Sustainable Syngas Production by High-Temperature Co-electrolysis

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High-temperature co-electrolysis shows comparable performance to steam electrolysis. Current densities above 1 A cm^{-2} can be reached between 700 °C and 800 °C. Tailor-made syngas is produced, mainly determined by the reactant ratio. The experimental results are supported by modeling. Durability tests with cathode-supported cells show increased voltage degradation rates during electrolysis compared to fuel cell operation. Nickel depletion is found to be the main cause.

Keywords: Cathode-supported cells, Durability, High-temperature co-electrolysis, Performance, Syngas production

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1 Introduction

The drastic climate change calls for a fast transition of the sectors energy, mobility and industry. A simple replacement by batteries or different energy conversion technologies is not simply applicable in all branches of the sectors. To reach a fully sustainable level in any case, renewable resources have to be exclusively used as the base. This cannot be achieved by the only straight forward approach of generating electricity from renewables. Energy and mobility are in urge for reliable energy carriers with suitable energy densities. Furthermore, chemical industry not only needs extensive energy, but also is relying on sources of carbon as a fundamental component. A solution for the problems of all sectors can be provided by the electrolysis of water to hydrogen and carbon dioxide to carbon monoxide. Hydrogen is an excellent energy carrier, whilst carbon monoxide is providing the material value generation potential. With this, Power-to-X scenarios are enabled. Especially Power-to-Syngas appears as a promising way towards synthetic fuels and sustainable base chemicals [1]. Electrolysis of carbon dioxide and water is simultaneously accomplished by high-temperature co-electrolysis [1, 2]. Its variability of usage opens up the routes to access ecologic carbon monoxide, hydrogen and syngas. With a high overall efficiency and possible tailoring of syngas compositions, this technology is providing an ideal solution for the defossilization of conventional chemical industry and coherent coupling of the sector of mobility.

To also increase the economic competitiveness of high-temperature co-electrolysis, the two most important factors are performance and durability. Both can be improved by examination of processes and mechanisms. The results can then be used to develop and optimize materials used for this technology. This contribution reports the results obtained in the framework of the Kopernikus project P2X: Flexible use of renewable resources – research, validation and implementation of ‘Power-to-X’ concepts. The behavior of cathode-supported high-temperature electrolysis cells was investigated, both on cell and stack level, under varying operation conditions with respect to performance and durability.

2 Experimental

For the experiments commercially available cells from the company CeramTec GmbH, originally developed for solid oxide fuel cells (SOFC), were used. These so-called cathode-supported cells (CSC) are composed of a NiO/8YSZ cermet support and cathode layer, an 8-mol % yttria-stabilized zirconia (8YSZ) electrolyte, a gadolinium-doped ceria (CGO) barrier layer and a (La,Sr)(Co,Fe)O_3 (LSCF) perovskite anode. For the single cell characterization, cells with a diameter of 20 mm were placed in a Probostat (NorCell) sample holder between Pt and Ni/Pt current collectors. An Au ring was used as sealant between the air and fuel compartment. Short stacks with cells in the size 10 cm × 10 cm were assembled in the so-called F-design of Jülich with interconnect plates manufactured from the commercially available

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Crofer 22 APU (ThyssenKrupp) steel. On the surface of the interconnect plates exposed to air an (Mn,Co,Fe)O_x protection layer to prevent chromium evaporation was applied using atmospheric plasma spraying. Cells were placed between the interconnect plates, with a Ni-mesh as contact layer on the Ni/8YSZ substrate side of the cell and a (La,Sr)(Co,Fe)O_3 contact layer on the other side. In the stacks a glass-ceramic sealant based on a (Ba,Ca,Al) silicate glass was used to separate the air and fuel compartments.

Prior to operation of the cells and stacks the NiO in the cermet support and cathode layer was reduced to Ni by stepwise increasing the amount of H_2 fed to the fuel side of the cell and/or stack. Performance tests were carried out on all cells and stacks according to the standard Jülich protocol. The performance of the single cells was investigated at 900 °C with various H_2O and CO_2 feed gas mixtures by recording current/voltage (i-V) characteristics from open cell voltage (OCV) to 1.4 V. In order to prevent the re-oxidation of the nickel a minimum amount of 10 to 20 % of H_2 was always part of the feed gas on the fuel, i.e., cathode side of the cell. Output gas compositions during co-electrolysis operation of cells were measured online with a mass spectrometer. The performance and durability of stacks were tested at 800 °C. Durability experiments on stacks were performed galvanostatically at 800 °C for at least 500 h under a constant current of $-0.5\,A\,cm^{-2}$ with variable feed gas compositions for steam (50 % H_2 + 50 % H_2O) and co-electrolysis (55 % H_2O + 35 % CO_2 + 10 % H_2).

