Title
A Thermodynamic Analysis of Electricity and Hydrogen Co-Production Using a Solid Oxide Fuel Cell

Permalink
https://escholarship.org/uc/item/56v8s8f7

Journal
Journal of Electrochemical Energy Conversion and Storage, 3(2)

ISSN
1550-624X

Authors
Leal, Elisângela M
Brouwer, Jack

Publication Date
2006-05-01

DOI
10.1115/1.2173669

Copyright Information
This work is made available under the terms of a Creative Commons Attribution License, available at https://creativecommons.org/licenses/by/4.0/

Peer reviewed
A Thermodynamic Analysis of Electricity and Hydrogen Co-Production Using a Solid Oxide Fuel Cell

Elisângela M. Leal
Combustion and Propulsion Laboratory, National Institute for Space Research (INPE), Cachoeira Paulista, SP, Brazil 12630-970
e-mail: elisangelaleal@yahoo.com

Jack Brouwer
National Fuel Cell Research Center, University of California, Irvine CA 92697
e-mail: jb@nfrcr.uci.edu

This paper presents the electricity and hydrogen co-production concept, a methodology for the study of SOFC hydrogen co-production, and simulation results that address the impact of reformer placement in the cycle on system performance. The methodology is based on detailed thermodynamic and electrochemical analyses of the systems. A comparison is made between six specific cycle configurations, which use fuel cell heat to drive hydrogen production in a reformer using both external and internal reforming options. SOFC plant performance has been evaluated on the basis of methane fuel utilization efficiency and each component of the plant has been evaluated on the basis of second law efficiency. The analyses show that in all cases the exergy losses (irreversibilities) in the combustion chamber are the most significant losses in the cycle. Furthermore, for the same power output, the internal reforming option has the higher electrical efficiency and produces more hydrogen per unit of natural gas supplied. Electrical efficiency of the proposed cycles ranges from 41 to 44%, while overall efficiency (based on combined electricity and hydrogen products) ranges from 45 to 80%. The internal reforming case (steam-to-carbon ratio of 3.0) had the highest overall and electrical efficiency (80 and 45% respectively), but lower second law efficiency (61%), indicating potential for cycle improvements. [DOI: 10.1115/1.2173669]

Keywords: solid oxide fuel cell, steam reforming, hydrogen production, energy analysis, exergy analysis

Introduction

Interest in hydrogen as a fuel has grown dramatically since 1990, and many advances in hydrogen production and utilization technologies have been made. Solid oxide fuel cells (SOFC) seem to be very promising for the direct conversion of chemical energy into electricity, attaining significantly higher efficiencies compared to similarly sized energy conversion devices, such as gas turbines and internal combustion engines, operated on natural gas. Furthermore, SOFCs produce high-temperature waste heat that can be used for cogeneration. The subject of this particular study is the analysis and investigation of how SOFC technology can be used to produce co-produce electricity and hydrogen for other uses.

The main processes for hydrogen production are presented in several literature sources [1–4]. Hydrogen production types include hydrocarbon-based processes (e.g., steam reforming, partial oxidation, gasification, catalytic decomposition), nonhydrocarbon-based processes (e.g., electrolytic, thermochemical, photochemical, photo-electrochemical), and integrated processes that may use renewable, nuclear, or other energy inputs. Steam-methane reforming is a very important and common industrial processes for hydrogen production. Steam reforming produces a hydrogen-rich gas that is typically on the order of 70–75% hydrogen on a dry basis, along with smaller amounts of methane (2–6%), carbon monoxide (7–10%), and carbon dioxide (6–14%) [5]. Typical hydrogen production plants purify the hydrogen rich stream after steam reformation through a pressure swing absorption (PSA) or other purifying device.

The hydrogen economy, and in particular the use of hydrogen as an energy carrier for transportation applications, will depend upon local consumer access to inexpensive and environmentally sensitive pure hydrogen product delivery. Since hydrogen is challenging to store with high energy density, transport, distribution and dispensing of hydrogen typically involves a significant energy and environmental impact. In addition, the infrastructure required for transport, distribution and dispensing is likely to be expensive and require several decades to introduce. Thus, attention must be paid to developing a means of providing hydrogen to consumers in an environmentally sensitive manner.

