentrated source.

For short and medium term applications the middle paths in Figure 1 via synthesis gas are favoured, because most of the produced fuels could use the existing fuel distribution infrastructure. This enables a gradually substitution of fossil fuels. Basic step of these paths is the production of synthesis gas from biomass. This could be done in a direct way by gasification or by an intermediate product bio-oil. Bio-oil can be produced by flash pyrolysis and in a subsequent step reformed into synthesis gas. The benefit of this two step process is that biomass can be first converted decentral into bio-oil and then

transported to large scale reformer plants where synthesis gas is produced and further processed.

3 Synthesis

As shown in Figure 1 the synthesis of renewable synthetic fuels could be divided in two main steps, synthesis gas production and fuel synthesis. The fuel synthesis processes from synthesis gas are well known and established on large scale plants of the petrol and coal industry. The application of these processes to a decentral biomass conversion needs downscaling and process simplification. The main barrier and technical challenge is the first conversion step from biomass to a suitable synthesis gas. Large number of ongoing R&D activities are focused on this task. In order to bundle and co-ordinate the activities in the field of biomass conversion and fuel production the Network Renewable Fuels "ReFuelNet" was established in Germany, May 2002.

3.1 The German Network Renewable Fuels "ReFuelNet"

The highest potential – due to a wide range of feedstock availability – have renewable fuels, generated from synthesis gas. Therefore R&D activities are concentrated on the production of synthesis gas, gas conditioning, gas cleaning as well as synthesis of renewable fuels. The use of renewable fuels with fuel cells is another technological challenge which will be addressed in the frame of the network.

ReFuelNet as an information and communication platform promots the co-operation of different disciplines like research, process engineering and system analysis.

The list of participants to the Network comprises university research institutes, governmental research units, industrial companies and distribution-marketing firms. This structure of the Network ensures a selection of research projects close to the market needs and allows a more easier transfer of

fundamental research results into industrial applications. The Network Renewable Fuels is supported by the German Federal Ministry of Education and Research. More detailed Information is given under www.refuelnet.de.

3.2 Synthesis gas via biomass gasification

For synthesis gas production of biomass different gasification technologies are in development. Due to the biomass availability and the low energy density of biomass the scale of plant size is limited. Gasifiers can work either with *direct heating* (partial oxidation/combustion of biomass supplies the heat for the gasification) or *indirect heating*, using heat exchanger or heat carriers for heat supply. Direct heated gasifiers generally deliver a nitrogen loaded product gas due to the use of air as gasification means. Indirect heated gasifier use a part of the produced gas or the coke in a separate combustion chamber to supply the heat for the gasification process. Therefore flue gas of combustion is not included in the product gas. Regarding the requirements for synthesis gas quality indirect heated or oxygen blown gasifiers are preferred. However, in most cases in a small biomass gasification plant the oxygen supply for gasification is too expensive.

Requirements on synthesis gas are:

- Adjusted stoichiometry
- Low N_2 content (< 5%)
- Particle and soot free gas
- Free of catalyst poisons

To achieve the above requirements for synthesis gas in most cases intensive gas cleaning is necessary after gasification. Here tar forming and behaviour is an important issue which is considered within the R&D activities of ReFuelNet.

Another possibility for synthesis gas production especially for wet biomass feedstock is the gasification in supercritical water. The gasification process

takes place under high pressure and temperature. The advantage of this process is the limitation of tar and particulate formation and the possibility to get a nitrogen free and hydrogen enriched synthesis gas.

3.3 Synthesis gas via Reforming of Bio-oil (flash pyrolysis)

An interesting concept for renewable fuel production is to produce bio-oil in decentral plants by flash pyrolysis followed by oil processing in centralised plants. As the energy density of bio-oil is much higher than that of biomass, it is more convenient to transport the oil to large scale synthesis plants for fuel production. For application of this conversion chain the reforming of bio-oil into synthesis gas is essential. However, due to the special feature of biomass the conversion into synthesis gas is not yet an up-to-date technology. Finding solutions to solve this problem is another aim within ReFuelNet.

3.4 Demonstration of renewable methanol synthesis

At the Centre for Solar Energy and Hydrogen Research (ZSW) Stuttgart two technologies for renewable methanol synthesis has been developed. The technologies are based on methanol production of CO_2 and H_2 and biogas respectively. The methanol production of biogas is schematically shown in Figure 2. At an existing municipal waste water treatment plant where biogas is forwarded for a combined heat and power plant (CHP), a part stream of the biogas was used for methanol synthesis.

The advantage of the combination of CHP plant with methanol synthesis as shown in Figure 2, is the possibility to operate the reactor in one through mode. The tail gas from the synthesis reaction is used for reformer heating or can be routed to the power generation in the CHP.

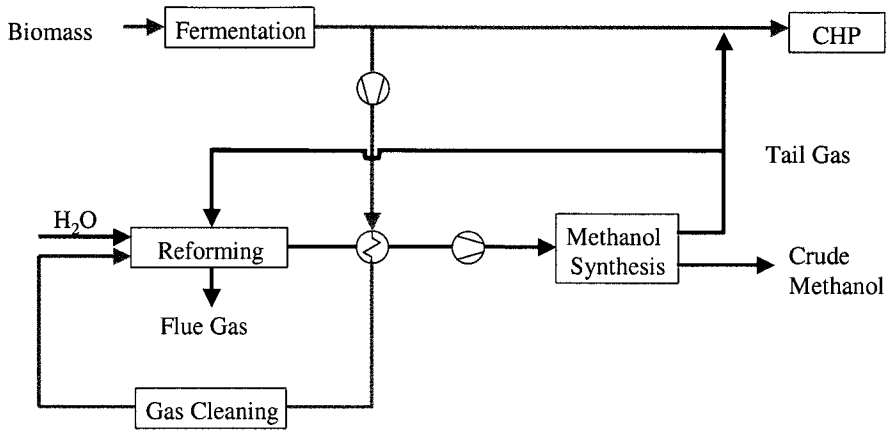

Figure 2: *Schematic process flow sheet of methanol synthesis from biogas in combination with CHP plant.*

3 Utilisation

The use of renewable fuels depends beside fuel costs on resource availability and environmental concerns. The most important options are bio-diesel, methanol, ethanol, synthetic petrol and diesel, methane and hydrogen.

Nowadays in western Europe and especially in Germany bio-diesel plays a significant role. The current share of bio-diesel in petroleum diesel is about 1.1 % (Germany 2001). Related to the total transportation fuel consumption it amounts to 0.55 %. The German consumption of biodiesel in 2001 was 600 000 t/a, corresponding to 680 Mio l/a.

In North America and Brazil ethanol production of sugar and starch containing plans is widespread. Ethanol can be used as blends with gasoline e.g. E10 (10 vol.% ethanol, 90 vol.% Gasoline) without engine modifications. Also higher blends are possible e.g. E85 (85 vol.% ethanol), however their use requires adapted engines. Furthermore ethanol could be used as substitute for MTBE (Methyl-Tertiary-Butyl-Ether) in gasoline or as a raw product for ETBE (Ethyl-Tertiary-Butyl-Ether) production.

An overview of different fuels concerning their CO_2 emissions and estimated specific costs are shown in Figure 3. For an evaluation of renewable fuels not only commercial aspects should be taken into account. Furthermore their CO_2 reduction potential, biodegradability and the security of supply should be considered. Nevertheless, looking at the costs of conventional petrol and diesel including tax, the renewable fuels, biogas, bio-diesel and methanol (from concentrated CO_2 and cheap hydropower electricity) are in the same cost range but their clear advantage is the much lower green house gas emission. The renewable fuel production costs increase by gasifying biomass with a subsequent fuel generation or if solar electricity from solar thermal power plants will be used as energy source.

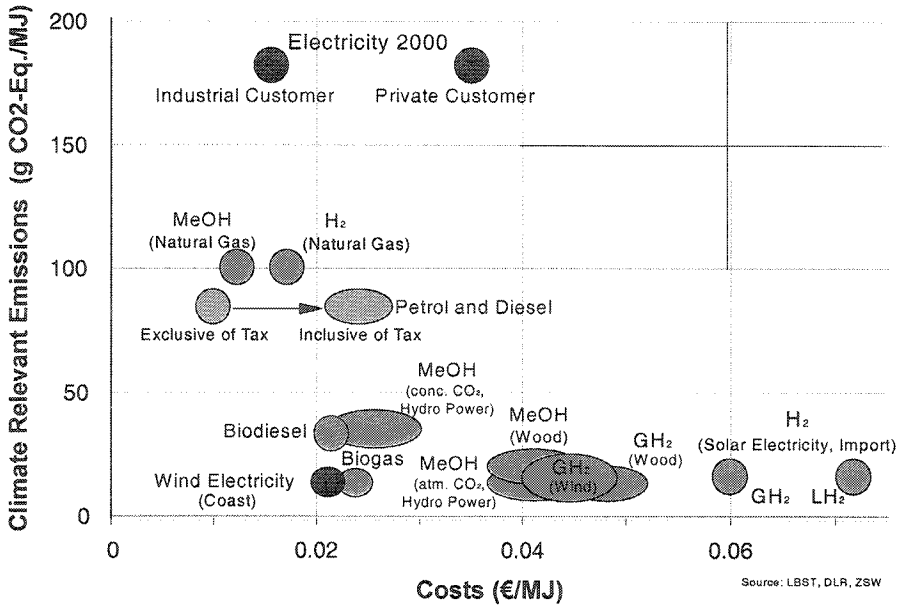

Figure 3: Climate relevant emissions and estimated specific costs of renewable fuels (in comparison with electricity produced in Germany) [5]

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Components and Manufactoring

NOBLE METAL FREE CATALYSTS FOR OXYGEN REDUCTION IN PEM FUEL CELLS

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A platinum free catalysts was prepared by mixing tetramethoxyphenylporphyrin cobalt with iron oxalate and by a subsequent heat treatment at 850 °C under inert gas for 2 hours. Afterwards, the product was etched in hot HCl to get rid of alloys and iron oxides formed. Kinetic current vs. voltage measurements inferred from rotating disc electrodes manifactured from this catalyst showed a catalytic activity for oxygen reduction which was comparable to platinum. The new catalyst, consisting of an in-situ generated carbon support with integrated catalytic Fe-Co centres, was stable within 100h under RDE operation conditions.

1 Introduction

In processes converting chemical into electrical energy under clean environmental conditions the development of polymer electrolyte electrode fuel cell (PEM-FC) system plays a central role.
The application of fuel cell stacks attracts interest not only for vehicles but also for stationary power generation. Regarding the decentralized electrical energy supply by stationary cell systems, a contribution to the electrical power generation of up to 10 % has recently been anticipated until 2010 (Grove Conference, London, 2001).
However, to manufacture a hydrogen-driven PEM-FZ and especially a Direct Methanol FC-module of 60 kW, 90 g platinum (1.5 g per kW) have to be employed at present. Using platinum for this application alone even the annual platinum world production of 150 t will not cover the requirements for a modul fabrication in a large scale. For this reason, alternative catalysts are in demand to decrease the price for the FZ-module at one hand and to guarantee a broad application of PEM-FC on the other.

2 Experimental

An alternative catalyst was prepared by impregnating an iron oxalate powder (FeC_2O_4 x 1.5 H_20; $3g \equiv 1.76 \cdot 10^{-2}$ mole) with tetrakismethoxyphenylporphyrin cobalt (CoTMPP, $C_{48}H_{36}CoN_4O_4$; 0.65g $\equiv 8.2 \cdot 10^{-4}$ mole) as a nitrogen-containing, organic transition metal complex and by subsequent thermolysis of this product at 450°C for 1h and 850° C for 2 hours in an argon gas flow. The reaction steps of catalysts formnation were investigated using a thermobalance (NETZSCH STA 409C), the gases released during the process were simultaneously analysed by means of a mass spectrometer coupled by a skimmer with the heated furnace. To characterise the catalytic centre and the morphology of the catalyst, X-ray diffractometry, scanning electron microscopy (SEM) and Extended X-ray Absorption Fine Structure EXAFS analysis were applied. The catalytic activity and the selectivity versus methanol was measured using rotating disc electrode (RDE) technique.

3 Results

3.1 Thermal Analysis Coupled with Mass Spectrometry

Fig. 1 shows the thermal behaviour of the oxalate – CoTMPP mixtur. In a first step, iron oxalate releases about 1.5 mole crystal water above 150°C prior to decompose in a second step into FeO (wustite) above 330°C releasing CO_2. At temperatures above 450°C CoTMPP starts to polymerise (release of $CH_3C_6H_5$) and to reduce iron oxide to iron visible as asymmetric tail in the CO_2 mass curve in Fig. 1. From XRD measurement it can be concluded that the iron reacted with cobalt forming a Co-Fe alloy (weirauite). Heating the mixture up to temperatures of 1000°C no further mass change occurred above 600°C.

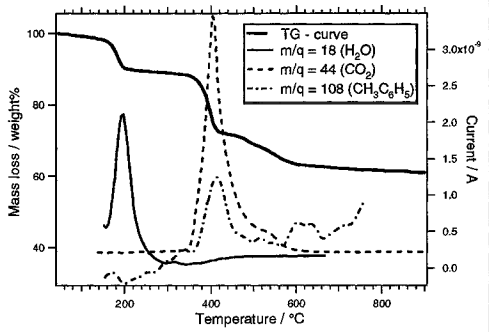

Figure 1: Thermogravimetric curve of thermally decomposed FeC_2O_4 x 1.5 H_2O and of its reaction with CoTMPP. The gas spezies H_2O and CO_2 and the methoxyphenyl groups evolved during the process were measured by mass spectroscopy.

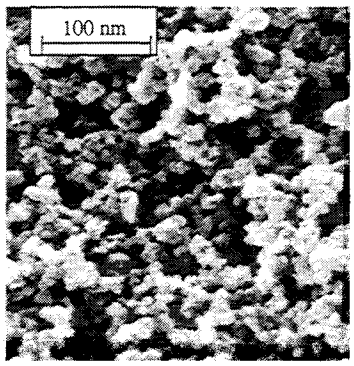

Figure 2: Scanning electron micrograh of a Co-Fe catalyst prepared by thermolysis of iron oxalate in presence of CoTMP and etched in HCl. The final product exhibits a highly porous structure with carbon particles of 10 nm size.

3.2 Scanning Electron Microscopy and X-ray Diffractometry

Using a GEMINI Scanning Electron Microscope the structure of the product was analysed. The catalyst obtained after heat treatment consisted of orthorhombic particles of dimensions 10 x 3 x 3 μm^3. X-ray diffractogrammetry using a SIEMENS D500 revealed that the material was composed of carbon, a cobalt-iron alloy (wairauite) and FeO (wustite). After treatment in hot HCl, wustite disappeared and only small graphite particles could be detected by XRD. This result was confirmed by a SEM micrograph (Figure 2).

3.2 Rotating Disk Electrode Measurements

A high activity studying oxygen reduction by RDE technique has been found which is comparable to a Pt/C-standard. The differences in the kinetic current density vs. voltage curves between both catalysts decrease with increasing current. However, these high catalytic activities could only be achieved when crystalline FeO and FeCo alloy phases formed during pyrolysis were etched away and the catalyst was tempered under inert gas afterwards.

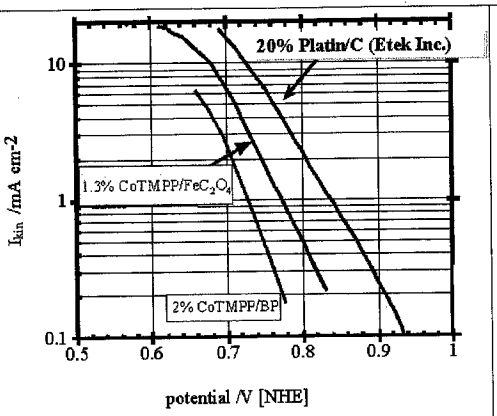

Figure 3: Kinetic current vs. potential curve of a platinum standard, a carbon supported Co catalyst (load 2weight%) and a carbon supported FeCo catalyst (1.3 weight%)..

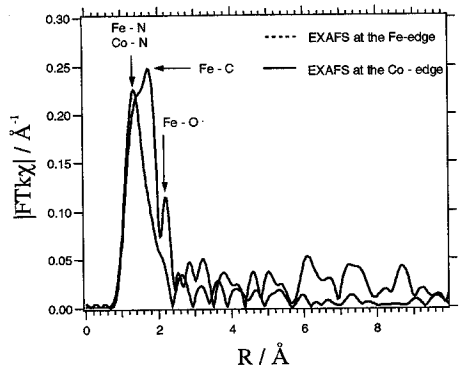

Figure 4: Fourier transformed EXAFS spectrum measured at the edges of iron and cobalt. Three different distances were found analysed as Fe-N, Co-N, Fe-C and Fe-O.

3.3 Extended X-ray Absorption Fine Structure EXAFS and Mößbauer Measurements

EXAFS measurements were performed at BESSY using the absorption edges of Fe at 7112 eV and of Co at 7709 eV. Analysis of the spectra elucidated that iron and cobalt atoms were bonded via nitrogen, oxygen and carbon in the carbon matrix (see Fig. 4). From the height of the absorption edges the cobalt to iron ratio of about 0.1 was inferred. To elucidate the coordination of Fe centres in the catalyst ^{57}Fe Mößbauer spectra were performed preparing a Co-free catalyst pyrolising FeTMPP-Cl [1]. The spectra were measured employing a constant accelleration of the absorber. The Mößbauer source was ^{57}Co/Rh. It was found that the iron bearing catalytic centres are characterised by sixfold coordinated Fe^{3+} ions.

4 Discussion

Tentatively, in the following an attempt will be made to explain the formation and the structure of the catalyst. Scanning electron micrographs of the iron oxalate before heating exhibited the identical particle shape as the highly porous product shown in Fig. 2b after HCl treatment. This means that in the decomposition process pyrolized CoTMPP pentrates via holes generated by release of CO and CO_2 into the decomposing iron oxalate gradually filling the shape of the orthorhombic particles. After treatment in hot 1N HCl, XRD only showed the typical pattern of nm-sized carbon. EXAFS measurements performed at the Fe- and Co-edge allowed a further inside into the bond distances of the metal centres, still present in the catalyst. The maxima of the Fourier transformed EXAFS spectra (Fig. 4) were interpreted as Fe-N, Co-N, Fe-C and Fe-O bond distances.

The catalytic activity of the material is depicted in Fig. 3. The kinetic current vs. potential plot exhibited a high performance of the electrode for the reduction of oxygen in acidic media compared to a commercial platinum catalyst. This activity did not degenerate during 100 h operation time. It is remarkable that such a high activity was observed although the metallic load of the catalyst was much smaller than in platinum catalyst from E-tek (2weight% for a pure Co and 2weight% for a Co/Fe catalyst, respectively). Therefore, it is assumed that Fe-Co-based catalysts could be more active than platinum as soon as the number of active sites could be increased. From XPS measurements it was inferred that iron and cobalt atoms are bonded via pyridinic nitrogen to the carbon matrix. The fact that mixed Fe/Co catalysts showed a better performance than pure Co catalyst allows the conclusion that the higher activity has to be corroborated with the presence of a complex catalytic centre. Further work will concentrate on the increase of the concentration of these centres.

5 Acknowledgments

Financial support by the BMBF under contract no. 0327067B and by DaimlerChrysler is gratefully acknowledged.

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INVESTIGATION OF THE INFLUENCE OF THE ELECTRODE STRUCTURE ON THE PERFORMANCE OF DIRECT METHANOL FUEL CELLS

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We present investigations to characterize the electrochemical processes in the DMFC, to measure the methanol permeation and correlate these results with the electrode structure. The metal loading is varied at the anode and cathode affecting the cell performance in a distinct way. Furthermore, it is shown that the methanol permeation can be reduced significantly by varying the anode structure but the changed electrode structure also leads to somewhat lower power densities. We discuss the optimum conditions for the DMFC operation considering the various important factors. The discussion is focussed on finding a compromise between fuel cell performance, fuel utilisation and metal loading. These factors are strongly influenced by the methanol permeation, the water permeation and electrode reaction characteristics.

1 Introduction

Direct methanol fuel cell (DMFC) provide the possibility to reduce the system complexity considerably. This concept may also be advantageous with respect to water management and stack cooling. Therefore, a high potential is foreseen in applications like transportation, in decentralized power generation and for portable devices[1]. The main problems associated with a liquid feed DMFCs are the low power density and low fuel utilization. This is related to the methanol and water permeation through the membrane and the slow electrode reaction kinetics. Due to the low reaction kinetics a high noble metal loading is necessary for acceptable performance[2].

The exploitation of the pronounced thermal activation of the electrochemical reactions is limited in liquid-feed systems since high temperatures are causing pressure build up in the

anode compartment which would also require high pressures at the cathode side leading to dramatically reduced system efficiencies[2]. Thus high catalysts loadings are often required to enhance the performance of the anode and cathode resulting in increased cost. Even though Nafion® and its variants are the most commonly used membranes against which other membranes are compared, membrane properties need to be improved with respect to water balance and methanol crossover which can lead to a loss of 30 % or more of the methanol fuel. Hence there is a need to diminish the catalysts loading in the DMFC at the cathode and anode and to prevent methanol crossover as well as water crossover by either new materials or adapted operating conditions. Furthermore, improved membrane electrode assemblies (MEAs) with defined microstructures to optimise the two phase transport at the anode (liquid feed, gaseous CO_2 removal) and cathode (gaseous feed and liquid water removal) in DMFCs are very important. In this paper, we discuss recent work at the ZSW in order to address these issues which are crucial for the success of DMFC systems.

2 Experimental

Membrane electrode assemblies (MEA) were prepared similar to the procedure reported by Wilson et al.[3]. The catalyst inks are prepared by dispersing unsupported or supported catalyst in suprapure water produced by Millipore filtration systems. Then Nafion solution is added to obtain the wanted Nafion content in the ink. Nafion is necessary both for the binding of the electrode as well as for providing proton conductivity to the active layer. The alcoholic solution in the spraying procedure was considered a potential hazard due to the possibility of inflammation. Therefore an alcohol-free Nafion solution was prepared in a rotation evaporator using a 15 wt% Nafion solution with a corresponding equivalent weight of EW 1100. During evaporation suprapure Millpore water was added and therefore a diluted solution with a Nafion content of 5 - 8% was obtained.

The preparation of the catalyst ink consisted in stirring the ink for least for three days. Only after this preparation procedure electrodes layers with sufficient binding to the electrolyte could be produced. However, if the ink is stirred too extensively (>2 weeks) lower power densities especially at higher temperatures were observed. It is assumed that this is due to an agglomeration of catalyst particles in the ink. Shortly before the cathode catalyst ink is sprayed, a PTFE suspension is added (Dyneon TF5032 PTFE, 60%) and stirred for a short period of time. If the solution is stirred to extensively (longer than 10 min.) in the presence of PTFE, gravy formation is observed which blocks the spraying nozzle. The PTFE addition is necessary in order to form hydrophobic regions in the cathode in order to avoid flooding of the pores in the DMFC operation. These hydrophobic properties improve considerably the air access to the active sites. This improvement is especially observed at the higher current densities, which involves the formation of considerable amount of reaction water.

The electrolyte membrane (Nafion® 105) is prepared in the usual way before being coated with catalyst[4]. The gas diffusion electodes are prepared by a spraying directly onto the

membrane: The wet membrane is fixed in a frame before being coated with catalysts. After fabricating the electrodes by spraying, a tempering step at 135°C for >25 min in an oven follows. The catalyst loading is calculated by comparing the weight of the MEA after drying with the weight of the membrane and the catalyst content of the ink.

The MEA is introduced in a dry state into a graphite cell from Electrochem, with an active area of 25 cm^2 and a serpentine flow field with 5 parallel channels of 1x1 mm, width of the ridge: 1 mm). As gas diffusion layers teflonized carbon papers are used (Toray TGP-60, 25% PTFE, compression by about 40% in the cell).

3 Results and Discussion

3.1 Performance versus methanol cross-over

The performance of our DMFC operated with 1 M methanol solution is shown as a function of temperature in Figure 1. A strong increase in power density with temperature is observed. At temperatures higher than 100 °C high power densities reaching 250 mW cm^{-2} at 0.5 V are obtained. The influence of the methanol fuel loss is also illustrated in Figure 1 were in addition to the cell voltage versus current density curves also the rate of methanol crossover is expressed in terms of current density. The methanol flux at the cathode is often given by an equivalent current for the total oxidation to CO_2 in order to directly relate it to the cell current density. The methanol permeation rates diminishes with increasing current density since the conversion of methanol at the anode causes a decrease in the concentration gradient. At 600 mV for the measurement at T= 110 °C the methanol lost due to permeation is in the range of 200 mA cm^{-2} and almost identical to the cell current density. This means that the faradaic efficiency $\eta_{far} = I_{cell} / (I_{cross\text{-}over} + I_{cell})$ corresponds to only 0.5 in this case which would lead to cell/stack efficiencies well below 30 %. At 0.5 V cell voltage, however, the faradaic efficiency is in the range of 0.85 which is acceptable and shows how careful the operating conditions of the DMFC have to be chosen with the present materials.

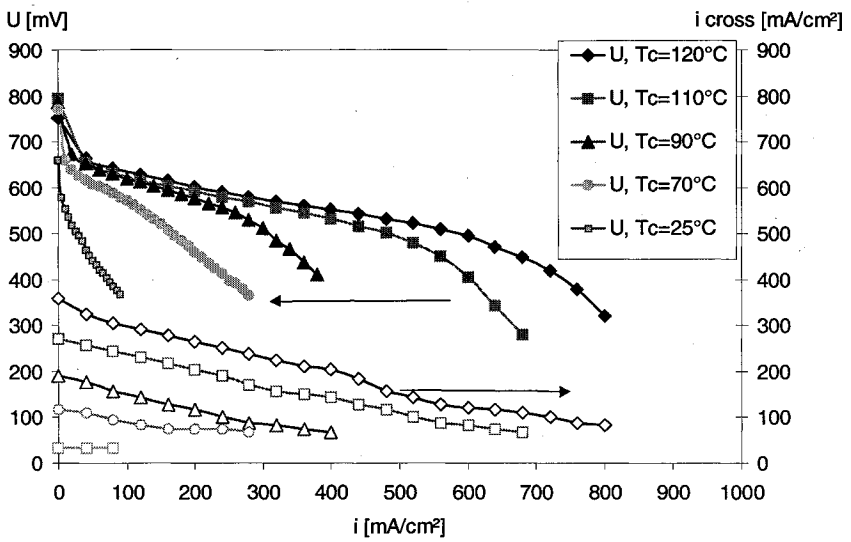

Figure 1: DMFC performance curves for MEAs with different cell temperature. Full symbols correspond to voltage versus current density whereas the open symbols correspond to the permeated methanol expressed in terms of current density (measured with a CO_2 sensor). Air flow is 4 l/min air flow, Nafion® 105, 1 mole/l methanol, Anode: unsupported 5.4 mg cm^{-2} Pt-Ru, 2.5 bar pressure, cathode: unsupported 6.3 mg cm^{-2} Pt, 5 bar pressure.

It is clearly seen in Figure 1 that the methanol permeation increases with temperature and at higher temperatures the polymer backbone expands due to softening of the fluorinated chain leading to increased permeation of methanol as well as water. The rate of methanol permeation with the present membranes restricts the concentration of methanol to values lower than 2 M solution [5,6].

3.2 Importance of Electrode Structure

In the measurement of Figure 2 different anode structures with high power density single cell DMFCs are compared. The square symbols correspond to a conventional anode structure which exhibits the highest power densities. The circles and triangles correspond to a anode structure in which the diffusion layer was highly hydrophobized. Again, the methanol permeation rates diminishes for all U-I curves with increasing current density since the conversion of methanol at the anode causes a decrease in the concentration gradient.

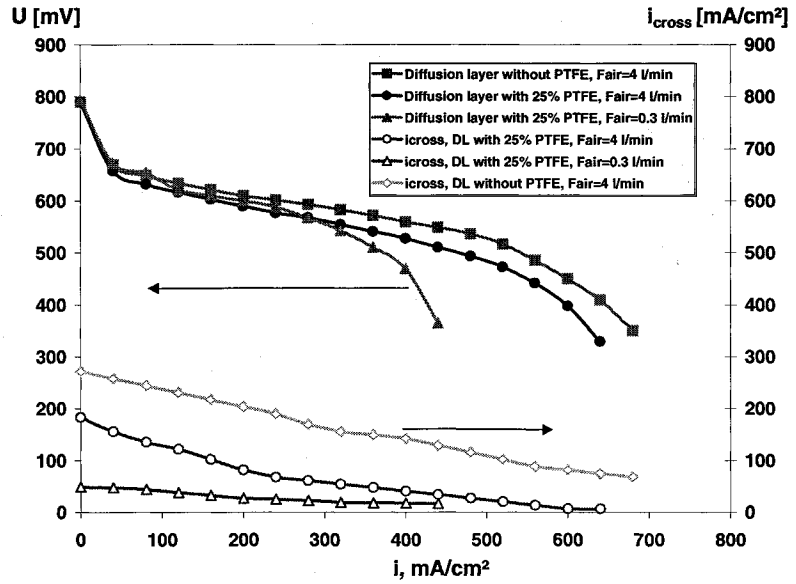

Figure 2: DMFC performance curves for MEAs with different anode structures and different air flows at the cathode. Full symbols correspond to voltage versus current density whereas the open symbols correspond to the permeated methanol expressed in terms of current density (measured with a CO_2 sensor). Cell Temperature 110 °C, Nafion® 105, 1 mole/l methanol, Anode: unsupported 5.4 mg cm^{-2} Pt-Ru, 2.5 bar pressure, cathode: unsupported 6.3 mg cm^{-2} Pt, 5 bar pressure.

A changed anode structure by introducing a high degree of hydrophobic components reduces the methanol permeation. A possible explanation is that methanol is oxidized more efficiently at the anode due to the formation and stabilization of gas bubbles in the active area. As a consequence the methanol concentration gradient across the membrane is reduced. However it has to be cautioned that the complex structure of the diffusion electrode obscures the causative relationships. It is noted that in Figure 2 a lower air flow leads to much reduced methanol permeation through the membrane consistent with a pervaporation behaviour of the membrane. Concurrently a reduced power density results. Nevertheless, an operation at reduced flow rates is advantageous regarding system efficiency. Although the MEAs which exhibited a reduced methanol permeation attain inferior power density their system efficiency is higher because of the better fuel utilization (see above). It has been reported that if the anode is sufficiently active to oxidize methanol electrochemically to CO_2 at a rate comparable to the supply of methanol, the concentration gradient and concurrently the methanol permeation drops to negligible levels [7].

3.3 Performance versus noble-metal loading

Precious metal alloys supported on carbon nano-composites of high surface area are the most commonly employed catalysts in fuel cells. There are reports existing in the literature on both supported and unsupported catalyst compositions and Figure 3 shows a comparison of supported and unsupported catalysts and the influence of reducing the cathode noble metal loading. Carbon supported catalysts have the advantage that the loading can be reduced without a concurrent decrease of electronic conductivity of the electrode. Unsupported catalysts have been shown to exhibit higher current densities for methanol oxidation, but the mass specific catalytic activity is higher for supported catalysts[1]. Supported catalysts offer a smaller crystallite size and relatively higher surface area compared to unsupported catalysts. The thickness of electrode made with supported catalysts play an important role in the mass transport of the fuel cell.

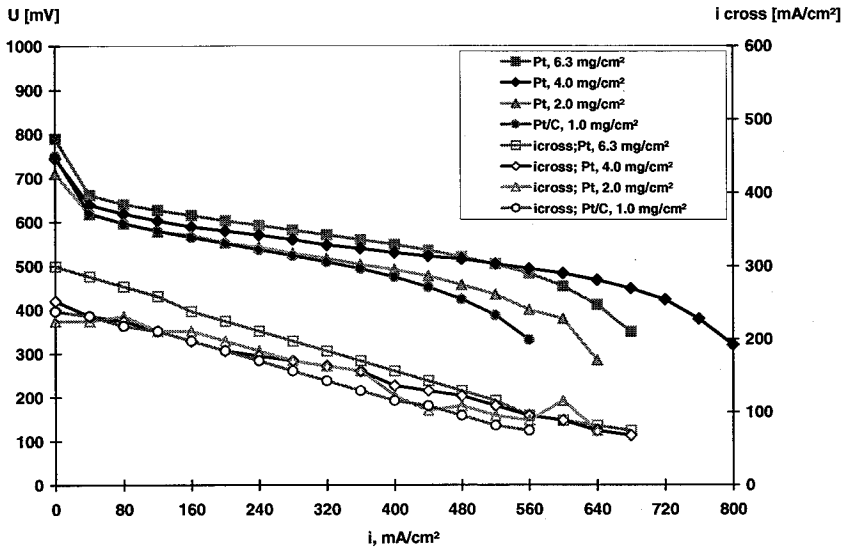

Figure 3: DMFC performance curves for MEAs with different cathode catalyst loadings of unsupported and supported catalysts. Full symbols correspond to voltage versus current density whereas the open symbols correspond to the permeated methanol expressed in terms of current density (measured with a CO_2 sensor). Cell temperature 110 °C, Nafion® 105, 1 mole/l methanol, Anode: unsupported 5.4 mg cm^{-2} Pt-Ru, 2.5 bar pressure.

