INTERNAL STEAM REFORMING OF PARTIALLY PRE-REFORMED NATURAL GAS IN SOFC STACKS

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ABSTRACT

Experiments have been carried out to determine the feasibility of operating Solid Oxide Fuel Cells with fuel gas mixtures of CH₄, H₂, H₂O, CO₂ and CO which would result from 6 to 16% pre-reforming of Victorian natural gas at steam/carbon ratios in the range 1.0 to 2.5. Electrode overpotentials and cell ohmic resistances were measured by the galvanostatic current interruption technique and anode off-gas composition was analysed by gas chromatography. Cell voltages under current load were recorded for up to 200 hours. The experimental data obtained on Ni based cermet anodes have been compared with modelled data using kinetic expressions derived in this laboratory and from the literature.

INTRODUCTION

Internal steam reforming of natural gas in SOFC stacks is an attractive option offering faster response to load variations and significant cost reductions in operating costs (due to higher efficiency) and capital investment (due to simpler balance of plant). This approach, however, may pose some problems such as carbon formation in the stack and, depending on the design, excessively large temperature gradients across an interconnect plate due to endothermic cooling. Partial pre-reforming of natural gas is considered to be one way of reducing the extent of these problems. In the most optimistic scenario only higher hydrocarbons need to be converted directly into CH₄, CO and CO₂ by steam-reforming while CH₄ in the fuel remains unconverted. For Victorian natural gas this corresponds to about 12% pre-reforming.

In recent years a limited number of papers have been published on studies of internal steam-reforming of methane (1-5) in solid oxide fuel cells. However, no experimental investigations of steam-reforming of partially pre-reformed natural gas have been reported. In the present work fuel-gas mixtures resulting from 6 to 16% pre-reformed Victorian natural gas at steam-to-carbon (S/C) ratios of 1.0 to 2.5 were fed into the single cell stacks and their performance monitored under load over a period of up to

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200 hours. The corresponding anode-off gas composition was analysed by gas chromatography after condensing and separating the steam. Ohmic and overpotential losses were measured for a range of conditions using the galvanostatic current-interruption technique. Cell performance parameters and anode-off-gas compositions were modelled using three methane reforming rate equations, two derived from kinetic studies in this laboratory and one from the literature.

METHODS AND MATERIALS

The experimental data were measured in an electrochemical reactor designed for planar solid oxide fuel cells. The data tabled in this paper were measured on a Nickel/zirconia based cermet anode which was optimised for methane internal reforming (Anode 1) at S/C ratios in the range 1 to 2.5. Kinetic data were obtained at S/C ratios 1 to 3 on Anode 1 and also on a standard Ni cermet anode. The anode and the LSM cathode were printed onto a 3YTZ electrolyte sheet, with an LSM reference electrode on the reverse side. The area of the working electrode was 10.2 cm². Current collectors were attached to both the working electrodes, and voltage probes were connected to all electrodes. The cell was sealed with glass on the anode side, and the cathode side was exposed to air. The reaction chamber as well as inlet and outlet tubes were constructed of alumina to avoid any aggravation of carbon formation by catalytically active wall materials in the fuel passage lines. The fuel gas (flow rate in the range 300-400 ml/min) entered the reactor in an up-flow direction after passing through a controlled temperature humidifier, while air was flowing over the cathode.

RESULTS AND DISCUSSION

The data in Table 1 show that cell voltages increase as S/C ratios are lowered, mainly due to higher open-circuit voltages at lower S/C values which outweigh the higher overpotential losses measured at lower steam-carbon ratios (see Figure 1). The open-circuit voltage is determined by the oxygen partial pressure difference between anode and cathode side which is controlled by the H₂/H₂O and CO/CO₂ equilibria on the anode side, both of which depend on the S/C value, and on the partial pressure of O₂ at the cathode.

Figure 1 shows an increase in anode overpotential with decreasing S/C whereas the IR drop is essentially independent of the S/C value for S/C>1. The trends in anode overpotential suggest increased electrode polarisation at lower S/C values. An interesting observation in Figure 1 is that cathode overpotentials also increased as the S/C values decreased. At high steam to carbon ratios both anode and cathode overpotentials approached the values measured for H₂ fuel. Whereas the increase in the anode overpotential with decreasing S/C value and thus increasing methane concentration is
plausible, the reason for the observed increase in cathode overpotential is not immediately obvious, and more work needs to be performed to explain this phenomenon.

