Achieving Autothermal Operation in Internally Reformed Solid Oxide Fuel Cells: Experimental Studies

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An integrated internal reforming solid oxide fuel cell (IIR-SOFC), in which the reformer is in good thermal contact with the SOFC, is an energy-efficient mode of operation. However, the rapid, highly endothermic methane steam reforming (SMR) reaction causes undesirable local cooling at one point or another within the SOFC system. Earlier simulation studies had indicated several system modifications that could eliminate this problem. Accordingly, experimental studies were carried out to find a suitable catalyst and reactor configuration that lowered the rate of the reforming reaction while retaining activity in the face of potential carbon deposition or sulfur poisoning. A 0.5 wt % $Rh/CeZrO_2$ has been identified as a catalyst that could provide the features that are suitable for the application in an IIR-SOFC. The catalyst showed good activity and stability toward the SMR. Kinetic studies provided overall information that was incorporated into the SOFC model developed to investigate its feasibility as the reforming catalyst. A further set of experiments investigated the use of the $Rh/CeZrO_2$ catalyst as the thin washcoat on the wall of the reformer. It was demonstrated that the coated catalyst had a suitably reduced but stable activity. It was shown that a barrier material (ZrO_2) could also be used to lower the catalyst activity and provide a mass transfer limited operation. The barrier material could be used to create a catalyst activity profile along the length of the reactor. By the addition of small amounts of oxygen to the feed, methane oxidation could be used to reduce the overall endothermicity of the reforming process; this can serve to improve the temperature profile within the reformer. Simulations indicated that typical methane-to-oxygen ratios of 10:1 to 20:1 were most effective. From the results obtained, $Rh/CeZrO_2$ has demonstrated its potential as the reforming catalyst in a SOFC, especially in a coated-wall configuration. The experimental results demonstrated that the configurations investigated by the simulation were achievable in practice.

Introduction

A fuel cell is an energy conversion device that produces electricity and heat directly from a gaseous fuel by electrochemical reaction between the fuel (at the anode) and an oxidant such as oxygen (at the cathode).[1] It has significantly higher theoretical energy efficiency in comparison to the conventional methods of power generation using internal combustion engines or power plants. This is because it bypasses the conversion of chemical energy of the fuel into thermal and mechanical energy.

A solid oxide fuel cell (SOFC) has an oxide ion conducting solid electrolyte requiring operating temperatures from 600 to 1000 °C.[2,3] An indirect internal reforming solid oxide fuel cell (IIR-SOFC) is a promising configuration for SOFCs because of the potentially high energy efficiency and the freedom to optimize the reforming catalyst and the anode material separately (Figure 1).

The reforming reaction occurs in a separate reformer that has a close thermal contact with the anode side of a SOFC, as shown in Figure 1. A good thermal contact between the reformer and the fuel cell allows the heat from the electrochemical reaction to be used for the endothermic reforming reaction. This gives rise to the high energy efficiency of the IIR-SOFC and reduces the excess air requirement at the cathode.

The high operating temperature allows SOFCs to reform a variety of raw fuels into hydrogen and CO, i.e., the gases required for the electrochemical reactions at the anode of a SOFC. Fuels such as natural gas, coal-derived gas, landfill gas,
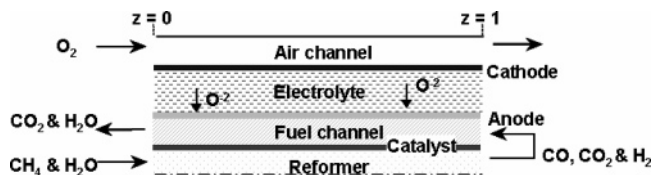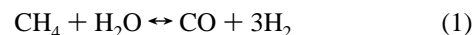
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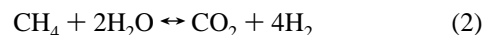
Figure 1. IIR-SOFC.

naphtha, gas oil, kerosene, biogas, methanol, and other low molecular weight liquid fuels containing hydrocarbons can be used; natural gas is usually the preferred source of fuel. Natural gas consists primarily of methane with a small amount of higher hydrocarbons, nitrogen, and carbon oxides and a trace amount of sulfur-bearing odorant. All the raw feedstocks need to be converted to hydrogen and/or CO rich fuel. In the present SOFCs, it appears that the reforming of methane to hydrogen predominates.