Figure 4 shows the DMFC power density at 0.5 V cell voltage as a function of reduced anode and cathode loading. It is shown that it is possible to obtain high power densities in the range of 200 mW cm^{-2} at 0.5 V with significantly reduced loadings. A stable operation was observed. Only when the cathode loading is reduced from 2 to 1 mg/cm^2 a pronounced

decrease was observed which, however, was not present when using supported catalysts. Therefore, one can hope that the utilization of supported catalyst and their optimization in the electrode structure will lead to a significantly reduced metal loading which will contribute to the cost reduction in DMFCs.

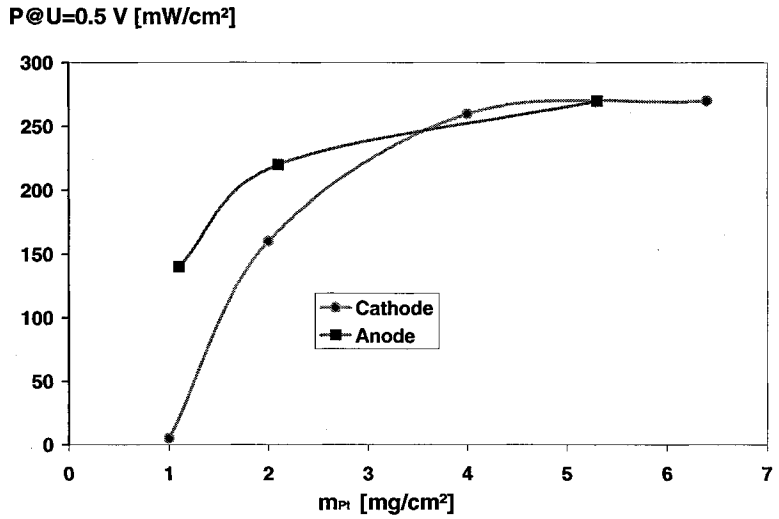

Figure 4: DMFC performance at 0.5 V for MEAs with different cathode and anode catalyst loadings of unsupported catalysts. Cell temperature 110 °C, Nafion® 105, 1 mole/l methanol.

3.4 Stack Design

In Figure 5 a stack development at ZSW with 12 cells and autonomous operation is shown. The stack is operated in the range of 70- 90 °C using standard materials like Nafion® 105 and high noble metal loading of about 11 mg cm^{-2}. The power density at 0.5 V corresponds to 55 - 60 mW cm^{-2}. The components of this stack are mainly graphite based, although some metallic components related to the sealing have been introduced. At present, the improvement of the MEA materials is generally given a higher priority in the development of DMFC compared to the stack development[1,2].

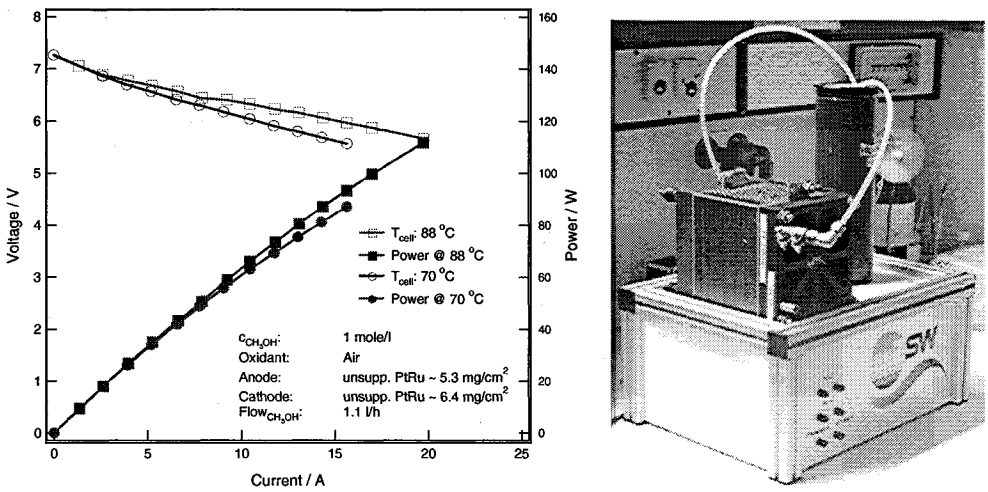

Figure 5: left:Performance curve of a 12 cell autonomous DMFC stack at T_{cell}= 88 °C and 70 °C.

right: Image of 12 cell autonomous DMFC system.

4 Summary and Conclusions

The direct methanol fuel cell is an attractive option for numerous applications. However, this concept is hindered in its use by limitations which are associated with the non ideal properties of the standard materials presently employed. This is essentially the insufficient activity of the catalysts and the high methanol permeation through the membrane. In this contribution it is shown that it is possible to improve on these non ideal properties considerably by optimizing the electrode structure and choosing the operating conditions carefully.

The temperature dependent U-I curves show that the operating temperature has a significant influence on DMFC performance because the activity of the electrodes is increased at higher temperatures but concurrently the methanol crossover is also increased. In this respect, the electrode structure is of paramount importance: e.g. a hydrophobic anode backing leads to an increase of power density and decrease of methanol cross-over (increase in faradaic efficiency). With such an optimized electrode structure stable operation of the DMFC at lower air stoichiometry is possible. This was not the case for the standard anode backing.

A general conclusion that can be drawn from the results is that the noble-metal loading in DMFC can be reduced significantly while maintaining a sufficient DMFC performance: E.g. reducing the loading to 3.2 mg/cm^2 (unsupported catalysts) and using a teflonized anode backing still yields power densities of ca. 150 mW/cm^2 at 500 mV with the following operating conditions: 110 °C, air flow 1.25 l/min (λ=9,6) or 130 °C, air flow 0.3 l/min (λ=2,3).

The use of supported catalysts is promising and should result in further reduction of the noble-metal loading if electrode structures are optimized.

5 Acknowledgement

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Energy Concepts for the Future and Coating Technologies for Fuel Cells

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Fuel cell technology is enjoying growing significance in the discussion on alternatives to conventional energy sources. This is the result of several factors: redoubled energy industry activities focussing on hydrogen technology, rising petroleum prices and ultimately the problem of global warming. The increasing interest – especially on the part of the automotive industry – has lent decisive impetus to developments in recent years.

Fuel cell technology is actually a relatively "old" development. In 1839 William Grove described the basic principle behind the fuel cell. Fuel cells did not find their first larger-scale practical application until the advent of NASA's moon landing program. Those units had only a limited service live but their "waste product" – water – could be used as drinking water for the astronauts.

Following the oil crisis in the seventies, efforts to substitute alternate forms of energy for dwindling fossil fuel resources were increased. The technology achieved its final breakthrough in the wake of the Low Emission Vehicle Act adopted by the State of California. It directs that – by the year 2003 – every vehicle manufacturer must include a 10% share of emission-free vehicles in its fleet. The consequence was a major boost to further development of the systems in regard to size, output and costs.

For many years now the Coatema Coating Machinery GmbH in Neuss has conducted research in this field and has garnered experience in coating technology which can be put to use in the three fuel cell application fields:
-- Stationary plant (output range of 2 to 5 kW or > 250 kW),
-- Automotive applications (output range >70 kW),
-- Mobile applications (output range < 1 kW).

Most of the systems in the pre-industrial stage are PEM (proton exchange membrane) and SO (solid oxide) fuel cell systems. It is expected that stationary and mobile fuel cells will reach maturity for marketing in 2004. General market introduction of automotive systems is anticipated for sometime in the period from 2005 to 2010.

How they Work

The great difference between this and traditional energy generation systems is found in the direct electrochemical conversion of a fuel (such as hydrogen) into electrical and thermal energy. In combustion engines the fuel is first converted chemically into thermal energy and then – in the engine or the turbine – into mechanical energy and, using a generator, is ultimately turned into electrical energy. A fuel cell system can reach efficiency levels of up to 40% in standard operations and as much as 70% when combined with thermal energy converters, this being in comparison to efficiency levels of from 20 to 30% in conventional systems.

The electrochemical process is essentially the reverse of electrolysis. The fuel cell itself comprises membrane electrode assemblies (MEA), bipolar plates and end plates. The MEA, where the electrochemical process actually transpires, comprises the anode, cathode and an electrolyte (polymer membrane) which separates the two electrodes and the systems feeding the reactants. Fuel is continuously fed to the anode. There, in the presence of a catalyst (platinum), it is split into electrons and ions, the ions being transported through the electrolytes to the cathode. Due to the difference in electrical potential between the fuel gas and oxygen, the electrons flow through an external circuit (where the electrical load is connected) to the cathode and in so doing perform electrical work. At the cathode, ions and electrons combine with the oxygen fed to the cathode to form water, which is discharged as water vapor. The operating temperature of such a PEM fuel cell is about 80°C; each cell will generate about 0.7 V.

Air or water cooling is required for operation since thermal energy is liberated during the electrochemical conversion process. In addition, the fuel and the air fed to the system will have to be humidified in order to keep the electrolytes moist, since the presence of water promotes proton conductivity in solid electrolytes.

Development Potentials

Fuel cell systems differ according to their operating temperatures and the electrolytes used. The PEM fuel cell is to be used to examine the development potentials:

- -- The costly catalyst (platinum) used here tends to suppress demand due to high raw material prices.
- -- The gas diffusion layers (paper, non-wovens, fabric) require improvement in regard to manufacturing costs and handling.
- -- As regards the electrolyte (polymer membrane), optimization is needed to optimize manufacturing costs, handling and temperature resistance.
- -- The material for the bipolar plates (graphite or coated metal) requires improvement of the coating technique.
- -- The system as a whole (stack, reformer, transformer, fuel) will have to be optimized throughout.

Major efforts are necessary in all these areas, and in particular in regard to costs, if the targeted goals are to be reached.

Coating technologies

Differentiation is made according to the coated substrates when discussing the coating methods used in fuel cell fabrication. On the one hand the gas diffusion layers made of paper, non-wovens or fabric are impregnated and coated; on the other hand, the coating is applied to the electrolyte itself. In addition the bipolar plates, if they are made up of metal, will have to be coated as protection against corrosion.

A MEA is made up essentially of a membrane located between two coated gas diffusion layers. Due to its simpler handling, non-wovens materials are currently being used in the main, although the use of carbon fabrics is increasing. Deposited on the membrane or the gas diffusion layers is a catalyst made of a mix of platinum and carbon black, applied for platinum density of between 8 and 0.25 mg/cm_. These figures are based upon publications available to

date. The goal in the future will have to be to reduce platinum loading in order to lower the costs for the system as a whole. The MEA manufacturing process includes six steps:

-- Impregnating,
-- Coating,
-- Drying / Cooling / Sintering,
-- Calenderization,
-- Laminating,
-- Assembly.

Coating Processes

There are two coating processes which are in common use. The first is the application of the catalyst to the gas diffusion layers. The substrate is first rendered hydrophobic for this purpose. This is followed by the coating of the catalyst layer, with the mix of platinum and carbon black. In the following process step they are laminated with the membrane. The catalyst may be applied in a repeating pattern or across the entire surface area. In addition, a gasket or seal is attached at the edges.

In the alternative process the gas diffusion layer is also made hydrophobic In contrast to the first variation, however, the catalyst is applied directly to the membrane, before the two gas diffusion layers are bonded to it.

All the processes are at present running in initial, discontinuous operations at laboratory scale or at smaller pilot plants. Coatema's approach is, with the assistance of continuous, short-run manufacturing plants, to explore the process parameters for a large production line so as to be able to offer – at a uniform quality standards – production lines such as this in coming years. Process standardization in stack manufacturing in particular represents great development potential for mechanical engineering firms and stack producers.

From the mechanical engineer's point of view, it is necessary to point out the necessity for intensive research and development work in process optimization and developing new coating techniques. The market players, who for years now have been investing massive effort and vast research resources, could in this way achieve a one- to three-year lead and thus a competitive advantage in development work. Thus, and only by way of major investments in process technology, it will be possible to reach the desired orders of magnitude and profit from the learning curve. To be emphasized here is the involvement of two of the German states – Baden-Württemberg and North Rhine-Westphalia. With the installation of working circles and competence centers they are successfully supporting these efforts and thus are ensuring successful implementation of this energy of the future.

Modelling and Simulation

AN EFFECTIVE AND RELIABLE METHOD FOR SINGLE FUEL CELLS EXPERIMENTAL TESTING AND RESULTS COMPARISON: TEST PARAMETERISATION AND PROCEDURE DEFINITION

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The great interest in Fuel Cell Systems, together with the novelty of the device itself, has determined a huge development effort aimed at attempting to make the steps that are considered necessary for future FC plant commissioning.
The Energy System Group of the University of Perugia is currently performing single cell testing. Since the beginning of this activity, therefore, particular emphasis has been put on testing procedures definition and test parameterization. The work team strongly believes that this is a winning key to effective system testing and reliable performance evaluation.
In this work the test procedures and parameters developed by the team are presented. The effort has been put in obtaining some relevant non-dimensional parameters to allow easy comprehension of the results and quick comparisons with other tests in different operating conditions or with results obtained on different cells eventually tested in different laboratories. All the parameters are in the range between 0 and 1 and are set in order to assume a value that equals to zero if the related quantity is not present. This implies the assumption of some test reference conditions. The authors strongly recall attention on this topic to avoid that all the data that both developers and research institutions are collecting will be of no practical use because of lack of common rules.
The parameters presented don't aim at giving rules that should be universally recognized but at driving attention on the most relevant issues that should be considered when testing a single cell and at constituting a reference work for future discussion. This should be considered the first effort on the way of defining standard testing procedures.

Introduction

The conversion of chemical energy directly into electrical energy without a combustion process have been known in concept since the middle of the 19th century, thus making fuel cells one of the oldest electrical energy conversion technologies. However, only in the last two

decades fuel cell devices have been recognized as one of the most promising technologies for power production, since they can be the answer in almost every field of energy requirement.
The tendency to increase the flexibility of electricity generation and the deregulated electricity generation market needs have led to a rapid development of more finely distributed power generation. Traditional power plants, however, are destined to fail in this field since they are characterized by a dramatic scale effect, with rapidly decreasing efficiencies with decreasing power outputs. On the other hand, the efficiency of a fuel cell is potentially superior to any other energy system and it is nearly unaffected by size. This allows their application for stationary power from few kWs (Sammes et al., 2000, King et al, 2000) to, in principle, many MWs (Lunghi et al., 2001[1], Lunghi et al., 2001[2], Lunghi et al., 2001[3], Ubertini et al., 2001, Lobachov et al. 1997). Smaller plants can be sited at the user's facility, while plants of few MWs are more suited for distributed power production.
The virtually absent scale effect make them also particularly attractive for miniaturized and portable power applications. Moreover, the limited emissions that characterize fuel cells systems can be the answer to the growing concern for the environmental issues requirements. The application of hydrocarbons for hydrogen production would anyway almost eliminate NO_x and CO emissions, that characterize conventional energy systems. Considering that their efficiency is higher than heat engines, the emissions of carbon dioxide are reduced too.
If hydrogen is produced by splitting water through processes involving renewable energy (Momirlan et al., 1999) and then used in a fuel cell, the only emission would be water vapor.
Fuel cells are also distinguished from traditional power generating technologies by other attractive characteristics including quite operation, low level of danger, rapid transient response and minimal requirements for maintenance (King et al, 2000).
Therefore, fuel cells market penetration is developing stepwise; from niche utilization in space and military applications, they are now entering the power production commercial markets at almost all levels. Fuel cells are being developed or are already in the market for stationary power, transportation vehicles, underwater and portable applications. Phosphoric acid fuel cells have entered the marketplace with several units with more than 40000 hours of operation. Polymer electrolyte fuel cells (PEM), solid oxide fuel cells (SOFC) and molten carbonate fuel cells (MCFC) are now at the stage of scaling-up to commercialization and many prototypes are being tested in pilot power plants in Europe and USA (Ali et al., 2000; Kordesh et al., 1996). MCFC full-scale power plants tests are needed to achieve 100% successful commercial-scale demonstration, which is foreseen in less than ten years (Hussey et al., 1999; Ito et al., 1997). Open access and competition are expected to increase the opportunities for fuel cell technology within the coming decade, as the deregulation evolves in USA and European markets. The Department of Energy Program in the USA is largely investing in fuel cell applications and the European Union has recognized the prospects of fuel cells with almost 100 Meuro allocated to fuel cell projects in the last decade (Borthwick, 1999). In Japan, the R&D of MCFC is carried out by the New Energy Industrial Technology Development Organization (NEDO) and, since 1993, a 1000 kW MCFC power plant installation has been performed (Ishikawa et al., 2000).
However the actual impact of fuel cells is strongly limited by durability, costs and, in automotive applications, by weight, volume and operational limitations. A number of technical problems such as corrosion and reliability still must be solved in some fuel cell types.

Furthermore, considerable additional progress in simplification of the product design, improvement of component performance and development of manufacturing processes is required. Questions have also been risen on requirements for connection to the grid, strongly affected by non-standardized procedures.
The fuel cell power units are made up of three major sections:

- the fuel processing section or reformer;
- the fuel cell stack;
- the power conditioning unit.

The fuel cell stack, made up of a certain number of single fuel cells, is the plant section where all the reactions that produce electricity take place. This paper deals with the experimental activity on single fuel cells or stacks.
In order to reach all the necessary targets in the relatively short times dictated by market rules, a synergy between researchers and institutions, developers and manufacturers is required. The greatest effort consists in experimentally validating computational predictions demonstrating the ability of the systems to achieve the calculated values of the relevant operational and life parameters. This is a long, time and resources consuming activity since every experiments constitutes a feedback for the design activity that should improve the system itself thus requiring further experimentation. In order to join resources to reach the ambitious target a virtual testing facility around Europe and around the world must be created.
It is obvious that the shift from site laboratory to a virtual facility, from enterprise work groups to net actions, from proprietary results to shared community knowledge requires a common language and common testing rules.
The Energy System Group of the University of Perugia is currently performing single cell testing. The presence of different and continuously renewing actors, like students working on the facility for their MSc or PhD thesis, and the need of data exchange with the partners in the various research projects attracted attention on this topic. Since the beginning of this activity, therefore, particular emphasis has been put on testing procedures definition and test parameterization. The work team strongly believes that this is a winning key to effective system testing and reliable performance evaluation.
The authors strongly recall attention on this topic to avoid that all the data that both the developers and the research institutions are collecting will be of no practical use because lack of common rules. In this work the test procedures and parameters developed by the team are presented. The effort has been put in obtaining some relevant non-dimensional parameters to allow easy comprehension of the results and quick comparisons with other tests in different operating conditions or with results obtained on different cells eventually tested in different laboratories. All the parameters are in the range between 0 and 1 and are set in order to assume a value that equals to zero if the related quantity is not present. This implies some test reference conditions assumption.
Let's we assume that the reference test condition has hydrogen in the anode side and carbon dioxide and oxygen in the cathode side. If we want to put Nitrogen in the gas streams we must consider its "role", if it is considered to be a diluting substance, then dilution parameters, one for the anode and one for the cathode, must be introduced: when theirs values are zero there should be no nitrogen in the anode and cathode streams. If, instead, we assume that the reference test condition has hydrogen in the anode side and air in the cathode side the cathode

dilution parameter should be zero, when in the cathode is present a nitrogen quantity which proportion to oxygen is 21/79. Things get more complicated when all possible input substances are considered. Nevertheless keeping the above parameter rules in mind it is possible to obtain a set of equations that, when resolved, gives the values of the parameters for each gas composition and vice versa.
The parameters presented don't aim at being at giving rules that should be universally recognized but at driving attention on the most relevant issues that should be considered when testing a single cell and at constituting a reference work for future discussion. This should be considered the first effort on the way of defining standard testing procedures.

Main assumptions

A fuel cell (Fig. 1) is an electrochemical device in which the chemical energy of fuel is directly converted to electrical energy without combustion.

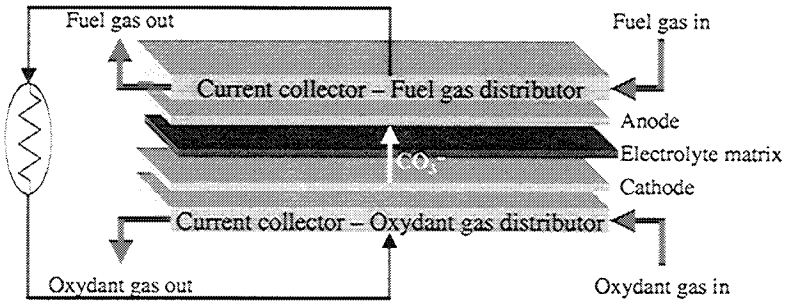

Fig. 1. Fuel cell operational principle

In a fuel cell gaseous fuels are fed continuously to the anode (negative electrode), where their direct oxidation occurs, and an oxidant (i.e. oxygen from air) is continuously introduced to the cathode (positive electrode). Electric charges are transported in the electrolyte (ion conductor) and electrons flow in the external circuit during these reactions.
The primary fuel source is hydrogen, which can be obtained for example from hydrocarbons through a steam reforming process. For the case of hydrogen/oxygen fuel cell the overall reaction is:

$$H_2 + 1/2O_2(+CO_2 \text{ in MCFC}) \rightarrow H_2O(+CO_2 \text{ in MCFC})$$

The Gibbs free energy change of the chemical reaction is related to the cell voltage through the following relationship:

$$\Delta G = -nF \cdot E_0$$

where F is the Faraday constant, n is the number of charges involved in the reaction and E_0 is the equilibrium cell voltage. The equilibrium cell voltage is the difference between the equilibrium electrode potentials, determined by the electrochemical reactions taking place at

the electrodes. The anodic and cathodic reactions, with their equilibrium potentials, varies for different types of fuel cells.
The ideal performance of the reversible fuel cell can be determined through the Nernst equation, that provides a relationship between the standard potential E_0 (potential at standard conditions 1.229 V) and the equilibrium potential E at various temperatures and partial pressures:

$$E=E_0+(RT/2F)\ln(P_{H2}\cdot P^2_{O2}/P_{H2O})$$

The physical behavior of a fuel cell depends upon different parameters and the structures of the diffusion electrode and of the electrolyte are quite complex, thus requiring considerable optimization for practical applications. Considering the great number of variables involved, their non-homogeneity and the huge amount of governing physical-chemical relationships, it is strongly believed by the authors that the principal independent parameters must be uniquely detected, in order to individuate homogeneous, unique and repeatable test conditions.
The fuel cell type (i.e. MCFC, PEM, SOFC and PAFC), age and operating temperature are, for instance, independent parameters and can be directly used for the definition of experimental tests. On the other hand, the same cannot be stated for gas flow rates or current.
To explain the purpose and the philosophy of this paper, let's consider a fuel cell directly fed with hydrogen. The current produced is not uniquely determined by the amount of hydrogen introduced since not all the hydrogen react in the anode; this means that the values of both quantities (current and hydrogen flow rate) must be specified in a test to relate the results to a test condition. It is nevertheless well known that a useful parameter to identify the cell working conditions is the fuel utilization that express the fraction of the fuel that has reacted in the cell. It is evident that one parameter among hydrogen flow rate, fuel utilization factor and current can be expressed by means of the other two. The necessity of establishing some rules for evaluating test conditions is evident.
In the reported example for instance, it seems convenient to eliminate the hydrogen flow rate since:

- the current density can be used to characterize both the anode and the cathode and is useful to express the global parameters (i.e. power output and overpotentials);
- the fuel utilization factor is non-dimensional and it allows to determine the partial pressure of the exhaust gases by means of those of the inlet gases; therefore, it allows to determine the fuel cell Nernst potential.

Considering that in some cases (i.e. MCFC) more than one fuel are sent to the anode and more than one oxidant are sent to cathode, the situation is more complicated.
What are the most relevant parameters that can be utilized to characterize a fuel cell ?
The complete answer to this question would take weeks of discussion and volume of notes. However, comforted by the specialized literature, we have assumed the following parameters as the most relevant:

- Type (MCFC, SOFC, PEM, AFC, DMFC, PAFC)
- Materials (electrodes, electrolyte and fuel);
- Age;
- Operating temperature;
- Operating pressure;

- Current;
- Oxidant flow rate;
- Fuel flow rate;
- Oxidant utilization factor;
- Fuel utilization factor;
- Dilution flow rates at both anode and cathode;
- Steam flow rate;
- Contaminants concentration.

The choice of the parameters to be utilized for a fuel cell characterization procedure should be orientated to distinguish the effects due to different causes, i.e. variation on current or on temperature or on cathode or anode input gas streams, and to distinguish the effects due to qualitative variations from those related to quantitative variations i.e. increase in anode flow rate or change in composition. In the present work the effort has been put in obtaining some relevant non-dimensional parameters to allow easy comprehension of the results and quick comparisons with other tests in different operating conditions or with results obtained on different cells eventually tested in different laboratories. The criterion pursued in the flow rate parameter definition has been that the parameters should be set to be null if the related quantity is absent and have a maximum value equal to 1. This implies some test reference conditions assumption.

The comments and the discussion made in this section become more clear after we have actually defined the parameterization procedure. The procedure starts from a standard test and is characterized by the minimum number of coefficients necessary to define any test.

Fuel cell types: materials and operating temperatures

The heart of a fuel cell is the electrolyte, where the charge carriers (ions) flow from an electrode to the other. The electrolyte can be made of a variety of substances (i.e. alkalines, solids, salts), that are usually employed to classify the fuel cells. An exception to this classification is the Direct Methanol Fuel Cell (DMFC) which identifies a fuel cell in which methanol is fed directly to the anode. The fuel cell type is the first information that should be given when fuel cell performances are provided. For sake of brevity, considering the real objective of this paper the fuel cells classification with their main characteristics is presented in tab.1.

Tab. 1 Fuel cell classification

	PEM	AFC	PAFC	MCFC	SOFC
Electrolyte	Ion exchange membrane	Potassium Hydroxide	Liquid Phosphoric acid	Liquid Molten Carbonate	Ceramic
Charge carrier	H^+	OH^-	H^+	CO_3^{--}	O^-
Operating temperature	80°C	70°C ÷ 220°C	205°C	650°C	700°C ÷ 1000°C

Even if each fuel cell type is characterized by a certain operating temperature range, its exact value has a fundamental importance for its strong effect on performances. The effect of operating temperature on the ideal voltage is easily detectable looking at the Nernst equation. Even if the ideal potential decreases with increasing temperature, the practical effect can be an increase in the operating voltage. The beneficial effect of increasing the operating temperature can be attributed to the increase of the reaction rate, to higher mass transfer rate and usually lower ohmic resistances. Details on temperature effects can be found in (Hirchenhofer, J. H. et al., 2000, Kordesh et al., 1996).
Looking at the operating temperature, a second fuel cells grouping can be done:

- low temperature fuel cells, where can be grouped the AFCs, the PACs and the PEMFCs;
- high temperature fuel cells, of two different types MCFCs and SOFCs.

The great advantage of high temperature fuel cells is that they make a high temperature heat available at the exhaust, that can be recovered in a bottoming cycle to obtain higher efficiency (60%-70%, Lunghi et al., 2001[1], Lunghi et al., 2001[2], Lunghi et al., 2001[3], Ubertini et al., 2001) or for cogeneration purpose (Silveira et al., 2001).

Global performances

The global performance of a fuel cell can be determined through the measurement of voltage and of current.
The operating voltage of a fuel cell is the difference between the reversible potential, given by the Nernst equation, and the losses, usually called overpotential or polarization (Hirchenhofer, J. H. et al., 2000, Kordesh et al., 1996):

- concentration polarization, caused by diffusion processes;
- activation polarization, caused by the fact that the charge transfer has a limited speed;
- ohmic polarization, which is simply the voltage drop across the resistive components of the fuel cell.

From a practical point of view the overpotential is the deviation of the terminal voltage from the open circuit voltage, due to the current flowing through the circuit and the electrolyte. Therefore, the open circuit voltage is an important parameter, but it must be underlined that it is different from the theoretical one, due to mixed potential formation and parasitic processes.
When more than one cells are put together in a stack, a single cell equivalent voltage should be introduced either by a simple average or some more elaborated techniques (cutting head and tails). The power production is anyway obtained from a fuel cell only when a reasonable large current is drawn.
Current is not the best choice as a global parameter, since if we put two identical cells in parallel we obtain the same values of voltage and double current. The problem raises from the fact that current is not an intensive variable. A very simple way of solving this inconvenience is to use current density, i, that is also very commonly (but not universally) used in literature. The parameter is very useful since losses can be related to current density and total current can be easily obtained through cell active area.

The best known adimensional parameter for the definition of the global performances of an energy converter is efficiency. For a fuel cell more than one efficiency can be used following the definitions given by Kordesh et al. (1996).
The thermodynamic efficiency can be obtained as the ratio between the free energy change, that can be totally converted to electrical energy, and the enthalpy available, that measures the chemical energy of the fuel:

- thermodynamic efficiency $\eta_t = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H}$.

Since a fuel cell is an electrochemical device, a measure of the quality of the energy conversion is the electrochemical efficiency, which can be used to adimensionalyze the operating voltage:

- electrochemical efficiency or non-dimensional voltage $\eta_e = \frac{E}{E_0}$

where E is the cell voltage for a single cell or the single cell equivalent voltage for a stack.
Even if we strongly believe that current density is probably the best current parameter to be used, its adimensionalization can be usefully done through the faraidic efficiency defined as the ratio between the effective current density and the theoretically expected current density on the basis of the amount of reactants consumed, assuming that the overall reaction in the fuel cell proceeds to completion:

- faraidic efficiency $\eta_f = \frac{i}{i_t}$.

Flow rates parameterization

The definition of flow rate coefficients that follows is based on the assumption that only the following species are contained in the anode and cathode streams:
H_2, CO, O_2, CO_2, H_2O and N_2.
In the formulas the flow rate of each specie is directly indicated with the specie symbol. The symbol TOT indicates the overall stream flow rate, that can eventually contain gases different from those already mentioned, that anyway do not take part to the reaction.
The standard test is based on a fuel cell in which the anode is fed with hydrogen and the cathode is fed with air and carbon dioxide with:

$$CO_2/O_2=2 \qquad (1)$$

Once the current is fixed, the definition of the fuel cell alimentation needs two utilization factors, one for the fuel flow rate at the anode and the other for the fuel flow rate at the cathode.
Referring to tab. 2, that summarizes the electrochemical reactions of all types of fuel cells, since each mole of hydrogen that reacts in the anode frees two moles of electrons, the fuel utilization factor is defined as:

Tab.2 Electrochemical reactions of fuel cells

Fuel cell	Anode	Cathode
PEM and PAFC	$H_2 \rightarrow 2H^+ + 2e^-$	$2H^+ + 1/2O_2 + 2e^- \rightarrow H_2O$
AFC	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$
MCFC	$H_2 + CO_3^{--} \rightarrow H_2O + CO_2 + 2e^-$ $CO + CO_3^{--} \rightarrow 2CO_2 + 2e^-$	$1/2O_2 + CO_2 + 2e^- \rightarrow CO_3^{--}$
SOFC	$H_2 + O^{--} \rightarrow H_2O + 2e^-$	$1/2O_2 + 2e^- \rightarrow O^{--}$

- hydrogen utilization factor $$U_{H_2} = \frac{e^-}{2 \cdot H_2}; \quad (2)$$

if eq. (1) is verified the cathode oxidant utilization can also be described by a single equation:

- oxidant utilization factor $$U_{ox} = \frac{e^-}{2 \cdot CO_2} = \frac{e^-}{4 \cdot O_2}. \quad (3)$$

The same procedure can be applied to fuel cells with more than one specie (i.e. hydrogen and carbon monoxide) oxidized at the anode. Operating a fuel cell with pure hydrogen gives the best performance, but pure hydrogen is expensive and difficult to store. The water splitting process used to simultaneously generate hydrogen and oxygen through renewable sources has been demonstrated, but the technology is not mature enough to bring it to demonstration level. Alternatives to pure hydrogen are natural sources such as natural gas or alcohols. These fuels, however, have to be reformed into hydrogen and even after clean up other species are still present. Even if in most fuel cells CO poisons the catalyst and then it has to be treated as a contaminant, in MCFC CO is a fuel.

Let us consider a MCFC anode alimentation with hydrogen, carbon monoxide and carbon dioxide. Two new coefficients must be defined for the oxidant section.