In Table 1 the experimental anode off-gas compositions for fuel-gas mixtures at different steam-carbon ratios were compared with calculated values using rate expressions derived from kinetic studies in this laboratory. Also shown in the table are computed and experimental cell voltages. The values obtained in this study were also compared with data modelled using the expression for steam reforming published by Achenbach et al (3).

The kinetic studies of steam reforming at S/C ratios in the range 1 to 3 show a dependence of the reforming kinetics on pH₂O and on the type of anode surface. On the standard Ni/ZrO₂ anode the reforming reaction was found to be fast, and the rate data fitted best the expression:

\[-r(CH₄) = 8542 \cdot (pCH₄)^{0.85} \cdot (pH₂O)^{-0.35} \cdot \exp(-95/RT) \quad [1]\]

This dependency is in contrast to the findings by Achenbach who reported a rate expression

\[-r(CH₄) = 4274 \cdot (pCH₄) \cdot \exp(-82/RT) \quad [2]\]

which is independent of the partial pressure of steam at S/C ratios in the range 2 to 8. In the steam reforming literature, kinetic expressions with partial pressure dependencies of first order in methane and zero order in steam such as Equation 2 as well as expressions with negative reaction orders with respect to steam have been reported (6), largely dependent on the type of catalyst and its microstructure. Notwithstanding the differences in the kinetic expressions on Ni/ZrO₂ of Achenbach [Equation 2] and ours [Equation 1], the model calculations yield fairly similar product distributions (see Table 1).

In order to open up the operational window for steam reforming over a wider range of S/C ratios, reforming catalysts are modified by addition of basic compounds (for example alkali and alkaline earth metals) for suppression of carbon deposition by improving steam retention (6). This approach proved effective also for SOFC anodes as demonstrated by Singh et al (7) who reported reduced carbon deposition tendencies in internal steam reforming in SOFC's when the Ni/zirconia cermet anode was modified by impregnation with salts of Mg, Ca, Al, Sr, Ce and Ba followed by calcination to form the appropriate oxides. However, modifications of this type, in general, result in lower reforming rates and increased negative reaction orders with respect to steam. Only Zhuang et al. (8) found low coking tendencies as well as higher steam reforming rates for ceria doped Ni/MgAl₂O₄ catalysts. In contrast, Belyaev et al (5) who studied the kinetics of steam reforming on a Ni-ZrO₂-CeO₂ anodes in SOFC at S/C > 2, found lower reforming rates and an activation energy of 163 kJ/mol which was somewhat higher than the more common values of 100 to 150 kJ/mol. The anodes developed for internal methane
reforming at CFCL (Anode 1) also show lower reforming rates and a higher activation energy. Furthermore, a stronger pressure dependence on both pCH₄ and pH₂O was observed compared to the standard Ni/YSZ anodes [Equation 3].

\[-r(CH_4) = 3.6 \times 10^8 (pCH_4)^{1.4} (pH_2O)^{-0.8} \exp(-208/RT)\]  

[3]

The data listed in Table 1 clearly show that both the kinetic expression of Achenbach [Equation 2] and our derived expression [Equation 1] on Ni/ZrO₂ predict higher amounts of H₂ in the anode off-gas for all S/C ratios, and the amounts of CO₂ predicted are less than the experimental value. In addition these expressions predict nearly complete consumption of methane whereas experimentally about 1-2% methane remained unconverted. Equation 3 gives a closer match to H₂ and CO₂ concentrations, but the predicted CO values are lower than the values measured experimentally and the methane concentrations are higher except at a S/C ratio of 1. In general, none of the kinetic expressions employed match perfectly the experimental observations over the complete range of S/C ratios. The discrepancies found may arise from (i) the omission of carbon-forming reactions in the calculations, and (ii) possible uncertainties in experimental measurements of inlet flow rates and exit-gas composition which could account for ± 5% error.