In general, fuels can be converted to hydrogen and CO using catalytic steam reforming or partial oxidation[2,4,5] as follows.
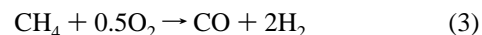
Methane steam reforming reaction:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (1)$$

Reverse methanation reaction:

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \qquad (2)$$

Partial oxidation reaction:

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \qquad (3)$$

Research Objectives

Earlier simulation studies[6] showed that a conventional reactor configuration for an IIR-SOFC (say, packed with a 15.2 wt %

nickel catalyst supported on magnesium spinel, Ni/MgAl$_2$O$_4$) led to unacceptably large temperature gradients near the reactor entrance or exit due to the mismatch in the rates of the (endothermic) steam reforming reaction and the (exothermic) fuel cell reaction. A coated-wall reactor was a more feasible configuration than a packed bed because a considerable reduction of the reforming reaction rate could be achieved; the thin layer of catalyst also provided a better heat transfer between the reformer and the fuel channel. However, the lower amount of catalyst available in this coated-wall configuration raised the potential problem of catalyst deactivation. The use of a precious metal catalyst with oxides as the support was identified as a possible solution to this problem. Although the precious metal catalysts are more active than nickel catalyst, they are more resistant to carbon deactivation. Through reduced loading and dilution with oxides, their activity can be reduced. Thus, a stable and relatively lower catalyst activity could be achieved.

A large number of precious metal catalysts on several oxide supports were examined in our laboratories as alternatives for the coated-wall internal reformer of an IIR-SOFC[7]. The most appropriate (in terms of activity and stability) was found to be 0.5 wt % Rh on CeZrO$_2$ support. In order to test the hypotheses from the earlier simulation studies, the overall kinetics of the methane steam reforming (SMR) reaction over the catalyst at high temperatures and near atmospheric pressure were investigated. The only kinetic information required was the apparent reaction orders in methane, hydrogen, steam, and oxygen, the apparent reaction rate constant, and the apparent activation energy for the reactions and catalysts of interest. Two types of reactor configurations were studied: a conventional packed-bed configuration with powder catalysts and an annular-flow configuration using a central rod bearing the coated catalyst.

Experimental System

Preparation of 0.5 wt % Rh/CeZrO$_2$. The 0.5 wt % Rh/CeZrO$_2$ was prepared by the incipient wetness or dry impregnation method. It involved filling the pores of the support with just enough precursor salt of rhodium chloride. The support used was commercial CeZrO$_2$ (a single-phase mixed oxide with composition 20% ceria and 80% zirconia, precalcined to 1000 °C) supplied by Daiichi Kigenso Kagaku Kogyo Co. Ltd. The dried catalysts were then dried further at 120 °C for 3 h under air flow before being heated up to 1000 °C and calcined for another 12 h. For the powdered catalysts, the calcined catalyst was crushed and sieved to the desired size range of 78−150 μm and had a Brunauer−Emmett−Teller (BET) surface area of 28.9 m^2 g^{-1}. For the catalyst rods used in the annular configuration, a 3.6 mm diameter α-alumina rod with a length of 200 mm was coated with Rh/CeZrO$_2$ close to the center of the rod for a coated length of 20 mm and then calcined. The coating and calcinations procedures were repeated to load a sufficient amount of catalyst (22 mg) onto the rod. The rod form of the Rh/CeZrO$_2$ catalyst was prepared to compare the global kinetic information obtained from the packed-bed and annular-flow configurations.

Reactor System. A reactor system, as shown in Figure 2, was constructed to carry out steady-state SMR at near-atmospheric pressure. An evaporator was used to deliver the required steam flow in running the SMR. A thermocouple was inserted into the heated, deionized water contained in the evaporator to measure the evaporating temperature. There was a pressure transducer located just before the inlet of the evaporator to measure the evaporating pressure. The outlet of the evaporator was trace-heated at 100 °C to prevent water condensation.
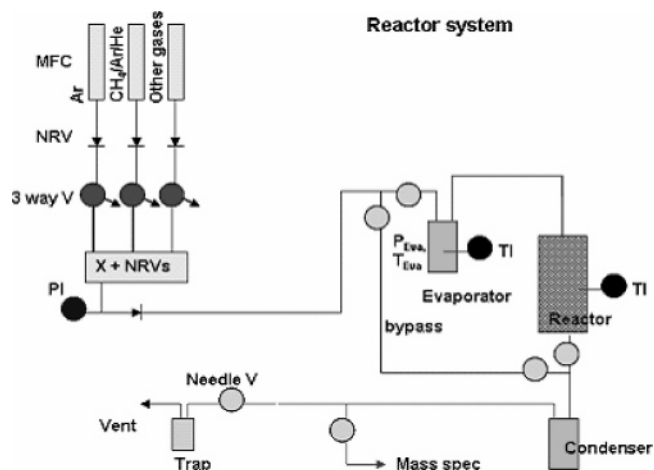

Figure 2. Reactor system.

A microreactor was mounted vertically at the center of a split-tube furnace (Lenton Thermal Design, Ltd.). The microreactors were 4 mm internal diameter quartz tubes. A type-K thermocouple, with its tip tied onto the external surface of the reactor at the center of the catalyst bed, was used to monitor the catalyst temperature. After reaction, the product gases entered a condenser maintained at 0 °C by a water/ice mixture.