Carbon monoxide is indeed a fuel in Molten Carbonate fuel cells and its presence must be considered with another fuel utilization factor. This implies that current and fuel mass flow rate are no more sufficient to characterize the extent of anode electrochemical reaction. A further coefficient must be introduced and probably the old one must be redefined. The idea is to define a coefficient that assumes equal values for those combinations of fuels flow rates that potentially make available the same amount of electrons and another coefficient that express the amount of one specie that is null when that specie is absent and equals to 1 when the other one is absent.

Therefore, a global fuel utilization factor must be defined as follows:

- global fuel utilization factor $$U_f = \frac{e^-}{2 \cdot (H_2 + CO)} \quad (4)$$

Considering that hydrogen and carbon monoxide are the result of fuel reforming and that a different fuel composition can make a difference in the fuel cell performances, another parameter has to be introduced to distinguish one fuel from the other:

- fuel carbon factor $$C_f = \frac{CO}{H_2 + CO} \quad (5)$$

which is null when CO is absent and is equal to unity when H_2 is absent.
Since CO_2 does not participate to the electrochemical reaction, but is in equilibrium with H_2, H_2O and CO through the shift reaction:

$$H_2 + CO \leftrightarrow H_2O + CO_2 \quad (6)$$

we can characterize its presence with the following parameter:

- CO_2 fuel factor $$CO_{2f} = \frac{CO_2}{H_2 + CO + CO_2 + H_2O} \quad (7)$$

The direct oxidation of hydrogen produces water that is therefore present in any anode stream. Moreover, most fuel cells need steam at the anode to avoid carbon deposition that can lead to plugging of the gas passage in the anode. Furthermore, methane formation in MCFC, regulated by the following reaction:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (8)$$

is detrimental to fuel cell performance because it represents a considerable loss of reactant. The addition of steam and carbon dioxide to the fuel gas modifies the equilibrium gas composition, thus inhibiting CH_4 formation.
Since carbon dioxide has already been considered, let us define a new parameter that take into consideration steam presence:

- humidification factor $$H_f = \frac{H_2O}{H_2 + CO + CO_2 + H_2O} \quad (9)$$

Fuel and oxidant can be diluted through inert species among which Nitrogen is the most common. The nitrogen dilution factor at the anode is given by:

- fuel dilution factor $$D_f = \frac{N_2}{TOT} \quad (10)$$

For the cathode a different approach must be considered. In fact, it must be noticed that, since the reference procedure utilizes air as oxidant, nitrogen is already present at the cathode and under reference condition, about 79 % of atmosphere is Nitrogen. Therefore, the dilution factor at the cathode is defined as follows:

- oxidant dilution factor $$D_{ox} = \frac{N_2 - \frac{79}{21}O_2}{TOT} \quad (11)$$

This implies that the oxidant dilution factor may assume negative values, which mean that there is an oxidant enrichment.
The definition of the flow rate parameters has been described considering a fixed carbon dioxide to oxygen ratio equal to 2. If this ratio is not equal to 2, that means:

$$\frac{e^-}{2 \cdot CO_2} \neq \frac{e^-}{4 \cdot O_2} \quad (12)$$

two oxidant utilization factors must be used. U_{ox} defined in (3) as the oxidant utilization factor now assumes the meaning of oxygen utilization factor:

- oxygen utilization factor $$U_{ox} = \frac{e^-}{4 \cdot O_2} \quad (13)$$

As it has been done at the anode for more than one fuel specie, we have to introduce a new parameter that takes into CO_2 utilization:

- carbon dioxide utilization factor $$U_{C2} = \frac{e^-}{2 \cdot CO_2} \quad (14)$$

The flow rate parameterization method is easily extendable if other species are involved in the reaction. More than two species as fuel or oxidant require that main utilization factor.

Measurements uncertainty

Every experimental measurement is affected by an error. Therefore, the experimental results must be accompanied by an uncertainty statement, which is an estimate of the largest error that is expected to remain with the experiment. The measurement uncertainty presented here have been evaluated with the law of propagation of uncertainty (Taylor, 1994; Doebelin, 1990) using the uncertainty on each single instrument, determined with statistical methods from calibration data. For the sake of brevity, the method of uncertainty calculation is not presented herein. The approach used follows the "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results" (Taylor, 1994; Doebelin, 1990).

A sample: experimental characterization of a single MCFC in the University of Perugia Test Rig

To show how the introduced parameters can represent a powerful mean to analyze fuel cells performances, the results of the experimental characterization of a single MCFC in the University of Perugia are reported.
First of all it is important to notice that fuel cells developers use to test the decrease of voltage while increasing the current flow with fixed anode and cathode input gas composition. While this test can be used to benchmark different cell types, it cannot be used to analyze cell performances like, for example, the increase in voltage internal losses. This happens because by increasing the current flow with fixed gas input the cell is forced to work with increasing utilization factors. By the use of the utilization factor in the test procedure it is possible to see how much of the voltage decrease is related to this effect and not to increasing losses.
In the first diagram (fig.2) in which tests with constant current density are reported, in fact, it can be seen how the utilization factor impacts on fuel cell performances. In all tests, made with different fuels (different H_2/CO ratios) there is a significant decrease in cell potential with the utilization factor ranging between 0,1 and 0,7. The decrease is around 0,26 V for all tested conditions.

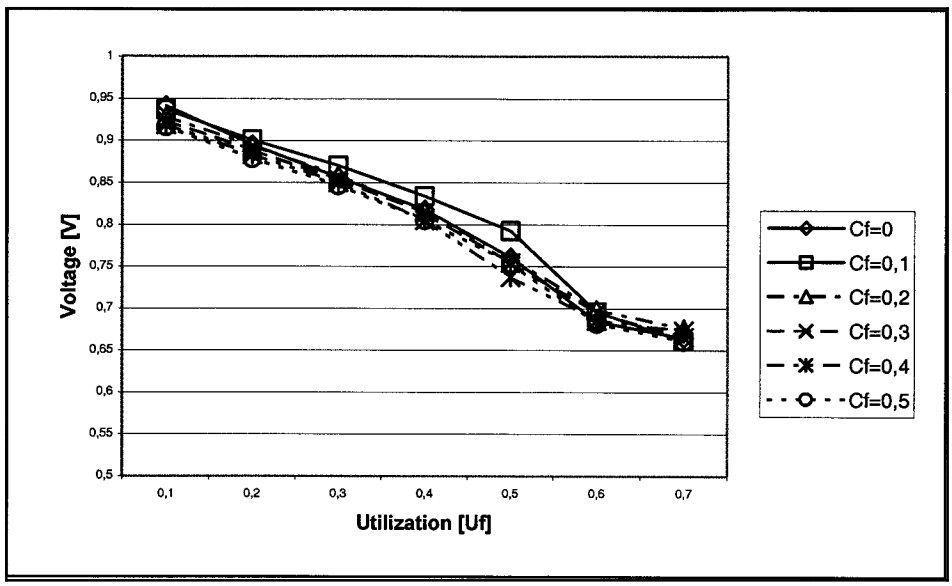

Fig. 2 Effect of fuel utilization on cell potential

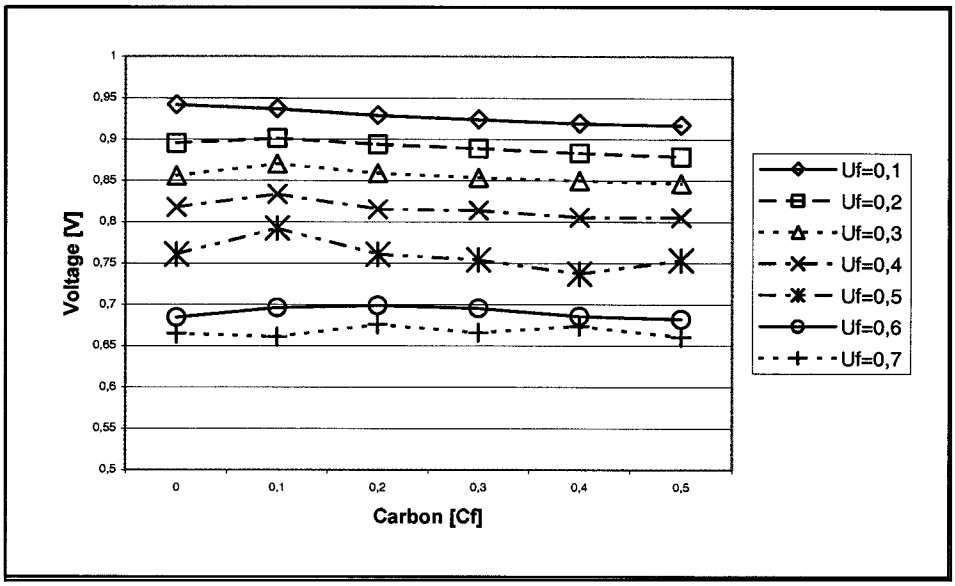

Fig. 3 Effect of alternative fuel on cell potential

The introduction of this factor and keeping it constant is therefore highly recommended while testing the effect of increasing current flows in fuel cells.

In the second diagram (fig.3) the effect of the introduction of CO as fuel is examined. This kind of test is very useful to investigate cell performances with alternative fuels. If we simply start to add CO at the anode while keeping constant the H_2 input flow rate and the flowing

current, we could observe an increase in cell performances. The erroneous conclusion that CO introduction can boost fuel cell performances could be drawn. This phenomenon, moreover would not be explained by theory since CO electrochemical oxidation is slower than H_2 electrochemical oxidation. This issue can be easily addressed by the redefinition of the fuel utilization coefficient as in (4) and by the introduction of the C_f coefficient as in (5).
As it is clearly evident by eq. (4), when the cell is fed with carbon monoxide, which is a fuel for a MCFC, and the current density is kept constant, the H_2 flow rate must be reduced to analyze fuel cell performances at a constant utilization coefficient. In fig 3 it is evident that the presence of carbon monoxide brings a small voltage decrease but is nevertheless a good fuel for the cell and this trend is confirmed for all utilization factors.

Conclusions

The great interest in fuel cell systems has determined a huge development effort. A relevant activity consists in experimentally validating computational predictions demonstrating the ability of the systems to achieve the calculated values of the relevant operational and life parameters. This is a long, time and resources consuming activity since each experiment constitutes a feedback for the design activity that should improve the system itself thus requiring further experimentation. In order to reach all the necessary targets in terms of duration, cost, reliability, performance, integration and flexibility, in the relatively short times dictated by market rules, a synergy across the continents is required and a virtual facility around the world must be created.
It is obvious that the shift from site laboratory to a virtual facility, from enterprise work groups to net actions, from proprietary results to shared community knowledge, requires the institution of a common language and common testing rules.
In this work the test procedures and parameters developed by our research team have been presented. Some relevant non-dimensional parameters have been introduced in order to allow easy comprehension of the results and quick comparisons with other tests in different operating conditions or with results obtained on different cells eventually tested in different laboratories. All the parameters are in the range between 0 and 1 and are set in order to assume a value that equals to zero if the related quantity is not present. Proper test reference conditions have been used.
The parameters introduced constitute a very powerful tool to analyze fuel cell performances as shown in the simple example of investigation of effect of fuel utilization factor and CO presence in the fuel for a Molten Carbonate single cell.

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SIMULATION AND MODELING: DISCOVERING THE POTENTIAL FOR STRUCTURAL OPTIMIZATION OF FUEL CELL STACKS

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General Survey

With the help of computer aided techniques, it has become much easier to analyze the mechanical behaviour of complex systems such as single elements of a fuel cell stack or even the whole stack itself. Thus, for example, the mechanical performance under loading caused by the manufacturing process or service conditions can be determined and assessed. A planar Solid Oxide Fuel Cell is a multimaterial composite system. Under thermal loading conditions significant internal stresses may occur due to the mismatch in the mechanical and thermal properties of the individual layers. Manufacturing shrinkage may fortify these effects. Therefore, the components and especially the joints have to meet high demands to preserve their mechanical integrity. By means of the theory of elasticity and numerical methods a structural mechanics analysis of the system leads to an understanding of the stress situation and possible failure mechanisms. In order to optimize the mechanical system, potential changes of the geometrical construction, such as layer thicknesses, and the characteristics of different materials are examined by sensitivity analysis. Because of stress concentrations, sealing joints belong to the most critical locations where stresses increase and may lead to fracture. Using simulation methods, the potential for optimization of the topological and geometrical design of the stack structure is explored, thus promising prolonged lifetime, enhanced performance and improved reliability of the fuel cell stack.

Mechanical Simulation of the Manufacturing Sequence

The manufacturing process of fuel cell stacks can be described by several single steps: First of all, the membrane electrodes assembly [MEA] is produced by sintering in a co-firing process. Therefore, the green compact is heated to about 1200° C. While it is plane at the beginning of this process, at temperature rise deflexion starts, caused by the mismatch of the different coefficients of thermal expansion [CTE] in the order of $1 \ldots 2 \cdot 10^{-6}$K. After cooling the MEA to room temperature, the whole stack is assembled. For the sealing of the stack a glass ceramic material is used. This material is sintered and crystallized while heating the completely assembled stack at a temperature of about 800° C. At the same time, the material of the substrate and the anode functional layer is chemically reduced while shrinking. Hence, the elastic properties of the material change, the elastic modulus is reduced to half, and kept so even after it is cooled to room temperature.

In order to better understand the shrinking process, it is possible to approach the problem by means of a finite element analysis: First the process of cooling after the sintering and the heating to the reduction temperature is simulated with oxidized anode material. The chemical process of the reduction of the substrate material and the following cooling is taken into account in the subsequent analysis assuming a virtual temperature. This additional temperature is drawn from experimental data. For this second calculation the material properties of the anode-substrate are considered as reduced as they really are in service.

On account of the non-linear behaviour of the CTE depending on temperature changes, the graphs of the resultant deflexion, figure 1, and the resultant stresses, figure 2, show a double curvature. Figure 1 shows the deflexion in the centre of a $200^2\,mm^2$ MEA. These deflexions correspond to the results of non-linear analysis as well as to the calculation of linearized theory [Landau/Lifshitz 1970]. The greater the deformation, the stronger this effect of non-linearity, which is, compared to the assumption of small deformations, the more exact one. Down to 1200° C the material is able to alleviate stress, but cooling below this temperature causes stresses. Together with increasing deformation, the stresses increase too. Therefore, the effect of shrinkage due to the de-oxidation process of the anode, where the deflexion increases rapidly as shown in figure 1, can even be found in the graph of the principal stresses in the electrolyte layer, figure 2. Only the effect of chemical reduction raises the stress level of the electrolyte to a maximal principal stress of about 200 MPa. Two different states of the MEA are shown in this figure, a MEA which is assembled in the stack, so that it cannot deflect in the direction of stack thickness anymore, and an unconstrained MEA. Though the compressive stresses are not low, the strength is not exceeded, as for the other layers. The stress level increases about 10 %, which can be explained by the effect of locked displacements.

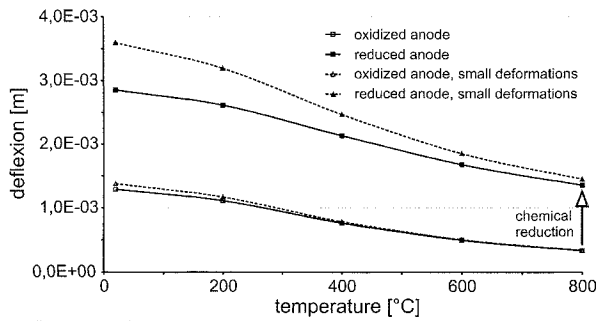

Figure 1: Maximum deflexion in the centre of the MEA during the manufacturing process.

Another result of the analysis is that the only way to keep the MEA plane is to transfer edge moments by the sealing joints. A surface load is not able to accomplish that. The influence of the cathode layer on the stresses was found to be almost negligible.

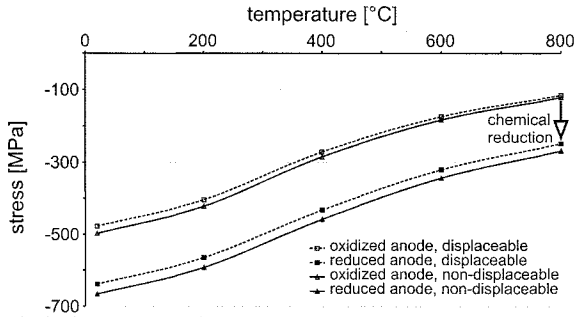

Figure 2: Maximum principal stress in the electrolyte-layer during the manufacturing process.

Minimizing Stresses caused by Service Conditions

Apart from charges due to the manufacturing sequence the inhomogeneous thermal loading under service conditions might also be a reason for failure. For a calculated distribution of the temperature under service conditions, shown in figure 3, which was based on a thermal analysis, the intention of optimization is to find a stack design which is as thin as possible.

The "objective function" then is the total thickness of the stack. As free parameters, so called design variables, the following parameters are used: thickness of the single layers, interconnect, electrolyte, anode, cathode. The optimization algorithm has to respect a number of constraints, because the stresses of the individual materials should not exceed the strength properties. Even the individual layer thickness is constrained for electro-chemical reasons by characteristic minimum and maximum values. These constraints put a limitation on the designs of every possible combination of layer thickness. Any design which violates these constraint boundaries is unacceptable [Vanderplaats 1984]. Starting with an initial set of design variables during an optimization procedure, the design is updated iteratively. Every single step requires an individual analysis of the whole stack and its stresses due to the manufacturing process. The optimization has been performed in view of the fact that the distribution of the temperature is dependent on the individual thickness of the single layers.

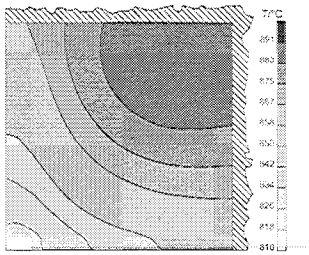

Figure 3: Temperature distribution of a quarter of the MEA for the initial stack design.

With respect to the periodic structure of the stack the whole analysis can be performed for a unit consisting of the individual layers of a single 100 mm² MEA and one interconnect plate. In figure 4, the graph of the resultant objective function, i.e. the total thickness of such a unit is shown. Already after few iterations, the total thickness approaches the minimum thickness. Responsible for this distinct decrement is the clearly reduced thickness of the interconnect plate, which was brought down to the lower limiting value. The thicknesses of the anode substrate and the cathode layer decrease during the optimization whereas the thickness of the electrolyte layer grows about 7.2%. In this manner, an optimal design was found which allowed to reduce the stack thickness and its whole weight considerably - about 30%.

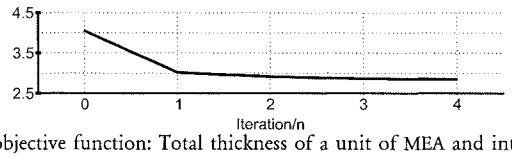

Figure 4: Graph of the objective function: Total thickness of a unit of MEA and interconnect plate during the iterative process of optimization.

Stress Concentrations at Sealing Joints

Deviating from this more general approach, the analysis of the sealing joints goes into detail. The essential problem is that at the interfaces of the joints, stresses increase in a singular manner. In order to analyse the underlying wedge or notch situations, an important issue in fracture mechanics is the knowledge of local mechanical fields. In the present study, a sealing joint situation is investigated in a general idealized geometrical configuration. Considering a bimaterial notch with an arbitrary opening angle, as outlined in figure 5, the singular behaviour at the notch tip can be determined in closed-form manner. An asymptotic analysis of a plane model using the complex potential method [Muskhelishvili 1975] is performed. This method works reliably even in the considered case of two dissimilar isotropic and linear-elastic materials where the material properties are discontinuous across the bond line. This analysis includes and confirms former investigations by Yang 1992 of special geometry and material configurations.

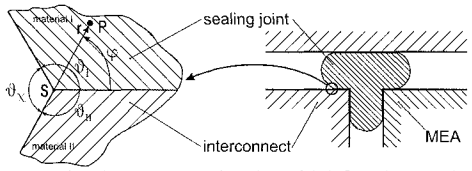

Figure 5: Localization of an example of the examined regions [right] and general model [left].

In the present approach, the corresponding stresses and displacements can be expressed by two complex potentials Φ and Ψ in polar coordinates by the Kolosov formulas:

$$\begin{aligned} \sigma_r+\sigma_\varphi &= 2\left[\Phi'(z)+\overline{\Phi'(z)}\right] \\ \sigma_\varphi+\sigma_r-2i\tau_{r\varphi} &= 2\left[\bar{z}\Phi''(z)+\frac{z}{\bar{z}}\Psi'(z)\right] \quad ; z\in\mathbb{C} \\ 2G\left[u_r+iu_\varphi\right] &= \left[\kappa\Phi(z)-z\overline{\Phi'(z)}-\overline{\Psi(z)}\right]e^{-i\varphi} \end{aligned}$$

where G denotes the shear modulus and κ is a constant depending on the plane stress or plane strain state. The complex potentials are represented by power law functions: $\Phi = A\,z^\lambda$ and $\Psi = B\,z^\lambda; A\in\mathbb{C}, B\in\mathbb{C}$. Eight real constants [$Re(A_I)$, $Im(A_I)$, $Re(A_{II})$, $Im(A_{II})$, ...] have to be determined with regard to the considered bimaterial conditions. The resultant stresses show a local behaviour of the following kind: $\sigma_{ij}(r,\varphi) = K^*\lambda r^{\lambda-1} f_{ij}(\varphi)$. The generalized stress intensity factor for non-crack configurations is K^* and the quantities f_{ij} are functions of the angular variable φ. In this section, the main emphasis is laid on the order of the singularity λ, which can be determined by solving a 8×8 system of equations that describes the boundary conditions [traction free boundaries] and the conditions of continuity at the interface.

Considering joint situations, two particular notch configurations are important [detailed sensitivity analysis in Müller et al. 2002]: First, the variation of the upper angle ϑ_I, which represents a wetting angle of contact, is considered. Secondly, sometimes it may be possible not to use a plane ground

[material II] but a tapered one. The angle ϑ_{II} is varied simulating this effect. Seeing that no exact data on the wetting angle is available yet, the parameter studies can only serve as hints in which direction design optimization should turn in order to reduce critical stress concentrations at local points.

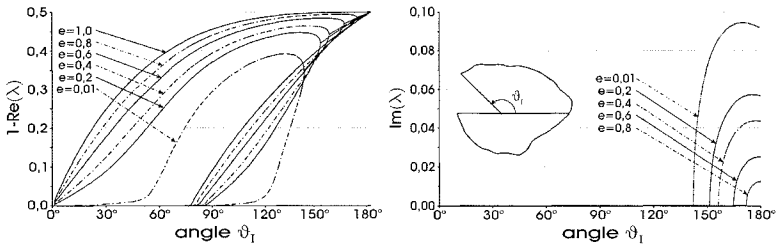

Figure 6: Joining material [material II] on plane ground [$\vartheta_{II} = 180°$], variable wetting angle of contact [ϑ_I].

Figure 6 shows the graph of the singularity exponent depending on the wetting angle of contact. The geometrical situation is that of a constant angle $\vartheta_{II} = 180°$ and the varied angle ϑ_I which stands for the wetting angle; therefore an angle $\vartheta_I < 90°$ means sufficient wetting. The different elastic behaviour of the notch materials is characterized by the ratio of the elastic moduli [$e = \frac{E_I}{E_{II}}$]. For a joint consisting of zirconia as electrolyte material and glass ceramic for the sealing, the value e = 0,4 is applicable. For the case of an interface crack, $\vartheta_I = 180°$, the order of singularity reaches the well-known value of 0.5. Starting from the crack situation and reducing the angle ϑ_I, the order of the singularity decreases with the increase of wettability. For bimaterial notches with a lower ratio of the elastic moduli, this effect becomes stronger. The graphs of figure 6 consist of two [homogeneous material] or three [bimaterial] regions: In the vicinity of the crack situation, a conjugate-complex pair of singularity exponents occurs, leading to a bifurcation point which is characterized by an additional logarithmic singularity. Towards lower angles two real singularity exponents are observed, the smaller one vanishes with a certain angle.

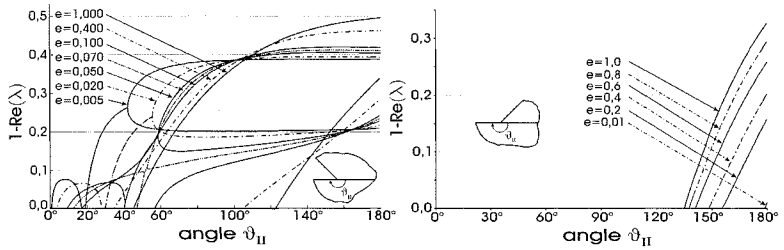

Figure 7: Inferior [$\vartheta_I = 135°$, left] and superior quality of wetting [$\vartheta_I = 45°$, left], variable angle ϑ_{II}; examination of the effect of tapering.

Assuming a relatively poor degree of wetting, i.e. $\vartheta_I = 135°$, singular behaviour of the stresses occurs for values of e smaller than one, even for values smaller than $\vartheta_{II} = 45°$ [smooth border]. The lower the ratio of the elastic moduli, the less the singular behaviour: Considering angles with $\vartheta_I > 60°$, the curves show only very little effect of the tapering measures. In the graph on the left in figure 7, only the real part of the singularity exponent is plotted. Similar to the curves presented in figure 6, the curves for lower values of e bifurcate in discrete points. The curves approach more and more, the lower e becomes and merge to a conjugate-complex pair of singularity exponents.
The diagram on the right side in figure 7 shows the graph of the stress singularity at a sufficiently good wetting, i.e. $\vartheta_I = 45°$. For homogeneous material no singular behaviour of the stresses is observed for angles ϑ_I below 135°: This corresponds to a smooth edge. For $e < 1$ it is obviously conservative to consider the case of homogeneous material. In other words: Tapering is the more to be favoured, the more similar the elastic properties of the bonded materials are. But in any case the singularity can be reduced by tapering.

Conclusions

After thorough examination, it can be ascertained that stresses in the individual components are caused by three main reasons: First, stresses of a SOFC-stack are caused by the manufacturing sequence, secondly, being in service, inhomogeneous temperature fields are a further reason for internal stresses. At the sealing joints additional local stress concentrations may occur. Examinations of the manufacturing process and the service conditions with regard to the resultant loads and stresses are necessary to find ways to optimize the SOFC-stack or its components, such as the sealing joints. Thus, improvements of the topological and geometrical design of the stack structure and its joints can be developed so that prolonged lifetime, enhanced performance and improved reliability may be reached.

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Fire Protection and Explosion Prevention for Hydrogen Safety Technology

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This paper describes main results obtained within the scope of joint project activities concerning the numerical simulation of reacting flow in complex geometries. The aim is the refinement of numerical methods for applied computational fluid dynamics (CFD) using high-performance computations (HPC) to study explosion processes in more detail, especially for hydrogen safety in technical systems. The R&D work is mainly focused on the modelling of the accident-related behaviour of hydrogen in safety enclosures ranging from slow to fast or even rapid flames. Therefore, we have established a modern field code cluster with supercomputing and special modules for specific studies. This new methodology allows the assessment of adequate safety measures to control deflagration-to-detonation transition (DDT) processes and to suppress fires or explosions for industrial safety.

1 Introduction and Objectives

The assessment of the integrity of safety enclosures under severe accident conditions is an important safety issue for industrial power plants. Such studies are under consideration to improve the safety behaviour of technical systems and to reduce the consequences of accidents for the environment as far as possible. To limit the increasing global climate problem and the greenhouse effect, hydrogen technology is a potential future energy option. However, increasing safety requirements have to be fulfilled to minimize industrial risks and to harmonize the safety culture. To control an accidental hydrogen combustion, different safety measures have been developed as part of the defence-in-depth concept with several accident management strategies. However, concerning flame acceleration or hot jet mechanisms, for example, a transition from deflagration to detonation (DDT) cannot be excluded a priori and may produce high explosion loads jeopardizing safety equipment and enclosure systems.

In general, fire and explosion protection is an important safety task in most areas of engineering. For instance, the prediction of hydrogen explosion loads in safety enclosures under severe accident conditions is relevant for hydrogen demonstration plants with fuel cells or hydrogen-powered vehicles. In this context, Fig. 1 shows a typical flow scheme of a solar H2-plant.

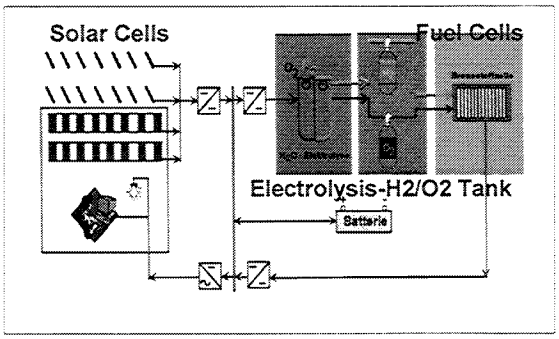

Fig. 1:
Flow scheme of the solar hydro-gen demonstra-tion plant opera-ting at FZJ with fuel cells used for an electrical consumption.

Whether or not an accidental transition from deflagration to detonation (DDT) could occur in safety enclosures depends on the specific plant design and the anticipated accident scenario due to the high hazard potential. The DDT phenomena have been studied so far that most of them are qualitatively understood. However, quantitative methods have not yet been established for the objective assessment in large-scale enclosures. DDT is a very complex process associated with turbulent reacting flows and shock wave interactions, and rigorous closure solutions are still in the distant future so that practical approaches are needed. Therefore, it is reasonable to subdivide DDT processes into essential stages, i.e. slow, fast, and rapid flames in the sub/super-sonic regime and to develop suitable software tools capable of numerically defining DDT conditions (criteria) to control the resulting combustion mode and the load response.

For the prediction of hydrogen behaviour, we established special computational fluid dynamics (CFD) modules in a modern field code cluster (MFCC) with supercomputing capabilities, which are suitable for research work as well as for end-user practice. The MFCC represents the state of the art of non-reacting flow simulations (distribution) and reacting flow simulations (combustion) in complex geometries. The establishment of new academic and commercial codes was based on a comprehensive literature review and on our own experience already gained in the EC-H2DDT, the HGF-H2 and the EC-EXPRO project work on CFD/DDT processes, Ref. [1, 2].

2 Computational Physics and Field Codes

The fluid motion can be described by field codes solving the conservation equations for mass, momentum, and energy, which form together with the equation of state a closed mathematical system, i.e. the so-called Navier-Stokes (Na-St.) equations. These governing equations for rate of change + convection - diffusion = source term can be expressed for a general variable (Φ) in the generic form as $\partial (\rho \Phi) / \partial t + \nabla (\rho \Phi \mathbf{u} - \Gamma \nabla \Phi) = S_\Phi$ with the closure terms: (a) Standard turbulence- and combustion models are based on the eddy viscosity (μ) and a two-equation turbulence model (k-eps): $\mu_T = C_\mu \rho k^2 / \varepsilon$ with the eddy life time $\tau_e = k / \varepsilon$. (b) A turbulent combustion model (S_T): $S_T = - A_T \rho (\varepsilon/k) m_{lim}$ and the Damköhler number being larger than unity ($Da = \tau_e / \tau_{ch} > 1$). (c) A shock compression heating (S_C) with a reaction model: $S_C = A_c (\rho / \tau_{ch})$ for $T > T_{ig}$ using the chemical induction time (τ_{ch}) and the ignition temperature ($T_{ig.}$).

The basic partial differential equations (PDEs) are integrated in a computing domain, using the conservative form of finite volume methods (FVM) with various accurate differentiating schemes and robust solver techniques for the convection, diffusion and source terms for ambient initial and boundary conditions. The resulting set of algebraic equations is solved with direct or indirect algorithms (i.e. iterative or coupled solver), as to: a(p) Q(p) = a(w) Q(w) + a(e) Q(e) for the residual reduction to the defined values and aimed at grid-independent solutions. Here, we distinguish between verification (code-to-code) versus validation (code-to-experiment) from an independent end-user side. For the numerical simulation of transient, compressible, turbulent, chemically reacting flows, we have developed special field codes for specific studies based on reactive Navier-Stokes and on reactive Euler flow solver codes. The software and hardware infrastructure of the modern field code cluster is displayed in Fig. 2 for CFD predictions of engineering flows in complex geometries using high-performance supercomputing systems.

