PROPAINE FUELED SOLID OXIDE FUEL CELLS

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ABSTRACT

This paper describes recent results on the operation of SOFCs with propane fuel. Two strategies have been employed. First, conventional anode supported SOFCs have been operated with propane-air mixtures. In this case, the cells operate by internal partial oxidation; for propane contents < 11% (oxygen-to-propane molar ratios > 1.7), there was no carbon deposition detected at 800°C. Power densities as high as 0.6 W/cm² were obtained at 800°C. Second, thick-GDC-electrolyte SOFCs with ceramic-based anodes have been operated with slightly humidified propane without coking, yielding power densities up to 0.14 W/cm² at 750°C. These cells were cycled between propane and air several times without anode degradation.

INTRODUCTION

Propane is interesting as a fuel for portable and remote fuel cell power generation applications because it is widely available, has a high energy density in liquid form, and also has a sufficiently high vapor pressure at ambient temperature to obviate the need for a fuel pump/blower. SOFCs are a logical choice for small-scale generators using propane as a fuel, since they can provide high power density and have good fuel flexibility. The energy densities of liquid propane (46.4 MJ/kg, 22.8 MJ/l) are considerably larger than for methanol (19.9 MJ/kg, 15.8 MJ/l), a fuel used in proton-exchange membrane fuel cells (PEMFC). In addition, methanol is normally mixed with water for use in PEMFCs, further reducing the energy density. Thus, propane-fueled SOFC portable generators have a fundamental advantage over direct-methanol PEMFC generators.

In principle, propane can be externally reformed to produce hydrogen-rich fuel for SOFC operation. However, this introduces unwanted additional size, weight, and complexity for small-scale generation applications. It would be more practical to directly introduce propane to the SOFC. Two approaches have been used with propane and a similar fuel, butane. First, single-chamber SOFCs have been reported where a fuel-air mixture is supplied to the cell and internal partial reforming generates hydrogen at the SOFC anode (1). Alternatively, SOFCs with novel anodes, based either on Cu (2) or conducting ceramics (3), have been reported to work with essentially pure propane or butane.

In this paper, we report on the operation of conventional anode supported SOFCs operated with propane-air mixtures, and thick-Ce₀.₉Gd₀.₁O₁.₉₅ (GDC)-electrolyte SOFCs with ceramic-based anodes operated directly on propane.
EXPERIMENTAL

Ni-YSZ anode supported cells were prepared using centrifugal casting of the YSZ electrolyte layer, as described elsewhere (4). LSM-YSZ cathode layers were painted onto the YSZ electrolyte and sintered at 1250°C.

For the electrolyte supported cells, GDC powders were pressed into pellets with ~ 3 wt% binder. In some cases, anode inks were painted onto the electrolytes and then co-sintered for 6 h at 1500°C. This yielded dense electrolytes = 0.3 mm thick with a diameter of = 12 mm. In other cases, the anodes were applied after high-temperature electrolyte sintering, and then sintered for 3 h at 1100°C. Anodes were a ceramic-based composite previously reported to work well with hydrocarbon fuels without coking (3). These novel anodes are a mixture of doped LaCrO₃ (either La₀.₈Sr₀.₂Cr₀.₉₇V₀.₀₃O₃₋₈, LSCM, or La₀.₈Sr₀.₂Cr₀.₉₇V₀.₀₃₀₃₋₈, LSCV), GDC, and = 4 wt% Ni. Finally, cathode inks, consisting of a mixture of LSCF (La₀.₆Sr₀.₄Ca₀.₂Fe₀.₈O₃₋₈) and GDC, were painted on and sintered for 3 h at 900°C. The electrode areas were = 0.5 cm² and thicknesses were 10-20 μm.

For cell testing, the anode sides of the pellets were sealed to alumina tubes using Ag ink. Current collector grids were painted on the electrodes using either Ag or Au inks. The SOFCs were tested in a tube furnace at temperatures from 500°C to 800°C. Fuels, either H₂ or C₃H₈, were supplied to the anode via an alumina feed tube, and ambient air was maintained on the cathode side. Current-voltage curves were obtained using a constant current power supply. Impedance spectroscopy was performed during these tests using a Solartron 1260 impedance analyzer. Exhaust gases were sampled using a differentially pumped mass spectrometer.

THERMODYNAMIC CALCULATIONS

A simple thermodynamic calculation similar to that reported by Koh (5) was carried out to predict expected results of SOFC operation on propane and propane-air mixtures. Equilibrium reaction products, including solid carbon, were determined, and expected open-circuit voltages were calculated. Figure 1 shows the equilibrium product distribution at 800°C versus the oxygen-to-propane ratio R. The main products at low R are C and H₂; i.e., the reaction is hydrocarbon cracking. With increasing R, carbon deposition decreases continuously as CO production increases, until C eliminated entirely for R ≥ 1.6. This is slightly greater than the stoichiometric ratio for partial oxidation, R = 1.5. At R = 1.6, the reaction is essentially partial oxidation, with only small amounts of H₂O and CO₂ produced. For R increasing above 1.6, H₂ and CO decrease continuously as H₂O and CO₂ concentrations begin to increase.

