A Novel Power Generation System Based on Combination of Hydrogen and Direct Carbon Fuel Cells for Decentralized Applications

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Abstract

Fuel cell (FC) based power generation systems are characterized by highest chemical-to-electrical (CTE) energy conversion efficiency compared to conventional power generators (e.g., internal combustion and diesel engines, turbines). Most efforts in this area relate to hydrogen-FC coupled with hydrocarbon fuel reformers (HFR). However, the overall CTE efficiency of the combined HFR-FC systems is relatively low (about 30-35%). The objective of this work is to develop a highly-efficient power generation system integrating a hydrocarbon decomposition reactor (HDR) with both hydrogen and direct-carbon FC. A unique feature of direct carbon FC is that its theoretical CTE efficiency is close to 100% and the practical efficiency could rich 80-90%. The concept of the integrated hydrogen and direct carbon FC system is discussed and the experimental data on the performance testing of a HDR coupled with PEM FC are presented in this paper.

1   Introduction

In view of dwindling resources of hydrocarbon fuels, it is imperative to substantially increase the efficiency of power generation systems. Fuel cells (FC) are considered the most efficient chemical-to-electrical (CTE) energy conversion devices. Most of R&D efforts in this area are focused on hydrogen-fuelled FC, including proton exchange membrane (PEMFC), alkaline (AFC), molten carbonate (MCFC) and solid oxide (SOFC) FC. Typically, FCs are coupled with reformation units that provide hydrogen-rich gas to the FC. Due to availability of hydrocarbon fuels and the convenience of their storage, hydrocarbon fuel reformers (HFR) are predominant type of reformers for a variety of applications. However, the overall CTE efficiency of the combined HFR-FC systems is relatively low (about 30-35%) mainly due intrinsic limitations of hydrogen-FC theoretical efficiency (70%) and significant losses (20-40%) in HFR.

FC utilizing elemental carbon as fuel (called direct carbon fuel cells, DCFC) have received relatively little attention, compared to H_2-powered FC. In DCFC, solid carbon is introduced to the anode compartment where it is electro-oxidized to CO_2 generating electricity:

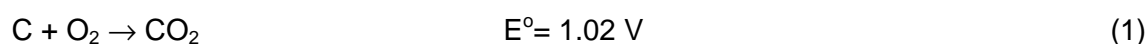$$C + O_2 \rightarrow CO_2 \qquad\qquad E^o = 1.02 \text{ V} \qquad\qquad\qquad (1)$$

Figure 1 depicts the comparison of different fuels in terms of their theoretical (maximum) and actual (or practical) efficiency (Cao et al, 2007). The actual efficiency of DCFC could be defined by the following equation:

$$\eta = \frac{\Delta G(T)}{\Delta H} \mu \frac{V}{V_o} = \frac{\Delta G(T)}{\Delta G + T \Delta S} \mu \frac{V}{V_o}$$

(2)

where, η is FC actual efficiency, ΔG, ΔH and ΔS are free energy, enthalpy and entropy of the reaction (1), μ is a fuel utilization coefficient, V and V_o are operating and open circuit voltages of FC, and V/V_o is a voltage efficiency.

Since for the reaction (1) $\Delta S \approx 0$, and assuming that for DCFC $\mu \approx 1$ (since the fuel-carbon and the product CO_2 exist in separate phases, allowing full conversion of carbon in a single pass) and $V/V_o \approx 0.8 \div 0.9$, the efficiency of DCFC could be as high as 80-90%.
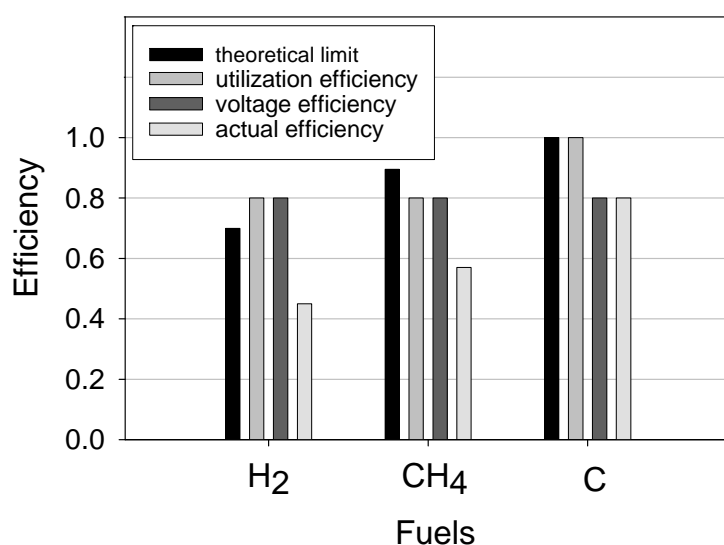
Figure 1:   Comparison of efficiencies of fuel cells using different fuels.

Recently, DCFC has been under the development and efficiencies reaching 80% have been demonstrated (Cherepy et al, 2005). The objective of this work is to develop a highly-efficient electrochemical energy conversion device based on the integrated operation of hydrogen- and carbon-powered fuel cells.

