CATALYST CONFIGURATIONS FOR INDIRECT INTERNAL STEAM REFORMING IN SOFCs

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ABSTRACT

Indirect internal steam reforming of CH₄ in SOFCs requires efficient thermal coupling of the endothermic reforming reaction to the exothermic electrochemical oxidation reactions. However, if the reforming reaction is too fast local cooling can result in thermally-induced fracture of ceramic components. This can be alleviated by controlling the reforming rate and the heat transfers.

Our approach to this problem is twofold. Firstly, to develop oxide-based steam reforming catalysts which have a lower activity than conventional steam reforming catalysts while being highly resistant to carbon deposition, and secondly to control the reaction rate by means of mass transfer. The latter can be achieved by the introduction of a diffusive barrier near the outer surface of the catalyst. This paper presents an overview of the current work, which includes both experimental and modelling studies. The modelling results demonstrate how the different strategies can fulfil the overall requirements for controlling heat flows and chemical reaction rates. In the case of controlled activity oxide catalysts, we present experimental data for steam reforming over ceria catalysts which show that they also approach the activity requirements.

Keywords: methane reforming, catalysis, modelling, ceria

INTRODUCTION

The solid oxide fuel cell (SOFC) operates at high temperatures (500-1000°C) and can use H₂, CO or hydrocarbons as fuel. Direct operation on methane has proved elusive due to deactivation of the anode by carbon deposition and therefore it is usual to reform the methane (fully or partially) using steam or partial oxidation. Internal steam reforming is the most efficient and there is sufficient heat available from the fuel cell reaction for the complete conversion of methane (1). The internal reforming can be carried out directly on the anode catalyst (which remains susceptible to carbon deposition (2)), or indirectly on a separate catalyst before the fuel gas reaches the anode. Indirect internal steam reforming of methane requires efficient thermal coupling of the endothermic reforming reaction to the exothermic oxidation reactions. However, such coupling is not easy to
achieve because of the high activity of conventional steam reforming catalysts at the higher SOFC temperatures. Significant local cooling can result leading to thermally-induced fractures of ceramic components. The simple solution of diluting the steam reforming catalyst to reduce its activity per unit volume is unsatisfactory because of the inevitable carbon (and sulfur) deposition, which leads to catalyst deactivation (3), and for which there is little capacity if the catalyst area is reduced.

Our approach to this problem is twofold. Firstly, to develop oxide-based steam reforming catalysts which have a lower activity than conventional steam reforming catalysts while being highly resistant to carbon deposition, and secondly to control the reaction rate by means of mass transfer. The latter can be achieved by the introduction of a diffusive barrier near the outer surface of the catalyst. Under mass transfer control, the rate of the reforming reaction is reduced whilst the overall activity (per unit volume) can remain steady in the face of possible deactivation (4). However, it is possible that a combination of approaches may be needed.

This paper presents an overview of the current work, which includes experimental study of steam reforming over oxide catalysts, in particular Ce$_{0.9}$Gd$_{0.1}$O$_2$-$x$, and modelling of indirect internal reforming in an SOFC employing various catalyst types: a Ni steam reforming catalyst, an oxide-equivalent catalyst, and mass transfer limited steam reforming.

STEAM REFORMING OF METHANE OVER Ce$_{0.9}$Gd$_{0.1}$O$_2$-$x$ CATALYST

Ceria is noted for its ability to resist carbon deposition and to catalyse the combustion of carbon (5). It has been investigated as an anode material (or a constituent of composite anodes) for SOFCs using fuels such as syngas, methanol and methane (6, 7, 8). Studies of the reaction of methane with undoped, Gd-doped and Nb-doped cerias (9) indicated that the Gd-doped material was likely to have the best steam reforming activity.

Ce$_{0.9}$Gd$_{0.1}$O$_2$-$x$ (CGO) powder (Rhodia, France) was calcined for 1hr at 1000°C in order to minimize sintering at the maximum reaction temperature. The nitrogen BET surface area after calcination was 7.1 m$^2$ g$^{-1}$. Temperature programmed reaction (TPRx) at 25°C min$^{-1}$ and isothermal reaction were performed on 300 mg specimens with 1-5% CH$_4$ in Ar at atmospheric pressure in a quartz tube flow micro reactor with quadrupole mass spectrometer (QMS) gas analysis. Steam pressures to give CH$_4$:H$_2$O ratios between 0.6-5.5 were established by passing the gas through a water evaporator at 90°C followed by a condenser controlled at a lower temperature. Lines downstream were maintained at 70°C to prevent condensation. Temperature programmed oxidation (TPO) after cooling to room temperature under argon was carried out in 10% O$_2$ in He at 10°C min$^{-1}$.