The compositions of the "dry" product gases (saturated with water at 0 °C) were then analyzed using a quadrupole mass spectrometer (European Spectrometry Systems (ESS)). The errors incurred by the mass spectrometer in calculating the rates of reactions were about 6%. Implicit in this analysis is the assumption that the solubilities of the reactant and product gases in the condensed water were negligible.

Experimental Method

The first objective of the experimental work was to determine the overall kinetics of the SMR over Rh/CeZrO$_2$ (and similar) catalysts in order to test the hypothesis put forward by simulation studies that such catalysts might allow the improved performance of an IIR-SOFC. The temperature investigated ranged from 850−1000 °C, typical of the operating temperature of a SOFC. Similarly, the relative compositions of the process stream (steam/methane/hydrogen) were kept at realistic ratios; however, the stream was substantially diluted with inerts in order to minimize non-isothermality in the reactor.

There were two further objectives of the experimental program: (a) to note the effect, if any, on the overall rates of steam reforming reactions if an inert diffusion barrier is deposited on to the outer surface of the catalyst and (b) to note the effect, if any, on the overall endothermicity of the steam reforming reaction if a small amount of oxygen is added to the reactor feed. Simulations had indicated that both of these modifications could significantly improve the operation of the system.

Reactor Configurations. For the case of powdered catalysts, the reactor was filled with a plug of quartz wool to support the catalyst loading. The reactor was then filled with a layer of 150 mg of SiC, placed on top of the quartz wool to avoid the slip-through of the catalyst particles. Catalyst (12 mg) was mixed with around 25 mg of SiC diluent before being loaded into the reactor. The SiC was used to enhance the heat transfer from the furnace to the catalyst and to minimize the localized cooling effect due to the SMR reaction, thus maintaining a more uniform temperature throughout the catalyst. In addition to that, the mixing of catalyst particles with the SiC particles of a similar
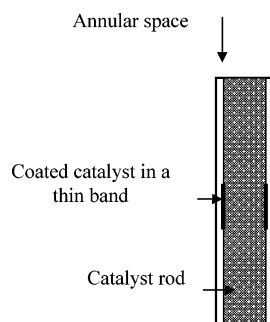
Figure 3. Long rod catalyst.

Figure 4. Rates of SMR with powdered catalyst; effect of methane (temperatures in °C).

Figure 5. Rates of SMR with powdered catalysts; effect of hydrogen (temperatures in °C).

size range reduced the bypassing of reactant gases. Another layer of approximately 150 mg of SiC was placed on top of the catalyst to condition the inlet flow of the reactants. The pressure drop across the packed bed was about 0.3−0.5 bar, depending on the amount of SiC loaded. Thus, by having approximately equal amounts of the SiC before and after the catalyst loaded, the operating pressure and its variation with the catalyst bed could be estimated. The residence time of the gases was around 0.04 s.

For the annular configuration, the catalyst rod was loaded without using any SiC. This created an annular-flow configuration with a lower pressure drop compared to the packed-bed configuration. The diameters of the long rods (Figure 3) were around 3.6 mm, while the internal diameter of the quartz reactor was 4.0 mm. This left a relatively thin annular space for the reactant gas mixtures to flow. The quartz wool, placed below and on top of the catalyst, was used to support the rod and to encourage better gas mixing. The residence time of the gases was approximately 0.02 s, and the Reynolds number for the flow in the annulus was around 4 (based upon average gas properties at 900 °C).

Catalyst Pretreatment. The loaded catalyst was heated to the required operating temperature under the flow of the reactant gas mixture. The data were collected after 2−4 days depending upon when the catalyst was fully reduced, and a steady state was reached. Steady state was assumed when the ion current readings of the mass spectrometer gave steady and repeatable readings.

Running the Experiments. For the SMR reactions, the experimental work was carried out at approximately 1.05−1.40 bar with an operating temperature varying from 830 to 950 °C. The temperature range was within the normal operating temperature of a SOFC. The reactant gas mixture used for methane steam reforming consisted of methane, steam, and hydrogen together with inert gases argon, as carrier, and a small amount of helium, as internal standard. The mole fraction of methane in the feed ranged from 0.7% to 2.5% with a total reactant gas flow of 145 ± 5 mL min^{-1}. Referring to Figure 2, both the feed streams met at the outlet of their respective mass flow controllers and were bubbled through the deionized water in an evaporator. The gases that left the evaporator were assumed to be saturated with water vapor at that temperature and pressure.