One environmentally sensitive means of addressing both local generation of power and the production and distribution of hydrogen is to co-produce hydrogen and electricity using a high temperature stationary fuel cell system. Internal reforming high temperature fuel cells, such as solid oxide fuel cells and molten carbonate fuel cells, are developed technologies with a few commercial products available. These systems do not require hydrogen; they are instead directly fueled by natural gas or renewable fuel such as landfill or digester gas. The natural gas is reformed either indirectly or directly in the anode compartment to produce hydrogen. Direct reformation results in both promoting hydrogen production and providing needed cooling to the fuel cell stack. Indirect reformation occurs in a separate but thermally integrated reactor. Significantly, these fuel cell systems do not electrochemically consume all the fuel that is supplied (a fundamental limitation) and they produce enough heat to reform much more than the amount of hydrogen they consume.

In the present work we present this novel concept and develop a set of integrated SOFC cycle configurations to study the impact
of reformer placement in the cycle on system performance. A comparison between six specific cycle configurations is presented in terms of both the First Law and Second Law of Thermodynam- 
ics analyses. The fuel cell heat is used to drive hydrogen production in an endothermic reformer using both external and internal reforming strategies.

We hypothesize that the local co-production of hydrogen and electricity will produce advantages compared to traditional hydrogen production strategies (e.g., steam reforming) in three ways: (1) production will be at the point of use avertting emissions and energy impacts of hydrogen transport, (2) the use of fuel cell waste heat and steam as the primary inputs for the endothermic reforming process will use less fuel, and (3) a synergistic impact of lower fuel utilization on fuel cell voltage that can be exploited to increase fuel cell electrical efficiency. One potential disadvantage of this concept is incompatibility with future CO2 sequestration options that are likely to be available only in certain locations.

**Thermodynamic Analyses Methods**

**Steam Reforming.** A very common method of hydrogen production is the steam reforming process. Methane steam reforming consists of the reaction of methane and steam over a supported nickel catalyst at around 700–800 °C to produce a mixture of H2, CO, CO2, and CH4.

First, a global reaction mechanism is required to analyze the thermodynamics of steam reforming of a hydrocarbon fuel at a basic level [6]:

\[
\text{C}_x\text{H}_y + x\text{H}_2\text{O} \leftrightarrow x\text{CO} + (2x + 0.5y)\text{H}_2 + (S - 2)x\text{H}_2\text{O} \quad (1)
\]

The term “global reaction” recognizes that the above reaction is actually the net result of a series of elementary reactions (including the water-gas shift reaction), some of which include catalytic interactions with surfaces. Some global reactions separate out the water-gas shift reaction as follows:

\[
\text{C}_x\text{H}_y + x\text{H}_2\text{O} \leftrightarrow x\text{CO} + (x + 0.5y)\text{H}_2 + (S - 1)x\text{H}_2\text{O} \quad (2)
\]

\[
x\text{CO} + x\text{H}_2\text{O} \leftrightarrow x\text{CO}_2 + x\text{H}_2 \quad (3)
\]

These reactions themselves are of no consequence to the overall thermodynamic analyses, but they are important to understand for reactor design and efficient operation and control of reformer systems. The overall balance of Eq. (1) conserves elements with two assumptions: there is sufficient steam to react with the fuel \(S \geq 2\), and the reaction goes to completion. Using Eq. (1), the formation enthalpies of the species can be added to determine the net enthalpy change [6] as follows:

\[
\Delta H_R = x\Delta h'_\text{CO}_2 + (S - 2)x\Delta h'_{\text{H}_2\text{O}} - [b'_\text{C}_x\text{H}_y + x\Delta h'_{\text{H}_2\text{O}}] \quad (4)
\]

Table 1 shows the net enthalpy change using a steam-to-carbon ratio equal to 2 and 3 for some hydrocarbon fuels.