Figure 1 shows a typical result of TPRx followed by isothermal steam reforming over CGO. Steam reforming began at 670°C producing H$_2$ and CO with a small amount of CO$_2$. The rate of CH$_4$ conversion increased rapidly with temperature passing through a maximum before reaching an approximately constant steady state level at 900°C after about 140 min. The reforming rate was proportional to the CH$_4$ concentration, but independent of the steam concentration (10). The steady-state turnover frequency at 900°C was 1.3 site$^{-1}$ min$^{-1}$, based on N$_2$ adsorption sites, (or 8.9x10$^{-5}$ mol min$^{-1}$ gm$^{-1}$).

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which is about $3\times 10^{-3}$ to $10^{-5}$ of the turnover frequency estimated for a Ni steam reforming catalysts at this temperature by extrapolation to 900°C and 5% CH$_4$ from measurements made at 500-600°C (11). The proportion of CO$_2$ in the products gradually increases with increasing H$_2$O/CH$_4$ ratio (Table 1) indicating an increasing contribution from the shift reaction. The temperature dependence (Figure 2) corresponds to an activation energy of 153 kJ mol$^{-1}$. No carbon deposition could be detected by TPO after steam reforming. The rate of steam reforming CH$_4$ at 900°C and activation energy are approximately equal to the values for the reaction with dry 5%CH$_4$ (12). This, together with the linear dependence on CH$_4$ concentration, suggests a steam reforming mechanism that is controlled by the reaction between chemisorbed CH$_4$ and lattice oxygen in the CGO surface.

![Figure 1](image.png)

**Figure 1** Mass spectrometer signal trends during TPRx / isothermal reaction of CGO with 5%CH$_4$. During the first 35 min the specimen was heated to 900°C at 25 °C/min as indicated by the temperature profile shown as a broken line. (Data have not been corrected for MS sensitivities).

| H$_2$O/CH$_4$ inlet | CO/H$_2$ outlet | CO$_2$/H$_2$ outlet |
|---------------------|-----------------|--------------------|
| 0.60                | 0.35            | 0.016              |
| 1.00                | 0.30            | 0.018              |
| 1.67                | 0.28            | 0.024              |
| 5.0                 | 0.17            | 0.030              |
| Theoretical reforming | 0.33          | 0                   |
| Theoretical with shift | 0.00           | 0.25               |
Figure 2  Arrhenius plot of turnover frequencies for reaction of dry methane with CGO and for steam reforming with 5 % methane / 5.5 % steam over CGO.

Figure 3  Schematic diagram of a solid oxide fuel cell with an indirect internal reforming reactor.

SIMULATION OF INDIRECT INTERNAL REFORMING

3.1 Coupled Fuel Cell and Reforming Reaction Reactor Modelling

In order to examine the interactions between indirect internal reforming and fuel cell reactions and evaluate various catalyst configurations, we have considered a generic tubular SOFC system illustrated schematically in Figure 3. The SOFC cathodes are on the outer surfaces of the tube and the anodes on the inner surfaces. There is a second inner tube of smaller diameter, concentric with the outer tube, which contains the reforming catalyst. Fuel is reformed as it passes along the inner tube reactor.
A conventional steady-state, heterogeneous, 2-D fixed-bed catalytic reactor model (13) was used for the inner reforming reactor and a steady-state 1-D model was used for the fuel cell reactions (14, 15). The SOFC model comprises mass balances of the fuel and air channels, energy balances of the same gas channels and the solid structure (cathode, electrolyte, and anode), and an electrochemical model that relates the gas stream compositions and temperatures to the current density, overpotentials, and cell voltage. The chemical species considered were CH₄, H₂O, CO, H₂, and CO₂ for the fuel, and O₂ and N₂ for the cathode gas. The molar flux in the gas channels was considered to be mainly convective in the flow direction. Simultaneous electrochemical conversion of H₂ and CO to H₂O and CO₂ was accounted for, the electrochemical reactions occurring only at the anode/electrolyte and cathode/electrolyte interfaces. On the anode side, it is assumed that the water gas shift reaction is at equilibrium. The thermal flux in the solid structure was assumed to be mainly conductive. In the gas channels, it was assumed mainly convective in the gas flow direction and conductive from the channels to the solid parts. An additional convective heat transfer between the anode gas stream and the adjacent inner reformer was also considered. It was assumed that all reaction enthalpies are released at the solid structure (16). Radiation was not considered explicitly at this stage, although it is likely to be significant at the high temperatures in the SOFC system.