During all electrochemical cell and stack tests air was supplied to the anode side of the cells. Post-test examination of the cells was performed using X-ray diffraction and SEM/EDX.

3 Results and Discussion

3.1 Performance

The comparison of the performance of CSCs on single cells during co- and steam electrolysis for gas mixtures of 50 % H_2O + 50 % H_2 and 25 % H_2O + 25 % CO_2 + 50 % H_2 has been reported earlier [3]. The gas feed used during co-electrolysis equilibrates due to the reverse water-gas shift reaction (RWGS) occurring at the nickel in the substrate and cathode layer to the thermodynamic equilibrium composition of 38.6 % H_2O + 11.4 % CO_2 + 36.4 % H_2 + 13.6 % CO at the operating temperature of 900 °C. In the i-V curves both mixtures show the same performance with respect to the area specific resistance (ASR) determined from the slope of the i/V curves and the current densities at the chosen maximum voltage of 1.4 V [3].

Similar results were obtained for the same type of cells build into short stacks. Fig. 1 shows the i-V characteristics of a 2-cell short stack operated with steam and co-electrolysis feed gas compositions shown in the figure, respectively. The performance is the same for both compositions and reaches close to $1.0\,A\,cm^{-2}$ at the thermoneutral stack voltage (2,75 V). This shows that power densities of over $1.3\,W\,cm^{-2}$ can easily be reached in SOECs.

The results were also compared to CO_2 electrolysis in single cells with 50 % CO_2 + 50 % CO as feed gas, which resulted in higher ASR values and lower current densities, hence, a lower overall performance. The observations are in good agreement with the results by Stoots et al. [4], who also state that co-electrolysis performs similar to pure steam electrolysis. Their conclusion was that steam is converted electrochemically while CO_2 is converted by the RWGS reaction. Our observations confirm the results for H_2O contents in the fuel feed down to 20 % [3]. For lower steam contents, however, the performance decreases and converges to that of pure CO_2 electrolysis. For low steam concentrations the CO_2 is converted electrochemically, which then results in the increase of ASR due to the slower kinetics of the CO_2 reduction.

The performance has also been investigated with a fuel gas feed of 40 % H_2O + 40 % CO_2 + 20 % H_2, i.e., increasing the fuel content (in electrolysis the sum of H_2O and CO_2) to 80 %. Compared to the mixtures with 50 % fuel + 50 % H_2 the ASR is similar and the current density at 1.4 V around 50 % higher. The mechanism seems to be comparable and only due to the higher fuel content the performance can be increased since concentration limitations do no longer arise at these higher current densities.

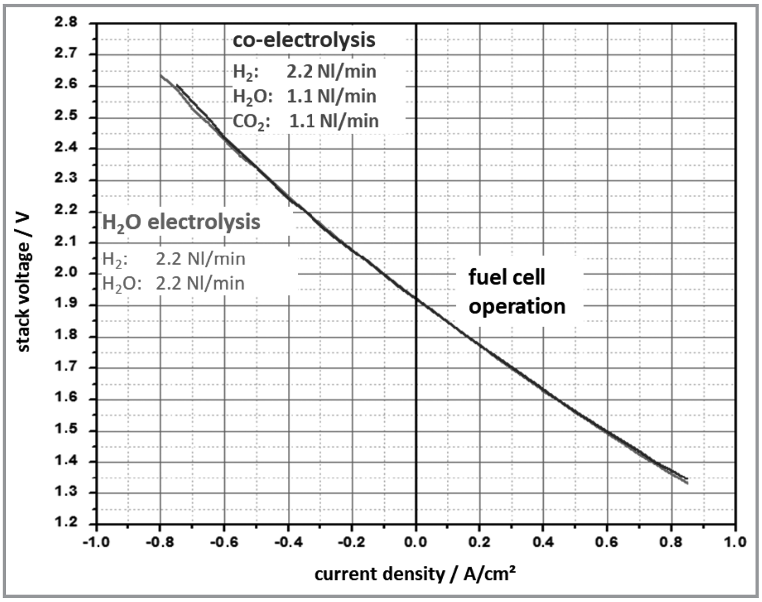

Figure 1. Current-voltage characteristics for a 2-cell short stack operated at 800 °C in both fuel cell and electrolysis mode with 50 % H_2O + 50 % H_2 (steam electrolysis) and 25 % H_2O + 25 % CO_2 + 50 % H_2 (co-electrolysis) as feed gas.

3.2 Syngas Tailoring

One unique advantage of co-electrolysis is the possibility to tailor the syngas ratio of H_2:CO in one process step by varying the process parameters such as inlet gas composition or flow rate. The gas composition was monitored by mass spectrometry and described in detail in previous work [3, 5]. The findings were that the ratio is mainly influenced by the inlet gas composition and determined by the fuel (H_2O + CO_2) utilization and the RWGS reaction. The flow rate does have only very little influence on the ratio and only increases the possible fuel utilization when decreasing the flow rate.