**Chemical Equilibrium Analysis.** There are two common methods used to express chemical equilibrium. One method is based on use of equilibrium constants, while the other is based on minimization of the free energy. One of the disadvantages of using equilibrium constants is that it is more difficult to test for the presence of condensed species in the reaction products. However, it is anticipated that solid carbon may be produced during the fuel reforming process, which can deactivate the catalytic reactions. Therefore, a method based on minimization of free energy is normally used in fuel reforming analysis.

Summarizing, for a given temperature and pressure, the equations for species conservation, atoms conservation, and condensed species are, respectively [7]:

\[
N = \sum_{k=1}^{m} N_k \quad k = 1, \ldots, m \quad (5)
\]

\[
b^0_l = \sum_{k=1}^{m} a^0_{lk} N_k = b_l \quad l = 1, \ldots, n \quad (6)
\]

\[
\frac{R_k T}{\sum_{l=1}^{n} \left( \frac{\lambda_l}{R_l T} \right)} a_{lk} = 0 \quad k = m + 1, \ldots, n \quad (7)
\]

Equations (5)–(7) form a set of \( n + l \) equations that can be simultaneously solved for the unknowns \( n, \lambda, \) and \( n \). The thermodynamic function is then solved by the Newton-Raphson method for the unknowns. Figure 1 shows an example for the solution of the chemical equilibrium equations for methane as a function of temperature. As can be seen in Fig. 1, the best temperature to run a reformer is between 700 °C and 800 °C, a temperature condition for which production of hydrogen is maximized.

**Solid Oxide Fuel Cell.** SOFC technology is promising for use in power generation applications, attaining significantly higher efficiencies compared to similarly sized energy conversion devices, such as gas turbines and internal combustion engines, when oper-

![Fig. 1 Results of production of hydrogen from methane as a function of temperature and steam-to-carbon ratio (solid line (S=3) and dashed line (S=2))](image-url)
ated on natural gas. Furthermore, SOFCs produce high-temperature waste heat that can be used for cogeneration, which in this particular case is used to produce hydrogen for other uses.

Independent of the fuel used in a SOFC, with an oxygen-ion-conducting electrolyte (the most common today) its operating principle relies on the continuous supply of fuel, containing H₂, CO, and CH₄ or other hydrocarbons, to the anode compartment while the cathode is supplied with air. According to this operation regime, the following reaction takes place at the cathode [8]:

$$0.5O_2 + 2e^- \rightarrow O^{2-}$$  

The oxide ion is transported across the electrolyte through the yttria-stabilized zirconia electrolyte. At the anode, the oxide ions are consumed by the oxidation of hydrogen to form steam releasing electrons to the external circuit [8]:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$  

Various fuel options are considered feasible for SOFC operation, especially after an appropriate external process in order to obtain a gas mixture that is rich in hydrogen, such as steam reforming. The electrochemically active species are H₂, CO, and CH₄, but it is common in system-analysis practice to assume that only H₂ contributes to power generation while CH₄ is consumed through in situ steam reforming, providing additional amounts of H₂ and CO, and CO is consumed through in situ water-gas shift reactions, providing additional amounts of H₂ [9].

Applying the steady flow energy equation and assuming negligible change of kinetic and potential energy, the First Law of Thermodynamics for a fuel cell system can be written as [10–13]

$$Q = W + \sum_k (N_k h_k)_R - \sum_k (N_k h_k)_P = 0$$  

The molar enthalpy of each component (h_k) at a temperature T in a mixture of gases is calculated as [14]

$$h_k = h_k^0 + \int_{298K}^{T} C_{P_k} dT$$  

where

$$C_{P_k} = C_{P_k}^0 + T \frac{dC_{P_k}}{dT}$$

The entropy terms are correspondingly defined as [14]

$$S_k = S_k^0 + \int_{298K}^{T} C_{P_k}^0 dT - R_a \ln \left( \frac{P_k}{P_k^0} \right)$$