In running the SMR, the concentrations of the methane or other gases were varied at each temperature. Usually, four temperatures were selected in conjunction with four methane concentrations. This gave a total of 16 operating conditions for each set of data. After varying the concentration of the gases at each temperature, the experiment with one of the gas concentrations was repeated to ensure the repeatability of the results. After running the whole set of conditions, the experiments were repeated at some of the previous operating condi-
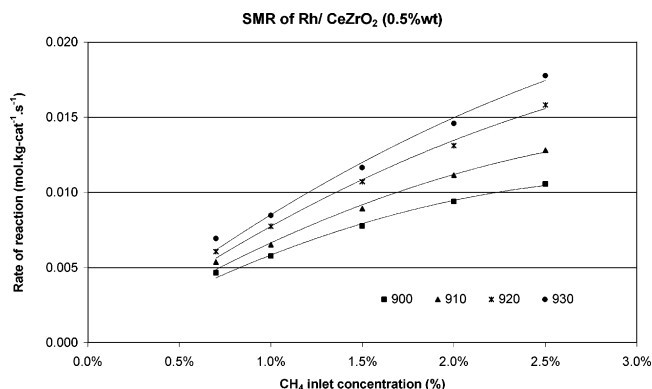
tions to double-check the repeatability of the data generated. The uncertainty of the reactant and product concentrations was approximately 5%.
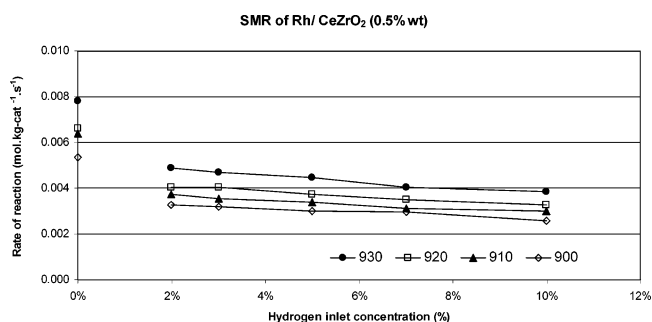
Experimental Results−Overall Kinetics

It is important to note here that no attempt was made to study the inherent fundamental kinetics of the steam reforming reaction for these catalysts. Instead, we wished to see if catalysts such as Rh/CeZrO$_2$ (especially when coated on the wall of a reactor) would have the desired activity and stability to reduce the large temperature gradients (of 50 K cm^{-1} or more) as found in simulation studies for an IIR-SOFC using conventional catalysts.[6] Accordingly, only the overall kinetics were studied− first in a packed reactor and then, more realistically, in a coated-wall reactor.

Powdered Rh/CeZrO$_2$ Catalysts. The kinetics of the SMR reactions over Rh/CeZrO$_2$ powder catalysts was investigated at temperatures between 900 and 930 °C and a total pressure of around 1.3 bar. The feed concentration of methane was varied from 0.7 to 2.5%, and the concentration of steam was varied from 3 to 12% (always keeping a steam/methane ratio of at least 3.0). In addition, some experiments were performed with hydrogen added to the feed with hydrogen/methane ratios up to 10, in order to simulate the compositions in the reforming section of a SOFC, where the methane concentration drops and the hydrogen concentration increases. In all cases, the methane conversion ranged from 3 to 13%. A typical set of results for a feed consisting of no hydrogen and a constant steam concentration of 8% is shown in Figure 4. Corresponding results were obtained for varying the concentration of steam in the feed.[7]

For the case of hydrogen, Figure 5 shows that, at low concentrations of hydrogen, there was a large negative effect of hydrogen concentration on the rate of the reforming reaction.
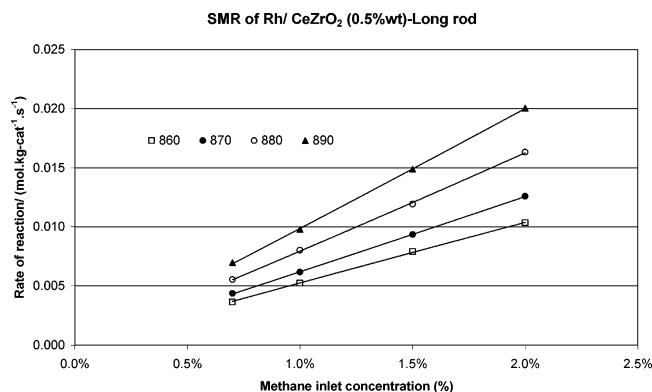
Figure 6. Rates of SMR with coated rod catalysts; effect of methane (temperatures in °C).

However, since the feed to the reforming section of an IIR-SOFC has a relatively high hydrogen concentration (because of the recycle of unreacted material leaving the SOFC), very low hydrogen concentrations are not of interest in this work and the low-concentration region can be ignored.

Coated Rod Rh/CeZrO₂ Catalysts. Because the inherent kinetics of the SMR reaction at the operating conditions of a high-temperature SOFC are extremely rapid, there could be significant local cooling of the catalyst due to the highly endothermic reforming reaction and internal mass transfer resistances through the catalyst pore structure. Because we were most interested in the overall performance of a coated-wall reactor, there was a significant advantage in obtaining the corresponding apparent kinetics in a more representative experimental configuration (although there could easily still be some masking of the "true" kinetics because of heat and mass transfer effects). Accordingly, for the purpose of this investigation, the experiments were repeated using a catalyst that was coated onto the external surface of a long rod, as indicated in Figure 3.