Investigations concerning the prediction of output gas compositions started with a thermodynamic modeling of the gas mixture. Assumptions in the model are an ideal gas and an ideal Faraday law for the electrons used in the electrochemical reactions. A continuous calculation of chemical equilibrium after each incremental increase of current is provided in order to account for the fast RWGS reaction. An example comparison for the mixture 40 % H_2O + 40 % CO_2 + 20 % H_2 is provided in Fig. 2. Although kinetic effects are not included, the thermodynamic prediction is close to the experimental outcome. Deviations are revealed in the amount of produced CO and H_2, which are subject to further microkinetic modeling in future.

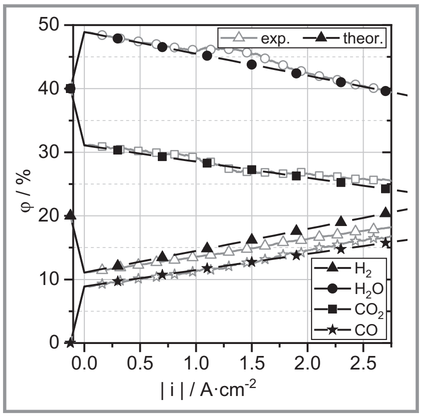

Figure 2. Comparison of output gas composition for the initial mixture 40 % H_2O + 40 % CO_2 + 20 % H_2 at 900 °C and a flow rate of 6 L h^{-1} between experimental results (transparent symbols) and theoretical calculations (filled symbols) up to an operation of 2.7 A cm^{-2}.

3.3 Durability Behavior

In Fig. 3 the time plot of the cell voltages and stack current density of a 2-cell short stack operated at 800 °C is shown. In the first durability test between 300 and 900 h of operation steam electrolysis was performed at a constant load of –0.5 A cm^{-2} with a feed gas composition of 50 % H_2 + 50 % H_2O. In this period a cell voltage degradation rate of around 17 mV kh^{-1} was observed. This degradation rate is substantially higher than observed with the same cells in a stack operating in fuel cell mode and also compared to steam electrolysis tests in the past [6]. In fuel cell mode degradation rates lower than 2 mV kh^{-1} can be reached for periods lasting several 10 000 hours of operation [7, 8].

After 900 h of operation co-electrolysis operation was investigated starting with a series of i-V measurements, electrochemical impedance spectroscopy (EIS) and gas analysis by gas chromatography, which included tests with varied feed gas flows. Since the usual measurement equipment had to disconnected during EIS measurements, the cell voltages of 0 V in Fig. 3 do not reflect the real cell voltages, which were always well above 0.6 V. It was observed that the cells experienced an accelerated degradation during the characterization at low feed gas supply, likely because of instabilities in the steam supply at the low flow rates.

In a second durability test starting at 1550 h of operation co-electrolysis was performed at a constant load of –0.5 A cm^{-2} with a feed gas composition of 55 % H_2O + 35 % CO_2 + 10 % H_2 and a conversion rate of 59 % at 800 °C. In this period the voltage degradation rate increased to around 40–50 mV kh^{-1}. Post-test investigations were performed on the cells in order to reveal possible causes for the increased degradation rates. One prominent cause found was the depletion of nickel at the electrode/electrolyte interface, which is described in more detail below. Other results obtained during the project also indicate a possible poisoning of the nickel electrode as a contributing factor for the increased degradation of the cells during electrolysis

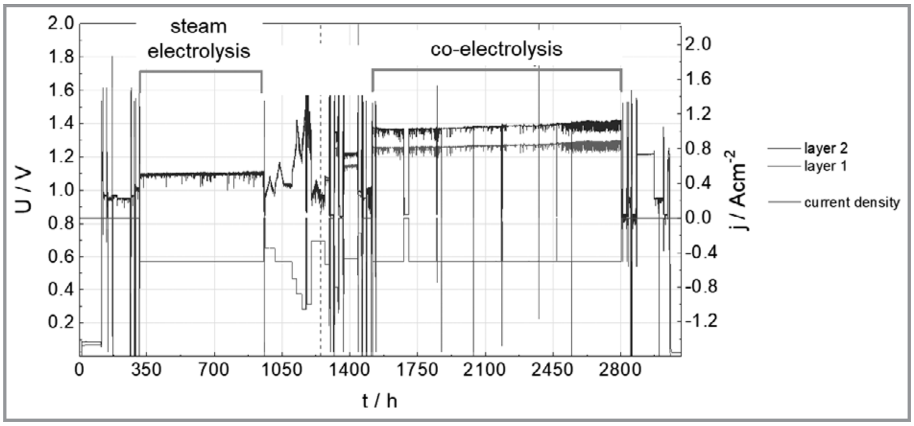

Figure 3. Time plot of the cell voltages and stack current density for a 2-cell short stack operated with steam and co-electrolysis. Details are explained in the text.

operation. The cause was likely an insufficient quality of the deionized water used for the steam generation.