2   Experimental

Methane (99.99 v.%) was obtained from Air Products and Chemicals, Inc. and used without further purification. Methane was catalytically decomposed over carbon-based catalysts at 850-900°C in a hydrocarbon decomposition reactor (HDR) to produce hydrogen-rich gas. All experiments were conducted at atmospheric pressure. On-line analysis of the effluent gas was performed gas chromatographically (TCD, Ar-carrier gas, silica gel column and FID, He-carrier gas, HysepD$_b$ column).   Analysis of carbon products was conducted by X-ray diffraction (XRD, Rigaku) and scanning electron microscopic (SEM, Jeol 6400F) methods. A single and four-cell PEMFC stack was assembled from parts provided by Fuel Cell Technologies Inc. and tested using different H_2-CH_4 mixtures and the effluent gas from the HDR. An individual cell consists of a 25 cm^2 single serpentine flow field on both anode and

cathode. In measuring polarization curves, current was stepped up from zero to the maximum test current density with an increment between 10 and 100 mA cm^{-2}. A 100A Model 890B Scribner load box (Scribner Associates, Southern Pines, NC) with a built-in current interrupt resistance measurement was used for the polarization measurements.

3   Results and Discussion

The proposed concept is based on the integration of a HDR, DCFC and H$_2$-powered FC (PEMFC or SOFC), as shown in Fig. 2. In the HDR, hydrocarbon fuel (e.g., methane or natural gas) is catalytically decomposed (T=800-900°C) to hydrogen-rich gas and carbon. The hydrogen-rich gas can be used in PEMFC or SOFC, whereas, the carbon product is withdrawn from the HDR and used in the DCFC with the efficiency of 80-90%. The combination of the HDR with SOFC is more preferable (than with PEM), because of better thermal integration of the HDR and SOFC operating in a close temperature range (850-900°C). High-temperature heat generated by SOFC could be used to drive the hydrocarbon decomposition reactions (in case of methane, about 20% of the SOFC heat output would be necessary). The remaining portion of the thermal output of the SOFC (steam + CO$_2$) could be used to produce additional electricity via a turbine (or a Rankine cycle) with the efficiency of 30-35%.
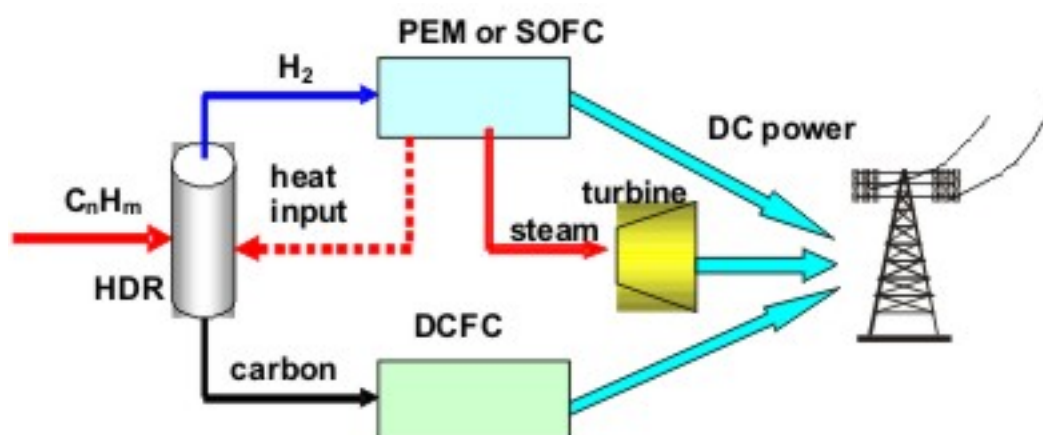

**Figure 2:   Simplified schematic diagram of integrated power generator.**

The concentration of hydrogen in the hydrogen-rich gas depends on the nature of hydrocarbon and operating temperature in the HDR; at the temperature range of 800-900°C, the hydrogen concentration is in the range of 40-80 vol%, the balance being predominantly methane along with small amounts of C$_2$+ hydrocarbons. If a low-temperature (80°C) PEMFC is used, H$_2$ is consumed with the efficiency of 40-45%, while methane exits the FC intact and is used as a heat source for the HDR (e.g., via its combustion). In the case of high-temperature (900°C) SOFC, both components of the H$_2$-CH$_4$ mixture are consumed as fuel with the average efficiency of 45-50%.