Combining Eqs. (8) and (10) and assuming that the electrochemical reaction is based on unit molar flow rate of the fuel yields [10,11]

$$W = \left[ \sum_k (N_k h_k)_P - \sum_k (N_k g_k)_R \right] \cdot T S_{cell}$$  

For a hydrogen fuel cell with known pressures of reactants and products [10–13] voltage can be calculated as

$$V = \frac{R_T}{2F} \ln K - \frac{R_T}{4F} \ln \left( \frac{p_j^0}{p_j} \right) + \frac{T S_{cell}}{2F}$$

$$\left( S_{cell}/2F \right) = \eta_{act} + \eta_{thm} + \eta_{conc}$$

The first term on the right-hand side of Eq. (16) shows the effect of operating temperature on the cell voltage while the second term shows the effect of reactant and product partial pressures on cell voltage. The irreversible voltage losses are accounted for in the third term of the equation and are expressed in terms of activation, Ohmic and concentration overpotentials. Activation polarization, which estimates losses due to slow electrochemical kinetics, is calculated by [9]

$$\eta_{act} = \frac{R_T}{n_a F} \ln \left( \frac{j}{j_0} \right)$$

where

$$j_0 = \frac{R_T}{n_a F C_l}$$

The Ohmic polarization, which estimates losses associated with ionic and electronic resistance throughout the fuel cell, can be calculated by [9]

$$\eta_{thm} = j R_i$$

The total exergy of a flow consisting of many components (neglecting the magnetic, electric and nuclear effects) is given by

$$Ex_{TOT} = Ex_{TM} + Ex_{CH}$$

The thermomechanical (Ex_{TM}) and chemical exergy (Ex_{CH}) can be written as, respectively [20]

$$Ex_{TM} = \sum_{k=1}^{n} N_k (h_k - h_k^0) - T_0 \sum_{k=1}^{n} N_k (s_k - s_k^0)$$

$$Ex_{CH} = \sum_{k=1}^{n} x_k Ex_{h,k}^0 + m R_T T_0 \sum_{k=1}^{n} x_k \ln x_k$$

Exergy analysis requires that the environment is defined. The temperature and pressure of the environment were set equal to the reference temperature and pressure (298 K, 0.101 MPa) in the current work. The atmosphere was modeled as an ideal-gas mixture with the composition shown in Table 2 [21].

The fuel utilization efficiency (ε_f) is the ratio of all the useful energy extracted from the system (electrical and process heat) to the energy of the fuel input while the second law efficiency (ε_2)

Table 1 Mole fractions and chemical exergy of the reference components in atmospheric air [21]

| Component | N₂ | O₂ | H₂O | CO₂ | Ar |
|-----------|----|----|-----|-----|----|
| Mole fraction | 0.7567 | 0.2035 | 0.0303 | 0.0003 | 0.0092 |
| Chemical exergy | 691.1 | 3,946.7 | 8,667.9 | 20,108.5 | 11,622.3 |

[kJ/kmol]
may be defined as the ratio of the amount of exergy of products to the amount of exergy supplied. This parameter is a more accurate measure of the thermodynamic performance of the system. Thus

\[
e_F = e_{el} + e_Q = \frac{W_{el} + Q_F}{E_F} \tag{24}
\]

\[
e_H = \frac{W_{el} + E_{x_F}}{E_S} \tag{25}
\]

Cycle Configurations

A solid oxide fuel cell system can be configured in many ways. Cycle configurations that include the potential for hydrogen co-production can be even more complex. In the current paper we present several possible generic cycle configurations that are considered for their potential electricity and hydrogen co-production capabilities. The detailed thermodynamic and electrochemical analyses are accomplished on these six specific cycle configurations, which use the high temperature fuel cell heat to drive hydrogen production in a reformer. Cycle configurations that consider both external and internal reforming options have been developed as shown in Figs. 2 and 3. Figure 2 shows the external reformer cycle configurations with the hydrogen production reformer placed in different positions in the cycle for each of the configurations 1–4. Figure 3 presents (a) a different configuration for external reforming (with combustion chamber after the air pre-heater), and (b) the internal reforming case. These generic cycle configurations were developed to examine the general impacts of system design on the thermodynamic performance of SOFC cycles for hydrogen and electricity production. Each of the cycles contains three preheaters for: (1) methane fuel preheat, (2) air preheat, and (3) water boiling and preheat. Each configuration also contains a reformer and combustor. In all of the cases, the thermodynamic analyses use the equations presented above, which comprise primarily overall energy and exergy analyses.