The trends shown in Figure 1 change considerably as the temperature is decreased, as illustrated in Figure 2 for R = 1.7. H₂ remains a prevalent product at all temperatures, but the CO content decreases to very low values for T < 550°C. The equilibrium fractions of H₂O and CO₂ become more substantial at lower temperature. An increasing amount of oxygen is required to produce these larger H₂O and CO₂ amounts, with the result that coking is expected for T < 750°C. Indeed, increasing R values are required to prevent coking as T decreases. This trend is shown in Figure 3. Coking is not eliminated until R > 4.5 at 400°C; this quite high value and the results in Figure 2 indicate that coking
occurs unless the fuel is almost entirely oxidized. Thus, from equilibrium considerations, operating temperatures > 700°C are actually most desirable for coke-free operation with propane fuel. Of course, the kinetics of the various reactions are expected to have significant impact.

**Figure 1.** Equilibrium products expected as a function of oxygen-to-propane ratio at 800°C. The fuel is a mixed gas of propane, oxygen and argon, and the ratio of argon to oxygen is 4.

**Figure 2.** Calculated product distribution at open circuit condition as a function of temperature for an inlet mixture of 10.7% propane, balance argon-oxygen in a 4:1 ratio, corresponding to an oxygen-propane ratio R = 1.7.
Figure 3. The critical oxygen-to-propane ratio R above which no carbon deposition is expected, versus temperature.

Finally, the equilibrium calculations were also used to estimate open circuit voltages expected for propane operation. For R = 1.7, the predicted OCV is 1.04-1.07 V. For R = 0.03 (i.e., humidified propane), the predicted OCV is 1.18-1.24 V.

INTERNAL PARTIAL OXIDATION RESULTS

A differentially-pumped mass spectrometer system was used to sample the anode exhaust gas. 80% Ar - 20% O2 mixtures were used with propane instead of air in order to avoid interference between N2 and CO at mass 28. Pure propane showed a large number of peaks including the singly ionized peak at 44 AMU and a strong peak at 29 AMU. The multiple peaks are due to cracking caused by electron beam bombardment in the mass spectrometer. Figure 4 shows an example of a mass spectrometer measurement versus cell temperature, taken with no current flowing through an anode-supported cell. The inlet mixture was 10.7% propane, with the balance being the 20% oxygen-Ar mixture (R = 1.7). The C3H8 and O2 amounts decreased with increasing temperature, but they were not completely consumed, showing that the reaction did not reach equilibrium, particularly at lower temperatures. CO and H2 increased with increasing temperature, in reasonable agreement with the equilibrium concentration predictions shown in Figure 2, but the H2 concentration was much smaller than expected. This may be due to the presence of significant quantities of higher mass ions in the mass spectrometer, which interfere with the observation of hydrogen, a phenomenon known as zero blast. H2O and CO2 stayed fairly constant, instead of increasing with decreasing temperature as in Figure 2, presumably because of the incomplete reaction of propane and oxygen. Substantial amounts of CO and H2 were produced over a wide range of temperatures, suggesting that effective SOFC operation should be possible.
Figure 4. Measured gas composition as a function of temperature for a propane-air mixture (10.7% propane) flowed over a Ni-YSZ anode at open circuit condition.

Figure 5 shows the anode-supported SOFC performance results in a 10.7% propane mixture. The maximum power density was ≈ 0.6 W/cm² at 800°C. Temperatures were measured by a thermocouple placed close to the cell; note that the measured temperature was typically ≈ 30°C higher than the furnace temperature due to the heat of partial oxidation. The concave-down curvature is rather unusual for the relatively low current densities shown here; the usual interpretation of this type of I-V curve is a gas-diffusion limitation in the anode. This may be related to the relatively slow diffusion expected for 10.7% propane in air. For comparison, the results for the same cell operated with hydrogen yielded similar power densities, but showed the typical concave-up curvature. The open circuit voltage obtained with the propane-air mixture, 0.9 – 0.95 V, was lower than observed with hydrogen, and lower than calculated for this gas composition assuming equilibrium is reached in the anode, ≈ 1.0V.