Experiments were carried out at temperatures between 860 and 890 °C and a total pressure of around 1.1 bar. In all cases, the methane conversion ranged from 13 to 21%. A typical set of results for a feed with a constant steam concentration of 6.5% is shown in Figure 6.

Analysis of Results. The objective of this part of the work was to test the feasibility of using the Rh/CeZrO₂ catalyst in an IIR-SOFC and, especially, to see if they could overcome the limitations of conventional catalysts and reactor configurations as indicated by our simulation studies. Accordingly, we sought an expression for the apparent overall kinetics of the SMR consistent with the data from all of the experiments. A multiple linear regression method was applied that considered the partial pressures of each of the relevant components in calculating the kinetic constants. Since all of the experiments were run under near-differential conditions, it was a reasonable approximation to consider the average partial pressure of each component in the reactor in each experimental run. For simplicity, an apparent power law rate equation of the forward SMR, as represented by eq 4, was used to describe the overall methane disappearance. This includes both the methane steam reforming and the reverse methanation reactions.

$$r = k(T)P_{CH_4}^{n1}P_{H_2O}^{n2}P_{H_2}^{n3}P_{CO}^{n4}P_{CO_2}^{n5} \qquad (4)$$

Analysis of the results showed that, at these low conversions, the effects of CO and CO₂ were minimal and subject to considerable uncertainty. Hence, the analysis was repeated ignoring the partial pressures of CO and CO₂.
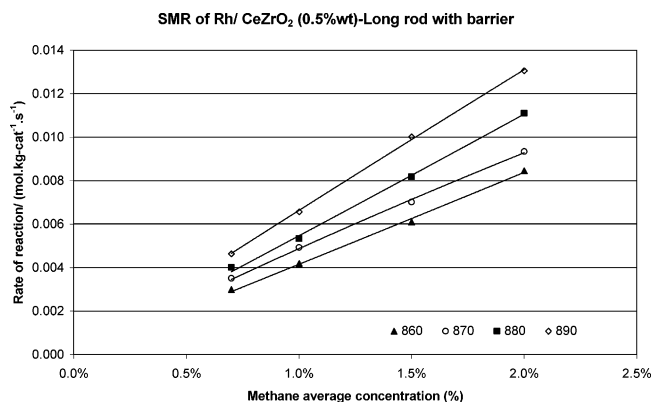

Figure 7. Rates of SMR with diffusion barrier; effect of methane (temperatures in °C).

By this method, the average values of the reaction orders with respect to CH₄, H₂O, and H₂ were 0.73, 0.41, and −0.15, respectively (with the result for hydrogen only valid for hydrogen concentrations above around 1%). The correlation coefficients for the data ranged from 0.94 to 0.98 (with 1 being defined as having perfect correlation). This led to an apparent rate expression as follows,

$$r = k''P_{CH_4}^{0.73}P_{H_2O}^{0.41}P_{H_2}^{-0.15} \qquad (5)$$

$$\ln(k'') = 15.8 - \frac{172\,000}{R_{gas}T_{reaction}} \qquad (6)$$

with k'' expressed in units (mol bar$^{-0.99}$ kg$_{cat}$$^{-1}$ s^{-1}).

Similar results were obtained when the results for the coated-rod catalyst were analyzed separately. However, in that case, the apparent order of reaction for methane was closer to unity and the apparent activation energy was much higher, around 279 kJ mol^{-1}. The discrepancy appears to be due to some masking of the overall kinetics in the case of the powdered catalysts because of the mass transfer and heat transfer limitations.

Experimental Results−Effect of a Diffusion Barrier

A diffusive barrier is intended to reduce the catalytic activity of the catalyst to provide a lower and more stable activity. Theoretically, it can be used to create a mass transfer controlled reaction in the SMR, depending on the properties of the barrier created. The previous modeling studies[6,8] investigated the use of a reduced activity catalyst and a profiled activity catalyst. Both of these configurations can be achieved through the use of a barrier material. The long rod was used to prepare this catalyst with a relatively thin layer of barrier of approximately 50 μm thickness. The barrier material used was a ZrO₂ suspension. The coating procedure for the barrier material was the same as the coating procedure for the catalyst onto the α-alumina rod, and it led to a similar thickness of the two layers.

The SMR reaction over a Rh/CeZrO₂ catalyst long rod with a layer of barrier material was studied at an operating pressure of 1.1 bar and temperatures from 860 to 890 °C at 10 °C intervals. The concentrations of methane were varied from 0.7 to 2.0% with an inlet steam concentration of 6.5%. It can be seen from Figure 7 that, as the methane partial pressures were increased, the rates of the SMR increased. As in the case of the coated rod without a barrier, the reaction order of methane in the SMR over the catalyst was close to one. The fractional conversions achieved ranged from 8.6 to 14.1%.
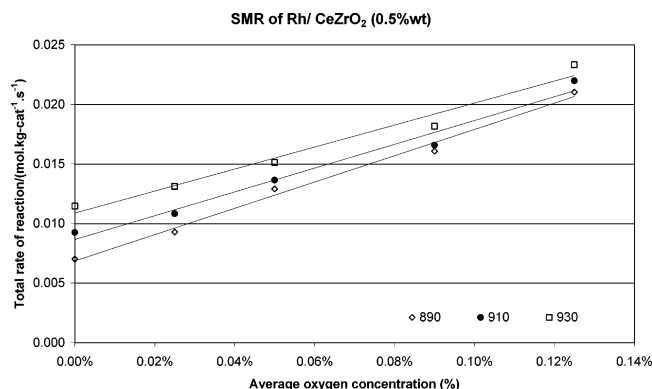
Figure 8. Total rate of reaction; effect of oxygen (temperatures in °C).