Results and Discussion

The following considerations and assumptions are made for the analyses presented herein:

- Fuel cell electrical power output is 1000 kW.
- Fuel cell operating temperature is 1000°C [9].
- All pre-heaters are 90% efficient [22].
- Fuel utilization in the anode compartment and oxidant utilization in the cathode compartment is 85 and 25%, respectively, in fuel cell units [23].
- All gas stream pressures are atmospheric [24].
When comparing the energy analyses amongst cycle configurations, Fig. 4 indicates that for the same amount of power produced by the fuel cell, configuration 6 (internal reforming) shows the highest potential for production of hydrogen (about 3.2 g/s for \( S=2 \) and 3.3 g/s for \( S=3 \)) as well as the highest overall efficiency. Also, configuration 6 achieves a remarkable overall efficiency of nearly 80% for the steam-to-carbon case of \( S/C=3 \). One of the reasons for this high efficiency is the synergy associated with internal reforming that is reflected in the higher electrical efficiencies for configuration 6. These higher electrical efficiencies are due to the higher exit hydrogen concentration in the fuel cell for configuration 6 leading to higher voltage potential.

Figure 4 shows that configuration 5 (combustion chamber after the air pre-heater) is the worst cycle configuration with the highest thermal losses on an energy basis. However, configuration 5 may be the most flexible configuration with regard to hydrogen production capacity (not studied in the current work). Configurations 2, 3, and 4 perform similarly with regard to hydrogen production and efficiency, but configuration 1 is slightly less efficient with lower hydrogen production capability.

Figure 5 shows the representation of a Sankey diagram for one of the cycle configurations. The configuration of Fig. 5 is the first configuration of Fig. 2 (with hydrogen production from a reformer module essentially placed in the exhaust of an integrated SOFC system). The parameters of energy performance shown in the Sankey diagram for configuration 2 emphasize the importance of analyzing the energy flows in the system. Energy is mainly lost in the exhaust gas. The exhaust gas losses are primarily a result of the combined thermal energy contribution of the fuel cell losses and combustor to the fuel cell system gas flows after thermal recovery in the preheaters (3) and reformer.

Figure 6 shows the results of overall exergy analyses for each of the six configurations for a fixed steam-to-carbon ratio of 2. It presents the exergy analyses for all of the configurations, indicating the components that contribute most significantly to exergy losses within each configuration. Components with high irreversibilities or low second law efficiency and the manner in which they are implemented in the cycle are those that designers should focus upon to improve system performance.

The exergy results of Fig. 6 show that the major destruction of exergy (irreversibility) was in the combustion chamber (CC) for all configurations. In all cases the combustion chamber is associated with the maximum temperature of the products in the integrated fuel cell system. Since the irreversibility in the combustion chamber is much larger than the other component irreversibilities the values for combustion chamber irreversibility are provided at the top of Fig. 6 for each configuration. Note that all of the component irreversibilities (exergy losses) are individually calculated on the basis of the same reference conditions (temperature \( =298 \text{ K} \), pressure=1 atm.). These results, therefore, represent relative component exergy losses on the same basis, but, cannot be summed or otherwise combined to calculate the overall second law efficiency. The overall second law efficiency is rather calculated by an exergy analysis with a control volume around the entire system that accounts for all chemical and thermal exergy inputs and outputs, which results are presented as "system" results in Fig. 6.

Several interesting results emerge from the second law analyses presented in Fig. 6. The variations in second law performance amongst the cycle configurations are primarily associated with the combustor, fuel preheater, and reformer components.

The combustor irreversibility of configuration 6 is lower than the other configurations because the product hydrogen is removed before the combustor. Hydrogen contributes to two moles of water for every mole of oxygen converted in the combustor compared to one mole for every mole of carbon converted to \( \text{CO}_2 \). Thus re-
moval of hydrogen from the inlet stream of the combustor leads to a lower number of moles in the product stream and the lowest combustor exit exergy compared to cases with hydrogen in the inlet gases. However, inlet exergy for the internal reforming case of configuration 6 is substantially lower than those of the other cases leading to lower second law efficiency for the combustor of configuration 6.

