OPERATION OF LOW-TEMPERATURE SOFCs ON PURE METHANE AND ETHANE WITHOUT CARBON DEPOSITION

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ABSTRACT

The feasibility of direct electrochemical oxidation of methane and ethane without carbon deposition was demonstrated at novel low-temperature solid oxide fuel cells (SOFCs). Power densities up to 0.37 W/cm² at 650°C were measured for single cells operating with pure methane as the fuel and atmospheric-pressure air as the oxidant. The measured power densities were competitive with fuel cells operated on hydrogen. Key factors for successful methane operation were the low operating temperatures and the incorporation of (Y₂O₃)₀.₁₅(CeO₂)₀.₈₅ − YDC in the Ni-based anodes. In addition, it was found that reducing the anode Ni content enabled carbon-free operation with ethane fuel at 500°C.

INTRODUCTION

Most potential near-term applications of fuel cells require the use of hydrocarbon fuels such as methane, for which a supply infrastructure is currently available. However, fuel cells typically operate only with hydrogen as the fuel. Fuel cells that could operate directly on hydrocarbon fuels would eliminate the need for a fuel reformer, providing considerable system and economic advantages and presumably improving the viability of the technology.

In prior examples where fuel cells have utilized hydrocarbon fuels directly, significant problems have been encountered. First, the direct-methanol polymer electrolyte fuel cell produces relatively low power densities, requires prohibitively large Pt loading of the anodes, and the methanol fuel can permeate the electrolyte (1,2). In addition, only alcohol fuels appear feasible. Second, solid oxide fuel cells (SOFCs) can utilize hydrocarbons directly via internal reforming. In this approach, a hydrocarbon fuel (e.g. methane) is combined with H₂O and/or CO₂, which are typically obtained by recirculating the fuel cell exhaust, and introduced directly to the SOFC anode. The commonly used Ni-based anodes provide the catalyst for the endothermic reforming reactions,

\[
\begin{align*}
\text{CH}_4 + H_2O & = 3H_2 + CO & \Delta H^{298} = 206kJ/mol \text{ CH}_4 \quad [1] \\
\text{CH}_4 + CO_2 & = 2H_2 + 2CO & \Delta H^{298} = 247kJ/mol \text{ CH}_4. \quad [2]
\end{align*}
\]

However, maintaining appropriate gas composition and temperature gradients across a large area SOFC stack is challenging (3,4). If the reforming reactions are slow, then
insufficient H₂ is supplied to the SOFCs. On the other hand, fast reforming reactions cause cooling localized near the fuel inlet, leading to poor cell performance and possible cell fracture. Thus, current demonstration SOFC stacks do not take full advantage of internal reforming; rather, they employ a combination of external and internal reforming of hydrocarbon fuels (5). Third, SOFCs can in principle operate by direct electrochemical oxidation of a hydrocarbon fuel. This approach would be desirable since it eliminates the problems with internal reforming mentioned above, and the theoretical maximum fuel efficiency is as good or better than that for reforming. However, prior attempts to operate SOFCs in this way have been largely unsuccessful, resulting in carbon deposition (6,7) at temperatures above ≈ 800°C and low power densities (6,8) (∼ 10 mW/cm²) below 800°C. Recently-developed SOFCs have produced high power densities with hydrogen fuel at relatively low temperatures (9-15) (Tc = 600-800°C); thus, they have the potential to provide good power densities with hydrocarbon fuels in a temperature range where carbon deposition can be avoided.

In this paper, we report results showing low-temperature (<700°C) operation of SOFCs using methane and ethane fuels. The addition of (Y₂O₃)₀.₁₅(CeO₂)₀.₈₅ (YDC) to the anode played a key role by increasing hydrocarbon oxidation rates. A generalization of the single-cell results to fuel cell stack operation is discussed.

EXPERIMENTAL PROCEDURES

Methane oxidation was studied in SOFCs that were fabricated on porous La₀.₈Sr₀.₂MnO₃ (LSM) cathode supports (16). The LSM pellets were ∼ 2cm in diameter and 1mm thick, and were produced using standard ceramic processing techniques. The SOFC layers, starting with a 0.5μm-thick YDC porous film, were deposited on the LSM pellet using dc reactive magnetron sputtering. The electrolyte, 8 mol% Y₂O₃-stabilized ZrO₂ (YSZ), was subsequently sputter deposited under conditions yielding a dense 8μm thick film. To complete the cell, another 0.5μm-thick YDC film was deposited, followed by a porous, 2μm-thick Ni-YSZ anode. Cell tests were performed at operating temperatures ranging from 550-650°C. Following the cell tests scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) were used to detect any carbon deposition that may have resulted at the anode.

To determine the role of YDC at the anode, fuel reactions were studied at Ni-YSZ and Ni-YSZ/YDC anodes using impedance spectroscopy. The impedance samples were prepared by sputter depositing an anode onto both sides of bulk YSZ single-crystal electrolytes (17). The measurements were collected in various fuel environments at 600°C.