Figure 9. Comparison of reformer temperature profiles of the SOFC with Ni and Rh catalysts (a) Ni/MgAl$_2$O$_4$, (■); (b) Rh/CeZrO$_2$, (▲).

By comparing Figure 6 with Figure 7, it can be seen that the rate of the SMR had decreased by about 20−35%. This showed that the barrier material was able to decrease the catalytic activity of the catalyst. Analysis of the temperature dependence of the rate constant for the long rod catalysts with and without the diffusion barrier showed that the barrier decreased the apparent activation energy from 279 to 206 kJ mol^{-1}. This suggests that the diffusive barrier was able to introduce a certain degree of mass transfer limitation. Not only did this reduce the endothermicity of the process, but it also made the reactor system less susceptible to catalyst poisoning, as demonstrated in our earlier studies.[8] Varying the thickness of the barrier on a coated wall is also a relatively simple way of introducing a variable catalyst activity profile as a function of length to a coated-wall reactor.

Experimental Results−Effect of Oxygen on the Reforming Rate

From the previous simulation studies using the SOFC model,[6] it was found that the addition of a small quantity of oxygen to the feed stream of the reformer could supply the reformer with part of the heat requirement of the endothermic SMR and, thus, reduce the thermal stress caused by the steep temperature gradient near the inlet to the reforming section of the fuel cell. Accordingly, the effect of small amounts of oxygen on the SMR over the Rh/CeZrO$_2$ catalyst powder was investigated with 1% methane feed at 1.35 bar pressure. The reaction temperatures studied ranged from 890 to 930 °C.

As a first approximation, it was assumed that the total rate of reaction at different reaction temperatures and oxygen concentrations was the sum of the reforming rate and the rate of total oxidation of methane. The total rate of methane disappearance as a function of temperature and oxygen concentration was measured experimentally. The oxygen feed concentration was varied from 0.05 to 0.25%, giving a methane/oxygen feed ratio between 4:1 and 20:1. In these experiments, the conversion of methane ranged from 8 to 28%. The rate of methane disappearance at each temperature was measured experimentally at zero oxygen concentration and again with different oxygen concentrations at the same temperature; the rate of oxidation was estimated by difference and fitted to a simple power law, and it indicated approximate first-order dependence upon oxygen concentration.

The total rates of reactions are presented in Figure 8. The average concentrations of oxygen were calculated as half the inlet concentrations, because all the oxygen was fully consumed in the oxidation reaction. It can be noted that even small amounts of oxygen in the feed have the ability to increase the overall
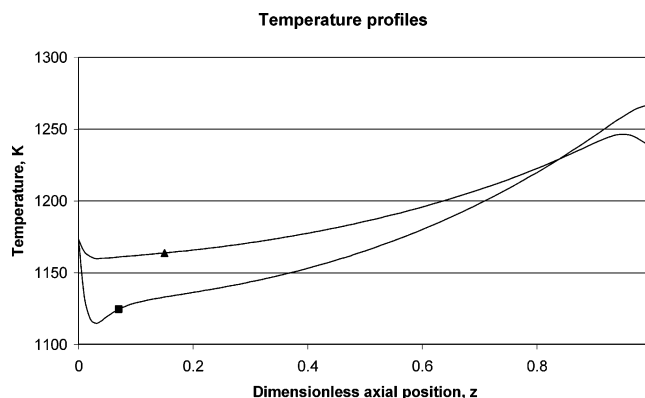
rate of methane consumption by 50% or more; this leads to a corresponding decrease in the overall endothermicity of the process, especially in the critical region close to the entrance to the reactor.

Simulation Studies on Rh/CeZrO$_2$

On the basis of the experimental studies described above, the various kinetic expressions obtained have been used in the SOFC models developed earlier[6] to investigate whether or not the problems of thermal mismatch can be eliminated or reduced with these catalysts and/or reactor configurations. Because the equations for the model have been given in an earlier paper,[6] they are not repeated here.