3 Computational Fluid Dynamics and Numerical Simulations

For hydrogen safety studies, we developed modern CFD methods for the analysis of hydrogen behaviour with supercomputing related to software optimization and special applications including improvement, validation, and performance tests. The modern field code cluster developed consists of new modules: **D3UNS, CFX, AIXCO, SHOCKIN, and IFSAS** with pre- and post-processing. Characteristics are hybrid grids, higher order turbulence and combustion models with various solver techniques, including multi-processing in the PVP and MPP mode executed on **the CRAY supercomputer complex** (J90, T90, T3E) of the FZJ. The modern field code cluster is capable of numerically simulating non/reacting flows of slow, fast, and rapid hydrogen flames in complex geometries and consists of the following innovative CFD methodology, as outlined below, related to main accidental phenomena: (1) Hydrogen distribution in complex geometries, (2) Hydrogen combustion with DDT, (3) Hydrogen explosion loads and resulting loads, and (4) Fire prevention and explosion protection with suppression agents. Major features and main results are, as follows:

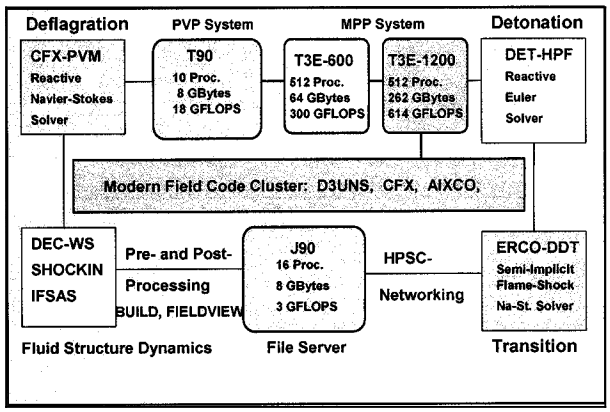

Fig.2: Modern field code cluster with high-performance supercompu-ting used for CFD flow simulations in complex geometries.

D3UNS code: We developed a new unstructured Navier-Stokes solver for non-reacting flow simulations (hydrogen distribution) consisting of classical turbulence modelling and large eddy simulations (LES) for in/compressible flows, including subgrid scale (SGS) modelling based on extended Smagorinsky models with wall damping and wall laws or dynamic modelling by Germano. The code works quite well on the T3E in the MPP mode and was successfully tested for benchmark cases reported in the literature (e.g. flow around obstacles). The D3UNS code is a sophisticated research tool for the large-scale simulation of engineering flows, especially for turbulent mixing with inertization, making full use of mesh refinement and adaptation using flow field parameters, Ref. [3].

CFX code: For the prediction of non- or reacting flows (hydrogen distribution and combustion) in complex geometries, we significantly improved the CFX software with physical-chemical models. This software consists of CFX-4 version (structured grids) on the T90 and CFX-5 version (unstructured grids) on the T3E with body-fitted coordinates. CFX-5 was extended for eddy dissipation combustion models (EDM) with flame quenching. Besides classical turbulence models, we implemented a new LES model for in/compressible flows based on a standard Smagorinsky model with modified wall functions. The CFX versions were ported

and optimized on the CRAY complex for parallel processing showing a good performance and scalability. The new versions were validated in experiments for hydrogen distribution and combustion (e.g. BMC, RUT, ENEL tests). Empirical parameters were fine tuned for the selected test cases indicating that the experimental results agreed quite well with the numerical simulations. The CFX code system is a comprehensive design and analysis tool for numerical simulations of turbulent reacting flows in complex geometries, Ref. [4].

AIXCO code: For the numerical simulation of hydrogen combustion (flame acceleration and DDT processes), we essentially improved the reactive Navier-Stokes code AIXCO. This code is based on the flamelet combustion model with flame front tracking and shock wave capturing. The flame front is described as a discontinuity between the burnt and unburnt gas, using a level set formulation with appropriate burning laws. The effects of turbulence can be taken into account through improved two-equation models. In addition, a two-step reaction model is implemented to study self-ignition characteristics of various hydrogen-air mixtures based on reduced chemical reaction schemes. We ported, parallized and optimized the AIXCO code on the CRAY-T3E, obtaining good performance tests and reasonable speedup factors. The code has been tested for large-scale RUT explosion tests performed at KI in Moscow with reviewing the DDT modelling. Finally, the code was extended for very large eddy simulation (VLES) using two-scales modelling with down-scaling and up-scaling between the integral and the subgrid scales (e.g. mixing layers). The AIXCO code is a modern research tool for the prediction of turbulent combustion, based on RANS and VLES flow solver options used for combustion engines and hydrogen safety, Ref. [5].

SHOCKIN code: For the numerical simulation of reacting flows related to hydrogen self-ignition (i.e. spontaneous thermal ignition), we developed a new adaptive reactive flow solver code with a two-step reaction model, including reduced or detailed chemistry. The code was validated in H2-DDT experiments performed at SWL of RWTH Aachen showing excellent agreement between experimental and numerical results with detailed insights into the shock wave behaviour. For the first time, H2-DDT test simulations were performed for self-ignition conditions in a large-scale containment model geometry. The code is an advanced research tool for analysing DDT conditions in complex geometries and for hydrogen-air mixtures with additives to prevent explosions, Ref. [6].

H2 safety: These modules of the modern field code cluster were used in hydrogen safety studies for technical systems. Hence, hydrogen control systems are based on mitigation, prevention, or protection measures. For fire protection and explosion prevention, effective suppression agents have been studied recently and already being used in industrial safety, public buildings, and high-tech equipment. The effectiveness depends on the special plant design and the specific requirements, which are still under investigation for process and industrial safety , Ref. [7], with different pros and cons for the safety concepts. Typical control systems studied for fire and explosion protection are, e.g.: (1) Auto-recombiner systems to avoid burnable mixtures, (2) Deliberate ignitor systems to control resulting explosion loads, (3) Dilution, inertization, micro-spray systems to suppress fires. In this context, Fig. 3 compares different fire suppression agents, such as Halon (rejected), FM-200 (modern), and CO2 or N2 (standard)

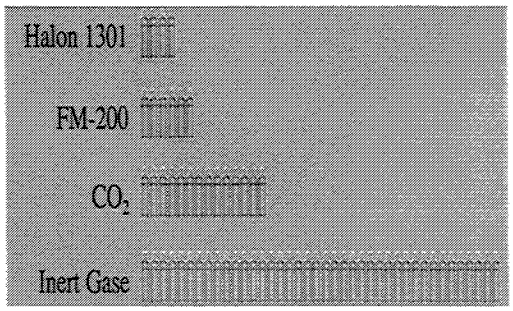

Fig. 3:
Comparison of dif-ferent fire extinguishing media, e.g. Halon, FM-200, CO2, and inert gas, with regard to a comparable con-sumption by Kidde-Deugra.

4 Summary and Outlook

We have established a modern field code cluster (MFCC) with new versions of the reactive Navier-Stokes/Euler flow solver codes: D3UNS, CFX, AIXCO, SHOCKIN and IFSAS, to predict fast flames (deflagration), DDT (transition), and rapid flames (detonation) using vector or parallel processing. Characteristics are hybrid grids, higher order turbulence and combustion models with supercomputing and networking. These new field code modules have been optimized on the heterogeneous CRAY-J90/T90/T3E computer complex at FZJ, running in the sequential or massively parallel mode with reduced computing times. With the applied computational fluid dynamics (ACFD) and supercomputing, it is now possible to explore scientific-technical aspects of reacting flows in more detail for realistic safety enclosures, especially for hydrogen safety technology as a future energy option, to limit the global climate problem.

5 Acknowledgments

This R&D work was performed within the scope of EC/HGF projects on H2-CFD/DDT including high-performance supercomputing (HPSC) for H2-safety. We acknowledge the support of EC Brussels, HGF Bonn, and FZ Jülich, especially of RWTH-ITM/SWL Aachen, AEA Technology, and INCAS Bucharest for their helpful contributions and kind collaboration.

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Poster Contributions

Analysis of the Process Advantages and Application Fields for Alkaline High-Pressure Electrolysis

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Abstract

At Forschungszentrum Jülich two alkaline high-pressure electrolysis units have been developed: a 200-bar electrolysis test facility (3x 75 watt cells) and a 5 kW electrolyser operated at 120 bar. The 5 kW electrolyser was developed for integration into the PHOEBUS Jülich facility, which is an autonomous energy supply system consisting of 43 kW_p solar fields, short-term energy storage (300 kWh lead acid batteries) and long-term energy storage (26 kW electrolyser, H_2/O_2 gas tanks and a 5.6 kW PEM fuel cell).

By using high pressure electrolysis it was possible to increase the overall system efficiency by dispensing with buffer vessels and compressors for H_2 and O_2 storage, which simultaneously lowers investment costs. It was shown that operating water electrolysis at pressures of 120 bar is not a disadvantage in energy terms compared to low- or medium-pressure electrolysis (1-30 bar). The thermodynamic disadvantage of pressure operation ($U_{cell} \sim \lg p_{tot.}$) is compensated by better electrolyte conductivity due to smaller gas bubbles. This was an unforeseen but fortunate result. Due to the absence of compressors the overall energy saving is around 10 percent.

A particular requirement of high-pressure electrolysis systems is the need for a pressure-stable peripheral system and a pressure vessel for the stack. Based on the design of the Jülich High-Pressure Electrolyser (HPEL), in the present contribution concepts will be presented to reduce material requirements for the pressure casing, and thus investment costs.

Material stability tests show that the NiO separators developed at FZJ (Ni-mesh support coated with NiO) are stable up to 60°C at 200 bar. Gas impurities, due to increased solubility of H_2 and O_2 under pressure and diffusion through the NiO separator, were always in an uncritical region so that process safety is assured.

Potential application fields for high-pressure electrolysis were identified. Especially for smaller applications (1-25 kW), high-pressure electrolysis is a promising approach because there are no commercially available compressors on this power scale. Cost calculations were carried out for 500 kW systems on the basis of normal commercial pressure electrolysers in combination with gas compressors. Calculating energy savings of 10-20% for a high-pressure electrolyser the break-even point for the sum of investment and running costs is reached after three and a half years. This makes high-pressure electrolysis attractive even for larger applications.

1. Introduction

At the present point in time, water electrolysis is a well-developed standard method for hydrogen and oxygen generation. Electrolytically generated hydrogen is of particular interest for low-temperature fuel cell systems because of its purity. Systems from a few kilowatts to the megawatt region are available commercially. Table 1 shows a small selection of manufacturers.

manufacturer	system	operating pressure	$Nm^3 H_2/h$ [1)]	source
Stuart Energy	alkaline	1 bar	3500	www.stuartenergy.com
Giovanola Freres	alkaline	1-30 bar	330-760	www.giovanola.com
Norsk Hydro	alkaline	1 bar	485	www2.hydro. com
HT Karlsruhe	alkaline	1 bar	250	www.ht-hydrotechnik.de
Hydrogen Systems	alkaline	10 bar	120	www.hydrogensystems.be
GHW	alkaline	30 bar	ca. 20	www.ghw-mbh.de
Proton	PEM	30 bar	10	www.protonenergy.com

[1)] maximum stated production rating

Tab. 1 Examples of commercially available electrolysers

Alkaline electrolysis (electrolysis of a KOH solution) has become accepted in preference to acidic PEM-electrolysis (electrolysis of demineralised water using a Polymer Exchange Membrane). The main reasons are that alkaline electrolysis does not require a cost-intensive polymer exchange membrane. Instead lower priced porous diaphragms are in use. Raney-nickel has proved appropriate as an electrode material for alkaline electrolysis. PEM-electrolysis is reliant on more cost-intensive noble metals like Pt, Rh, Ir or Ru as electrode material, at least at the anode (oxygen) side. Also the life-time and operational reliability of alkaline electrolysers are higher according to a 12-year field survey by Solar-Wasserstoff-Bayern GmbH [1].
Commercially available electrolysers are all operated at pressures from 1 to 30 bar. The advantage of operating the electrolyser at 30 bar is the saving of the first compressor stage, which is the most energy-intensive part of the gas compression. For larger electrolyser systems hydrogen compressors are available commercially in contrast to smaller power rating regions below 5 Nm^3/h H_2.
By using high-pressure electrolysis it is possible to increase the overall system efficiency by dispensing with buffer vessels and compressors for H_2 and O_2 storage, which simultaneously lowers investment costs. Operating water electrolysis at pressures of 120 bar is not a disadvantage in energy terms compared to low or medium-pressure electrolysis (1-30 bar). The thermodynamic disadvantage of pressure operation (equation 1, increasing cell voltage U_c with increasing total pressure p_{tot}),

$$U_c = E = E_o + 0.045 \lg p_{tot} \qquad (1)$$

is compensated by better electrolyte conductivity due to smaller gas bubbles [2]. Due to the absence of compressors the overall energy saving is around 10 to 20 percent depending on compressor type [3].

At the Institute for Materials and Processes in Energy Systems (IWV 3) a 5 kW electrolyser prototype has been developed which operates at 120 bar (alkaline technology). The electrolyser is integrated into the PHOEBUS Jülich plant, which is an all-year self-sufficient energy supply system based on solar fields as the primary energy source [4]. A power rating of 5 kW corresponds to a H_2 generation rate of approx. 1 Nm^3/h. The prototype has Ni/Co/Fe-activated anodes and Ni/C-Pt-activated cathodes developed at IWV 3. A porous NiO diaphragm is used. These diaphragms have also been developed at IWV 3. In a detailed study it could be shown that the NiO diaphragms are stable up to 200 bar at 60 °C [5]. At 120 bar operating pressure and a current density of 400mA/cm^2 an efficiency of 75% was measured, for a current density of 100 mA/cm^2 the efficiency is approx. 87% [3].

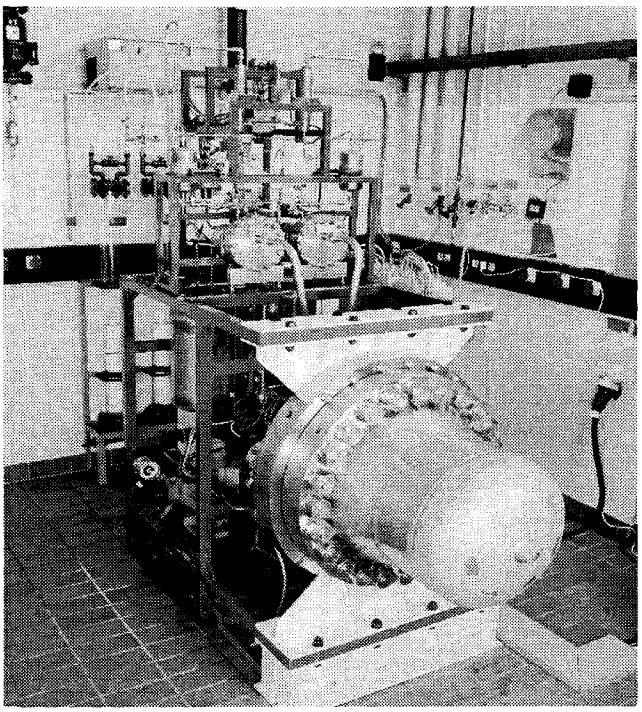

Fig. 1 High-Pressure Electrolyser Prototype

2. Construction features of the High Pressure Electrolyser Prototype

The most noticeable feature of the Jülich High Pressure Electrolyser (HPEL) is the pressure containment consisting of stainless steel with an overall weight of 1151 kg. The electrolyser stack consisting of 15 single cells with an electrode area of 500 cm^2 each is situated inside the containment (figure 2). All pipes leading into and out of the containment and the gas separators are pressure-resistant. The pressure-resistant parts represent a high investment cost factor, besides a more complicated, and therefore more expensive, pressure and filling level control. Additionally pressure-resistant pumps are needed for adding water to the running system. The strategy to improve power/cost ratio is as follows:

- Weight reduction of the pressure containment

- structural
- material (steele vs. composite materials)

- Performance increase

- operating pressure increase (from 120 to 200 bar)
- power rating increase (by lowering the single cell width)

- System simplification

- inside the containment (current lead in)
- outside the stack (pipe guide, instrumentation)

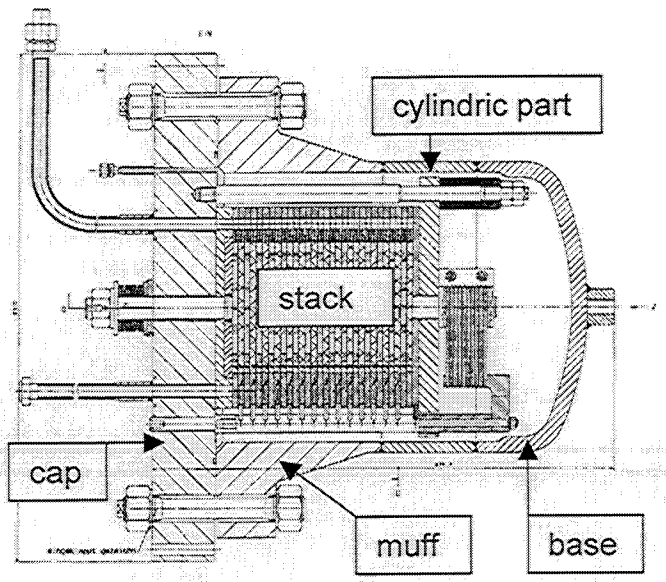

Fig. 2 Longitudinal section of the HPEL

It is possible to reduce the weight of the Jülich prototype because the pressure containment was constructed using all the maximum safety parameters [6]:

$$s_w = \frac{D_a\, p}{20\frac{K}{s}v + p} + c_1 + c_2$$

s_w: wall thickness of cylindrical part [mm]
D_A: outer diameter [mm]
p: pressure [bar]
K: stressability value [N/mm^2]
s: safety factor
v: lateral contraction value
$c_{1,2}$: safety adds [mm]

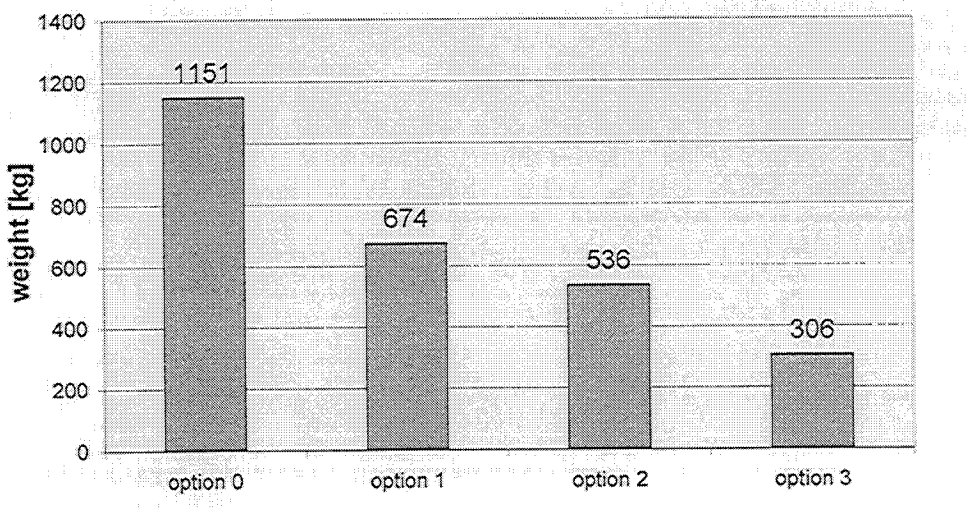

Fig. 3 HPEL pressure containment weight savings by parameter changes

For the thickness of the containment base, muff and cap similar equations are classified [6]. Reducing these parameters to more realistic values for the wall thickness s_W leads to a decrease of the overall containment weight. The result for different parameters and design changes are shown in figures 3 and 4.

option	weight [kg]	D_A [mm]	s_W [mm] pipe/cap	remarks
0	1151	559	20/30	double pipe force + s=1.5
1	674	559	15/15	s=1.5
2	536	489	15/15	s=1.5
3	306	412	12/12	s=1.5

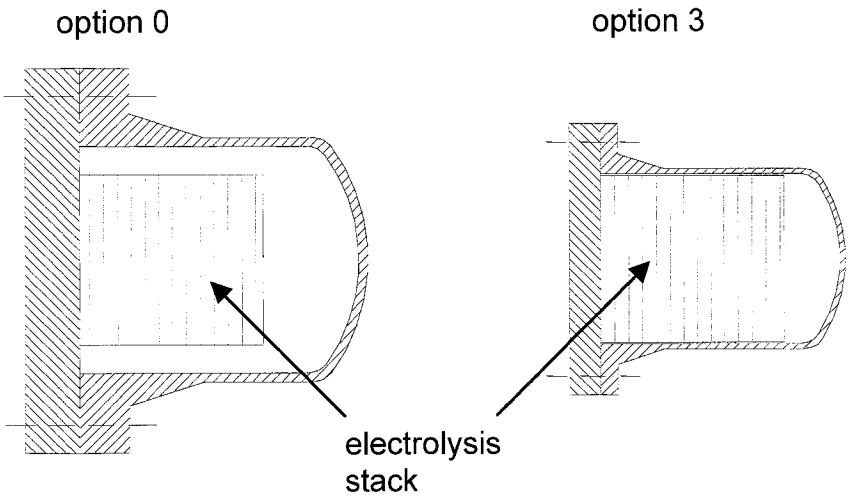

Fig. 4 Basic data for pressure containment weight reduction

It therefore seems to be possible to reduce the weight of the stainless-steel container from 1151 kg to approx. 300 kg. A further weight reduction is possible by using composite materials instead of steel.

3. Application fields

At the present point in time only one percent of the hydrogen produced worldwide is generated by electrolysis [7]. Producing hydrogen by other methods like partial oxidation or steam reforming is less expensive than electrolysis, even when the current is produced on a large scale by water power. Thus a mass production of hydrogen by large electrolyser systems is unprofitable at the moment.
For small self-sufficient energy supply systems, where hydrogen is needed as a long-term energy carrier, high-pressure electrolysis is an alternative to normal pressure electrolysis and exhibits the following advantages:

- higher reliability by dispensing with H_2/O_2 compressors
- no need for buffer vessels between electrolyser and compressors
- energy saving of 10-20% by dispensing with compressors [3]

- less maintenance.

The following diagram shows possible application fields for a high-pressure electrolyser integrated into an energy self-sufficient system (figure 5).

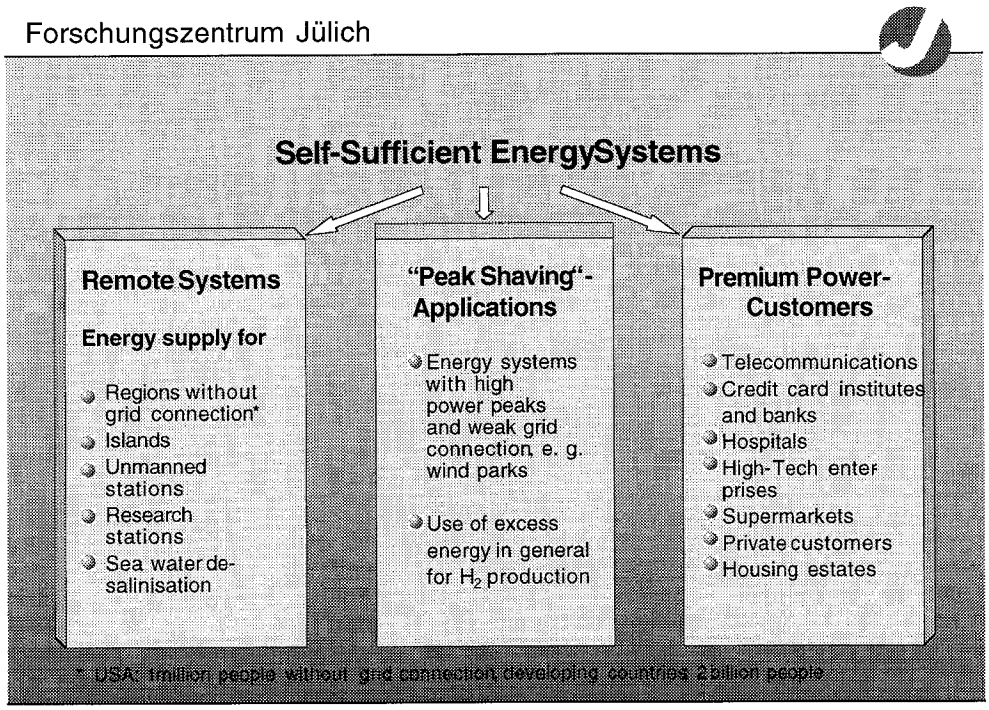

Fig. 5 Application fields for high pressure electrolysers

4. Cost situation

A cost estimate for the Jülich 5 kW HPEL , called the "pre-prototype" in table 2, was carried out on the basis of costs for material and production (staff- and machining-costs). The costs for the "pre-prototype" are real costs. Investment costs for the 5 kW prototype, 5 kW small series production and 500 kW series production are estimates. Large uncertainties in the cost estimate are represented by the real costs for the electrolysis stack because there is no series production of the Fe/Co/Ni and Ni/Pt-C electrodes, NiO diaphragms and cell frames [8]. It follows that a small series production of the Jülich 5 kW HPEL would come to 253,000 Euro. A comparable low-pressure electrolyser involves investment costs of about 100,000 Euro including the peripheral instrumentation but without the compressor. As already mentioned, no compressors are available in the region of 5 kW electrolysis power (5 kW electric power corresponds to a H_2 production of approx. 1 Nm^3/h).

	"pre-prototype" 5 kW [Euro]	prototype 5 kW [Euro]	Small series 5 kW [Euro]	series product 500 kW [Euro]
MATERIAL COSTS				
cell block	21,000	21,000	21,000	160,000
pressure vessel	37,500	20,000	20,000	150,000
gas separators	5,000	4,000	4,000	20,000
electrolyte system	4,000	4,000	4,000	10,000
water supply system	4,000	3,000	3,000	15,000
pipes	31,500	21,500	21,500	60,000
control systems	75,000	45,000	45,000	45,000
gas cleaning	13,000	13,000	13,000	25,000
SUM 1	**196,000**	**126,500**	**126,500**	**322,500**
Staff- and Machining- Costs				
construction	201,500	25,000	-	-
instrumentation	504,000	25,000	-	-
working scheduling	7,000	7,000	1,000	1,000
production	196,500	150,000	50,000	100,000
test engineering	18,500	18,500	5,000	10,000
assembly	90,500	90,500	22,500	45,000
SUM 2	**1,018,000**	**316,000**	**126,500**	**156,000**
SUM1 + SUM 2	**1,214,000**	**442,500**	**253,000**	**478,500**

Tab. 2 Investment cost estimate from "pre-prototype" to series production [8]

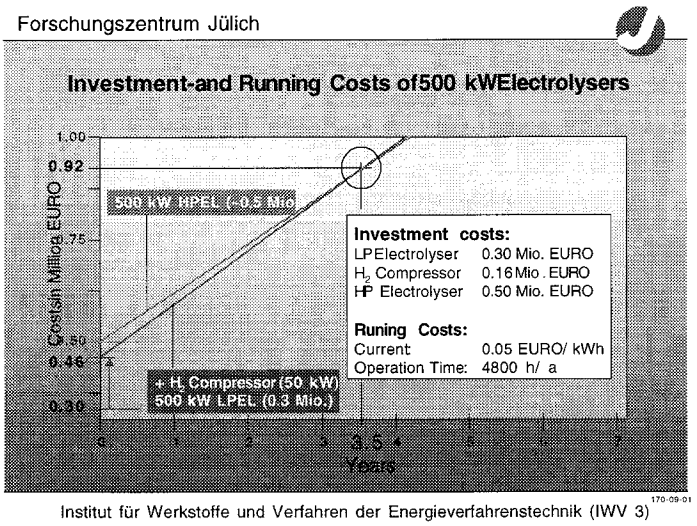

Fig. 6 Costs versus time for 500 kW systems

A flow-rate reduced metal membrane compressor, used in the Jülich PHOEBUS plant, amounted to around 50,000 Euro. For small systems an HPEL (250,000 Euro) is more expensive than a low pressure electrolyser/compressor (150,000 Euro). On the other hand, this system will have better energy efficiency, expected higher reliability and lower maintenance.

Comparing the costs of an 500 kW HPEL to a pressure electrolyser/ ONE compressor (only for H_2, Andreas Hofer Hochdrucktechnik GmbH [9]) combination from the German electrolyser manufacturer HT- Hydrotechnik GmbH [10] showed that the investment costs for the low-pressure system are only little lower that for a 500 kW HPEL. Taking into account an energy saving of only 10% the break-even point (point of time when the sum over investment- and running-costs is equal, figure 6) is reached after 3 _ years.

5. Conclusion

At Forschungszentrum Jülich it was shown that it is possible to operate of a high-pressure elecrolyser at up to 120 bar. Further investigations showed that an operating pressure of 200 bar at temperatures up to 60 °C is also realisable. The pressure containment of the Jülich 5 kW HPEL is overdimensioned for safety reasons. A weight reduction by nearly factor 4, from 1151 kg to 306 kg, is possible on the basis of design changes and reduction of the wall thickness. In this way a modified HPEL would have nearly the same weight as a combination of low-pressure electrolyser and compressor. A cost estimate showed that a 5 kW HPEL, manufactured in a small production series, is competitive with low-pressure systems taking energy savings and reliability into account. Pure cost deficits of the HPEL may be balanced by low maintenance, which is particularly important for self-sufficient energy supply systems.
Also a 500 kW HPEL could compete with commercially available electrolyser/compressor combinations. Taking into account the energy savings of a 500 kW HPEL in comparison to low-pressure systems the break-even point is reached after 3 _ years. The advantages of HPEL´s are their lower maintenance requirements due to the absence of mechanically moving parts (compressor) and the consequent higher reliability.

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MULTI-FUEL PREMIXING TECHNOLOGY FOR LIQUID HYDROCARBONS APPLICABLE FOR E.G. FAME, FATTY ACIDS, IGO AND MIXTURES

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ABSTRACT

Modern mixture preparation systems for liquid fuels require a homogeneous fuel vapour air mixture. To make this possible a separation of the combustion- and mixing zone from the high temperature oxidation zone is necessary. Simultaneously the requirement of a simple and inexpensive construction has to be fulfilled.

The use of cool flame reactions offers the opportunity to establish a technical vaporisation system for various fuels. Through such systems pre-mixing technologies can be applied for a number of liquid hydrocarbons such as FAME, n-heptane, fatty acids and mixtures with IGO. The chemical reaction is investigated in a glass reactor that offers an optical approach and the possibility for temperature measurement in the reaction zone. Samples of the reaction gas can be taken and analysed by gas chromatography.

INTRODUCTION

In case of an oxidation of hydrocarbons the implementation of a premixing technology is favourable for different reasons. The quality of the fuel air mixture has a substantial influence on the development of products and pollutants. By means of separating the mixing zone from the oxidation process a selective creation of products can be achieved.

In the application of liquid fuels a simple technical execution of such systems exists in the injection of fuels into a preheated air flow. For a number of fuels this can be combined with the occurrence of exothermal reactions before the actual ignition. A significant feature of a set of liquid hydrocarbons is a temperature range where the conversion due to these reactions is decreasing with increasing temperature. This area is characterized as the negative temperature coefficient NTC [1]. So called cool flames appear. These are combined with a partial oxidation of the fuel and a partial consumption of oxygen. A number of complex chemical chain reactions appear within the cool flames with the involvement of free radicals and a multitude of different intermediate products that show different life times. Stimulated aldehydes emit a weak blue light within the reaction [2]. The cool flame reaction can be determined for a number of liquid hydrocarbons, especially representative pure chemicals have been studied. Also technical fuels such as industrial gas oil (IGO) and diesel as well as fuels from renewable energy sources e.g. rapeseed methyl ester (RME) show cool flames [3].

The heat released within the reaction makes an autothermal and at the same time residue free evaporation of the liquid fuels possible. Autoignition of the fuel air mixture can be securely avoided by the chemically restricted cool flames. Thus the apparent contradiction with liquid fuels can be handled which is that the temperature necessary for the complete evaporation of the fuel exceeds the theoretical ignition temperature.

The evaporation of fuels using cool flames enables the application of liquid fuels, renewables in particular in the fields of application including the burner technology, fuel processors, the technique of turbines and engine technology. An exact understanding of the ongoing processes is necessary for the design of technical apparatuses.

EXPERIMENTAL

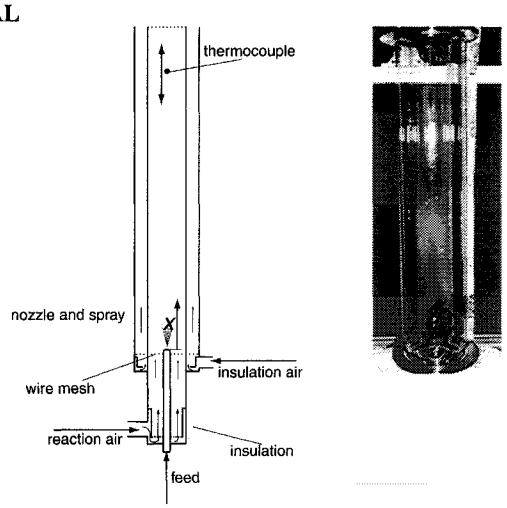

Figure 1: experiment apparatus and picture of cool flame reaction

The investigations were carried out in a double-walled glass reactor. Thus an optical approach of the reaction was possible, which allowed a recording of the pale blue light of the reaction products. A photograph could be taken with a ten minutes exposure time. The fuels RME, IGO a mixture of IGO and 5% RME and the representative fuel n-heptane were sprayed into a preheated air flow by means of a simplex nozzle. A geared pump provided the necessary fuel pressure. The temperature of the gas flow was measured along the reactor axis. At the end of the 0.7 m long reactor samples of gas could be taken from the reaction and analysed by gas chromatography.