Although small amounts of carbon may be formed during the internal steam reforming experiments reported in this study, short term stability data at various steam/carbon ratios are encouraging. Figures 2 and 3 show the performance of a single cell stack operated on 6 and 16% pre-reformed Victorian natural gas over a period of up to 200 hours at S/C ratios of 2 and 1 respectively. The figures clearly demonstrate the feasibility of operating with low steam/carbon ratios with partially pre-reformed natural gas.

CONCLUSIONS

This study demonstrated the feasibility of operating Solid Oxide Fuel Cells at steam/carbon ratios of 1.0 to 2.5 with natural gas which is pre-reformed to relatively low extents. No significant drop in cell voltage was observed during tests of up to 200 hours. Both anode and cathode overpotentials increased with decreasing steam/carbon ratios, but cell voltages at lower steam/carbon ratios were still higher, and therefore yielded higher electrical and overall efficiencies.

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Table 1: Cell Voltage and anode off-gas composition at 200 mA/cm² over Anode 1 with a) S/C=2.5, b) S/C=2.0, c) S/C=1.5 and d) S/C=1.0.

(a) S/C=2.5, OCV=915 mV

|                | Measured | Eqn(1) | Eqn(2) | Eqn(3) |
|----------------|----------|--------|--------|--------|
| Cell Voltage (V) | 0.66     | 0.68   | 0.68   | 0.63   |
| H₂ (%)         | 68.9     | 74.3   | 74.3   | 67.3   |
| CO (%)         | 17.4     | 18.6   | 18.6   | 14.5   |
| CO₂ (%)        | 11.0     | 7.1    | 7.1    | 9.2    |
| CH₄ (%)        | 2.7      | 0.0    | 0.03   | 9.0    |

(b) S/C=2.0, OCV=940 mV

|                | Measured | Eqn(1) | Eqn(2) | Eqn(3) |
|----------------|----------|--------|--------|--------|
| Cell Voltage (V) | 0.69     | 0.70   | 0.70   | 0.65   |
| H₂ (%)         | 70.7     | 74.3   | 74.3   | 68.5   |
| CO (%)         | 19.4     | 20.4   | 20.4   | 16.8   |
| CO₂ (%)        | 8.1      | 5.3    | 5.3    | 7.1    |
| CH₄ (%)        | 1.7      | 0.0    | 0.04   | 7.7    |

(c) S/C=1.5, OCV=976 mV

|                | Measured | Eqn(1) | Eqn(2) | Eqn(3) |
|----------------|----------|--------|--------|--------|
| Cell Voltage (V) | 0.70     | 0.73   | 0.73   | 0.68   |
| H₂ (%)         | 70.1     | 74.2   | 74.1   | 69.8   |
| CO (%)         | 22.0     | 22.7   | 22.7   | 19.8   |
| CO₂ (%)        | 5.8      | 3.1    | 3.2    | 4.5    |
| CH₄ (%)        | 2.2      | 0.0    | 0.06   | 6.0    |

(d) S/C=1.0, OCV=1070 mV

|                | Measured | Eqn(1) | Eqn(2) | Eqn(3) |
|----------------|----------|--------|--------|--------|
| Cell Voltage (V) | 0.75     | 0.80   | 0.79   | 0.75   |
| H₂ (%)         | 69.1     | 73.9   | 73.9   | 72.2   |
| CO (%)         | 27.4     | 25.5   | 25.4   | 24.3   |
| CO₂ (%)        | 1.6      | 0.6    | 0.6    | 1.1    |
| CH₄ (%)        | 1.9      | 0.0    | 0.1    | 2.4    |

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Fig. 1 Electrode overpotentials and ohmic resistance values on Anode 1 as function of fuel composition (hydrogen or methane-steam at various S/C ratios)

Fig. 2 Internal steam reforming over Anode 1 using 6% pre-reformed Victorian Natural Gas with S/C=2 at 900°C (j=200 mA/cm²; U_f=49%)

Fig. 3 Internal steam reforming over Anode 1 using 16% pre-reformed Victorian Natural Gas with S/C=1 at 900°C (j=200 mA/cm²; U_f=40%)