In summary, for the reformer, the mass and energy balances in the gas phase were modeled as being one-dimensional and axial dispersion was ignored. The gas flows in the reformer, the air channel, and the fuel channel were effectively modeled as plug flow, giving, as an approximation, a constant concentration and temperature in the radial direction. The ideal gas law was used to reflect the changing velocity and density profiles along the axial direction due to the reactions that occurred. Overall heat and mass transfer coefficients linked the concentration and temperature profiles of the gas and solid phases. Radiant heat transfer between the reformer catalyst surface and the fuel cell solid structure, as well as convective heat transfer to both the reformer and the fuel channels, was taken into account.

General fuel cell principles were applied to develop a steady-state, one-dimensional, planar SOFC model. For the Ni yttria-stabilized zirconia cermet anode assumed here, the electrochemical reactions of both H$_2$ and CO were considered. The air and the fuel channels had separate mass and energy balances. An energy balance equation and an electrochemical model that related the current density and the potential achievable to other operating variables described the behavior of the solid structure. The kinetics of the electrochemical reactions at the electrolyte/electrode interface were assumed to be controlling; thus, the transport of reactants through the cermet electrodes was not modeled.

Characteristic Profiles for Coated-Wall Rh/CeZrO$_2$ Catalysts. Figure 9 shows the simulated temperature profiles of the SOFC model with both the Rh/CeZrO$_2$ and conventional nickel catalysts.[9] The highest average temperature gradient for the Rh catalysts is around 10 K cm^{-1} in comparison to 50 K cm^{-1} for the SOFC model with the Ni catalyst. The moderately high temperature gradients near the exit of the reformer are due to the direct methane steam reforming reaction at the anode of
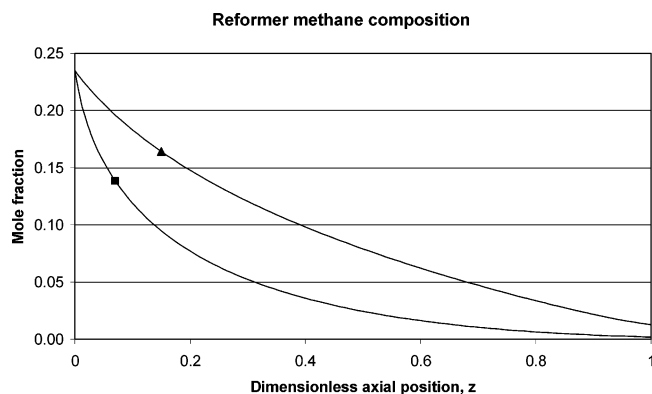
Reformer methane composition

Figure 10. Comparison of reformer methane mole fraction profiles of the SOFC with Ni and Rh catalysts (a) Ni/MgAl$_2$O$_4$, (■); (b) Rh/CeZrO$_2$, (▲).
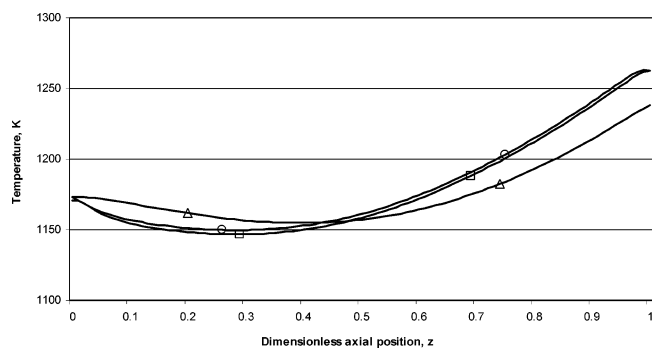

Figure 11. Behavior of a coated-wall SOFC reactor whose activity increases linearly from the inlet to the exit regions: temperatures in the reformer (□), fuel channel (○), and air channel (Δ).
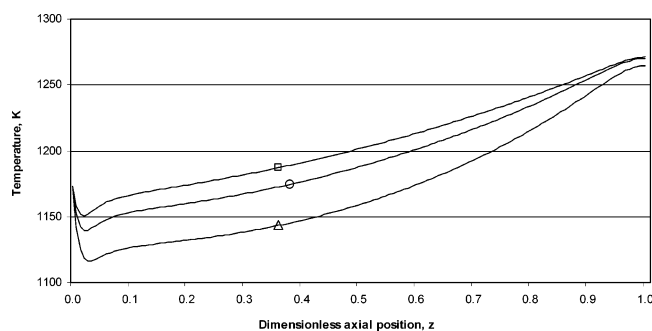

Figure 12. Reformer temperature profiles of a SOFC with different oxygen concentrations in feed: 6% (□); 3% (○); and 0% (Δ) (note: methane concentration in feed was 23%).

Table 1. Comparison of SOFC Performance Factor

	power density (A·cm^{-2})	operating voltage (V)	efficiency (%)
Ni/MgAl$_2$O$_4$	0.198	0.66	47.7
Rh/CeZrO$_2$	0.204	0.68	49.0

the SOFC. The corresponding changes in the simulated methane composition profiles are shown in Figure 10.