Configuration 5 has irreversibility in the combustion chamber that is similar to configurations 1–4. However, the second law efficiency of the combustion chamber of configuration 5 is the lowest of all configurations due to the high temperature rise in this component placed after all of the preheaters. All other cases have similar second law efficiency and irreversibilities in the combustor.

The preheater irreversibility for configuration 5 is higher and its second law efficiency is lower compared to all of the other configurations. This is due to the high hydrogen content of the stream entering this pre-heater for this case, since the chemical exergy of hydrogen is high compared to the water that is present in this stream for the other configurations.

Configuration 5, which shows the worst energy and hydrogen production performance, has better exergy performance in the reformer component than all the other cycle configurations because the combustor is placed immediately before the reformer leading to a better reformer operating temperature. Configuration 6 has the second highest reformer second law efficiency, also due to a better reformer operating temperature. The reformer of configuration 6 operates at the 1000°C temperature of the SOFC, which results in good conversion of fuel to hydrogen as indicated in Fig. 1. The reformer performance of configuration 6 also benefits from concurrent electrochemical and chemical reactions in the anode compartment.

The second law efficiency (and exergy losses) in the fuel cell component is very similar in each of the cycle configurations. As a matter of fact, the irreversibilities and second law efficiency of the fuel cell component is the worst for configuration 6, which had the highest fuel cell energy efficiency due to internal reformation. The difference in second law efficiency for the fuel cell of configuration 6 is slight (30% versus 33% for configurations 1–5). The fuel cell irreversibility of configuration 6 is about 10% higher than the other configurations primarily due to higher fuel throughput for the same power output.

The overall second law efficiency of configuration 1 is highest and configuration 6 is lowest among all the configurations considered. The second law efficiency of configuration 1 is high due to cumulative better exergy performance of the components as integrated in configuration 1. This is primarily manifested in lower irreversibilities in the fuel cell (compared to configuration 6), and the reformer (compared to all other configurations except configuration 5).

Configuration 6, which shows the best energy performance and hydrogen production capacity, exhibits the worst exergy performance due to a higher inlet exergy requirement. That is, more fuel is required to achieve the higher hydrogen production of configuration 6. However, what this result indicates is that there is the potential for significant performance improvements for the internal reforming option of configuration 6. These potential improvements will be addressed in future studies.

To directly compare the proposed concept to stand-alone steam reformation one final set of calculations was performed. Strict hydrogen production thermal efficiency was calculated on the basis of hydrogen energy out divided by the fraction of methane fuel input that was used to produce the hydrogen. That is, the quantity of fuel that directly produces electricity (in the fuel cell) was subtracted out of the denominator. The resulting strict hydrogen production efficiency of configurations 1–6, for steam-to-carbon ratio of 2.0, were 85.6, 84.2, 84.3, 83.7, 60.8, and 85.6%, respectively. These thermal efficiency values, except for the configuration 5 value of 60.8%, are clearly superior to typical small-scale steam reformation [2] and even compete with large-scale steam methane reformation efficiencies reported in the range of 75 to 80% [2].

Further research is justified using the insight gained through the present investigation. This research should focus on those subprocesses having large exergy losses and should include, for example, transport integration, design and optimization, temperature profile changes, etc.

Summary and Conclusions

The high efficiency and lower pollutant emission features of fuel cells compared to other technologies make them an attractive technology for energy generation. Hydrogen is one of the most abundant elements in our universe, but it is difficult to obtain in its pure form. Hydrogen is also difficult to store and transport due to its low volumetric energy density. Thus, novel means of hydrogen production, distribution, and delivery are required. Hydrogen can be extracted from water or hydrocarbons using chemical or electrochemical processes. There are relatively simple procedures for obtaining hydrogen from both of these sources, but both require a significant amount of energy. A very common method of hydrogen production is the steam reforming of natural gas.