DIRECT PROPANE RESULTS

Tests were also carried out with GDC-electrolyte supported cells with humidified (3% H₂O) propane, R = 0.03, as the fuel. A ceramic-based anode with a small amount of Ni was used in order to minimize coking (3). Figure 6 shows the performance at different
Figure 5. Performance of an anode supported fuel cell NiO – YSZ | YSZ film | LSM-YSZ fueled by 10.67% C3H8 – 89.33% (O2 – 4 Ar) at a flow rate of 300 sccm at different temperatures.

temperatures. The open circuit voltage (OCV) decreased with increasing temperature, a direct result of the mixed conductivity of the GDC electrolyte (6). The cell resistance also decreased rapidly with increasing temperature, resulting in an increase in power density despite the lower OCV. Impedance spectroscopy measurements during the cell test showed that both the electrolyte ohmic loss and the polarization resistances decreased with decreasing temperature, as expected. The electrolyte portion of the cell resistance was 60-70% of the overall resistance. The relatively low power densities shown in Figure 6 were due to this relatively high ohmic loss and the low OCV of the GDC electrolyte.

Figure 7 compares the results for cells with LSCM-GDC-Ni and Ni-GDC anodes operated with hydrogen or propane as the fuel. For hydrogen, the cell performance was very similar for the LSCM-GDC-Ni and Ni-GDC anodes. Thus, the ceramic-based anodes work as well in hydrogen as conventional Ni-based anodes – this is important since a portion of a propane-fueled stack will operate with substantial hydrogen, produced by reforming with cell reaction products, in the fuel. For propane, the power densities were lower than for hydrogen. The LSCM-GDC-Ni anodes produced higher power densities with propane than the Ni-GDC anodes.

Visual observation after running the cells on propane showed no obvious carbon deposition on the LSCM-GDC-Ni anodes, but heavy carbon deposition on the Ni-GDC anodes. Energy-dispersive x-ray (EDX) analysis of LSCM-GDC-Ni anodes showed no detectable carbon deposition after cell operation for \( \approx 3 \) h in propane near the maximum power point (or higher) currents. After the same cells were maintained at open-circuit condition in propane for \( \approx 3 \) h, the anodes showed no visual evidence of carbon deposition, but a small amount of C was observed by EDX. Note that the propane flow...
rate of 10 sccm corresponded to a fuel utilization of only \(= 2\%\) at the maximum power point, such that \(R < 0.1\). This is still well within the range where carbon deposition is expected at equilibrium (see Figure 3). We speculate that carbon nucleation was suppressed on ceramic-based anodes, relative to Ni-GDC, by the lower Ni content and different Ni morphology. In addition, oxygen-containing species produced by cell operation increased \(R\) at the anode, decreasing the driving force for coking.

Figure 6. Performance of the LSCV-GDC-Ni anode SOFC in propane fuel for different temperatures.

Figure 7. Voltage and power density versus current density for SOFCs with LSCM-GDC-Ni and Ni-GDC anodes, operated at 750°C with air as the oxidant and either \(H_2\) or \(C_3H_8\) fuel.
In small-scale SOFC generators that are turned on and off frequently, it is important that the anodes can be redox cycled without degradation. The Ni-YSZ anodes normally used in SOFCs degrade severely over a few redox cycles (7). Figure 8 shows an example of cell performance during a number of redox cycles between air and propane. (Note that short Ar purges were used during the switches between propane and air, to avoid having an explosive mixture in the gas-feed lines). The current density rapidly returned to its initial level after each of the redox cycles. Similar results were obtained for redox cycling between hydrogen and air. It is not clear whether the short transient decrease in current at the beginning of propane operation was real, or an artifact of changes in gas composition in the gas-feed lines. In any case, Figure 8 demonstrates that the ceramic-based anodes can be successfully used without degradation during redox cycling.

![Figure 8. Cell voltage at 80 mA as a function of time during cycling of the fuel gas between propane and air, with a short gas-line flush with Ar during the switch.](image)

**SUMMARY AND CONCLUSIONS**

The present paper discusses two regimes of SOFC operation on propane fuel. Equilibrium calculations suggest that operating temperatures ≥ 700°C are actually most favorable, as oxygen/propane ratios as low as 1.7 yielded coke-free conditions and high H2 and CO fractions. At lower temperatures, higher oxygen/propane ratios were required to prevent coking, and more of the fuel was converted directly to H2O and CO2. Anode-supported SOFCs operated at 800°C with an oxygen/propane ratio of 1.7 yielded reasonably good power densities, ~ 0.6 W/cm², without coking.

The other regime for direct-propane operation was with humidified propane (R = 0). This was well within the range where coking was expected, and heavy coking was indeed observed for Ni-GDC anodes. However, by using ceramic-based anodes with small Ni content, coking was suppressed, allowing stable operation over several hours. Cell operation was also stable over several propane-air redox cycles, indicating little or no anode degradation. These results are promising for potential portable SOFC generator applications.
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