Apart from the improved temperature profiles, there is no major difference in the expected performance of the SOFC, based upon a simulation of the entire fuel cell system. For these runs, the operating potential for the fuel cell system was 0.68 V with an open circuit potential in the range of 0.84−0.92 V along the axial position. The power output of the fuel cell was 0.20 W cm^{-2} while the fuel efficiency was 49.0%. A summary of various performance indicators is shown in Table 1.

Characteristic Profiles for Rh/CeZrO$_2$ Catalysts with Linear Activity Profiles. A comparison of Figures 6 and 7 has shown that, by varying the thickness of a ZrO$_2$ diffusion barrier,

one can easily reduce the catalytic activity of a coated-wall reactor to obtain an activity profile that is a function of reactor length. An obvious way of capitalizing on this is to reduce the activity near the reactor entrance where the endothermicity is highest and the temperature gradient would otherwise be steepest.

Figure 11 reproduces the results from our earlier simulation study[6] showing the expected temperature profiles for a reactor whose catalyst has a uniform activity and compares it with a reactor whose catalyst activity varies linearly (from zero at the entrance) but with the same average activity. Although that simulation is a rather extreme case, the experiments demonstrate that achieving such a range of activities is achievable by the introduction of variable-thickness diffusion barriers.

Characteristic Profiles for Rh/CeZrO$_2$ Catalysts with Combined Reforming/Oxidation. Figure 12 reproduces the results from our earlier simulation study[6] showing how a small amount of oxygen added to the feed can have a marked effect on the endothermicity and steep temperature gradients at the entrance section of an IIR-SOFC. The experimental results obtained here confirm that such behavior can, indeed, be achieved with a very small amount of oxygen in the feed and that the Rh/CeZrO$_2$ catalysts serve equally well for steam reforming as for total oxidation.

Conclusions

The concept of autothermal operation has been applied to a high-temperature solid oxide fuel cell in order to increase its overall efficiency. The possible configuration of the SOFC is the indirect internal reforming SOFC (IIR-SOFC) in which the reformer section is separated but adjacent to the fuel cell anode and in good thermal contact with the SOFC. However, there could be undesirable local cooling at the reformer entrance due to the thermal mismatch between the endothermic reforming reaction and the exothermic electrochemical reaction at typical SOFC operating temperatures. The main objective of this work was to eliminate or reduce the thermal stress caused by the thermal mismatch, through the study of factors that influence the design and feasibility of the IIR-SOFC. The local cooling can be possibly alleviated by the use of a lower activity catalyst. The feasibility of using a precious metal catalyst supported on oxides has been investigated in both experimental and modeling studies.

The intrinsically lower activity catalyst can be fabricated through the manipulation of the metal content of a precious metal catalyst. The kinetics of the reforming reaction over 0.5 wt % Rh/CeZrO$_2$ have been studied. In particular, an overall kinetic expression for the methane steam reforming over the Rh/CeZrO$_2$ has been obtained. It has a relatively lower activity than the 15.2 wt % nickel catalyst of Xu and Froment[9] used in previous modeling studies[6] and shows good stability. The simulated results from the SOFC model developed show that the temperature gradients of the SOFC can be further reduced. The highest average temperature gradient is around 10 K cm^{-1}, in comparison to 50 K cm^{-1} for the SOFC model with Ni catalyst.

The earlier modeling results[6] showed that the decrease of the reforming catalyst activity can reduce the temperature gradients near the entrance of the reformer. The use of diffusive barrier washcoats can locally reduce the rate of reforming of a more concentrated catalyst and provide a more stable activity through mass transfer limited operation. A mass transfer barrier material was coated onto the external surface of the Rh/CeZrO$_2$ catalyst. The experimental results show a reduction in the reaction rate

of the SMR and a decrease in the activation energy, indicating that mass transfer limitation may have been achieved. The reduction in the reforming activity through the use a barrier material provides one of the possible approaches to create a linearly distributed catalyst profile in the future.

The addition of a small amount of oxygen to the feed allows the exothermic partial oxidation reaction of methane to occur simultaneously with the endothermic steam reforming reactions. Part of the heat requirement can be supplied by the methane oxidation reaction. The partial oxidation reaction has been studied over the 0.5 wt % Rh/CeZrO$_2$, and the catalyst shows sufficient activity for both SMR and partial oxidation. Simulation results show that the temperature profiles improve and large temperature gradients can be virtually eliminated.

Thus, on all of these counts, the use of coated-wall precious metal catalysts in the reforming section of IIR-SOFCs shows significant potential and is worthy of more detailed studies.

Acknowledgment

Nomenclature

k, k'' = apparent rate constant
$n1$, $n2$, $n3$, $n4$, $n5$ = reaction order
P_i = partial pressure of component i, bar
r = rate of reaction, mol·kg$_{cat}^{-1}$·s^{-1}
R_{gas} = gas constant, kJ·mol^{-1}·K^{-1}
SMR = steam methane reforming reaction
SOFC = solid oxide fuel cell
T = temperature, K

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