Ethane fuel reactions were studied in SOFCs with anodes of low Ni content. Various cells were made using Ni-YDC anodes containing 10, 20, and 40 weight percent Ni. The porous Ni-YDC anodes were ∼ 2μm-thick. The cell structure and processing was similar to that described above, except that the cathode was an LSM-YSZ mixture. In order to identify carbon-free operating conditions, the Ni-YDC anodes were tested in ethane fuel environments at temperatures ranging from 500-700°C. Current-voltage measurements of cells were taken under operating conditions that avoided carbon deposition.

1002 Electrochemical Society Proceedings Volume 99-19
RESULTS AND DISCUSSION

Methane Fuel Utilization

Single-cell current-voltage measurements were carried out in air and methane. The results for dry and wet (with 3% H₂O) methane were nearly identical. Cell performance was stable in our preliminary 100 h life tests, except for wet methane at low voltages where the anode Ni gradually oxidized. Figure 1 shows the measured current density and power density vs. voltage. The open-circuit voltage (OCV) was 1.06V. The current density vs. voltage curves were non-ohmic indicating a substantial electrode overpotential. Based on prior studies of these cells operated on hydrogen fuel (14), the current densities were limited primarily by cathode overpotential. Current densities increased with increasing temperature, such that maximum power density increased from 250 mW/cm² at 600°C to 370 mW/cm² at 650°C. Similar results were obtained for cells operated with humidified hydrogen fuel, except that the power densities were ~ 20% greater (14). Visual observation, EDX, and SEM observations of the anodes, carried out after the cell tests, showed no evidence of carbon deposition after ~ 100 hrs of operation.

Successful cell operation on dry methane indicated that direct electrochemical oxidation,

\[
\text{CH}_4 + 2\text{O}_2 = 2\text{H}_2\text{O} + \text{CO}_2 \quad \Delta G^\circ(600^\circ\text{C}) = -800 \text{kJ/mol} \quad [3]
\]

was the primary anode reaction mechanism. The OCV values measured in methane, typically =1.06V, were typically very close to the values measured for these cells operated with 97%H₂+3%H₂O fuel. This is reasonable given that the \( \Delta G^\circ(600^\circ\text{C}) \) values are similar for eq. 3 and hydrogen oxidation. The exact Nernst potential for eq. 3 cannot be calculated since the H₂O and CO₂ partial pressures are not known, but the measured OCVs suggest reasonable values, <0.18 atm for H₂O and <0.09 atm CO₂.

Methane reforming may have also played a role in the cell operation, but only after H₂O and CO₂ were produced by reaction [3]. Reforming rates were probably too low to contribute significantly to the anode reaction, because of the small anode area (= 1cm²) and low temperature (3). Furthermore, relatively high fuel flow rates were used that tended to flush any reformation reactants and products from the anode compartment.

Direct methane oxidation is further evidenced by impedance spectra (Figure 2) obtained from these same Ni-YSZ/YDC anodes in humidified methane (a) and humidified dilute H₂ (b). This 3%H₂+3%H₂O+94%Ar mixture, which was used to simulate a slightly reformed methane fuel, yielded electrode arcs with a much different shape than those for methane. This indicated the primary anode reaction with methane was not oxidation of hydrogen produced by reforming. Also shown in Fig. 2 is the impedance result for the anode operated in 97%H₂ + 3%H₂O (c). This electrode arc was much smaller than that for methane, indicating a lower anode overpotential and explaining why the SOFC current densities were higher for hydrogen than methane.
The rapid direct electrochemical oxidation of methane at these temperatures was due to the unique anodes employed in these SOFCs (17), which combined Ni-YSZ and YDC layers. This is illustrated in Fig. 3, which compares the impedance spectra taken in humidified methane for Ni-YSZ/YDC and Ni-YSZ anodes. The YDC layer causes a factor of $\approx 6$ decrease in the electrode resistance. This agrees with prior studies indicating that ceria promotes hydrocarbon oxidation (18), and is probably related to the capability of ceria to store and transfer oxygen (19). A recent study has shown that the oxygen storage capability of ceria is enhanced by the addition of zirconia (19). The present anodes have two ceria/zirconia interfaces where enhanced oxygen storage may increase methane oxidation rates.

Another important result from the cell tests was the absence of carbon deposition. In general, carbon deposition can occur by methane pyrolysis,

$$CH_4 = C + 2H_2, \quad [4]$$

or disproportionation,

$$2CO = C + CO_2. \quad [5]$$

On the other hand, the oxygen flux arriving at the anode during SOFC operation tends to react with any carbon, suppressing carbon deposition (7). The role of methane pyrolysis was tested by flowing pure methane over SOFC anodes, without SOFC operation, such that no oxygen ion flux or reaction products were present. No carbon deposition was observed at <700°C, and the amount of carbon deposited increased with increasing temperature above 700°C. Thus, carbon deposition via the methane pyrolysis reaction did not occur readily at low temperatures.

