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Abstract

In this paper we describe the development of Cu/CeO₂/YSZ anodes for solid oxide fuel cells (SOFCs) that are active for the direct electrochemical oxidation of dry hydrocarbon fuels. A novel method for synthesizing thin-electrolyte, anode-supported cells is described. This method uses tape-casting of YSZ layers with graphite pore formers, followed by impregnation with aqueous solutions of Cu(NO₃)₂ and Ce(NO₃)₂. The performance of model SOFCs with Cu/CeO₂/YSZ anodes while operating on a variety of dry hydrocarbon fuels, including methane, butane, decane, and synthetic diesel is reported.

Disciplines

Automotive Engineering | Biochemical and Biomolecular Engineering | Catalysis and Reaction Engineering | Chemical Engineering | Engineering

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ANODES FOR DIRECT OXIDATION OF HYDROCARBONS IN SOLID OXIDE FUEL CELLS

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ABSTRACT

In this paper we describe the development of Cu/CeO₂/YSZ anodes for solid oxide fuel cells (SOFCs) that are active for the direct electrochemical oxidation of dry hydrocarbon fuels. A novel method for synthesizing thin-electrolyte, anode-supported cells is described. This method uses tape-casting of YSZ layers with graphite pore formers, followed by impregnation with aqueous solutions of Cu(NO₃)₂ and Ce(NO₃)₂. The performance of model SOFCs with Cu/CeO₂/YSZ anodes while operating on a variety of dry hydrocarbon fuels, including methane, butane, decane, and synthetic diesel is reported.

INTRODUCTION

The vast majority of solid oxide fuel cells rely on the use of a Ni/YSZ cermet as the anode. These anodes are easy to manufacture, have good electrical conductivity and are catalytically active for hydrogen oxidation. A major drawback of Ni/YSZ anodes, however, is that they do not allow for the use dry hydrocarbon fuels. This is due to the fact that Ni is an excellent catalyst for the formation of graphite from dry hydrocarbons at temperatures above 600°C. Operating a SOFC with a Ni/YSZ anode on a dry hydrocarbon fuel results in irreversible, rapid cell deactivation due to carbon deposition on the anode. In the case of methane (CH₄) this limitation has been partially overcome by internal steam reforming to produce hydrogen. Since Ni is an excellent catalyst for the steam reforming of CH₄ to CO and H₂ it is possible to run a SOFC with a Ni/YSZ anode on a mixture of CH₄ and H₂O. The CH₄/H₂O mixture is reformed on the anode to produce H₂, which is then electrochemically oxidized. The addition of water also suppresses carbon deposition on the anode. Although this approach allows for the use of a CH₄/H₂O mixture as the fuel, it still has several significant limitations. Temperatures in excess of 800°C are required in order to obtain high equilibrium conversions for the steam reforming reaction. Thus, high operating temperatures must be used. An even more significant limitation of this approach is that it only works for methane. It is not possible to operate SOFCs with Ni/YSZ anodes on fuels containing higher hydrocarbons such as those found in gasoline and diesel.

Clearly an SOFC that can directly utilize dry hydrocarbon fuels, such as gasoline and diesel would have significant advantages over current SOFC designs which require hydrogen as the fuel. As will be shown below, this goal has recently been achieved (1,2). In this paper we provide an overview of our studies of the use of Cu/YSZ cermet

anodes in SOFCs. Unlike Ni, Cu is a relatively inert metal and is not active for the formation of graphite from dry hydrocarbons. Results are presented below which show that SOFCs that have Cu-based anodes are active for the direct oxidation of a wide range of dry hydrocarbon fuels.

CELL CONSTRUCTION

The cells used in this study were produced using tape casting. A detailed description of the procedure used to construct a cell has previously been reported (2,3) and only a brief description will be given here. Each cell was fabricated using two tape cast layers of YSZ. The yttria content in the YSZ was 8 mole %. The first layer was cast using an aqueous slurry of YSZ which also contained binders (Duramax B-1000 and B-1014) and a dispersant (Duramax D-3021). After allowing the electrolyte green tape to dry in air, a second tape of YSZ was cast on top of it. This tape was cast using the same YSZ slurry used for the electrolyte layer with the addition of up to 40 wt.% of graphite particles (Alfa, 325 mesh). The tape cast bi-layer was then sintered in air at 1550°C for 4 hrs. During sintering the graphite particles were oxidized and removed as gaseous CO₂, leaving a highly porous YSZ layer on top of a thinner dense YSZ layer. The cathode was produced by pasting a slurry containing a 50:50 mixture of YSZ and La(Sr)MnO₂ (Praxair Surface Technologies) on the exposed surface of the electrolyte tape and then sintering in air at 1250°C for 2 hrs. Copper and ceria were then added to the porous anode layer using wet impregnation of aqueous solutions of Cu(NO₃)₂ (Fisher Scientific Co.) and Ce(NO₃)₂ (Alfa). Copper and ceria were added to provide electrical conductivity and catalytic activity, respectively. After adsorption of the nitrate solutions into the porous YSZ layer the electrolyte disk was annealed in air at 950°C for 2 hrs. Electronic contacts were formed using a Pt mesh and Pt paste on the cathode and Au mesh and Au paste on the anode. The anode side of the structure was then attached to an alumina tube using Au ink and the edges were sealed using ceramic adhesives (Aremco 516 and 571).