This paper presents a novel method for the local co-production of hydrogen and electricity from high temperature fuel cells. Several generic cycle configurations are presented. In addition, a methodology for analyzing this concept is presented that includes thermodynamic and electrochemical analyses. The energy analyses of these cycles show that the configuration in which the fuel is combusted inside the fuel cell has the best energy efficiency and co-production of hydrogen capacity. However, the exergy analysis of this same configuration shows that much effort should be invested to further improve this cycle configuration.

The electrical efficiency (ratio of the electric energy produced to the fuel thermal energy) of the systems was about 41–44%, showing the highest value for the internal reformation option. The overall energy efficiency (ratio of the electric energy and hydrogen produced to the fuel thermal energy) ranges from 45% to 80%. The lowest overall energy efficiency was for a case that combusted fuel in the exhaust of the fuel cell system for hydrogen production in an external reformer. The highest overall efficiency was for the internal reforming configuration.

The hydrogen co-production concept presented in this paper is clearly worthy of further investigation, development, and demonstration. Thermodynamic analyses suggest a clear advantage of net fuel savings compared to separate generation of electricity and hydrogen, which is only augmented by the avoidance of transport energy and emissions benefits.

Fuel cell technology is advancing with several commercial products emerging into the market that may become amenable to testing the hydrogen co-production concept. But significant challenges remain, including the need for more robust high temperature fuel cells that can internally reform methane-based fuels, integration with small-scale hydrogen separation, compression and storage technology, and cost reduction.

Acknowledgment

The authors would like to acknowledge CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil) for the financial support in this project.

Nomenclature

\[ A = \text{area, m}^2 \]
\[ a_{ik} = \text{number of atoms of element } i \text{ in species } k \text{ in the products, kmol} \]
\[ b_i^0 = \text{number of atoms of element } i \text{ in the reactants, kmol} \]
\[ C_p = \text{specific heat at constant pressure, kJ/kmol K} \]
\[ E_F = \text{thermal energy of the fuel, kW} \]
**Greek Symbols**

- \( \alpha \): Transfer coefficient
- \( \delta \): equivalent thickness of diffusion layer, m
- \( \eta_{act} \): activation polarization, V
- \( \eta_{conc} \): concentration polarization, V
- \( \eta_{el} \): electrical efficiency
- \( \eta_{2} \): Second Law efficiency
- \( \mu_{k} \): molar chemical potential of species \( k \), kJ/kmol
- \( \lambda_{L} \): Lagrange multiplier
- \( \eta_{ohm} \): Ohmic polarization, V

**Subscripts and Superscripts**

- \( f \): formation
- \( g \): gas
- \( i \): initial
- \( k \): species
- \( l \): liquid
- \( p \): products
- \( R \): reaction or reactants