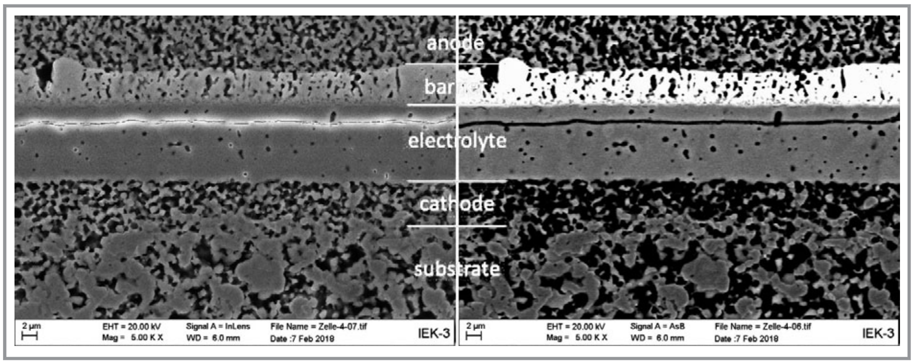

Figure 4. SEM images (left: SE, right: BSE) of a cross-section of a cell from a short stack operated in steam- and co-electrolysis mode over 1000 h at 800 °C.

3.4 Dynamic Load Following Behavior

The dynamic load following behavior of cells and stacks, important in future scenarios using renewable energy sources, was investigated using a load profile predicting a week of energy consumption of Germany in the year 2050, which was developed by the partner Wuppertal Institute in the Kopernikus P2X project. The load profile consisted of four distinct levels (50 %, 75 %, 100 % and 125 %), with durations between 4 and 10 h. The total load profile lasted about one week, in which the current on the cells and stack was switched between the subsequent levels without changing the other operating parameters, like gas flow and temperature. Both single cell and short stack respond very fast (within seconds) to the load changes. The load cycling did not have a noticeable effect on the voltage degradation in both tests compared to the durability tests performed under constant load. These results on the dynamic load following behavior will be published in more detail separately.

3.5 Post-test Analyses

Cells were examined post-test with SEM in order to reveal possible causes for the increased degradation rates observed during electrolysis. In Fig. 4 exemplary SEM images of a cross section of a cell are shown. The crack in the cell across the 8YSZ electrolyte layer is most likely due to SEM sample preparation. Fig. 4 reveals in addition one possible cause for the increased degradation rate: in the cathode functional layer at the interface to the 8YSZ electrolyte layer severe Ni depletion is observed. Since only the 8YSZ backbone of the cermet layer remains, this results in an increased thickness and ohmic resistance of the electrolyte layer. The Ni depletion also reduces the number of triple phase boundaries in the cathode functional layer. Both will cause a substantial loss in the performance of the cell. A possible solution could be the introduction of a Ni/CGO cermet cathode layer. These types of cermets are often used in electrolyte-supported cells. They do not show Ni depletion and the voltage degradation rates are considerably lower.

4 Conclusions

The results show that high-temperature co-electrolysis can produce tailor-made syngas compositions in the area relevant for downstream catalytic processes. The syngas composition is determined mainly by the educt ratio H_2O to CO_2. It has been shown that in co-electrolysis mainly the water vapor is electrochemically reduced to hydrogen with a Faraday efficiency of nearly 1. The carbon dioxide is reduced by the so-called reverse water-gas shift (RWGS) from hydrogen to carbon monoxide. The composition of the product gas is consistent with the thermodynamic equilibrium of the RWGS reaction.

Co-electrolysis at operating temperatures between 700 and 800 °C in the range of the thermoneutral voltage (1.3–1.4 V) can reach current densities well above 1 A cm^{-2}. The power density (~1.5 W cm^{-2}) is independent of the educt composition. This means that the required syngas composition in the co-electrolysis has no effect on the performance of the cell or the stack.

Dynamic load profile tests were performed on a cell and short stack on the basis of an exemplary residual load profile for one week each. The cell and stack could follow these load changes very well. In these first tests no serious increase of the voltage degradation rate was observed. This successful dynamic test shows the high potential of co-electrolysis as a flexibilization option and further for process integration and sector coupling.

The results show that the cathode-supported cells with a Ni/YSZ cermet substrate and cathode layer show significantly higher voltage degradation rates when operating in electrolysis mode compared to fuel cell mode. As one major reason for this degradation, the nickel depletion in the cathode functional layer could be identified. A possible solution could be the introduction of a Ni/CGO cermet cathode layer. These types of cermets are often used in electrolyte-supported cells and do not show Ni depletion. Additionally, voltage degradation rates are considerably lower.

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