The electrochemical model was based on the approach of Achenbach (17), using kinetic parameters for reactions at the anode and cathode without modification. Full details of the combined model for the SOFC and internal reformer will be presented elsewhere (18). The resulting system of differential and algebraic equations was solved using gPROMS (Centre for Process Systems Engineering) with the orthogonal collocation on finite elements method (19).

3.2 Simulation of Indirect Internal Steam Reforming Using Ni and CGO

The coupled model described above was used to simulate the influence of reforming catalyst characteristics on the performance of the tubular SOFC; with emphasis on the temperature profile and methane conversion along the tube. The length of the module was taken as 0.3 m and the diameter of the steam reforming inner tube was 2-3 mm. The diameter of the steam reforming catalyst particles was 0.2 mm. Steam reforming of CH₄ on the anode was neglected, as the concentration of CH₄ was very low in most cases. Inlet CH₄/ H₂O ratio was 0.5 with small amounts of hydrogen (essential for the modelling (20)). Air inlet temperature was 950°C, current density = 4x10³ A m⁻², and fuel utilization = 0.75

The base case catalyst was a Ni steam reforming catalyst for which the kinetics of the steam reforming and shift reactions were based on the work of Xu and Froment (20). Using the Ni catalyst diluted by 500, Figure 4, and a fuel inlet temperature of 900°C, the simulations show methane is rapidly converted resulting in a temperature minimum near the fuel inlet and a temperature difference of approximately 180°C along the length of the tube. Greater catalyst concentration resulted in almost instantaneous CH₄ conversion.
Figure 4. Simulation using a diluted (by 500) Ni catalyst for fuel inlet temperatures, $T_0$, of 900°C and 775°C.
(a) Temperature: -------- Reformer ($T_0 = 900$°C), ........... SOFC fuel channel ($T_0 = 900$°C),  --------- Reformer ($T_0 = 775$°C), .............. SOFC fuel channel ($T_0 = 775$°C).
(b) Reformer CH$_4$ mole fraction: _______ $T_0 = 900$°C, __________ $T_0 = 775$°C.

Figure 5. System behaviour using a Ni catalyst diluted by a factor $10^4$ to simulate an oxide catalyst for a fuel inlet temperature, $T_0$, of 900°C.
(a) Temperature: _____ Reformer ---- SOFC fuel channel; (b) Reformer CH$_4$ mole fraction
Reducing the fuel inlet temperature while maintaining the air inlet temperature, Fig. 3, smoothed the temperature profile, but increased the temperature difference along the tube to approximately 250°C.

The performance of oxide catalysts was simulated by approximating the activity to that of a Ni catalyst diluted by a factor of $10^4$. This also smoothed the temperature profile, Figure 5a, spread the CH$_4$ conversion more uniformly along the length of the reactor and reduced the temperature difference along the tube to about 120°C. The CGO catalyst studied experimentally had a significantly lower activity, see above, and gave predicted methane conversions approaching 40%.

![Figure 6](image)

(a) Temperature: -------- Reformer ----- SOFC fuel channel;
(b) Reformer CH$_4$ mole fraction

### 3.3 Simulation using a mass transfer limited catalyst

The mass transfer limited catalyst particle consisted of a core of conventional Ni catalyst surrounded by a porous mass transfer barrier. The characteristics of the mass transfer barrier and active catalyst distribution within the catalyst particle were taken from Aguiar et al (4) and had been optimised to maintain an approximately constant rate of reaction despite a reduction of the intrinsic catalyst activity because of deactivation. The effect of controlling the reaction rate by the mass transfer barrier is shown in Figure 6. This catalyst gave a smoother temperature profile, with a temperature difference along the tube of approximately 120°C. Clearly, the temperature profile requires an optimisation of the barrier properties.
CONCLUSIONS

A computational steady state model has been developed for analysing the coupling of reforming and electrochemical reactions in SOFCs, and evaluation of catalyst configurations. Simulation of the performance of an indirect internal reforming tubular SOFC has demonstrated that local temperature minima associated with rapid steam reforming over Ni (and by implication other metal) catalysts can be alleviated by mass transfer control or use of oxide catalysts, such as Ce$_{0.9}$Gd$_{0.1}$O$_{2-x}$.

Gd-doped ceria has useful catalytic activity for indirect internal steam reforming of methane in high temperature SOFCs and is extremely resistant to carbon deposition. The rate is proportional to methane concentration and independent of steam concentration (over the range investigated) and the activation energy is 153 ±10 kJ mol$^{-1}$. The reaction rate appears to be controlled by the reaction of chemisorbed methane with lattice oxygen in the ceria.

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