**References**

1. Ahmad, S., and Krumpelt, M., 2001, “Hydrogen from Hydrocarbon Fuels for Fuel Cells,” Int. J. Hydrogen Energy, 26, pp. 291–301.
2. Ogden, J. M., 2002, “Review of Small Stationary Reformers for Hydrogen Production,” Technical Report No. IEA/H2/2/TR-02/002, International Energy Agency.
3. Hammerli, M., 1984, “When Will Electrolytic Hydrogen Become Competitive?,” Int. J. Hydrogen Energy, 9(1/2), pp. 25–51.
4. Morse, S., 2004, “Hydrogen—The Fuel of Today,” Technical report, available at www.eng.usf.edu/rnm/ret_revet_004/HYDROGEN_FUEL_OF_THE_FUTURE.doc
5. Lipman, T., 2004, “What Will Power the Hydrogen Economy?,” Technical Report No. UCD-ITS-RR-04-10, The Natural Resources Defense Council.
6. Lütz, A. E., Bradshaw, R. W., Kellera, J. O., and Wittmerb, D. E., 2003, “Thermodynamic Analysis of Hydrogen Production by Steam Reforming,” Int. J. Hydrogen Energy, 28, pp. 159–167.
7. Gordon, S., and McBride, B. J., 1994, “Computer Program for the Calculation of Complex Chemical Equilibrium Compositions with Applications: I. Analysis,” NASA Reference Publication 1311.
8. Hirschenhofer, J. H., Stauffer, D. B., and Engleman, R. R., 1994, *Fuel Cells: A Handbook*, 3rd ed., Gilbert and Commonwealth, Inc. Philadelphia, U.S. Department of Energy, Contract No. DE-AC02-82CH10587.
9. EG&G Technical Services, Inc., 2002, *Fuel Cell Handbook*, 6th ed., DOE/NETL-2002/1179, Under Contract No. DE-AM26–99FT40575 U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory.
10. Chan, S. H., and Xia, Z. T., 2002, “Polarization Effects in Electrolyte/ Electrode-Supported Solid Oxide Fuel Cells,” J. Appl. Electrochem., 32, pp. 339–347.
11. Chan, S. H., Khor, K. A., and Xia, Z. T., 2001, “A Complete Polarization Model of a Solid Oxide Fuel Cell and its Sensitivity to the Change of Cell Component Thickness,” J. Power Sources, 93, pp. 130–140.
12. Kanamura, K., Yoshioka, S., and Takehara, Z., 1991, “Dependence of Entropy Change of Single Electrode on Partial Pressure in Solid Oxide Fuel Cell,” J. Electrochem. Soc., 138(7), pp. 2165–2168.
13. Takehara, Z., Kanamura, K., and Yoshioka, S., 1989, “Thermal Energy Generated by Entropy Change in Solid Oxide Fuel Cell,” J. Electrochem. Soc., 136(9), pp. 2506–2512.
14. Herle, J. V., Membrez, Y., and Bucheli, O., 2004, “Biogas as a Fuel Source for SOFC co-Generators,” J. Power Sources, 127(1–2), pp. 300–312.
15. Matsuzyki, Y., and Yasuda, I., 1999, “RelAtionship Between the Steady-State Polarization of the SOFC Air Electrode, La0.6Sr0.4MnO3-y/YSZ, and its Com-plex Impedance Measured at the Equilibrium Potential,” Solid State Ionics, 126(3–4), pp. 307–313.
16. Costamagna, P., Costa, P., and Antonucci, V., 1998, “Micro-Modelling of Solid Oxide Fuel Cell Electrodes,” Electrochim. Acta, 43(3–4), pp. 375–394.
17. Sunde, S., 1997, “Calculations of Impedance of Composite Anodes for Solid Oxide Fuel Cells,” Electrochim. Acta, 42(17), pp. 2637–2648.
18. Tanner, C. W., Fung, K. Z., and Virkar, A. V., 1997, “The Effect of Porous Composite Electrode Structure on Solid Oxide Fuel Cell Performance: I—Theoretical Analysis,” J. Electrochem. Soc., 144(1), pp. 21–30.
19. Chan, S. H., Low, C. F., and Ding, O. L., 2002, “Energy and Exergy Analysis of Simple Solid-Oxide Fuel-cell Systems,” J. Power Sources, 103, pp. 188–200.
20. Utkigak, P. S., Dubey, S. P., and Prasad Rao, P. J., 1995, “Thermoeconomic Analysis of Gas Turbine Cogeneration Plant—A Case Study,” Proc. Inst. Mech. Eng., Part A, 209(5), pp. 45–54.
21. Bedringås, K. W., Ertesvåg, I. S., Byggstøyl, S., and Magnussen, B. F., 1997, “Energy Analysis of Solid-Oxide Fuel-Cell (SOFC) Systems,” Energy, 22, pp. 403–412.
22. Iwahashi, T., Yoshida, N., and Kosaka, H., 1998, “High Efficiency Power Generation From Coal and Wastes Utilizing High Temperature Air Combustion Technology: Thermal Performance of Compact High Temperature Air Preheater and Meet Boiler,” Proceedings of the International Symposium on Advanced Energy Technology, Sapporo, Japan, Hokkaido University, pp. 455–462.
23. Larminie, J., and Dicks, A., 2003, *Fuel Cell Systems Explained*, Wiley, London.
24. Dunbar, W. R., Lior, N., and Gaggioli, R. A., 1991, “Combining Fuel Cells with Fuel-Fired Power Plants for Improved Exergy Efficiency,” Energy, 16(10), pp. 1259–1274.