Besides the fuels the air inlet temperature and the air ratio were varied. The adjustment of the thermal boundary conditions was made by the regulation of the temperatures of the insulation and reaction air. Figure 1 shows the reactor design and a picture of the reaction zone of the cool flame reaction for IGO.

RESULTS AND DISCUSSION

The requirements for initiation of the reaction were determined in the system by the variation of the thermal boundary conditions. The fuel was sprayed into the thermally conditioned reactor. The initiation of cool flames was determined by means of temperature measurement at the end of the reactor. If no reaction occurs, the gas temperature decreases due to the evaporation of the liquid. Raising the inlet temperature of the reaction air successively you reach the limit when an initiation can be observed detecting a temperature jump at the end of the reactor which is due to exothermal reactions. The limit divides the

thermal boundary conditions of the system into an area of the cool flames and the area, within which no exothermal reactions are to be determined.

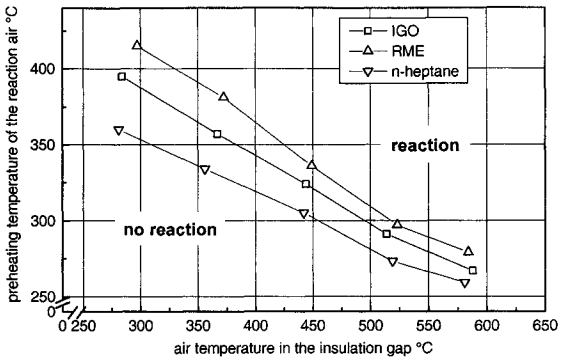

Figure 2: Initiation conditions for the cool flame reaction, different fuels are sprayed into a preheated air stream, p = 10 kW, λ = 1.4

The beginning of cool flame reaction can not be assigned to characteristic temperature in this apparatus after figure 2. Rather the energy balance of the system is decisive. The reaction can be started up either with enthalpy transport through reaction air using high inlet temperatures in the reactor or through heat transfer to the reaction zone from the reactor walls.

With regard to the fuels the observed behaviour is rather comparable. N-heptane indicates the lowest starting up temperatures. The necessary temperatures increase around 15 K to 30 K for IGO which could be due to the high percentage of aromatic content of 28%. Aromatic hydrocarbons tend to react at much higher temperatures than alkanes. Starting up the reaction for RME still on around 20 K higher temperatures are necessary which is due to the boiling range of 330 to 340 °C.

In case the thermal boundary conditions are chosen so that cool flame reactions occur in the respective area from figure 2 stationary temperature profiles establish, which were measured with the aid of the adjustable thermocouple. Figure 3 presents the axial temperature profile for the injection of RME as a function of the distance from the fuel atomizer. The thermal output was 10 kW. The air ratio was varied between 0,68 and 1,49.

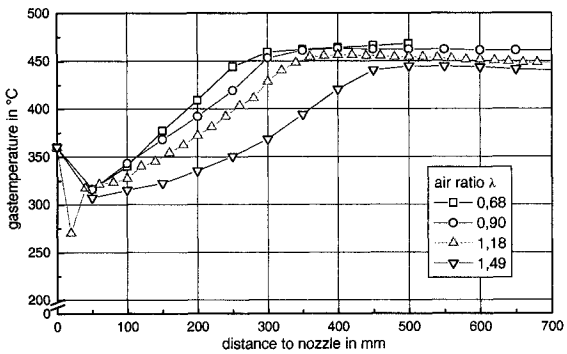

Figure 3: temperature distribution on the axis of the reactor as a function of the distance to the nozzle, fuel RME, p = 10 kW, influence of the air ratio

Close to the nozzle low temperatures are measured due to the evaporation of the liquid fuel. After that the temperature rises again due to mixture effects between fuel vapour and hot air. The starting of the cool flames is connected with a distinct temperature gradient, which ends apparently later at high air ratios. In this part of the gas flow the pale blue light of the reaction is visible as shown in figure 1. The final temperatures reach approximately 450°C almost independently on the air ratio. This originates in the chemical limitation of the reaction. Since the fuel conversion within the cool flame is in a first approximation proportional to the amount of air, more fuel conversion is to be determined with higher air ratios.

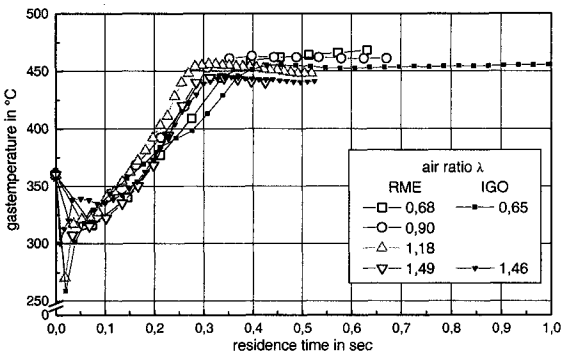

Figure 4: temperature distribution on the axis of the reactor as a function of the residence time, RME and IGO, p = 10 kW

Figure 4 shows the appropriate temperature distribution as a function of the residence time. The conversion of the local temperatures into the temporal distribution was done using the local flow velocities. According to the figure the reaction of the cool flames starts independently of the air ratio after a time of approx. 0,15 seconds. This time represents the sum of the chemical and physical induction time, until the cool flames starts. The reaction is finished after a time of 0,3 to 0,5 seconds. These characteristic values are valid for any executed air ratio under the given thermal boundary conditions.

For comparative reasons some temperature distributions for the fuel IGO are included. The final temperatures of the reaction are slightly lower than that of RME. For this fuel the characteristic reaction times are comparable. The same is valid also for n-heptane, here the final temperatures however are approx. 20 K higher, and a mixture of IGO with 5% RME which shows no significant difference to the behaviour of pure IGO.

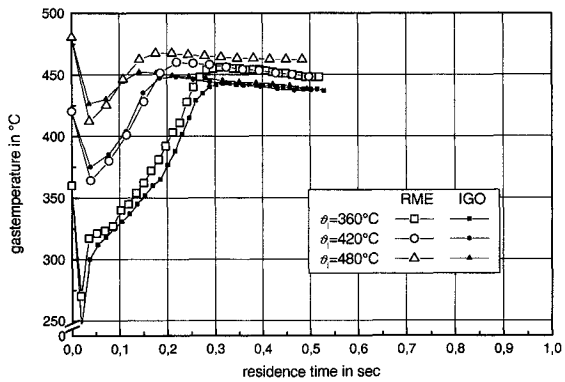

Figure 5: temperature distribution on the axis of the reactor as a function of residence time, RME and IGO, p = 10 kW, influence of inlet temperature

Figure 5 shows the temperature distribution for the injection of RME and IGO with different inlet temperatures. The processes are very much comparable for the fuels. Due to the chemical limitation the final temperature of the reaction is not only independent of the air ratio but also of the inlet temperature and amounts in all cases around 450°C. The cool flame reaction of RME reaches higher temperatures. The results show that the temperature rise within the cool flame reaction decreases with rising inlet temperature. The reaction time is decreasing with increasing inlet temperatures accordingly. Assuming that the temperature rise is proportional to the fuel conversion (same mass flows assumed), a reduction of the fuel conversion with rising temperature can be determined. This is the reason why the evaporator can be run safely without autoignition.

The correlation between inlet temperature and conversion rate in the reaction can also be established analysing the gas chromatography studies of the reaction products. The surveyed RME consists to 87 % of C_{18} fatty acids. In the reaction a molecular chain shortening and a partial oxidation take place, so that a set of different hydrocarbons can be detected in the gaseous phase of the reaction. These compounds are partially unstable. Besides a number of oxidation products are detected.

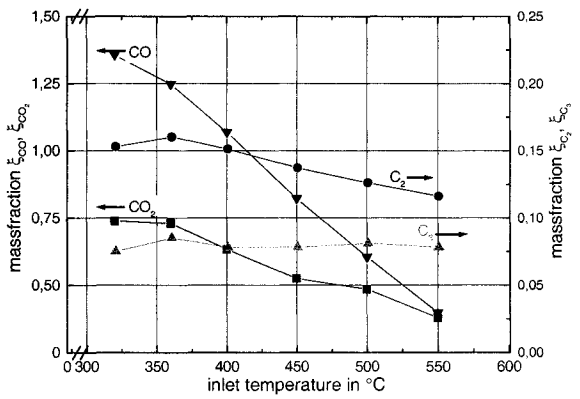

Figure 6: Massfraction of different reaction products, fuel RME, p = 10 kW, λ = 1.2, influence of inlet temperature

Figure 6 shows the analyses by gas chromatography by means of a heat conductivity detector, with which a limited number of species can be determined. Apart from small quantities of ethane and propane carbon monoxide, a maximum of 1.3 percentage, and carbon dioxide in larger proportions are found within the cool flame. The portion of these oxidation products decreases with rising inlet temperature; accordingly the remaining oxygen content increases. This pronounced NTC-behaviour can thus be proven also with the fuel RME.

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STUDIES ON THE ACTIVITY AND STABILITY OF COLLOID-BASED CATALYSTS IN POLYMER ELECTROLYTE FUEL CELLS

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Pt/Ru colloidal catalysts exhibit a slightly improved activity and CO-tolerance as well as a pronounced improved long term stability compared to an industrial standard catalyst (E-Tek). Furthermore, an improved composition of the catalyst ink used for Membrane Electrode Assembly (MEA) preparation with optimum ionomer in the range between 30 and 50 wt % depending on the catalyst system has been found. Already under neat hydrogen operation the commercial reference system showed significant degradation whereas the colloidal system maintained a high power density. Also when operating the cell with reformate gases the deteriorating effect was strongest on the reference catalysts and led to a termination of the long-term test after 950 hours. At the end of the measurement the reference system from E-Tek showed only about 36 % of the original power density. In contrast, the Pt/Ru colloid system still obtained 80 % of the original power density.

1 Introduction

Highly active and stable catalyst layers are a prerequisite for technical applications in Polymer Electrolyte Fuel Cell (PEFC) technology. Deposition of nanoscale noble metal particles on carbon supports as proposed by Bönnemann et al. [2-5] provides a promising method for the synthesis of active catalysts. The work here is focussed on the evaluation of the catalytic properties of the colloid based catalysts under realistic conditions, which means here in full cell measurements (single cell tests). This includes the fabrication of MEAs from the conditioned catalysts as well as the electrochemical characterization of these MEAs, mainly of their electrocatalytic activity, CO tolerance, and long-term stability. The latter was done, e.g., via current-voltage curves in different feed gas compositions (pure H_2 and CO contaminated H_2) and in long-term measurements. In these measurements it turned out that it is extremely important to adapt the procedure for MEA fabrication to the colloid based catalysts. Therefore a considerable amount of work and time was spent on optimizing the composition and structure of the MEA and hence the procedure for MEA preparation.

2 Experimental

All colloid samples were prepared according to the methods described by Bönnemann et al. [2-5]. They were supported on XC-72 carbon particles and were conditioned at the group of Prof. Bönnemann. The conditioning procedure consists in of eliminating the ligands by oxidative treatment and a consecutive reductive pretreatment and conditioning. As reference catalysts for the comparison of the novel catalysts a commercial catalysts from the company E-Tek (Pt/Ru (1:1) 20 % on XC-72) was used. On the cathode of the investigated electrode membrane assemblies (MEA) a new experimental catalyst (40 % Pt on carbon, H1) was used which exhibited superior performances.

MEA-manufacturing has been carried out according to the following procedure:

1 g of the catalyst powder was gently dispersed in an agate mortar followed by dispersion in approximately 10 to 15 ml of distilled water. The slurry was homogenized by sonication and intensive stirring. An aliqout amount of a 15 % alcoholic Nafion solution (Ion Power Inc. Delaware, USA) was added, thus adjusting the Nafion to catalyst powder ratio (3.3 g of Nafion solution results in a 50 % Nafion content in the dried catalytic layer). The optimum Nafion to catalyst ration proved to be 45 % in the case of cathode catalyst H1. In case of the E-Tek materials (supported on Vulcan XC-72) the optimum amount was 50 %. The same Nafion® concentration was typically used for colloid catalysts since they were supported on the same material (Vulcan XC-72) which is assumed to determine the optimum amount of Nafion®. Normally catalyst suspensions containing Nafion were intensively stirred for at least 24 h and afterwards used within one day. Before the coating of the membrane the suspensions are stirred again.

Nafion® 105 was used as electrolyte membrane. Before coating, the membrane was conditioned by boiling in 3 % H_2O_2 in order to remove organic contaminants. Subsequently, the membrane was boiled for approximately 1 h in analytic grade 20 % H_2SO_4 to remove cationic impurities followed by boiling in suprapure water (Millipore quality).

The membranes were stored in Millipore water until further use. Before coating, the membrane was fixed in a Teflon coated frame and heated to 100 °C until the weight remained constant. Subsequently, the assembly was weighed. Catalyst was deposited in several thin layers using an air brush. The catalyst loading was determined by drying at 100 °C followed by weighing. Further catalyst layers were added by the same procedure until the desired catalyst loading was reached. The second catalytic layer was prepared accordingly. Normally, the anode was prepared first followed by the cathode. After finishing both catalytic layers, the MEA was cured for 20 minutes in an oven at 135 °C. The MEA active area typically was 25 cm^2. In case no other values are given in the following chapters, the anode noble metal loading was 0.35 mg cm^{-2}, cathode noble metal content was 0.50 mg cm^{-2}.

CO stripping voltammetry has been performed according to the following procedure:

After measurement of the current-voltage curves in pure hydrogen the cell is connected to the potentiostat of an electrochemical testing station (IM 6, Zahner corporation, Kronach) and purged on both sides with nitrogen. The previous cathode is exposed to humidified hydrogen

at 10 ml/min and acts as reference and counter electrodes (reversible hydrogen electrode) for the cyclic voltammetry experiments. The cell temperature was controlled at 70 °C and the humidifying of the hydrogen was performed at 75 °C. For the determination of the active surface area the anode side (working electrode) is exposed to a mixture of 5 % CO in hydrogen at 100 ml min^{-1} for 60 minutes with at 0 V vs. RHE (measured with respect to the reference and counter electrode). Next, the gas supply of the working electrode is changed to dry nitrogen and is the working electrode is purged for 6 minutes. During the purge, the potential of the working electrode is monitored and rises. When it reaches 100 mV vs. RHE the control of the potentiostat is activated and the potential of 100 mV is held. Subsequently, the recording of the cyclic voltammetry takes place. Three cycles are recorded from 50 mV to 1.0 V starting from 100 mV. The scan rate is always 10 mV s^{-1}, The last cycle is terminated at 100 mV. In the first cycle the currents associated with the oxidation of the CO ad-layer adsorbed on the catalyst surface are recorded. The area of the CO oxidation peak corresponds to the area of the particles contacted by the electrolyte.

Measurement of current-voltage characteristic has been performed according to the following procedure:

For measurement of the current-voltage curves the dry catalyst coated membranes (CCM) prepared as described above were fixed in a graphite cell housing having an active cell area of 5 cm x 5 cm). Teflonized graphite paper (Toray TGP 120, 26 % PTFE-content) was used as the gas diffusion layer. During slow heating of the cell by electrical heat pads fixed to the housing to the final operating temperature of 70 °C, the membrane was rehydrated by passing humidified gasses (hydrogen and oxygen). The temperature of the anode humidifier was set to 75 °C, cathode humidifying was carried out at 65 °C. After reaching the operating temperature, gradually increasing current was drawn from the cell within 2 h ending at a current density of 700 mA cm^{-2}. The cell voltage was kept above 500 mV during this period. Subsequently, the initial current-voltage curve was recorded. Recording of current-voltage curves was carried out by stepwise increase of the current density at controlled gas stoichiometry. (Anode: 1.25 fold excess of hydrogen, cathode: 2 fold excess of oxygen). Voltage data was taken after a minimum stabilization time of 2-5 min.

3 Results and Discussion

3.1 Variation of the Nafion Content in the Electrode Layer

The influence of the composition of the electrode layers on the performance of the electrode membrane assemblies was investigated in order to improve the preparation procedures with the colloidal particles. It was noted that a higher performance of the MEAs could be obtained by optimizing the Nafion content in the active layer of the MEAs. A clear relationship between the properties of the carbon supported catalyst (wt % and specific active area) and the Nafion content of the catalyst ink is observed which yields superior performances of the MEAs. The fraction of the catalyst area which was electronically and ionically contacted and

therefore electrochemical active in the layer was used as a measure of optimizing the ionomer (Nafion) content in the layer. The utilization of the catalyst active area is measured by cyclic voltammetry of the oxidation of a pre-adsorbed carbon monoxide ad-layer which is proportional to the active surface sites (CO stripping voltammetry). The evaluation of the active electrochemical area by CO stripping voltammetry is possible by minor adjustments of the experimental conditions in the full cell set-up.

The optimization of the ratio between catalyst loading and Nafion content is exemplary described for the case of a Pt catalyst (40 % Pt on carbon) from Heraeus in the following. Starting with the usual composition of 33 wt. % Nafion with respect to the total catalyst weight (noble metal + support) higher and lower Nafion contents in the ink were investigated. Membrane electrode assemblies with similar metal loading were prepared from the differing inks in order to maintain similar electrode thicknesses (anode 0.35 mg cm^{-2}, cathode 0.5 mg cm^{-2}). As cathode catalyst the Heraeus catalyst mentioned above was used.

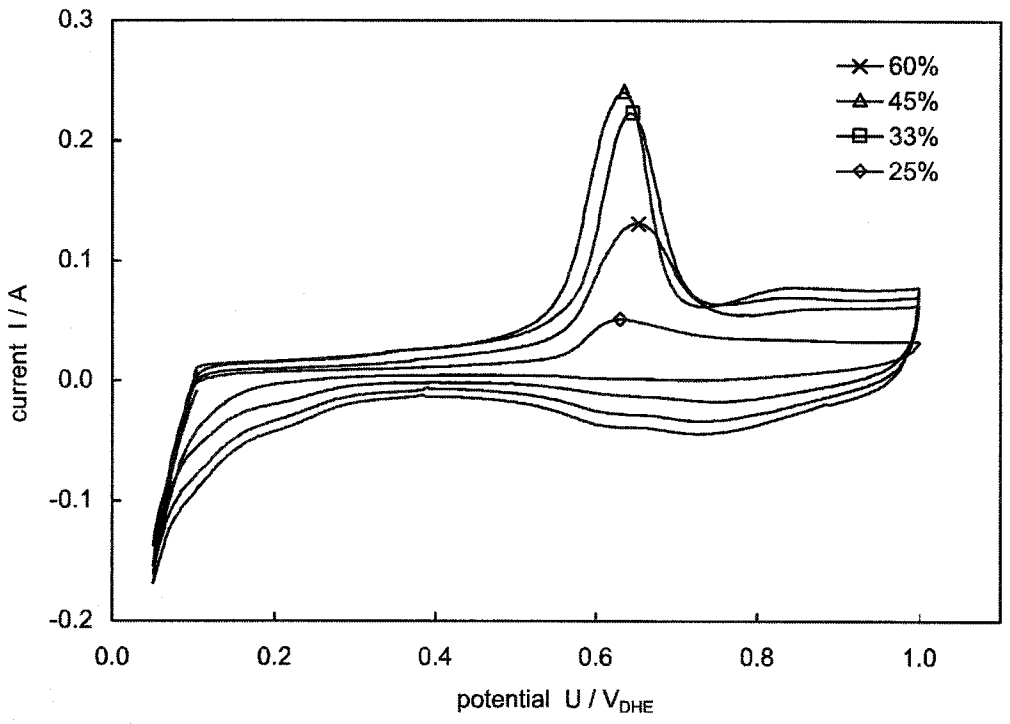

Figure 1: Influence of the Nafion content in the electrode on the active suface area as measured by CO stripping voltammetry.

According to the results from the CO stripping voltammetry (see Figure 1), the membrane electrode assembly with 45 % Nafion content should also possess the highest active surface area (superior catalyst utilization) and therefore also a superior performance in the fuel cell operation. The corresponding current-voltage curves are shown in Figure 2.

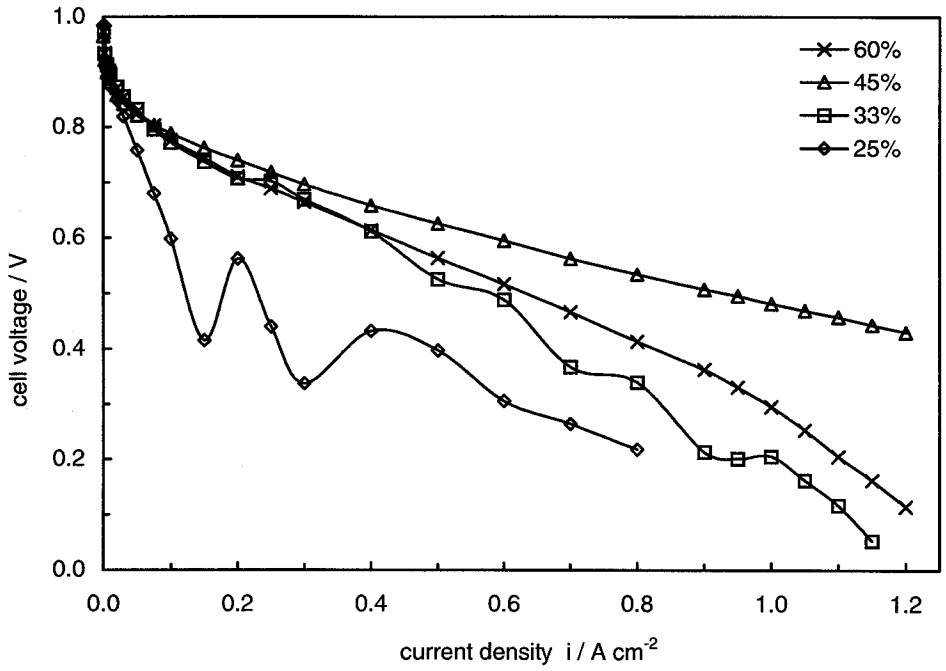

Figure 2: Current-voltage curves of electrode membrane assemblies (MEAs) using Pt-catalysts from Heraeus, 0.35 mg cm^{-2} metal loading and varying Nafion contents on the anode, 0.5 mg cm^{-2} metal loading and 50 wt. % Nafion on the cathode.

An increase of MEA power starting from a Nafion content of 25 wt. % showing a peak at 50 wt. % and dropping back at 60 wt. % ionomer content is found. Besides, lower voltage within the whole range of current densities, also unstable MEA humidifying is observed at a Nafion content of 25 wt. % and 60 wt. %. Therefore, it is concluded that adaptation of the ratio between Nafion and catalyst powder dramatically influences MEA performance. This behavior is also seen in the reference system consisting of commercially available E-Tek catalyst materials. As shown in Figure 3, cell performance considerably improved by optimization of the electrolyte content inside the catalytic layer even when commercial catalysts were used.

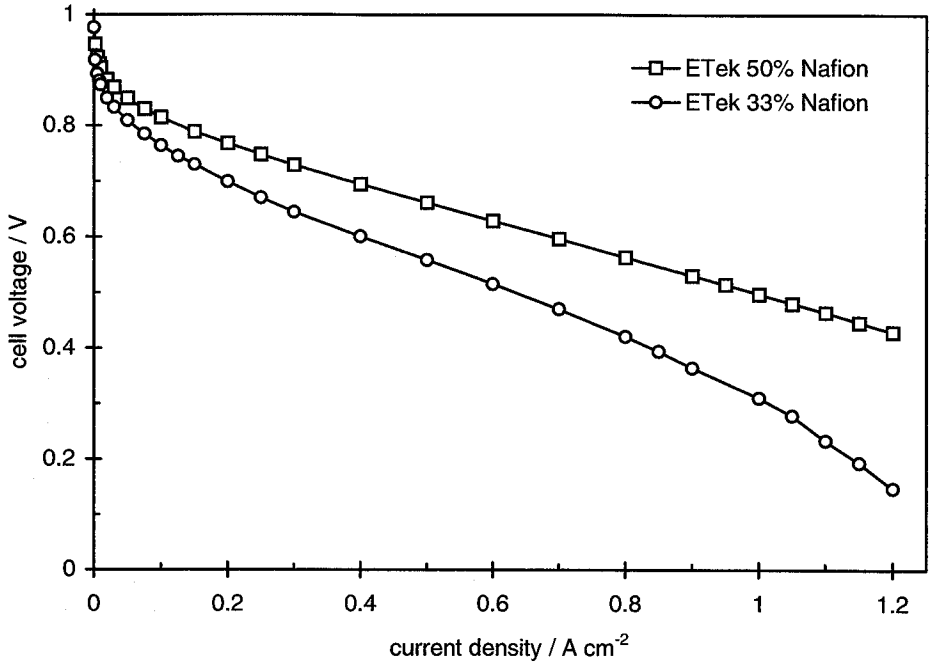

Figure 3: Variation of anode Nafion content using an E-Tek Pt/Ru catalyst with a loading of 0.35 mg cm^{-2}. The cathode catalyst was an E-Tek 20 % Pt / Vulcan with a loading of 0.50 mg cm^{-2} and a Nafion content of 50 wt. %.

3.2 NR_4^+ stabilized Pt/Ru Colloid

The NR_4^+-stabilized colloid (Pt:Ru=1:1) treated as described above with a Nafion content of 50 wt. % shows a performance comparable to 50 wt. % Nafion containing MEAs prepared from the commercial E-Tek material (see Figure 4). From these results it is concluded that rigorous control of the conditioning parameters is a prerequisite for high activity catalysts.

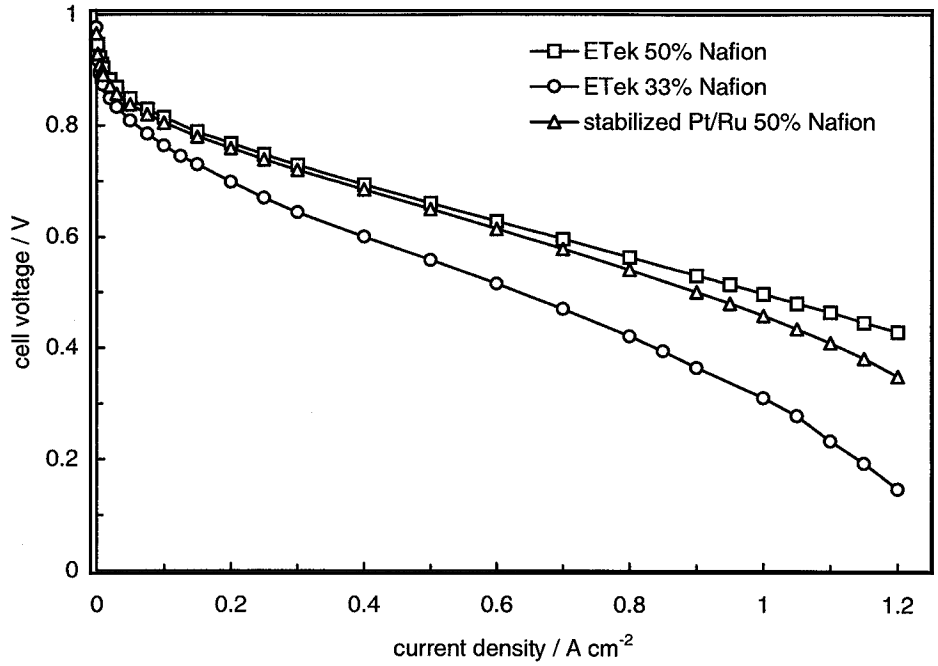

Figure 4: Comparison of the NR_4^+ stabilized Pt/Ru colloid with the E-Tek reference in pure hydrogen. Noble metal content: anode 0.35 mg cm^{-2}, cathode 0.50 mg cm^{-2}, anode Nafion content as indicated.

A comparison of the long term performance during 1000 h of the NR_4^+ stabilized colloid catalyst with the commercial E-Tek material will be shown in the next section. Similar performance of the freshly prepared MEAs will clearly show the influence of long term operation and different gas compositions on MEAs prepared from these catalyst materials.

3.3 CO Tolerance of Pt colloids decorated with 5 % Sn

In Pt/Ru-alloy catalysts a reduction of the potential of CO-oxidation is observed, therefore these materials show enhanced CO-tolerance as compared to pure Pt-catalysts. Formation of stable alloys and intimate contact of both metals on the catalyst surface are considered as a prerequisite. Adsorption of hydroxy species at the surface of the alloying element allow the transfer of oxygen containing species to neighboring Pt-sites. This process allows the electrooxidation of CO bonded to Pt sites at lower potential. In principle, this effect should be enhanced when using multivalent alloying elements having a redox potential lower than Ruthenium.

To obtain a similar effect, 5 % Sn was decorated to the surface of a Pt based catalyst. The catalyst had a noble metal content of 20 %.

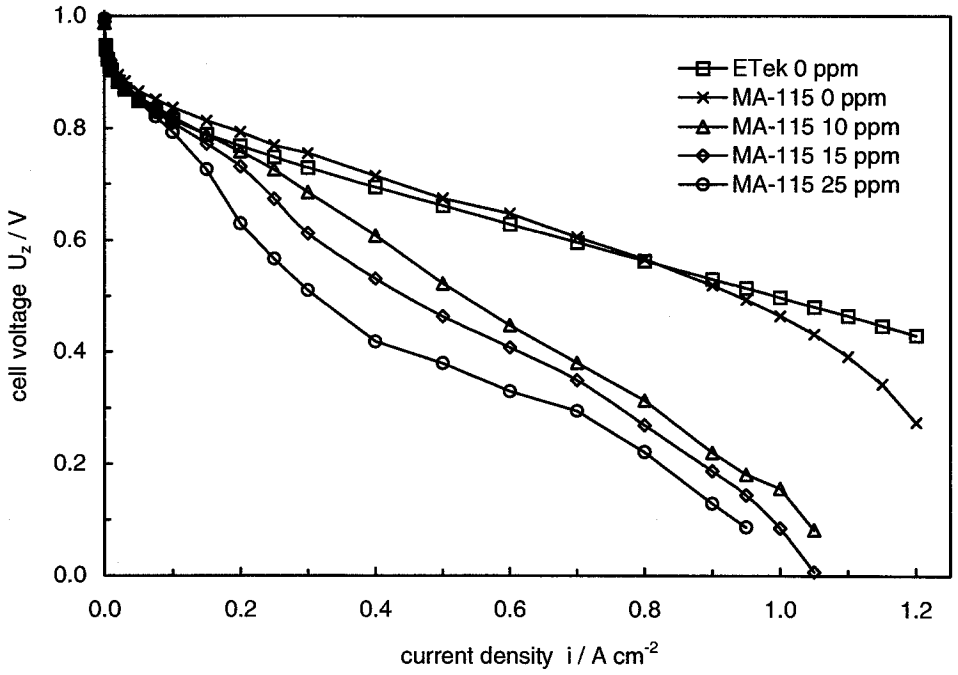

Figure 5: Current voltage curves of MEAs made from 5 % Sn / Pt catalyst under increasing CO concentration compared to a MEA with E-Tek catalysts. Noble metal loading: anode 0.35 mg cm^{-2}, cathode 0.5 mg cm^{-2}, anode Nafion content: 50 wt. %.

As shown in Figure 5, the Sn decoratd Pt-catalyst shows similar performance as the commercially available E-Tek Pt/Ru catalyst when operated under pure hydrogen. Addition of CO however, reveals differences in performance. Similar to Pt/Ru-catalysts lower cell voltage is observed when increasing the CO concentration. When compared to MEAs containing Pt/Ru, the MEA made from the Sn decorated Pt catalyst showed higher voltage over the complete current range. After completion of the measurements under CO-contamination, faster recovery was observed when operating under neat hydrogen.

4 Comparison of Pt/Ru Catalysts in Long Term Experiments

Catalyst materials showing high activity in full cell measurements were further characterized in long term experiments for 1000 h. Commercially available catalysts from E-Tek were used as a reference. Furthermore, the NR_4^+-stabilized Pt/Ru-catalyst was investigated.

The cell temperature was kept at 70 °C during the complete duration of the long term test. Anode humidification was set to 73 °C, cathode humidification was set to 63 °C. The cathode

was operated under neat oxygen at a stoichiometry of 2. The anode gas composition has been modified during the duration of the experiment. At the beginning, the anode stoichiometry was set to 1.25. At the end of the long term test, the anode stoichiometry had to be increased to 1.5 in order to maintain a stable cell voltage. This behavior indicates changes in the properties of the gas diffusion layer or the electrode microstructure or the electrode composition.

The cell was operated in galvanostatic mode using a manually set current density. After initial operation under pure hydrogen increasingly harmful anode contaminants were added. After 200 h approximately 20 ppm CO were added to the anode gas. After 300 h 50 ppm CO combined with 0.5 % O_2-bleed were added. After approximately 550 h the anode gas was diluted by 20 % N_2. Finally, after approximately 800 h N_2 was exchanged to 20 % CO_2 thus approaching the gas composition expected from CH_4 steam reformate. The current drawn from the cell was adapted in order to achieve the highest possible current density at a cell voltage in the range of 400 mV to 600 mV. Casually, current voltage curves using pure hydrogen were recorded during the long term experiment in order to follow MEA degradation.