H$_2$-CH$_4$ mixtures with the hydrogen concentration of 40-50 vol.% were obtained by thermocatalytic decomposition of methane as a feed at 850-900°C and atmospheric pressure. High-surface area amorphous forms of carbon were used as catalyst for the

process (Muradov et al., 2005, 2009). Before introducing H_2-CH_4 mixture to PEMFC, it is necessary to purify it of possible CO impurities (although there is no oxidant is present in the feed, CO could be formed in the HDR due to presence of moisture and oxygenated groups on the surface of carbon catalyst). Reduction of CO concentration in the hydrogen-rich gas down to 10 ppmv and below was accomplished via the methanation reaction by passing the gas over Ru/Al_2O_3 catalyst at $350^{o}C$, as follows:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad\qquad (350\ ^{o}C)$$
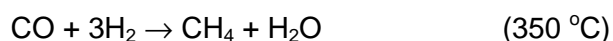
Two series of experiments were conducted: with a single cell and four cell stack PEMFC. The experimental set-up for testing the four-cell stack PEMFC is shown in Fig. 3.
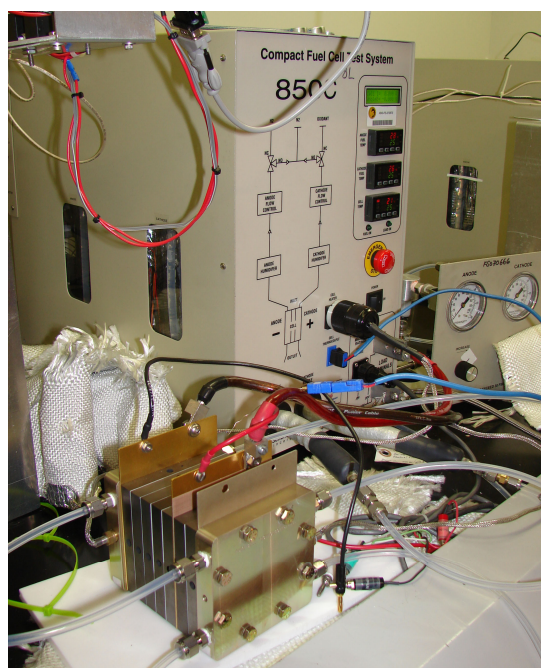
Figure 3:   Experimental set-up with a four-cell PEMFC stack with an internal humidifier.

The H_2-CH_4 mixture could be directly fed to PEMFC without a need for an elaborate gas conditioning and purification systems such as water gas shift and preferential oxidation units required by conventional reformers. Figure 4 shows the results of performance testing of a single-cell PEMFC using the hydrogen-rich gas produced in the HDR. The HDR-PEMFC system ran for several hours without deterioration. These data indicate that PEMFC could be successfully operated on the H_2-CH_4 feed produced from hydrocarbon fuels.

We have conducted extensive studies on the characterization of carbon products of the process. The data indicate that carbon exhibits certain three-dimensional ordering, however, it lacks the perfect structural order characteristic of graphite (which is typical of turbostratic carbon). It has been reported that turbostratic carbon exhibited unusually high electrochemical reactivity in molten carbonate-based DCFC (Steinberg et al, 2002).
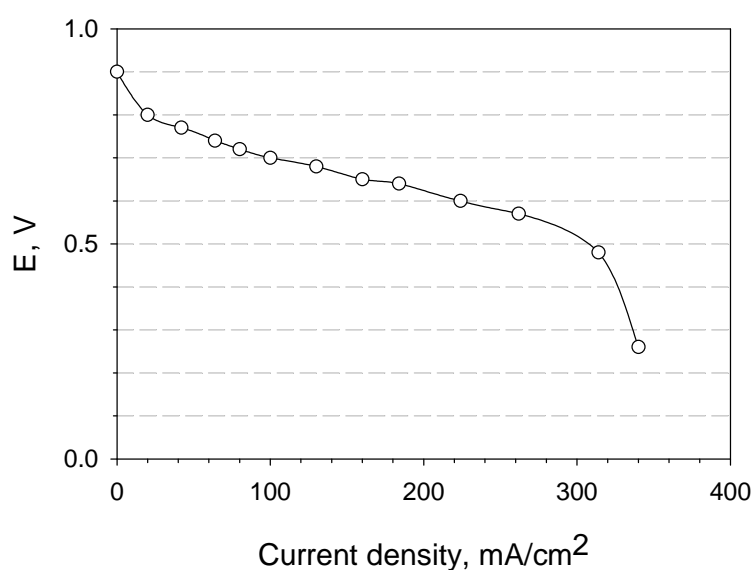
Figure 4: **Performance testing of a single cell PEMFC using hydrogen-rich gas produced by hydrocarbon decomposition reactor operating on methane as a feedstock.**

The overall CTE of the integrated system (including a turbine) operating on methane was estimated at 49% and 79% with PEMFC and SOFC options, respectively. Thus, the CTE of HDR-SOFC-DCFC integrated system is about two times higher than that of a conventional reformer-FC system.

Concluding, the advantages of the proposed integrated power generator over conventional reformer-FC based power generators are as follows: (1) significantly higher overall CTE efficiencies, (2) thermal integration, which simplifies the thermal management of the system, (3) the lowest amount of CO_2 emissions per kWh produced, (4) production of sequestration-ready CO_2 (since CO_2 is produced in FCFC in a concentrated form), which obviates the need for costly and an energy intensive capture of CO_2.

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