During cell operation, product gases are present in the anode compartment, and carbon deposition can occur via reaction [5]. As noted above, the present cell tests provide data for nearly pure methane in the anode compartment, since the small-area cells and relatively high fuel flow rates resulted in small concentrations of reaction products. However, it is important to consider the situation that would be encountered in a SOFC stack, where the products of reactions [1]-[3] would be present at substantial partial pressures. Thus, we have carried out a simple equilibrium calculation to determine the conditions where one would expect carbon-deposition-free stack operation in CO-CO$_2$ mixtures. Figure 4 shows the CO/CO$_2$ partial pressure ratio at equilibrium with graphitic carbon (eqn. 5) vs. temperature, for two CO + CO$_2$ total pressures. For sufficiently low CO/CO$_2$ ratios, carbon deposition will not occur. Based on this figure, the optimal temperature range for SOFC stack operation on dry methane is 500-700°C. That is, if the temperature is <500°C, carbon deposition proceeds by reaction [5] unless CO/CO$_2$ ratios are very low. While temperatures $\geq$700°C would tend to suppress carbon deposition by reaction [5], they would allow carbon deposition by direct pyrolysis of methane (eq. 4).

Some internal reforming would be necessary in a SOFC stack to produce a small amount of CO and H$_2$. These would balance the CO$_2$ and H$_2$O produced by direct oxidation, preventing too low CO/CO$_2$ and H$_2$/H$_2$O ratios where the anode Ni may oxidize. Ni oxidation was indeed observed under some cell test conditions when 0.03atm
H₂O was intentionally added to the methane fuel. This presumably indicates that reforming rates were too low to produce substantial H₂.

**Ethane Fuel Utilization**

Ethane oxidation was studied at Ni-YDC anodes using low Ni concentrations intended to limit carbon deposition. Table 1 summarizes carbon deposition results at the various Ni-YDC anodes exposed to dry and wet (3% H₂O) ethane from 500 - 600°C. These reaction studies were made without cell operation and indicate the onset of carbon deposition for the given conditions. In wet ethane, anodes with lower Ni content (10-20wt%) were more resistant to carbon deposition at higher temperatures. For dry ethane fuel, carbon deposition occurred even for low temperatures and anodes with low Ni content. These observations suggest that carbon-deposition-free cell operation should be possible using wet ethane with any of the above anode compositions at 500°C, and up to 550°C for anodes with 10-20wt% Ni.

The performance of a cell operating with wet ethane fuel at 500°C is illustrated in figure 5. In this case the Ni-YDC anode contained 40wt% Ni. The cell current densities were relatively low because of the low temperature. Current densities for ethane fuel were typically about 35% less than for hydrogen fuel. A maximum of ≈35mW/cm² was obtained with ethane. No carbon deposition was detected. Carbon-deposition-free cell operation with anodes of lower Ni content (10-20wt%) was achieved up to 600°C, which is beyond the temperature range indicated by the carbon reaction studies given in Table 1. This suggests that the oxygen flux arriving at the anode during cell operation reacted with any carbon, thereby suppressing carbon deposition. However, cell power densities were quite low in these cells, either because of low anode electrical conductivity or low Ni catalyst content.

**SUMMARY AND CONCLUSIONS**

In summary, we have demonstrated high power density SOFCs that operate by direct electrochemical oxidation of methane without carbon deposition. The YDC/Ni-YSZ anodes played a key role in providing rapid methane electrochemical oxidation rates. The results, combined with a simple thermodynamic analysis, suggest that SOFC stacks could operate in the temperature range from ≈500 to 700°C without carbon deposition. Direct oxidation provides a desirable method for utilizing methane fuel, avoiding the difficulties associated with reforming. Indeed, this may be the only feasible approach for low-temperature SOFCs, since extrapolation of internal reforming rate data below 750°C suggests that reforming rates become prohibitively small (3). In addition, the preliminary findings for ethane fuel indicate that the direct use of ethane is possible in low-Tc SOFCs. As low-Tc SOFC current densities improve, such cells may become a viable option.

**ACKNOWLEDGEMENTS**

We thank the Illinois Minority Graduate Incentive Program for providing the funding that supported Erica Perry Murray on this research project.
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Table 1. Conditions that limit and promote carbon deposition are shown for the various Ni-YDC anodes. The (number) indicates Ni weight percent.

| Fuel          | Anode  | 500°C | 550°C | 600°C |
|---------------|--------|-------|-------|-------|
| wet ethane    | Ni(10)-YDC |      |       |       |
|               | Ni(20)-YDC |      |       |       |
|               | Ni(40)-YDC |      |       |       |
| dry ethane    | Ni(10)-YDC |      |       |       |
|               | Ni(40)-YDC |      |       |       |

1006 Electrochemical Society Proceedings Volume 99-19
Figure 1. Cell voltage and power density vs. current density for an SOFC operated on air and methane.
Figure 2. Comparison of electrode impedance spectra for Ni-YSZ/YDC anodes measured at 600°C in a) 97% CH₄ + 3% H₂O, b) 3% H₂ + 3% H₂O + 94% Ar, and c) 97% H₂ + 3% H₂O.

Figure 3. Impedance spectroscopy results for Ni-YSZ and Ni-YSZ/YDC anodes in 97%CH₄ + 3% H₂O at 600°C.
Figure 4. CO/CO$_2$ ratios at equilibrium with graphitic carbon calculated based on reaction (5).

Figure 5. Cell power density vs. current density for an SOFC operated on air and ethane.