4.1 E-Tek Pt/Ru catalyst

The E-Tek Pt/Ru reference material already shows significant degradation within the first 200 operating hours under pure hydrogen (see Figure 6). During the following test further degradation is observed. Particularly under the influence of O_2-bleed starting after 320 operating hours a steady performance loss is observed. Dilution of the anode gas by N_2 shows no significant effect. However, substitution of N_2 by CO_2 after 750 operating hours has a significant effect. After a short initial period, a series of transient voltage breakdowns is observed. After such a breakdown, the voltage shows a fast recovery to its initial level. This behavior can be explained by the so called retro-shift-reaction or CO_2 reduction at the catalyst surface. Decrease of the CO_2 concentration or increase of the O_2-bleed reduce frequency and intensity of these voltage dips. However, it was not possible to completely suppress them when E-Tek-catalysts were used. After completion of the 1000 h long term test, only 36 % of the initial performance were recovered under operation in pure hydrogen (see Figure 6). Table 1 shows the evolution of the cell voltage at 500 mA cm^{-2} during the long term test.

Table 1: Evolution of the cell voltage at 500 mA cm^{-2} during the 1000 h test.

t / h	anode gas	voltage at 500 mA cm^{-2} / mV	
		E-Tek Pt/Ru	**NR_4^+ stabilized**
0	H_2	660	655
500	$H_2/CO/O_2$	450	600
800	$H_2/CO/O_2/N_2$	350	580
950	$H_2/CO/O_2/CO_2$	very unstable	450 ± 20
End	H_2	330	620

4.2 NR_4^+ stabilized Pt/Ru Colloid

The overall performance of the colloid catalyst during the long term test proved to be superior to the E-Tek reference material. In pure hydrogen only a small decrease of the cell performance is observed. Addition of CO also leads to a lower voltage decrease. O_2 bleed however, leads to a gradual continuous reduction of cell voltage. However, time the voltage curve in pure hydrogen still yields 90 % of the original value (Table 1). The influence of subsequent N_2 dilution is comparable to the one observed using E-Tek catalysts. Substitution of N_2 by CO_2 also results in the observation of transient voltage dips, however, at lower intensity and frequency, permitting air O_2 bleed at a lower level as compared to the E-Tek reference. After 1000 h of operating time still 80 % of the original performance are observed (see Figure 6).

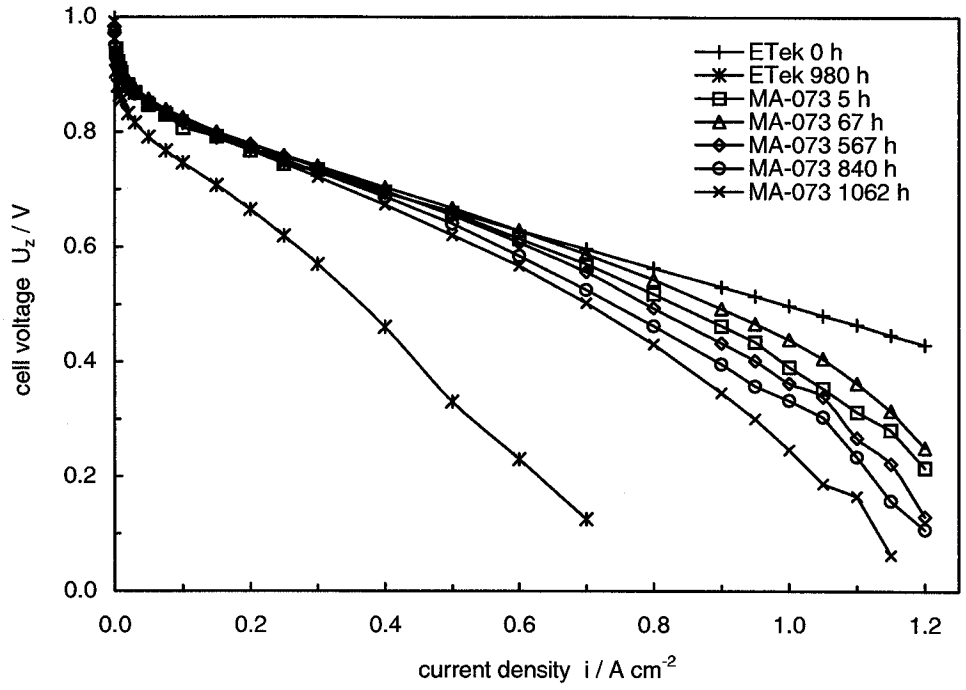

Figure 6: Current voltage curves in H_2 of the NR_4^+ stabilized colloid and the commercial E-Tek catalyst during the long term test (1000 h).

5 Summary and Conclusions

Colloidal catalysts were used which showed a high power density in subproject 2 regarding the electrooxidation of neat and CO containing hydrogen. Furthermore, four carbon supported catalyst systems were investigated which were synthesized at MPI Mühlheim, and activated by a new conditioning procedure.

A much better performance of the colloidal catalyst could be obtained by adjusting and optimizing the preparation of the catalyst inks. The ionomer (Nafion) content of the ink was found to dramatically influence the performance of the MEAs. The electrochemical active surface area of the catalyst was measured by CO stripping voltammetry and an excellent correlation between the performance and the electrochemical surface area is derived. Optimum ionomer contents were found in the range between 30 and 50 wt % depending on the catalyst system. At low ionomer content in the active layer the utilization of the catalyst is low because a significant amount of catalyst particles have no ionic contact to the membrane: The proton conductivity of the layer is insufficient. At higher Nafion content the active area increases due to a better ionic contact whereas at high ionomer content the active area significantly decreases which is explained by the decrease in the electronic conductivity of the layer

and again a reduced utilization of the catalyst. The reduced utilization is due to the covering of the catalyst particles with ionomer films leading to an electronic insulation..

The so far most active colloidal catalyst system was the NR_4^+ stabilized Pt/Ru colloid that was investigated in a long-term measurement over 1000 h and compared to the commercial reference system Pt/Ru from E-Tek. Already under neat hydrogen operation the commercial reference system showed significant degradation whereas the colloidal system maintained a high power density. The addition of 20 ppm CO to the fuel induced on both systems the well-known decrease in performance due to poisoning of the catalyst surface. In addition, the reference system, however, showed an unstable cell voltage with a tendency to oscillate. The addition of 0.5% oxygen from air (air-bleed) to the CO containing anode gas (50 ppm) leads as expected to an increase of the cell voltage. However the degradation of the catalysts, especially of the commercial system, progresses further also under air-bleed conditions. The adaptation of the fuel composition to a more realistic operation with reformer gas leads to further changes in the behavior of the cells. The influence of the dilution of the fuel by nitrogen was relatively small compared to the influence of the addition of CO_2. In the latter case, transient breakdowns in the performance of the cell are observed that lead often to the emergency shut-down of the cells. However, after these sudden losses of performance the original power densities can be recuperated. The reason for these effects are probably an additional CO concentration on the catalyst surface or in the feed gas due to either CO_2 reduction reaction at the catalyst surface or a retro-shift reaction from gas phase. This interpretation is also supported by the influence of the CO_2 concentration on the frequency and magnitude of the breakdowns in the cell voltage. An improvement in the stability of the cells can be achieved with a higher air-bleed (0.7-0.9 % O_2). Again the deteriorating effect was strongest on the reference catalysts and led to a termination of the long-term test after 950 hours. At the end of the measurement the reference system from E-Tek showed only about 36 % of the original power density. In contrast, the Pt/Ru colloid system still obtained 80 % of the original power density. Both aged and used electrode membrane assemblies were sent to the University of Bonn (subproject 3) for further analysis.

It is noted from the U-I curves of the investigated MEAs that in the case of the E-Tek catalyst a significant voltage drop is observed at relatively low current densities indicating a loss of catalytic activity. It can not be derived, however, if these losses originate mainly from the anode or cathode electrodes. In the case of the NR_4^+ stabilized Pt/Ru colloidal catalysts no significant effect at lower current densities is observed. The catalytic properties seem to remain constant over the measurement time. Changes and losses are observed in the region of intermediate and higher current densities which can mainly be attributed to the electrolyte resistance and the mass-transport properties of the electrode. Therefore, it is imperative to investigate changes in the microstructure of the gas diffusion electrodes which will be performed in the future.

6 Acknowledgement

We thank our collaborators Bönnemann, Behm, and Hormes for providing, conditioning, and characterising the colloidal catalysts. Financial support by DFG under contract Ga 625/1-3 is gratefully acknowledged.

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THE FIRST 250 kW PEM FUEL CELL IN EUROPE INITIAL OPERATING EXPERIENCES

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1. INTRODUCTION

In June 2000, the Berlin power company Bewag put the first European proton exchange membrane (PEM) fuel cell in the 250 kW class into operation. The successful performance of this demonstration project is regarded as a significant step towards the market introduction of PEM fuel cells in the electric power and heat supply applications.

The details given in the following describe the objectives of the project. The technology and basic parameters of the measuring program are explained, and experience gained during the planning, approval and startup phase is described. This documentation ends with a summary of the initial operating experiences.

2. CONCEPT AND OBJECTIVE OF THE PROJECT

PEM fuel cells are considered to represent a substantial contribution towards energy supply in the future. The wide-ranging activities of industry towards the development of PEM systems – from small plants with an output of 1 kW to large-scale system with an output capacity of 250 kW – reflect the great interest in this technology.

A prerequisite for the market introduction of new systems is the gaining of practical experience. Demonstration plants and field tests serve this purpose. The Berlin demonstration project is an integral part of the tests with 250 kW aggregates planned by ALSTOM and its partner Ballard on a Europe-wide scale. Field-related specialists are showing great interest in this plant – the first of its kind in Europe.

2.1 The reason for PEM

Five different fuel cell technologies are presently in the development phase:

- **A**lkaline **F**uel **C**ell (**AFC**)
- **P**hosphoric **A**cid **F**uel **C**ell (**PAFC**)
- **P**rotone-**E**xchange-**M**embrane **F**uel **C**ell (**PEMFC**)
- **M**olten **C**arbonate **F**uel **C**ell (**MCFC**)
- **S**olid **O**xide **F**uel Cell (**SOFC**).

They differ with regard to the structure of the electrolyte and the working temperature (Fig. 1).

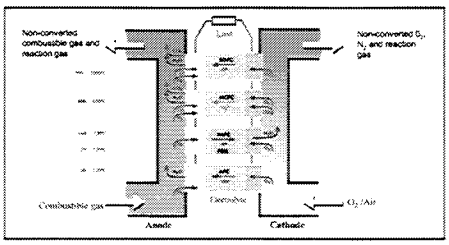

Fig. 1: Fuel cell systems

During the planning of the project, the participating parties decided in favour of the PEM technology. A series of advantages which are attributed to this technology are decisive in this case:

- PEM fuel cells can be used in mobile and stationary plants. This varied range of application options speaks out in favour of synergy effects with cost advantages for the stationary application.
- PEM fuel cells, as compared with competitive technologies, indicate the highest performance density, with further development potential. This allows the construction of small and space-saving systems as required in the decentralised supply.
- The application options of PEM fuel cells in the electric power supply cover a range from small-scale applications in the watt range, to decentralised applications in the cogeneration of heat and power and application cases in the emergency power supply. Accordingly, this technology is universally applicable.

The operating temperature of a PEM fuel cell is approx. 80 °C. The attainable heating water temperatures are in the region of 75 °C and comply with the requirements for the existing room heat supply and warm water generation. In addition, PEM fuel cells comply with the requirements for future heat supply systems to a high degree. The objective here is the reduction of heat losses, utilisation of environmental energies and the optimisation of cogeneration processes. This favours the development of low temperature heating systems, as available with PEM fuel cells.

2.2 Project partners, supplier and financing

5 partners are participating in the Berlin fuel cell project:
- Bewag - Berlin, as Project Leader
- Electricité de France (EdF) - Paris,
- Hamburgische Electricitätswerke (HEW) -Hamburg,
- E.ON - Munich and
- VEAG Vereinigte Energiewerke AG, Berlin.

The decision of the partners to realise the Berlin project together provides the prerequisite for combining the financial potential of the individual participants. At the same time, the partnership ensures that the existing know-how of the individual partners is purposefully applied to the project execution on a larger scale.

The Canadian company Ballard is the manufacturer of the plant. The supplier is ALSTOM. The decision for the Ballard system takes the circumstance into consideration that this system was the most further developed at that particular time. At the same time, cooperation with Daimler Benz and the forth-coming partnership with ALSTOM as well as the objective of producing comparable plants in Europe, indicated a future-orientated development. The stationary plants presently planned by Ballard in the performance range of 1 kW to 250 kW confirm this expectation.

The project costs amount to approx. 3.8 million €. Of this amount, 94.7% are investments, 1.9% approval costs and 3.4% for project-accompanying work and operating costs. The level of approval costs reflect the innovative character of the project. These costs concern the expenditures allocated to the project partners; additional costs for special tests are allocated to the manufacturers.

The project is financed together with the European Commission. Brussels is participating in the overall expenditures of the project with approx. 40%. The innovative character of the project and the positive effects for the European economy are the decisive factors for the Commission to give financial support to this pioneering enterprise.

2.3 Time-schedule planning of the project

Planning operations for the project began in early 1998 (Fig. 2). On the whole, about 30 months have passed up to the official startup in June 2001. The long planning duration period is attributable to problems which occurred during manufacture in Vancouver. They resulted from delays in delivery and control-technical optimisation of the plant. The long approval process was also responsible in this respect. The difficulties involved with the examination and testing of a new technology led to a substantially more sophisticated technical evaluation.

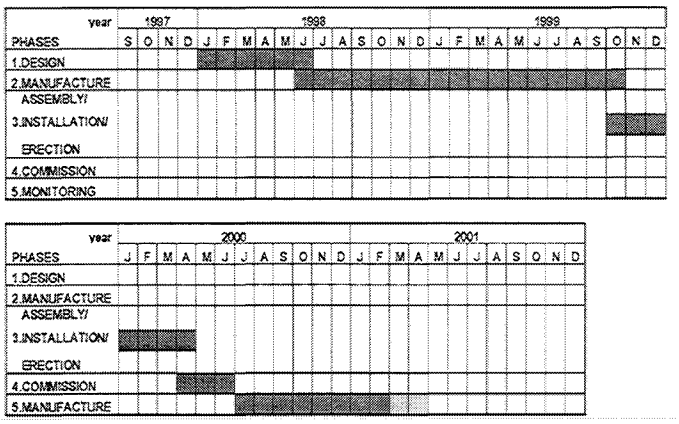

Fig. 2: Time-schedule of the fuel cell project

3. PLANT CONCEPT

The objective of the project is the verification of the functioning capability of the plant under practical conditions. This requires the integration of the fuel cell into an existing supply system.

The Treptow heating station was selected as a site location. It supplies a local district heating network with a max. winter load of 25 MW and a minimum summer requirement of 500 kW. The electrical requirement over the full year is about 200 kW. With an electric generating output of the fuel cell of about 212 kW and a thermal capacity of up to 250 kW, the heating station provides for optimum preconditions for operating the fuel cell over the full year independently of the requirement.

3.1 Structural layout of the plant

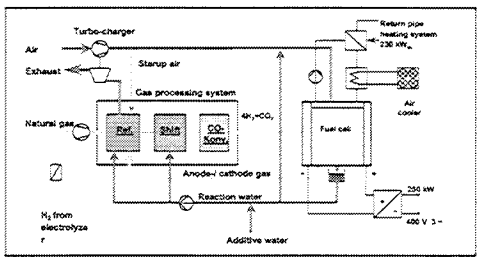

Fig. 3: Flow diagram of the 250-kW-PEM-fuel cell plant

The plant operates on the basis of natural gas. As it is the case with all systems without internal reformation, the plant concept includes four part systems: the gas processing for converting natural gas into hydrogen, the PEM fuel cell, the inverter and the control unit. Compared with competitive systems, a characteristic of the plant is the fact that it is operated under pressure. The operating pressure of up to 4 bar allows a more compact plant design with smaller structural sizes. Where the stack is concerned, and compared with atmospheric operation, this results in a higher performance and a higher degree of efficiency. The disadvantages are the complex non-lubricated natural gas compressor, the technologically sophisticated turbocharger as well as the complex process pattern. This results in, among other things, an additional oil circuit for lubricating the turbocharger and an increased self-requirement which partially compensates the energetic advantage of the stack. In order to avoid unacceptable noise levels, more complex sound insulation measures are necessary.

The concept for the future commercial product envisages the full coverage of the water requirement for reformation by means of condensation of the water-vapor-containing anode and cathode exhaust gases coming out of the fuel cell. The plant going into operation in Berlin complies with this requirement only in part. In particular, where partial load is concerned, it requires make-up water from the heating plant. It is recovered from a deionate plant installed there.

3.2 Integration in the periphery

The process serves the extraction of heat for heating purposes. In order to accomplish this, cooling water flows through the fuel cell in a primary cycle. This cooling water discharges its energy to the return line of the connected district heating network by way of a heat exchanger. In the event of a non-existing heat requirement, an emergency cooler provides for adequate re-cooling of the primary cycle.

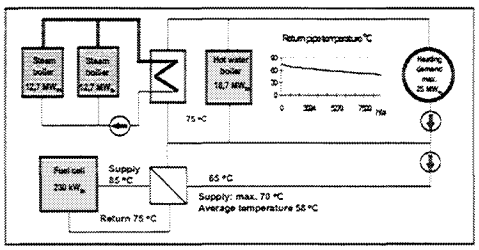

Fig. 4: Integration of the fuel cell in the Treptow heating station

The complete plant goes into service as a package unit. The container contains all the components required for the process: gas processing, fuel cell, inverter and control system. Also required for operation are: the natural gas connection, the hook-up to the district heating system, the supply with operating gases such as nitrogen and high-pressure air and the supply with deionate.

3.3 Approval procedure

The basis for the approval procedure is the Federal German Emission Protection Law. This procedure complies with the circumstance that the fuel cell is erected in a heat plant approved according to this law. Furthermore, it takes into account the circumstance that the approval authorities do not have sufficient experience with the new technology at the present time. As in the case of the power suppliers, a certain process of learning is required here also. With the concentration of the approval procedure on one location – instead of being split up and distributed over several facilities – the advantage of having only one contact partner is evident. The experience gained during the processing confirms the correctness of this approach.

The internal structural layout of the plant corresponds to American and Canadian requirements with regard to approval and supply aspects. This concerns the material selection, the concept of the installed valves and pumps as well as the form of electric wiring. On the customer´s side, the plant is designed according to European legislation, meaning, all electrical outlets are in accordance with VDE to the greater extent. The power inverter required for generating the network-synchronous output signal (frequency 50 Hz, voltage 3 x 400 V) is supplied directly from the fuel cell and discharges its outlet capacity to the low voltage distributor of the heating station.

The installed structural elements such as pumps and fans work at 60 Hz. Their supply is taken over by a second inverter which receives its supply from the outlet voltage on the customer´s side.

The objective of the approval procedure is the verification that the plant, in the furthest sense, conforms with European codes and standards. The tests of the TÜV are concentrated accordingly on the conformity verification.

The main milestones of the approval procedure concern the following:

- Technical expertise inspection by the TÜV-Rheinland/Berlin-Brandenburg together with the TÜV North America
- Safety tests according to the new European directive for pressure equipment and according to Canadian Standard (CSA)
- Component tests in Canada
- Function and safety tests in Berlin

The applied directives concern the steam boiler regulations and the pressure vessel regulations, directives for the selection and application of materials, the ex-proof protection regulations, measurement and control instrumentation, electromagnetic compatibility, machine directive, low voltage directive and the rain compatibility.
The preliminary test of the pressurised parts was performed in Germany by the TÜV Rheinland/Berlin-Brandenburg. The basis for the evaluation was the new European directive for pressure equipment. The remaining tests – with the exception of the functional and safety tests – took place at the manufacturer Ballard´s works in Canada with the support of the American TÜV. They were decisively responsible for the high costs and the time-consuming work involved.

The safety tests locally in Berlin include the testing of the peripheral facilities such as high-pressure air, nitrogen and natural gas supply, as also safety checks of the complete plant. These include leakage integrity testing of the stack and the gas processing system, testing of all pressure and temperature sensors as well as testing of the internal burners of reformer and turbocharger with regard to adherence to start sequences. The results of the TÜV test show that the plant in all points conforms to European safety requirements.

The application was submitted for the approval procedure end of June 1998. On the whole, the entire approval duration period was almost 2.5 years. The procedure was completed in November 2000.

3.4 Measuring program

The project has the objective of covering and evaluating all essential operating and process parameters within the framework of a comprehensive measuring program. The program comprises the following items:

- Verification of operational safety
- Efficiency (35 .. 40 %), verification of a constant process sequence
- Partial load behaviour
- Efficiency of the single components reformer, stack, inverter
- Ageing and voltage decline
- Determination of the theoretical degradation of 40.000 h
- Verification of the long-term functional safety of stack and plant
- Transient behaviour and starting behaviour
- Testing of availability and reliability

- Optimal integration in power and heat supply plants
- Influencing of the network quality

The required measuring variables are covered by a large number of internal and external measuring probes. The internal variables include gas mass flow, pressures, temperatures and composition of the reformat. The external variables are understood to include electric power and heat generation, natural gas as well as deionate requirement and consumption of compressed air and nitrogen. In particular, compressed air is required for starting the plant. With this, the turbocharger is put into operation and the related auxiliary burners are supplied with starting air. The volume of the air requirement is of great significance because expensive synthetic air is use to avoid damage to the stack.

Nitrogen is used to purge the plant after it is shut down. In addition, the gas is used for stack pressing. A piston under gas pressure provides for a evenly distributed pressing together of the individual cells and supports the stack threaded union. Both variables are of interest from technical as well as from economical aspects because highly pure gases are used here also.

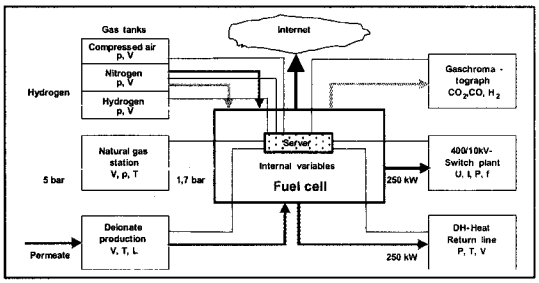

Fig. 5: Data processing

All measuring variables – internal and external – are recorded in second intervals and stored on a server (Fig. 5). At the same time, the complete operation of the plant is visualised with the possibility of an online monitoring by PC. The wonderware visualisation program is adopted here. Based on the overall concept, the plant is controlled from the control room. In addition, all project partners have the opportunity of checking the operating status of the plant on an online basis via Internet. Information transmission is by Internet; the data is coded in order to avoid data losses.

4. PROJECT AND OPERATING EXPERIENCES

4.1 Startup of the plant

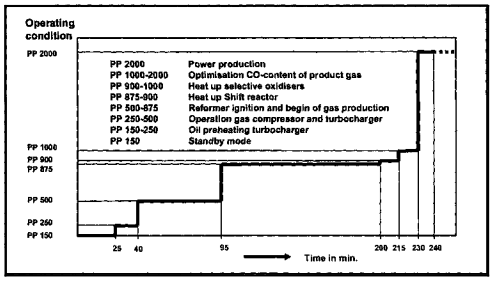

Fig. 6: Cold start mode

From the cold state, the plant requires about 4 hours before it can be connected to the grid. The concept of the plant envisages defined operating modes which are characterised by PP-values as illustrated in Fig. 6. They make possible a targeted capacity increase and decrease/shutdown of the plant as well as the control of the individual operating mode.

Proceeding from the basis value PP150, (control function of the plant in operation), the first step is to start up the oil cycle for the lubrication of the turbocharger and the oil is heated up. After reaching the operating temperature (PP260) the natural gas compressor together with the turbocharger can be started. Compressed air is applied here for the air supply to the turbocharger and the auxiliary burner arranged upstream. After completion of this process step (PP500) the plant is now capable of accomplishing all further startup steps without external utilities.

For heating up the reformer up to the time of the gas production (PP875), there is a time duration of about 55 minutes. After this, the shift converter is heated up to operating temperature (PP900). The indirect form of the heatup requires a duration period of 105 minutes and has a substantial influence on the starting time of 4 hours. The following time period for heating up the CO-cleaning stages (Solex and Polisher), arranged after the shift converter, from PP900 through PP1000 up to the time of power production (PP2000) serves to optimise the gas quality and to ensure the lowest possible CO-value.

4.2 Performance

The plant went into operation in June 2000. Despite about 24 months service period, the actually registered operating time of about 4.000 h is relatively short. Various outages resulting from measures towards process optimisation and elimination of infancy ailments were responsible here. These problems included leaking valves, malfunctioning sensors, earthing faults and failures of the data processing system as well as problems with the external gas analysis system (gas chromatograph) for the observation of the gas quality at the inlet to the stack. However, all faults involved only the peripheral or conventional facilities. Disturbances of the core system, consisting of gas processing and stack, do not belong to these.

On the whole, the plant produced 446 MWh electric power and 457 MWh heat over the entire service period up to the end of June 2002

Fig. 7 shows the actually obtained efficiency and utilisation degrees for the individual load conditions

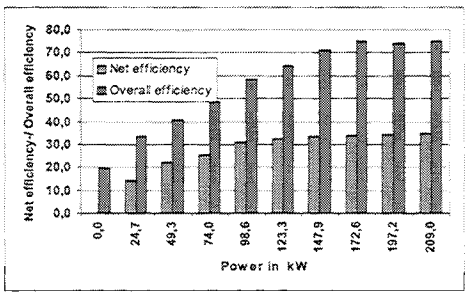

Fig. 7: Efficiency and utilisation degrees at various loads

Accordingly, the plant reaches as from an output of 140 kW an overall utilisation degree of 70% . As from 170 kW, over 75% can be taken for granted. At 50% full load capacity, the electric net efficiency degree is minimum 30%, as from 175 kW about 35%.

From the Bewag´s point of view, the plant with its achieved values fulfils satisfactorily the expectations in the new technology. A fact to be taken into account with this evaluation is that it is the first European plant of its kind and the second in the world. The main objective here is not to demonstrate a high performance system trimmed to energy efficiency, but to provide the verification of functionality and technical reliability. System optimisation must be reserved for the second generation.

5. SUMMARY

The Berlin demonstration plant is the first European PEM plant in the 250 kW class. It is a completely new design concept where no adequate experience has been gained up to the present time. In this sense, this project has a pioneering function.

The objective of the project is to gain operating experience. Within the framework of a comprehensive monitoring program, all relevant process and operating parameters are recorded and evaluated. Though the results available at present are limited they confirm the positive expectations which all project partners associate with the project.

The past operating period of 24 months was characterised by interruptions for eliminating infancy ailments and for optimising the system. As a result, the effective operating time was low and, subsequently, no factual statements on availability, maintenance and operational problems can be made at the present time. However, Bewag and partners are confident that adequate experiences will be gained in the coming months.

COST EFFECTIVE SITE SELECTION FOR A RENEWABLE ENERGY SYSTEM WITH HYDROGEN AS LONG TERM STORAGE

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The stand-alone renewable energy systems with hydrogen as long term storage have been a subject of various study in recent years. Such a system consists of a long term storage and a short term storage systems. In a battery energy is stored for short term where as the electrolyser, H_2-tank and fuel cell combination is used for long term energy storage. When the battery is fully charged the surplus energy in the system is diverted through the electrolyser and hydrogen is produced. The produced hydrogen is stored in a high pressure (~200 bar) tank for long term use. The stored hydrogen is utilised by the fuel cell to supply energy when the battery reaches to the minimum discharge level and increases the reliability of supply. The same purpose can be achieved by a hybrid system in which a diesel generator is used in addition to the battery. The advantage of such a system is that it needs low investment cost. But the main disadvantage is that it needs to supply fuel for the operation of the generator. Sometimes, for the stand-alone applications in remote places, consumers pay high fuel cost due to the transportation of fuel. The advantage of a hydrogen based long term storage over diesel generator is that it does not need any supply of fuel. Thus the fuel cost can be eliminated fully. The investment cost of the system is higher than the diesel system. In photovoltaic-diesel or wind-diesel hybrid systems, the surplus energy in the system is not stored. Sometimes for some of the remote applications the surplus energy is too much which is wasted in hybrid system without long term hydrogen storage.
In the present study, the possible sites for renewable applications are specified depending on the seasonal renewable energy variation and also fuel cost at the site of application. To find out the fuel cost at the location of application, the transportation cost is also included. The seasonal energy difference is plotted along the x-axis which represents the renewable energy scenario at the site of application. The fuel cost at the site of application is plotted along the y-axis which depends on the accessibility of the site. Different sites can be specified by different points on the diagram. A boundary curve is obtained which divides the entire possible region of application into two parts. The use of hydrogen based long term storage system is cost effective in one part of the divided region whereas on the other part a hybrid system with diesel generator is cost effective.

1. Introduction

Because of the varying nature of the output of the photovoltaic and the mismatch between the energy supply and demand, it is imperative to have a energy buffer system. Lead acid battery

is widely used as energy buffer in such a system. Some of the remote applications like telecommunication, medical or light house which demand higher reliability, are powered by the photovoltaic. To achieve the highest level of reliability of supply either energy supplying component (photovoltaic) or energy buffering component (battery) in the system is oversized (Samimi et al., 1997). Even some times both of them are oversized to fulfil the higher level of reliability of supply. Such a system has very high potential to generate energy in comparison to demand but can not be stored because of the limited battery capacity. Indirectly, a high amount of energy is wasted in the whole life time of the system and the energy cost of the system increases. It is not always possible to reach the highest levels of reliability only with battery. Combining the diesel generator with the photovoltaic along with the battery the highest levels of reliability of supply can be achieved. In case of total failure of renewable system and battery, the diesel generator system can operate by itself and provide the electricity.

In many remote areas, the cost of fuelling and maintenance of the diesel generator is too high (Butler, 1996). The high cost of the delivery and often dubious quality of the fuel places a premium on effective utilisation of the resources and makes the value of energy far higher. It was reported by Muselli (1999) that the transportation cost by air is 40 times higher than ground transportation. In hybrid systems 40% of the total energy loss is contributed (Peterson, 1999) by non-optimal sizing of the system. To supply a highly reliable system, the non-optimal sizing losses are even higher. Because of the finite battery capacity, this energy can not be stored.

Along with the battery, some other storage system is needed which will be able to store the excess energy in the system and will supply it back when needed. Hydrogen, as an energy carrier can be chosen as a solution to reduce the losses in the system and also to provide higher reliability of supply. Hydrogen is a highly clean fuel when it is produced by a renewable source like photovoltaic. During peak season, the surplus energy which is not stored in battery can be used in electrolyser to produce hydrogen and it is stored in a gas tank or metal hydride tank. Stored hydrogen can be utilised in fuel cell to supply the shortage of energy when battery is not sufficient to fulfil the requirement. Thus solar hydrogen system is another option to achieve highest levels of reliability. In present work, a comparison between the solar hydrogen system and photovoltaic-diesel hybrid system is carried out for cost effective application.

2. Seasonal solar energy variation

The solar radiation at a particular place changes with the time of the day as well as year. This is because of the position of the sun in the sky. The total daily solar energy at a particular position depends on the day length at the position. Though the total sun shining hour per annum at any location on the earth is same, the distribution of sun shining hour is dependent on the latitude of the location. The day length depends on the position of the location mainly on the latitude and also on the time of the year. On the equator there is no effect of seasonal variation on the day length. With the increase in the latitude the variation of the day length also increases. For the northern hemisphere it is minimum in December and maximum in

June. To estimate the average seasonal difference in the day length, the whole year is divided into two parts depending on the earth motion around the sun. One part contains the months with longer days and the other part contains the months with shorter days. The difference between the average day length varies from zero to twenty four hours per day. Due to the variation in the day length, the daily incident solar energy also varies with the time of the year as well as the latitude of the location. The total seasonal solar energy difference on the horizontal plane and also on a inclined plane at the different locations on the earth is plotted in figure 1. To calculate the energy difference on the inclined plane, the inclination angle is considered equal to the latitude of the location. The energy difference is obtained from the following relation,

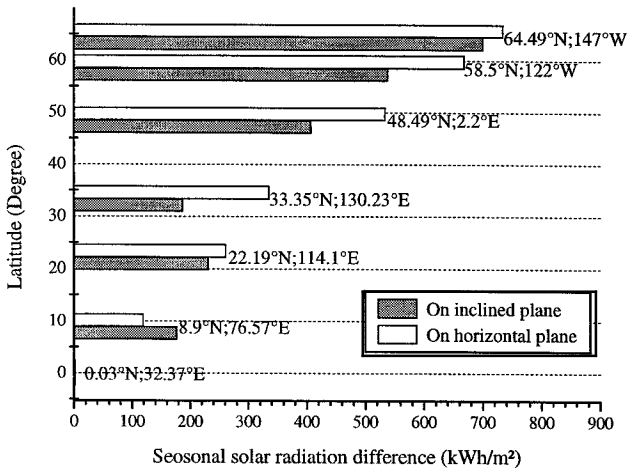

Figure 1: Seasonal solar energy difference calculated on the basis of monthly average solar radiation

$$E_{diff,solar} = E_{s,solar} - E_{w,solar} \quad (1)$$

3. Surplus energy in photovoltaic system

The surplus energy in a solar photovoltaic system increases with the increase in the latitude. For a hybrid system with a diesel generator, the surplus energy is wasted. Thus the wasted energy in the system increase with the increase in the latitude. The wasted energy can be utilised in a long-term storage system and stored as hydrogen. On the other hand, increase of latitude indicates higher operational and maintenance cost of diesel generator for hybrid system.

The surplus energy in a photovoltaic-diesel hybrid system for 100% reliability of supply can be written in terms of energy difference,

$$E_{solar,xs} = E_{diff,solar} \cdot A_{PV} \cdot \eta_{PV} \cdot \frac{1}{(1+\eta_{LTS})} \quad (2)$$

This is the amount of surplus energy which is wasted in a system with photovoltaic-diesel hybrid system.

4. Site specification

The renewable energy scenario varies with the position on the earth. For the hydrogen based long term storage system the seasonal energy difference is one important factor. The other important factor for the cost-effective long-term application is the accessibility to the site. It can be specified by the effective fuel cost at the site which includes the transportation cost of the fuel. On the basis of accessibility the remote sites can be classified in the followings categories:

- *Remote village:* Such locations are connected to the main land by road and it is not so far away. The remotely located villages are the example of this category.

- *Isolated location:* Such locations are not directly connected to the main land by road. Generally fuel is transported to the location by water. The distance of the location from the main land can be as high as 3000 km. Mainly Islands are referred by this category.

- *Remote mountain:* In such location the fuel is transported by road and air. The distance of the location from the main land is not so far.

- *Highly isolated location:* These locations are far away from the main land and the fuel is transported by air. Mainly the polar regions are belong to this category.

The fuel cost at the site of the application depends on the mode of the transportation as well as the distance of the site from the main land. It also depends on the ground fuel cost which depends on the energy policy of the country. The ground price of the diesel may vary from $US 0.3 per litre to $US 0.9 per litre (IEA, 1999). In figure 2, the seasonal solar energy difference is plotted along the x- axis and the fuel cost including transportation cost at the site is plotted along the y-axis. The different points on the plot represent the different sites on the earth.

5. Cost analysis

The surplus energy calculated in the above mentioned section can be recovered by introducing a long-term storage in the system. To recover the surplus energy, an investment for the electrolyser, fuel cell and tank would be needed. For such a system, the operational cost is negligible. The total cost for the long-term storage is,

$$K_{LTS} = K_{EL} + K_{Tank} + K_{FC} + K_{Others} \quad (3)$$

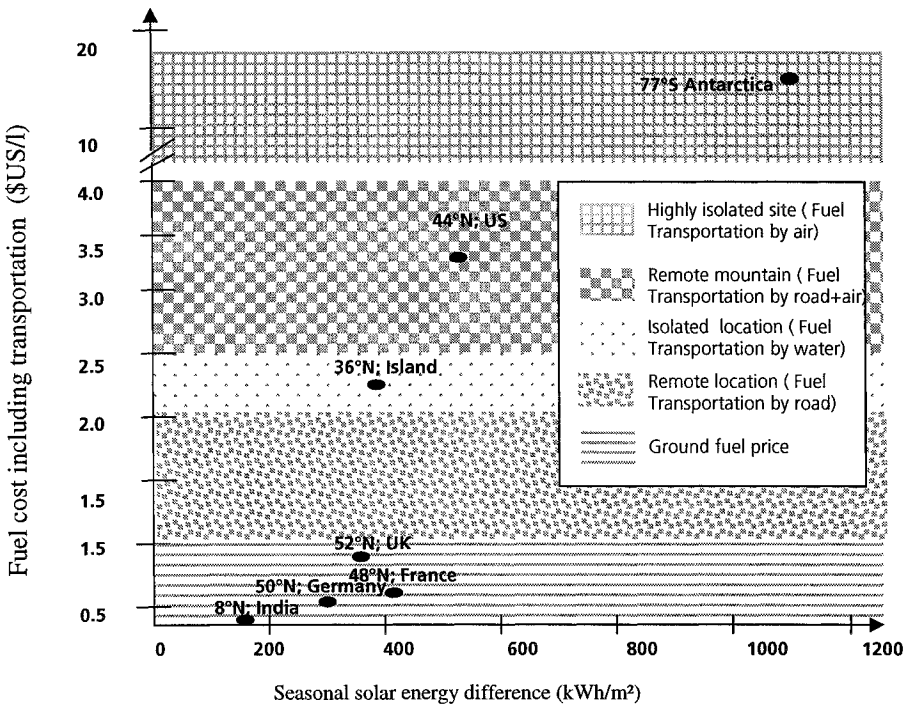

Figure 2: Specification of different sites in terms of seasonal energy difference and fuel cost.

The cost of the electrolyser and the fuel cell are defined with respect to the nominal power. For small scale application, the present cost of the electrolyser and fuel cell are consider to be $US 12500/kW and $US 20000/kW respectively. The target cost of electrolyser and fuel cell was reported to be $US 3000/kW by Meurer (2000). Electrolyser and fuel cell have no moving parts. In such cases, generally the life time is consider as high as 40,000 operating hours. For present calculation it is considered that no replacement of electrolyser and fuel cell takes place in the whole life time (20 years) of the system.

The hydrogen tank can be specified by the volume and the maximum attainable pressure. The cost of the hydrogen bottle (maximum pressure=200 bar) is considered equal to $US 5470/m³. In present calculation, the tank cost is converted in terms of energy considering the maximum attainable pressure (200 bar) and the higher heating value of hydrogen. The cost for the hydrogen tank considered for calculation is $US 7.7/kWh. The life time considered for tank equal to 20 years.

The other costs in long term storage loop includes compressor, various valves and sensors. The major cost intensive component is compressor. For the solar-hydrogen systems with the photovoltaic sizes in the range 2.5 kW to 10 kW the same membrane compressor with maximum flow hydrogen rate of 3 Nm³/h can be used. The other cost may vary in the range from 100% to 10% of the total investment cost of long term storage. For present calculation, the other cost is considered as $US20000 in whole life time of the system.

For a photovoltaic-diesel hybrid system the same amount of surplus energy should come from the diesel generator. As in a hybrid system most of the energy from the diesel generator, flows through battery, the efficiency of the battery is taken into consideration. In such a system along with fuel cost, the energy storage cost in battery should be included for operational cost. The total life time cost for the hybrid system to provide the same amount of surplus energy in whole life time of the system is given by,

$$K_{DG} = K_{fuel} + K_{bat,hy} + K_G + K_{GR} + K_{GM} \tag{4}$$

The surplus energy in the system with the long term storage system will come from the generator in hybrid system. The cost of diesel in the whole life time of the system can be obtained from the relation,

$$K_{fuel} = \frac{E_{s,xs} \cdot \eta_{LTS} \cdot T_{life}}{\eta_{DG}} \cdot \left(\frac{Bat_{use}}{\eta_{bat}} - \{1 - Bat_{use}\} \right) \cdot \frac{K_{fuel/l}}{PCI_v} \tag{5}$$

The efficiency of the generator depends on the output power. The average efficiency of the different generators reported by Museli (1999) is given in table1.

Table 1. Average efficiency of different generators

Generator	Average efficiency
Gasoline	21.1
Diesel (3000 rpm)	35.3
Diesel (1500 rpm)	29.9

A part of the energy produced by the generator is used to boost the battery during bad weather in a photovoltaic-diesel hybrid system. The battery cost during the whole life time of the system is given by,

$$K_{bat,hy} = E_{s,xs} \cdot \eta_{LTS} \cdot T_{life} \cdot K_{bat,sp} \cdot Bat_{use} \tag{6}$$

The specific battery cost is the storage cost in battery per unit energy which depends on the battery investment cost and also the average full life cycle of the battery. The average effective life cycle of lead-acid battery is reported to be 535 cycles by Ashri (1999). The storage cost in battery ($K_{bat,sp}$) considered for present calculation is \$US 0.37/kWh.
The life time of the diesel engine is expressed in terms of the operating hours. This is the time after which the engine should be rebuilt. The total rebuilt cost in the whole life time of the generator is given by,

$$K_{GR} = K_{PR} \cdot \frac{E_{s,xs} \cdot \eta_{LTS} \cdot T_{life}}{P_G \cdot T_{engine}} \tag{7}$$

It is assumed that the engine is needed to be rebuilt after 6000 hours operation. The cost of each rebuild is set to $US 1500 (Siemens,1996).
Beside the rebuilding cost, some of the components are needed to be replaced at a regular interval. At the time of installation, the investment cost of the generator is relatively low. But the maintenance cost of such system is high. Biermann et al., (1995) estimated the maintenance cost as a function of the total hardware cost, which varies from 5% to 20%. Museli (1999) estimated the maintenance cost on the basis of operating hours, which is more realistic. The maintenance cost of different engines can be calculated from the following relations (Museli, 1999):

i) for 3000 rpm diesel engines,

$$K_{GM} = \frac{\left(\{0.747 + 0.1184 \cdot P_G\} \cdot 15.2 + 120.8\right) \cdot 1.184}{P_G \cdot 400} \quad (8)$$

ii) for 1500 rpm diesel engine

$$K_{GM} = \frac{\left(\{0.242 + 0.3505 \cdot P_G\} \cdot 15.2 + 120.8\right) \cdot 1.184}{P_G \cdot 600} \quad (9)$$

The value of the different parameters used in present calculation is given in table 2.

Table 2. Value of different parameters

Parameters	Value
η_{bat}	0.93
η_G	0.3
η_{LTS}	0.4
Bat_{use}	0.98
$K_{bat,sp}$	0.37
PCI_V	10.08

6. Boundary curve for cost effective system selection

Comparing the life cycle cost of the long-term storage and the diesel generator a boundary curve is obtained as a function of the seasonal solar energy difference on which both the system is equally reliable and cost effective. On the one side of the boundary curve the hydrogen based long-term storage system is cost effective and on the other side the photovoltaic-diesel hybrid system is cost effective. In figure 3, the boundary curves are plotted for two different systems of different sizes. The present cost of electrolyser and fuel cell is considered for the calculation of the boundary curves. The upper side of the boundary

curve is cost effective for the solar-hydrogen system. The boundary curve corresponds the small system (PV = 2.5 kW) lies above the boundary curve corresponds to the relatively bigger
system (PV = 10 kW). With the increase in the size of the system the surplus energy in the system also increases. As a result, the operational and maintenance cost as well as the fuel cost in whole life time also increases in the photovoltaic-diesel hybrid system. In the case of solar hydrogen system the cost of electrolyser and fuel cell is only increased but the other cost remains same. The boundary curves considering the target cost of fuel cell and electrolyser which is relatively low is shown in figure 4. Because of the lower cost of the electrolyser and the fuel cell the boundary curves are shifted towards the lower fuel cost and increases the cost-effective area for hydrogen based long-term storage system.

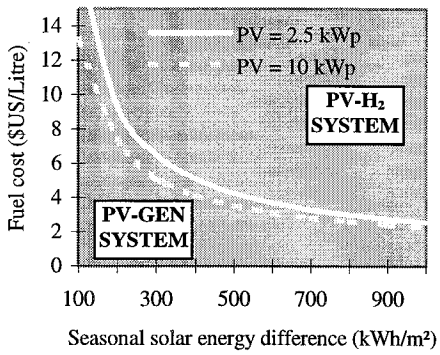

Figure 3. Boundary curve on the basis of present cost of electrolyser and fuel cell

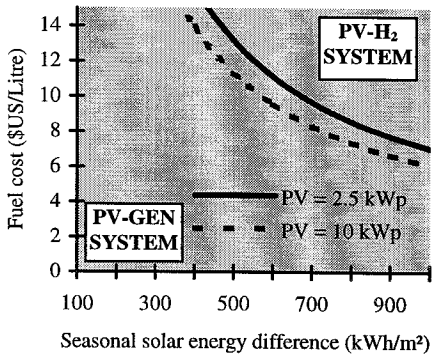

Figure 4. Boundary curve on the basis of target cost of electrolyser and fuel cell

7. Cost effective site selection

Combining the boundary curves with the diagram shown in figure 3 different sites can be identified where the hydrogen based long term storage is cost-effective over photovoltaic-diesel system. It is shown in figure 5. It is found from the figure that in spite of the present high cost of the electrolyser and the fuel cell, the applications in the highly remote areas like Antarctica is cost-effective for hydrogen based long term storage. At present, the application on the mountain top or island are not cost effective for hydrogen based long term storage. But in near future when the target cost of the electrolyser and fuel cell will be achieved these sites will be also cost effective.

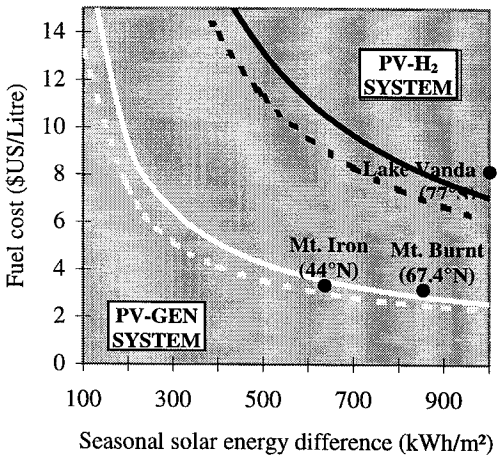

Figure 5. Cost effective site selection for solar-hydrogen system

8. Conclusion

In this present study, the solar hydrogen system is compared with photovoltaic-diesel hybrid system to find the cost effective sites. It is found that the seasonal variation in the solar energy increases with the increase in the latitude. The surplus energy in the system increases with the increase in the latitude. In a photovoltaic system with diesel generator this surplus energy is wasted. The cost effectiveness of the hydrogen based solar system increases with the increase in the latitude. In spite of higher present cost of the electrolyser and the fuel cell, the hydrogen based solar system is cost effective for the polar region. When the target cost of the electrolyser and the fuel cell is achieved, the scope of the hydrogen based solar system will also increase in near future.

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10. Nomenclature

$E_{s,solar}$	Total solar energy during good radiation	(kWh/m²)
$E_{w,solar}$	Total solar energy during bad radiation	(kWh/m²)
$E_{diff,solar}$	Seasonal solar energy difference	(kWh/m²)
$E_{S,XS}$	Surplus energy in good season	(kWh)
A_{PV}	Area of photovoltaic array	(m²)
η_{PV}	Efficiency of photovoltaic array	

η_{LTS}	Overall efficiency of long term storage	
K_{EL}	Investment cost of electrolyser	($US)
K_{Tank}	Investment cost of tank	($US)
K_{FC}	Investment cost of fuel cell	($US)
K_{Others}	Other investment cost	($US)
K_{fuel}	Cost of fuel	($US)
$K_{bat,hy}$	Energy storage cost in battery	($US)
K_G	Cost of diesel generator	($US)
K_{GR}	Generator rebuilt cost	($US)
K_{GM}	Generator maintenance cost	($US)
T_{life}	Life time of the system	(Year)
η_{bat}	Battery efficiency	
Bat_{use}	Battery use factor	
η_{DG}	Efficiency of diesel generator	
$K_{fuel/l}$	Cost of the fuel	($US/litre)
PCV_v	Heating value of fuel	(kWh/litre)
$K_{bat,sp}$	Specific energy storage cost in the battery	($US/kWh)
K_{PR}	Cost per rebuilt of engine	($US)
T_{engine}	Life time of the engine	(Hour)
P_G	Power of the generator	(kW)

PREPARATION, STRUCTURE AND PERFORMANCE OF RU-BASED OXYGEN REDUCTION CATALYSTS IN PEM FUEL CELLS

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Ruthenium-based catalysts supported on carbon have been prepared by three different methods using ruthenium oxalate, $Ru_3(CO)_{12}$ and ruthenium colloids as precursor. X-ray diffractometry (XRD) and transmission electron microscopy (TEM) revealed that the particle sizes ranged from 7 to 2.5 nm. The most homogeneous distribution was found employing colloidal technique. It was found by rotating disc electrode measurements (RDE) that the number of surface sites on the carbon support limits the concentration of catalytic particles to 20% Ru. Ruthenium particles, surface modified by selenium, became stable against oxidation and showed a higher current density at an increased overvoltage of 0.12 V compared to platinum. The results will be compared with the catalytic activity of Fe-Co catalysts.

1 Introduction

Recently, it was shown that catalysts based on ruthenium meet the requirements as catalysts for direct methanol fuel cells, because of their high selectivity in oxygen reduction [1]. Therefore, we have developed and tested different methods for the synthesis of carbon supported ruthenium particles and studied the effect of incorporated selenium. In combination with the analysis of the resulting morphology and catalytic activity this allows an evaluation of requirements for replacing platinum with ruthenium based catalysts for oxygen reduction in direct methanol fuel cells.

2 Experimental

2.1 Preparation of Catalysts

Ru catalysts were prepared by three techniques:
A: High surface area carbon (Vulcan XC 72R) was impregnated with a ruthenium oxalate complex. Thermal treatment at 300°C for 1 h of the impregnated carbon powder and subsequent purification yielded the final catalyst.

B: High surface area carbon (Vulcan XC 72R) was impregnated with $Ru_3(CO)_{12}$ and thermally treated at300°C for 2h to obtain a mixture of 23% ruthenium metal and 77% carbon. For the incorporation of Se, the catalyst powder was dispersed in H_2SeO_3 containing solution. The powder was afterwards filtrated and dried.

C: For the preparation of a catalyst via colloidal Ru nanoparticle we followed a preparation procedure given in ref. [2]. The incorporation of Se was achieved as described above.

2.2 Structural and Chemical Characterisation

The catalysts were investigated with a Philips CM12 transmission electron microscope. Analysis of the TEM pictures to obtain particle size distribution was performed with standard public domain NIH software. XRD was carried out with a SIEMENS D500/5000 diffractometer operated with a Cu anode at 45 kV and 30 mA. A secondary graphite monochromator was used to select the $k\alpha_1$ and $k\alpha_2$ lines. Thermal stability of the catalyst prepared by method B was investigated by a thermal balance coupled with a mass spectrometer (TG-MS). Extended X-ray Absorption Fine Structure (EXAFS) measurement elucidated the bond distances and coordination numbers of the catalytic centres using synchrotron radiation (RÖMO II X1.1 station at HASYLAB).

2.3 Electrochemical Experiments

The electrocatalytic activity of the powder materials was tested via standard cyclovoltammetry and rotating disc electrode (RDE) measurements using a three electrode set up. In the laboratories of DaimlerChrysler Ulm Gas Diffusion Electrodes GDE were manifactured to test the catalysts in a Polymer Electrolyte Fuel Cell.
The catalyst electrodes were prepared by pipetting an ethanolic catalyst suspension onto glassy carbon electrodes to obtain a Ru loading of 70µg Ru/cm^2. The so obtained electrode was dried in air and was afterwards electrochemically cycled (50 mV/sec) from 780 mV to 0 V vs NHE for 10 min under N_2 in 0.5 M H_2SO_4 electrolyte to obtain stable cyclovoltamograms. For measurements under oxygen, the solution was saturated at least 10 min with oxygen and rotating disc experiments were performed with different rotations at a scan rate of 5 mV/sec.

3 Results and Discussion

The preparation procedures listed above yielded catalyst particles on carbon with different mean particle sizes as summarised in table 1. With decreasing particle size the active surface area of the catalyst was increased and should therefore led to corresponding increase of specific current density for oxygen reduction. However, the apparent overvoltage for the oxygen reduction decreased less significantly as expected from the increase in relative surface area. Therefore, it is assumed that the quality of the electrical contact of the nanoparticles to the carbon electrode is current limiting. Interestingly, an increase of current densities by a factor of 2 to 3 was found by the incorporation of selenium. Under the best conditions achieved in this way, the activation barrier for the overall oxygen reduction is approximately 0.12 V higher than for platinum.

Table 1: Comparison of different catalytic active ruthenium catalysts

Prep.	median particle size (TEM)	tafel slope	curr. dens. at 600 mV	tafel slope mod. with Se	curr. dens. at 600 mV mod. with Se
A	7 nm	125 mV/dec	2.7 mA/cm^2	-	-
B	4 nm	125 mV/dec	4 mA/cm^2	100 mV/dec	12 mA/cm^2
C	2.5 nm	110 mV/dec	5 mA/cm^2	110 mV/dec	10 mA/cm^2

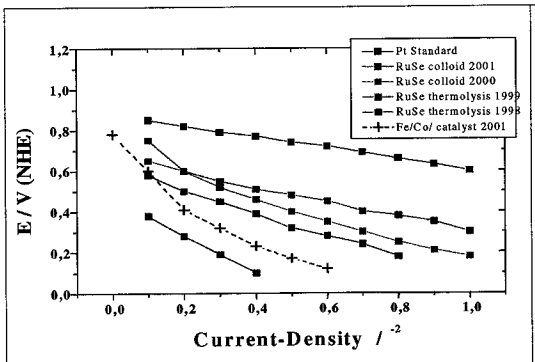

Figure 1: Current-voltage-characteristic of H_2-PEM fuel cells using Ru-Se and Fe/Co catalysts at the cathode site (cathode: C / Ru_xSe_y (20%Ru / C, load 0.14mg/cm²); Fe/Co (5%Co/C, load 0,2mg/cm²) operation pressure 3bar of compressed air; anode: Pt, load 4mg/cm², fuel: H_2; operation temperature: 80°C, active area: 50cm².

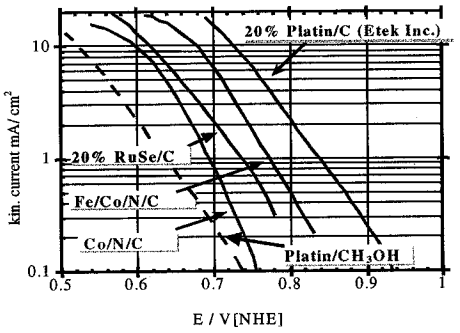

Figure 2: Tafel plots of Ru-Se/C and Co-Fe-N/C catalysts obtained from rotating disc electrode measurements. Please, note the shift of the platinum curve in the presence of methanol.

Fig.1 shows the progress of the catalytic activity achieved in PEM fuel cells over the last four years improving the catalysts structure and the performance of Gas Diffusion Electrodes (GDE) carried out by the project partner DaimlerChrysler. Although the activity of the best catalyst, prepared by colloidal technique, remained below the output characteristic of platinum, the Ru-Se catalyst has advantages using methanol as fuel in Direct Methanol Fuel Cells due to the fact that Ru-Se catalysts are stable against depolarisation by methanol, verified under laboratory conditions (see Fig. 2). The related Tafel plots given in Figure. 2 also show that recently prepared Co- and Fe-Co catalyst (see also contribution NOBLE METAL FREE CATALYSTS FOR OXYGEN REDUCTION IN PEM FUEL CELLS in this proceedings) exhibit higher activity than the best Ru-Se catalyst in RDE measurements but not employing the catalyst in GDEs so far (see Fig. 1). This behaviour is presently affected by different mesoscopic structures of the catalysts studied.

XRD and TEM measurements revealed that the catalyst prepared from $Ru_3(CO)_{12}$ in the presence of an optimized selenium concentration consists of metallic Ru-particles with a particle size ranging from 2 to 6 nm. No other crystalline compounds, such as $RuSe_2$ or RuO_2, could be detected. In TG-MS measurements, it was found that the samples released considerable amounts of CO and CO_2 upon heating, which presumably belong to an amorphous layer covering the Ru core. A release of selenium is observed at 800°C and at about 1100°C.

All Ru-Se catalysts showed the EXAFS pattern of Ru metal and additional features that can be addressed as Ru-Se, Ru-C and Ru-O bondings. Adjusting EXAFS profiles it was found that the distance in the as grown material amounts to a value of $d_{Ru\text{-}Se} \approx 2.56$Å which is typical for metal organic compounds such as $Ru_4Se_4(CO)_{12}$. The Ru-C and Ru-O distances are 1.95Å and 1.97Å, respectively. This behavior can be explained by the presence of amorphous ruthenium oxides or hydroxides and metal organic complexes covering the surface of the Ru nanoparticles.

Conclusively, the concentration of surface sites which bind catalytic particles as well as the presence of selenium, which may act as electron transfer bridge, was found to have a significant effect on current density.

5 Achnowledgment

Financial support by the BMBF under contract no. 0327067B and by DaimlerChrysler is gratefully acknowledged.

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A FUEL CELL WORKSHOP FOR SAARLAND'S SUPPLIERS: OUR GOALS COMPARED TO OUR RESULTS

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Today, fuel cells and their technical potential are a major topic, discussed in public. Often the fuel cells are considered to be the energy saving technique that will solve all our future supply problems. Through the study of daily papers and different energy related journals, one can get the impression that today, fuel cells can be bought in a discount store already. The actual technical level of the fuel cells is however in the stage of prototyping and pilot- and/or field tests. Only the American company ONSI has produced a 200kW phosphoric acid fuel cell unit in series.

Because of the importance of the fuel-cell-system technique, the institute IZES received order by the Ministry of economy of the land Saarland to organize an industrial workshop on the subject: "The market for fuel-cell-systems: A chance for the Saarland economy!" Such a Workshop is considered to be a chance for the suppliers in Saarland to establish themselves with their products in the fuel-cell-system engineering field. It makes sense to do this in an early stage of development. The main goals of this event were the presentation of new possibilities and the practical benefits of the fuel-cell-system technology for the Saarland economy. Besides today's big success in e. g. IT and material technology, Saarland's traditional competences is located in the fields of energy, electrical engineering, metal processing and plant engineering.

INTRODUCTION

A first industry questionnaire has shown that a lot of companies in Saarland are interested in the topic "fuel-cells". On the other hand, the major result of the interviews was that the topic "fuel-cell" has mainly medium or even long-term priority. By setting a first priority to the topic "fuel-cell", an information initiative was created to perform a workshop for the supplying industry. In many ways, this contact with the fuel-cell-system engineers was recognized to be the first in a course of many other discussions and workshops to follow with regional suppliers.

The destination of this workshop was first, to inform interested companies and institutions about the state of-the-art of fuel cells, and second to demonstrate their supplying- potential to the fuel-cell-system producers, in order to initiate new projects with the Saarland industry. Four months after the Workshop the participants were asked for impulses of the workshop to their company activities. The number of the newly created business contacts between the Saarland industry and the manufacturers of fuel-cell-systems is rising and will finally be an indication for the success of such a workshop.

STATE OF THE ART OF FUEL CELL SYSTEMS

TABLE 1
FUEL CELL SYSTEMS

low temperature fuel cells	operating temperature	field of application	availability
alkaline fuel cell (AFC)	60 – 80 °C	military and aerospace technology	presently no commercial use
polymer exchange membrane fuel cell (PEMFC)	70 – 90 °C	stationary combined heat and power (CHP) units mobile applications	1st generation of stationary of CHP units pilot and demonstration vehicles
direct methanol fuel cell (DMFC)		mobile applications	pilot and demonstration vehicles
medium temperature fuel cell			
phosphoric acid fuel cell (PAFC)	190 – 210 °C	stationary combined heat and power units	200 kW unit in series
high temperature fuel cells			
molten carbonate fuel cell (MCFC)	600 – 650 °C	stationary combined heat and power units, power plants	1st generation of stationary CHP units
solid oxide fuel cell (SOFC)	850 – 1000 °C	stationary combined heat and power units, power plants	1st generation of stationary CHP units

One distinguishes today mainly five different fuel cell types, in accordance with the kind of their electrolyte. The distinction of these different systems can be done in accordance to their process- and/or operating temperature. A division in accordance with their process temperature is more reasonably, because simultaneously, the field of application of the respective fuel cell is determined. The five different systems and their state of-the-art is described in table 1.

Fuel cell systems are of very high interest for both, stationary and mobile applications. The individual features of the five (there is no distinction between PEMFC and DMFC) fuel cell systems are for example the material of the electrolyte and the therefore defined possible operating temperatures. Also the fundamental demands for the fuel gas quality are depending on the process temperatures of the different techniques. The technical key data for the individual fuel cell techniques are fully described in [1].

AFC systems were developed particularly for aerospace and military (high cost) applications. Because of their high requirements on gas quality at the present time, there is minor market potential for this technique. For stationary systems, particularly, the PAFC, the MCFC and the SOFC fuel cell technique will be considered. PEMFC units up to 250 kW electrical power are of interest for stationary CHP. Today, for mobile applications, the polymer electrolyte membrane and also the direct methanol fuel cells are the preferred technical concepts.

PARTICIPATING MANUFACTURERS OF FUEL-CELL-SYSTEMS IN THE WORKSHOP

The Institut fuer ZukunftsEnergieSysteme IZES (institute for future energy systems) and the Ministry of Economy of the Land Saarland were responsible for the co-ordination and organisation of the Workshop. Two leading fuel cell system manufacturers, the European Fuel Cell GmbH (EFC) and the Motoren- und Turbinen-Union Friedrichshafen GmbH (MTU) and one leading high performance plastic manufacturers were present as invited speakers. The contents of these lectures were arranged prior to the Workshop in close co-operation with both, the speakers and the participating supplying companies from the Land Saarland. On one hand, the fuel cell manufacturers EFC and MTU specified, as detailed as possible, the systems and peripheral components that are of urgent need for the improvement of the presently actual units. A detailed list of the needed components and their present state of-the-art can be found in reference [1]. On the other hand, the TICONA GmbH described the purpose of high performance plastic materials in fuel cell systems and their peripheral systems too.

In the field of house heating systems, the EFC presented their product and the required components for the improvement of the complete fuel cell system. The EFC GmbH was founded in 1999. The goal of the company is the manufacturing of complete fuel cell aggregates in Germany. The company acts as a system integrator and produces fuel cell house heating systems together with partners and subcontractors. As a central unit, they use a PEM fuel cell stack with net 1.5 kilowatt electrical power. Furthermore, on EFC´s side , the wish exists to set-up a marketing partnership for the fuel cell units with local energy suppliers.

In the field of the stationary fuel cell units, the MTU GmbH, an enterprise of the Daimler Chrysler AG, presented their product, a complete system and peripheral components for the improvement of the MCFC hot module. A European consortium was founded in 1990 for the development of a highly integrated compact carbonate-direct fuel cell system with net 250 kilowatt of electrical power. This consortium carried out the largest European program for the commercialisation of the molten carbonate fuel cell technology. MTU acts as the consortium leader. The developed hot module concept was first tested in the years 1997/98. The complete fuel cell power unit operated at the test facility of Ruhrgas AG, a member of the consortium, in Dorsten, Germany.

In the field of high performance plastic materials, the company TICONA GmbH, an enterprise of the CELANESE AG, presented their product range with regards to the fuel cell technology. In the broad product spectrum of the TICONA GmbH, there are many high tech plastic materials for the production of components in both, stationary fuel cells and mobile applications. For example, materials for the reformer unit or components of the water cycle are available by the TICONA GmbH. These materials are characterised for example by their low density, the high resistance against chemicals, humidity and temperature.

GOALS VERSUS RESULTS OF THE WORKSHOP

The primary goal of the Saarland´s workshop, from the viewpoint of the IZES and the Ministry of Economy of the Land Saarland was, to motivate potential producers of single components, subsystems or complete systems to produce for fuel cell systems. By listing the most important qualities of the required products, the suppliers in Saarland were motivated to visit the workshop and to contact the fuel cell manufacturers. In addition to the lectures of the speakers, a booklet including the specific details and state of-the-art of the actually used system components and their potential for improvement, as well as information about the companies of the participating

speakers. This information booklet will assist the Saarland's enterprises in their decision process and to establish closer contacts with fuel cell system manufacturers, if it appears reasonable.

Due to the successful creation of new business relations between the enterprises from Saarland and the fuel cell manufacturers, the local companies will start new spheres of activities. In case that the fuel cell technology will have a major part in the decentralised energy supply in near future, this means simultaneously the creation of new jobs and also securing of existing jobs.

The success of the Workshop can be demonstrated now, some five months after the workshop by the following examples.

In the near future, one manufacturer and a local power plant operator, want to implement the fuel cell technique in the Land Saarland. Together with the institute IZES, a concept for a new generation of urban housing shall be developed and brought into action as soon as possible.

The efficiency and selectivity of the currently applied catalyst materials are still in the stage of development with respect to costs and lifetime. One fuel cell manufacturer intends to develop a suitable catalyst for his product, together with the scientific staff of the chair of technical chemistry at the university of Saarland. A central topic in the scientific work of this institute is the research for new more effectively working catalysts and materials. For example, catalysts for the selective oxidation of hydrocarbons are one of their major topics.

SUMMARY

In conclusion, the workshop was successful for both, the participants of the suppliers of the Land Saarland and for the companies of the invited speakers too. New business relations arose with regard to the available industrial supplying-potential of companies in the Land Saarland. A further pleasant result of the event was that the participating enterprises from Saarland created new contacts also between each other. Because of these first successes alone, it can be said definitively, that the idea to create new jobs and also to secure existing jobs has become true already. At the present time the final benefit is hard to be estimated, because the evaluation process is not yet completed.

ACKNOWLEDGEMENT

IZES thanks Elisabeth Weber from the Ministry of Economy of the Land Saarland for the support during the organisation of the Workshop.

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AN EFFECTIVE AND RELIABLE METHOD FOR SINGLE FUEL CELLS EXPERIMENTAL TESTING AND RESULTS COMPARISON: ADVANCED CONTROL TECHNIQUES

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The Energy System Group of the University of Perugia is currently performing single cell testing. The authors strongly believe that test parameterisation, procedure definition and advanced control techniques constitute the three main steps toward achieving standardization of test conditions and results. Advanced control techniques issues are dealt with in this part of the paper. The advanced control system for the test facility was developed by the authors in order to reach two main objectives: an easy and remote setting and modulation of all required parameters to make the cell work at the chosen conditions; a continuous check of all security parameters in order to reveal breakdowns of the test rig or dangerous conditions, both for the system and for the operators. The results showed how test standardization and automation can enhance the amount of information that can be obtained and drastically reduce time and cost required for testing thus fostering fuel cell technology development.

Introduction

Fuel cells are known to be very promising energy conversion devices. Great expectations rely on them thanks to their potential high efficiencies and very low emissions.
The great interest in Fuel Cell Systems, along with the novelty of the device itself, fostered strong research effort aimed at making the development steps considered necessary for future FC plant commissioning. Great experimental activity is required both for fuel cells evaluation and for theoretical and numerical data validation.
Given the large amount of activities required in order to attain all the necessary targets in terms of duration, cost, reliability, performance, integration and flexibility, in the relatively short times dictated by market rules, a synergy across the continent is required. The greatest effort concerns experimentally validating computational predictions which must demonstrate the ability of the systems to achieve the calculated values of the relevant operational and life parameters. This is a long, time and resources consuming activity since all experiments constitute feedback for the design phase that should improve the system itself thus requiring further experimentation. In order to combine resources to achieve the ambitious target, a virtual testing facility throughout Europe must be created. It is obvious that the shift from site laboratory to a virtual facility, from enterprise work groups to net actions, from proprietary results to shared community knowledge requires the adoption of a common language and common testing rules. Another major requirement consists in reliability and accuracy of experimental results that can only be guaranteed by rigid test procedures and proper error

handling. Lastly, the increase of facilities capabilities is needed in terms of ease of use and reduction in time and resources required for tests as well as increase in data post analysis capabilities.
The Energy System Group of the University of Perugia is currently performing single cell testing. The presence of different and continuously renewing performers, like students working in the facility on their MSc or PhD thesis, and the need of data exchange among partners in the various research projects, attracted attention to this topic. The authors strongly believe that test parameterisation, procedure definition and advanced control techniques constitutes the three main steps toward achieving standardisation and reliability of test conditions and results.

System description

The facility for fuel cells testing has been conceived, already in the design phase, in order to allow immediate reading of all required quantities and easy manipulation of all individual parameters. Besides, in every procedure, or every test activity, the possibility to set and control all the needed parameters from a remote location and in an automated fashion should be guaranteed.
The first requirement, i.e. easy reading, setting and controlling, means that during a test run, the parameters that have to be read or varied are all fed into a data acquisition system and can be directly managed by a software installed on a local computer. The second step means that reading and even controlling can be performed by a computer placed far from the facility, by means of data exchange procedure through the internet.

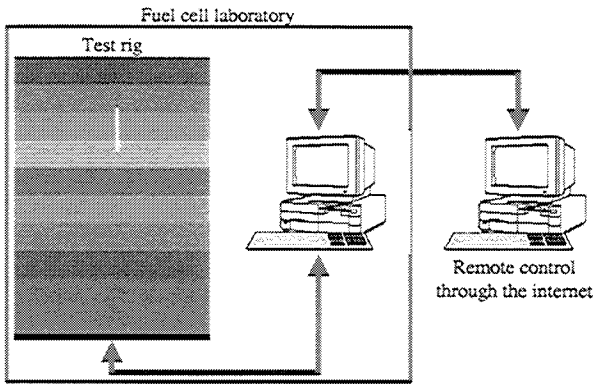

Fig. 1 – Data and information flow through test rig and Control System

Finally, the possibility to design and insert test procedures in the software, allows to perform unattended activities on the test rig without any chance of nonconformities from test procedures.
Obviously, the possible absence of operators during the test activities implies that a certain amount of data, comprising environment and test devices conditions, has to be put under software control in order to monitor possible system failures or accidents. Then, automatized interventions have to be implemented to avoid dangerous conditions.

The above stated is particularly important in a University laboratory, where several and continuously changing people work inside, such as students on their MSc or PhD thesis and where there is need to exchange data in real time with industrial partners involved in research projects. This prompts the need for automatization and standardization of test procedure and facility management.
The first activity in this field has performed on the defining common rules for test conditions as specified on the (Lunghi, 2001). Hereby, test procedures and parameters were developed by the team to try to obtain an easy and quick comprehension of the results and to allow effective comparisons with other tests performed in different working conditions or in different laboratories.
In order to clarify the system definition, attention has to be paid on what a single fuel cell test rig has to monitor and control.
A fuel cell is an electrochemical device that converts chemical energy directly into electrical energy. The principle of an MCFC operation is shown on fig. 2.
The process involves the oxidation of a fuel (hydrogen, but also CO for MCFC) and the reduction of an oxidant (O_2, CO_2) according to the following reactions:

at the anode:

$$H_2 + CO_3^{--} \rightarrow H_2O + CO_2 + 2e^- \quad (1);$$

$$CO + CO_3^{--} \rightarrow 2CO_2 + 2e^- \quad (2);$$

at the cathode:

$$1/2\,O_2 + CO_2 + 2e^- \rightarrow CO_3^{--} \quad (3).$$

At the anode CO is mainly involved in the water-shift reaction, hence increasing the concentration of hydrogen:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (4);$$

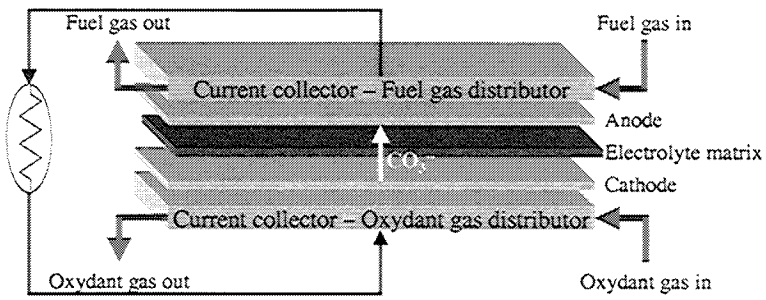

Fig. 2 – MCFC operation principle

Electrons flow from the fuel electrode (anode) to the oxidant electrode (cathode) through an external load. The electrical circuit is closed by the ionized particles ($CO3^{--}$) crossing the electrolyte filled with carbonates. The reactant gases, fuel and oxidant, are separately fed to the anode and cathode manifolds; the electrolyte matrix prevents gas crossover and guarantees the correct ionic conduction and electronic insulation between the two electrodes. The maximum electrical work obtainable in a single fuel cell operating at a set temperature and

pressure is given by Nernst's equation, thus depending on the concentrations of the flowing gases into the cell, and on the working temperature and pressure.
However, the working voltage available at the cell electrodes is considerably lower than the Nernst potential, due to the irreversible losses caused by the ohmic resistance and the activation and diffusion polarization (Fuel Cell Handbook, 2000, Lunghi et al. 2001).
On the basis of the brief description above, it is evident that a fuel cell test rig should first yield the measurement of the cell voltage (final output), the gas flow rates and the flowing current.
The specifications of the designed control system have been noticeably ambitious, particularly because it was intended not only to perform measurements but also to control the cell behaviour by means of an integrated software that allows to verify data, benchmark their values and modify the operating conditions in order to obtain a defined performance from the cell under test. To get the goals specified above, a test rig unit has been designed and implemented as reported in a full description in (Lunghi et al. 2001). The simplified scheme of the system is reported in figure 3.

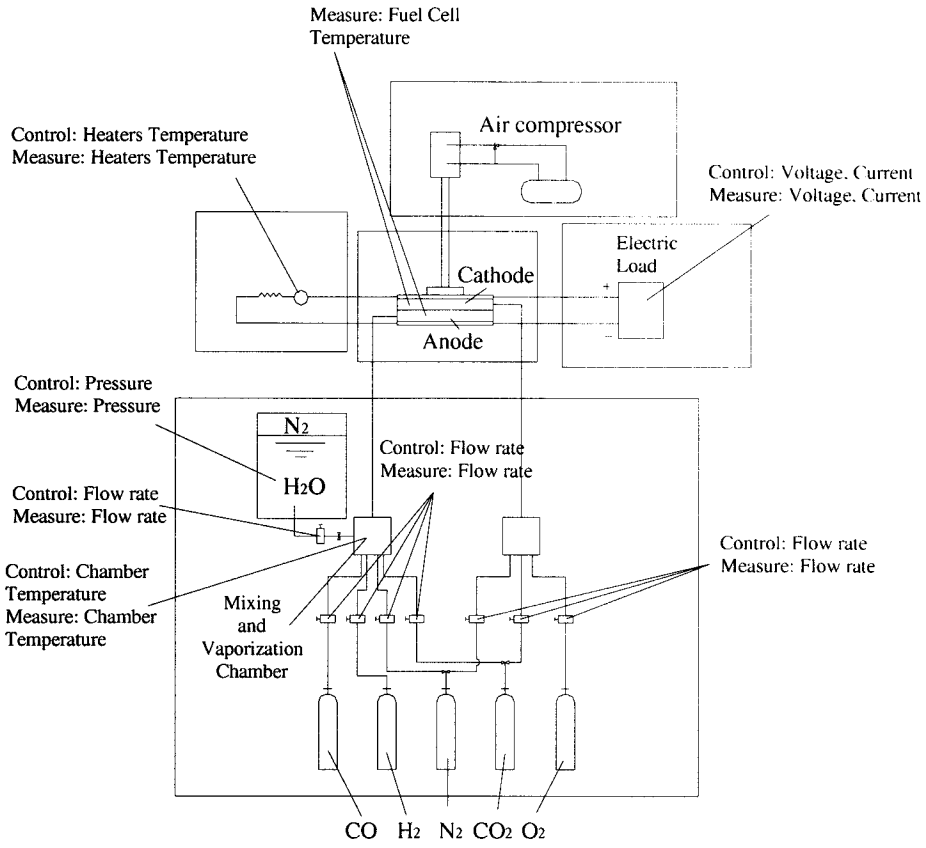

Fig. 3 – Test rig scheme

The main output, i.e. the cell voltage, is directly measured at the two electrodes and its value processed by a National Instruments board, which yields other analogical measurements such as temperatures through specific sensors and hydrogen or carbon monoxide environment concentrations. The type of the board is the PCI-6035E characterized by two analog outputs, 16 analog inputs with an acquisition range between 610 V and 6 50 mV and a sampling rate of 200 kS/s. The gases and water flow rate are measured and controlled by Brooks 5850E Digital Mass Flow Controllers, chosen for their high accuracy and for their characteristic to be managed by software through serial PC ports.
The vaporizer system provides the measurement and control of the water vapour directed to the anode and, through a serial port, is possible by the software to manage temperature and flow rate. The load Agilent N3301A has been chosen since it is extremely accurate and it can work in constant current or constant voltage or constant resistance mode. Furthermore, the load is also remotely controlled by the serial PC port. Finally the temperature of the system is subjected to external control, and local temperatures collected by thermocouples present in various position of the cell, are processed by the PC board.
Even if the test rig system has been designed and the components chosen for full remote and programmable management, all components are separately controllable. Once the test rig was built, the control system logic was implemented so attain the main defined goals.

Logic of the Control system

The control system of the fuel cell test rig works according to the scheme reported in figure 4.

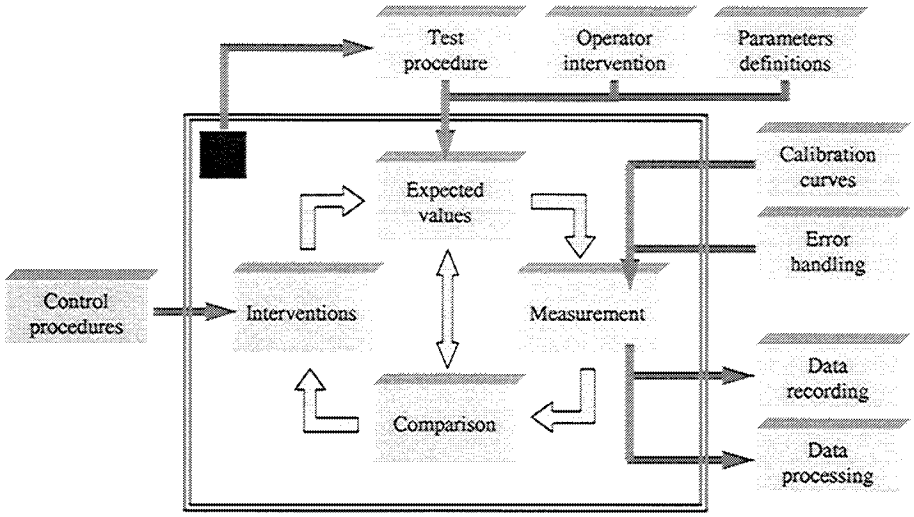

Fig. 4 – Flow diagram of the control system logic

The heart of the system is the cycling unit constituted by the four following main blocks:

- Evaluation of expected values of parameters;

- Measurement of the controlled parameters;
- Comparison between the measured values and the expected values;
- Interventions in order to minimize the gap between the expected and the measured values.

This unit is retried with a frequency which depends on the minimal time required by the instrumentations in order to get all the values and to process them as per the set working conditions.
The first cell (evaluation of expected values of the parameters) is a section where all controllable parameters, are set according to their definition and test procedure e/o operator intervention. For example, through the analytical definition of current density and fuel utilization factor and through the value introduced by the operator and through some procedures, the expected values for current flow and H_2 flow rate are evaluated. It is obvious that, at the actual unit iteration, the new expected value of the parameter can be the same as the former, if there are no interventions from external, or it can be different, if some procedure has been changed or the operator changed its value.
The second cell provides the measurement of every relevant parameter. The first set concerns measuring a theoretical value by means of specific protocols for data exchange between the instruments and the software. For example, the theoretical mass flow rate is derived from the degree of aperture of a valve inside a mass flow controller. After the reading, post elaboration is performed. In the case of mass flow controller, calibration curves (obtained by calibration protocols implemented in the software) are used to correct read data. Other routines have also been developed and implemented in the software to take in account measuring chain inaccuracies.
Then, in the third cell, a comparison between the expected values and the read values is performed and the gaps are determined. If the value of these gaps is lower than the maximum set, the single parameter is left in the same condition. If the value of the gap is higher than the maximum allowed, then an intervention on the related instrument is performed in order to attain the defined value. The interventions can be realized by specific procedure in order to allow better regulation (for example a proportional, integral, derivative regulation can be chosen).
The cycling of the main unit is under the control of a clock, with which, it is possible to interact with the external procedure that, at prefixed times, modifies the expected values of some parameters as it will be seen in the next paragraph. Then, the data recording is thus labelled by the time description.
It is important to notice how the implemented control system allows analysis routines that are not easy with manual systems. For instance, in order to yield the evaluation of voltage losses related to current density increase, it is necessary to work keeping all the other parameters fixed, first of all the utilization factor. This implies increasing gas flow rates as the current density increases. It is not feasible to perform such a test with manual control system since, for each current density value, all the required values of the other input parameters (i.e. mass flow rates) should be evaluated and set in the system taking also into account calibration curves and necessary rounding off due to devices stepwise regulation. Finally, manual recording should be made keeping in mind that the set value differs from the wanted one. Only the automated system can manage this complexity and attribute an output value to the correct real input value (not the desired one) and then analyse the results thanks to dispersion curves.
In order to increase the potentiality of the system, some routines have been implemented which allow easy and powerful controlling of the system. Some examples follow. One of the

mentioned routines involves flow controllers management. During the tests or start-up, shut down, re-start procedures of the single cell, the need to use different flow controllers was highlighted. In fact, for different working conditions, different gas flow rates or even different gases are required, hence the instruments have to be changed. This need involves a mechanical modification of the system and a consequent software implementation in order to take into account the new instrumentation. In order to avoid continuous software modifications and consequent related errors, a routine has been implemented through which a quick choice of the working instruments is possible by simply inserting the related TAG number (i.e. a label of the instrument) in a dedicated dialog window. The characteristics of all the flow controllers needed by the software are stored in a routine and called according to the defined TAG. The software then allows to use the chosen flow controller for different gases, giving the possibility to insert several specific calibration curves. This functionality is easy to use thanks to the possibility to store the related curves in specialized routines.
Another implemented routine deals with errors from measuring chain inaccuracies. It is possible to introduce inaccuracies of every measuring instrument in terms of measure average shift from true value and measure standard deviation to obtain automatic corrections and estimation of the overall error.
An important advantage of the control system is the possibility to make real time data processing in compliance with defined procedures, and thus to make available in real time - from the basic values as voltage, current, gases flow rates - derived parameters. This functionality reduces the time required for post-analysis and, above all, allows immediate understanding of some phenomena.
The measured values can then be recorded in a file. This allows to analyze and process data after the test conclusion. Different kind of data (measured values, processed parameters, environment conditions, and so on) can be recorded and the possibility to make "off-line" analysis allows to use more powerful analysis tools, given the abundance of available elements.
Finally, the system provides protection against system failures and against environmental dangerous condition.
In case of particular conditions, for example with the cell voltage dropping below a security limit, the software performs some planned interventions. Several steps can be chosen which prompt, in case of serious failure risk, to the termination of the test-run and the inertization of the cell by feeding nitrogen in the electrode comparts, thus preventing irreparable break down.
The utilization of hydrogen and carbon monoxide for fuel cells testing, encouraged the adoption of gas concentration sensors in the ambient. They provide a current signal proportional to the considered gas concentration. The signal is directed to the PC and in case of over-concentration an alarm is switched on.

Automated procedures

The most relevant feature of the designed control system regards the possibility of unattended operation thanks to automated test procedures. For the characterization of a fuel cell, the group of the university of Perugia has defined some relevant parameters fully described in Lunghi, 2002. The choice and definition of these parameters was made with the aim to distinguish cell performance variation in relation to different causes as current, temperature, cathode or anode stream gases modifications.

First of all, the most relevant parameters for cell behaviour have been recognized as the following: type of fuel cell, electrodes and electrolyte materials, age, operating temperature, operating pressure, current, oxidant flow rate, fuel flow rate, oxidant utilization factor, fuel utilization factor, dilution fuel flow rate, dilution oxidant flow rate, steam flow rate, contaminant concentration. The reasons of this choice and a complete description is reported in (Lunghi, 2002). On the basis of this, some relevant non-dimensional parameters were determined with the criterion to make their value equal to 0 if the related quantity is absent and equal to 1 if the related quantity is set to the maximum value. Particular attention has been focused on the flow rates parameterisation, in order to yield immediate and easy understanding of the operating condition of the fuel cell.
In tab. 1 the defined factors U_f, U_{ox}, C_f, CO_{2f}, H_f, D_f, D_{ox} and a brief description are reported.

Description	Symbol	Definition	Note
Fuel utilization factor	U_f	$\frac{e^-}{2\cdot(H_2+CO)}$	It indicates the rate of fuel (H_2 and CO) reacting vs the total fuel flowing through the anode.
Fuel carbon factor	C_f	$\frac{CO}{(H_2+CO)}$	It indicates the ratio between the CO flow rate and the total fuel (H_2 and CO) flow rate
CO_2 fuel factor	CO_{2f}	$\frac{CO_2}{(H_2+CO+CO_2+H_2O)}$	It indicates the ratio between the CO_2 flow rate and the reactant gases flowing through the anode.
Humidification factor	H_f	$\frac{H_2O}{(H_2+CO+CO_2+H_2O)}$	It indicates the ratio between the H_2O flow rate and the reactant gases flowing through the anode.
Fuel dilution factor	D_f	$\frac{N_2}{TOT}$	It indicates the ratio between the inert gas N_2 flow rate and the overall stream flow rate through the anode.
Oxygen utilization factor	U_{ox}	$U_{ox}=\frac{e^-}{4\cdot O_2}$	It indicates the rate of oxidant (O_2) reacting versus the total oxidants flowing through the cathode.
Carbon dioxide utilization factor	U_{C2}	$U_{C2}=\frac{e^-}{2\cdot CO_2}$	It indicates the rate of CO_2 reacting vs the total CO_2 flowing through the cathode.
Oxydant dilution factor	D_{ox}	$\frac{N_2-79/21 O_2}{TOT}$	Ratio between the inert gas N_2 flow rate and the overall stream flow rate through the cathode.

Tab. 1 – Relevant parameters for Molten Carbonate fuel cell operation

With these factors in mind, test procedures have been planned in order to analyse the cell performance by varying the defined parameters. Then the procedures have been implemented in the software tanks to specific routines, in order to make the control system able to perform fully automated trials.
The software allows the operator i) to define the range inside which every parameter can vary, ii) to define the step for every parameter variation and, iii) to define the duration of the trial for every single combination of parameters.
The flow diagram for the test routine is schematised in figure 5.

After the definition of the test procedure, performed thanks to the specification of the parameters range variation, the step wideness and the duration of every combination of parameters, by inserting the relative values in the specific dialog box, the trial can start.

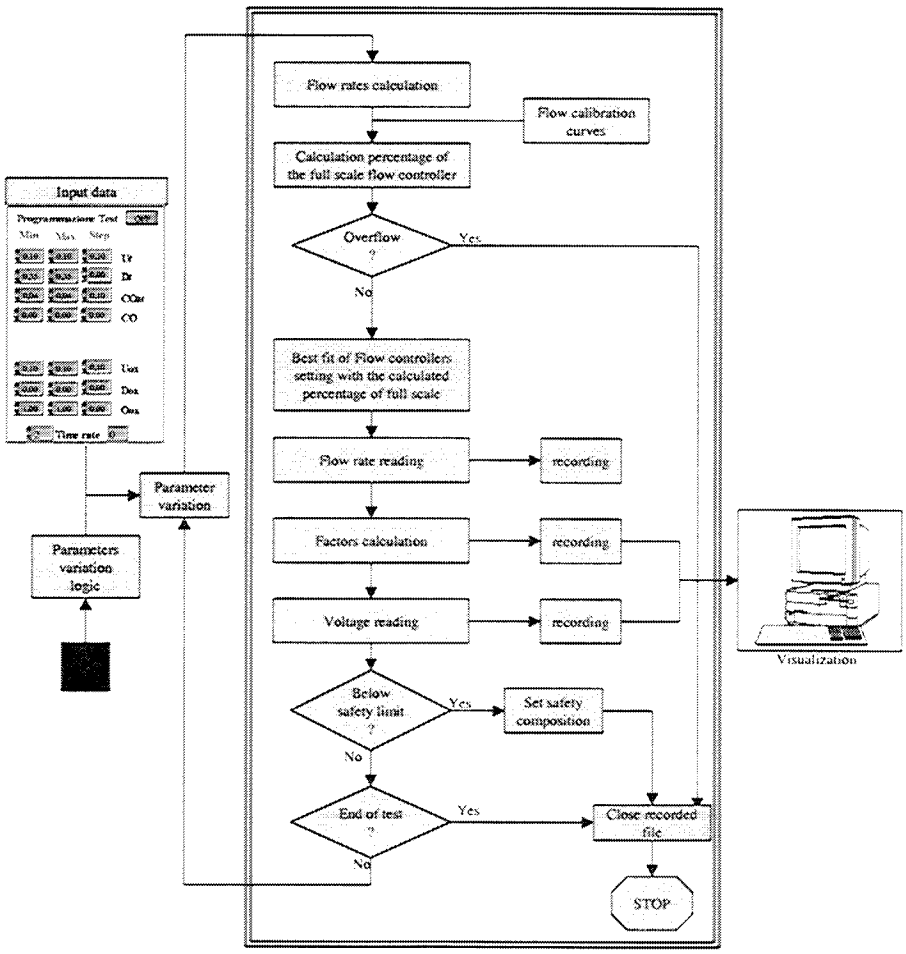

Fig. 5 – Flow diagram of the test procedure

Usually a test is planned in order to characterise the cell according with the variation of several parameters. The "parameter variation logic" algorithm sets all the parameters at the initial value and nests all loops necessary to provide the variation of each parameter between the fixed range at every time step. In this paper, reference will be made to flow rates quantities but the concepts here explained are general and used in the control system to control all relevant quantities i.e. temperatures, pressures, current flow, voltage...In the case of flow rates the routine works like the example below.

Let's suppose that a test should be conducted aiming at evaluating cell performance with U_f varying from 0,5 to 0,8, C_f varying from 0 to 0,4, D_f varying from 0 to 0,2, with constant

current and with all parameters varying with a step of 0,1. As said, this information has to be set on the front panel of the control system (figure 6). Once the procedure has been started, the considered factors are set at the initial value (U_f = 0,5, C_f = 0, D_f = 0) and the other non specified factors at their default value. According to the fixed sequence (which allows in this case the variation of D_f first, then C_f and finally U_f), D_f starts from 0 and varies up to 0,2, then C_f changes its value of one step and D_f varies again along the full range, hence C_f increases another step and so on, till the complete variation of U_f along its range. Every possible combination is thus performed in a predefined time and the cell can work under several conditions in a fully automated mode. As reported in the scheme of fig. 5, the routine calculates the gases flow rate related to every parameters combination. Since the flow controllers need to be set with the percentage of their full scale, the percentage value is calculated thanks to flow controllers nominal data (automatically recognized by the control system by the TAG) and calibration curves. It can happen that, for some parameters, the flow controllers are not able to provide the related flow rates due to overflow conditions or working conditions that, requiring too little valve opening, do not guarantee test required accuracy. In this case, the test is aborted.

In normal operation, flow controllers valves are set by the routine to the best fit condition using the calculated expected values for flow rates, then the true flow rates are measured and comparison and intervention phases follow (this procedure follows the general scheme of the figure 4). An important feature is that the system, together with the desired parameter value, records the "true" parameter value obtained by the measurement and eventually corrected by calibration curves. All outputs, like voltage are also recorded. This allows error reduction since curves are then plotted like dispersion curves thus avoiding the contribution to inaccuracy in output measurements due to the differences between real input values and the expected ones.

If the cell potential is found below a safety limit, the trial is terminated thus avoiding cell break down .

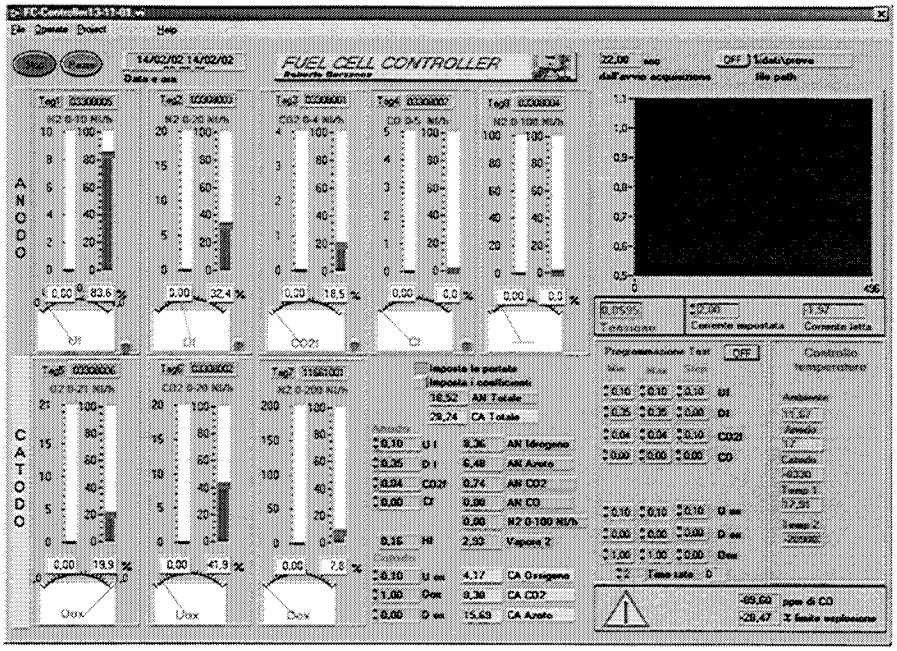

Fig. 6 – Front panel of the control system

Test case

The main front panel of the control system is shown in fig. 6. On the front panel different sections for different input/output data are present. A large part of the panel is dedicated to the flow rate gas control with slides indicating related values and percentages of full scale of every controller. Tension vs time is displayed through a plotting curve during the test. A section provide the parameters and/or flow rate setting, while an other section allows their variation by a planned procedure. Cell and ambient temperatures are also shown. Data can be recorded in a defined path. In case of dangerous conditions (system failure, high toxic gases concentration) alarms switch on and related procedure starts.

Fig. 7 – Dialog window for text planning

The software, realized by the visual program LabView, has been validated and several single cell tests have been performed.
The results of a sample test will follow. The test procedure has been accomplished in automatic way, simply setting a specific dialog window (fig. 7). Every combination of factors has been proved for a time duration of 10 minutes.

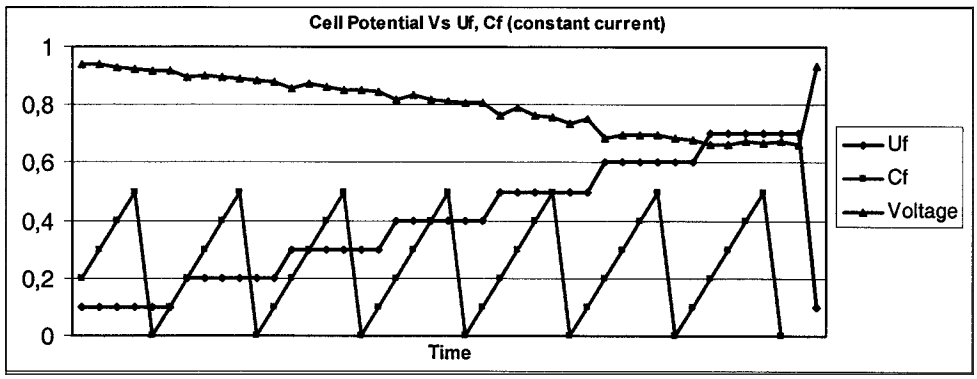

Fig. 8 – Cell voltage vs U_f and C_f factors

The test verified the influence of the Utilization Factor (real utilization of fuel) and Carbon Factor (presence of CO in the fuel mixture) on the cell potential. As can be seen, the voltage at the electrodes drops as U_f increases. A diminution of about 30% of the starting value of voltage has been found with an increase from 0,1 to 0,7 of U_f (fig. 8).
The C_f factor seems to modestly affect the performance of the cell (only minimal decrease of the voltage with increase of C_f was found) thus proving that CO effectively contributes, through the shift reaction, to the current flow ending up in the global reaction (2). This allows, in the case of sulphur free anode input gases, good performances of the cell even with CO rich gas mixture.

Conclusions

The need of reliable experimental data requires strong effort in fuel cells test standardization. An advanced control system has been developed by the authors that allows complete management of all relevant parameters.
The control system for fuel cells test facilities guarantees three main features: an easy and remote setting and modulation of all required parameters, to make the cell work at the chosen conditions; possibility of automatized test procedures; a continuous check of all security parameters in order to reveal breakdowns of the test rig or dangerous conditions, both for the system and for the operators. The control system works through the continuous repetition of a feedback unit. The system features a continuous reading of the main data such as cell voltage, temperature, pressure, gas composition, electric load, H2 and CO ambient concentration, utilization factors, etc., a measurement of the gap between those values and the target values, the required consequent modulation of instruments or even the shutdown of the operation test

in case of dangerous conditions. During the unit operation, all expected and real data are elaborated in order to show the operators the chosen control parameters. At every loop unit, the system modifies the values of the parameters according to real time operator input or to a previously defined test schedule given as a file input. In this operating mode, it is possible to plan a complete test campaign and make the system work with a predefined procedure comprising the variation and manipulation of all data.
The control system has been validated and used for several tests on fuel cells resulting to be reliable, accurate and a powerful mean for fuel cells performances evaluation.

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