For performance testing the fuel cell was attached to either to a gas manifold or a liquid syringe pump and then placed in an oven and heated to the desired operating temperature. The cathode of the cell was left exposed to air and fuel was flowed over the anode. The flowrate of fuel to the anode was such that the overall conversion of the fuel was less than 5 %. These conditions were chosen in order to operate under conditions where the rate of carbon deposition should be highest.

RESULTS AND DISCUSSION

The current density and power density versus voltage characteristics for a fuel cell with a Cu/CeO₂/YSZ anode operating at 700°C on pure butane (C₄H₁₀) are displayed in Figure 1. The electrolyte layer in this cell was 60 μm thick and the YSZ anode matrix was 50% porous prior to being impregnated with Cu and CeO₂. After impregnation the anode contained 30 wt.% Cu/CeO₂. The data in this figure illustrate several points. The most important being that the Cu/CeO₂/YSZ anode is active for the direct electrocatalytic oxidation of higher hydrocarbons. The open circuit voltage for the cell is 0.97 V, which is close to that predicted by the Nernst equation for the oxidation of

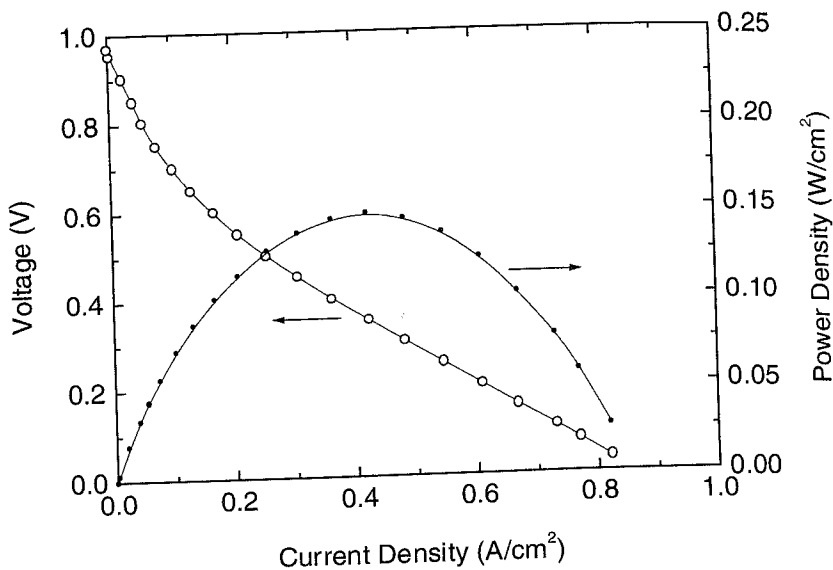


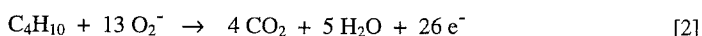
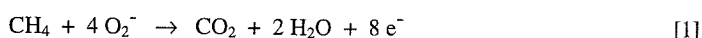
Figure 1. Voltage and power density versus current density for an SOFC operating at 700°C on pure C₄H₁₀. This fuel cell had a Cu/CeO₂/YSZ anode and a 60 μm thick YSZ electrolyte layer.

C₄H₁₀ to CO₂ and H₂O. The power density produced by the cell is 0.125 W/cm² at a voltage of 0.5 V, which is within in the range required for a commercially viable device. Note that the overall performance of this cell is at least partially limited by the relatively thick electrolyte layer. Significant improvement in cell performance would likely be obtained by using a much thinner electrolyte layer.

The performance of the cell was highly reproducible. Experiments were performed in which a similar cell was operated at 0.5 volts while using butane as the fuel for 70 hrs. No change in cell performance was observed over this time period. Thus, the cell performance was stable while operating with C₄H₁₀ as the fuel and did not degrade over time. Visual inspection of the anode after the long-term testing revealed that the anode was carbon free. In addition to butane we have tested cells with Cu/CeO₂/YSZ anodes on a variety of gaseous dry hydrocarbon fuels including methane, propane, and ethylene. In all cases stable operation without carbon deposition on the anode was observed.

Figure 2 displays the amount of CO₂ produced in an SOFC with a Cu/CeO₂/YSZ anode at 750°C versus current density for operation on hydrocarbon fuels. Data for a cell operating on pure CH₄ and pure C₄H₁₀ are included in the figure. The CO₂

production rate was measured using GC analysis of the effluent gas from the fuel cell. The two lines in the figure correspond to the CO₂ production rate versus current density which would result from the following two chemical reactions:



Note that the data for CH₄ falls directly on the line predicted by reaction [1]. The data for C₄H₁₀ is close to the line predicted by reaction [2] although there is some deviation at high current densities. The slight deviation for butane is likely to be due to gas phase reactions involving the butane that result in the production of a more complex hydrocarbon mixture in the gas phase. These results are again consistent with the direct electrochemical oxidation of hydrocarbons on the Cu/CeO₂/YSZ anode.

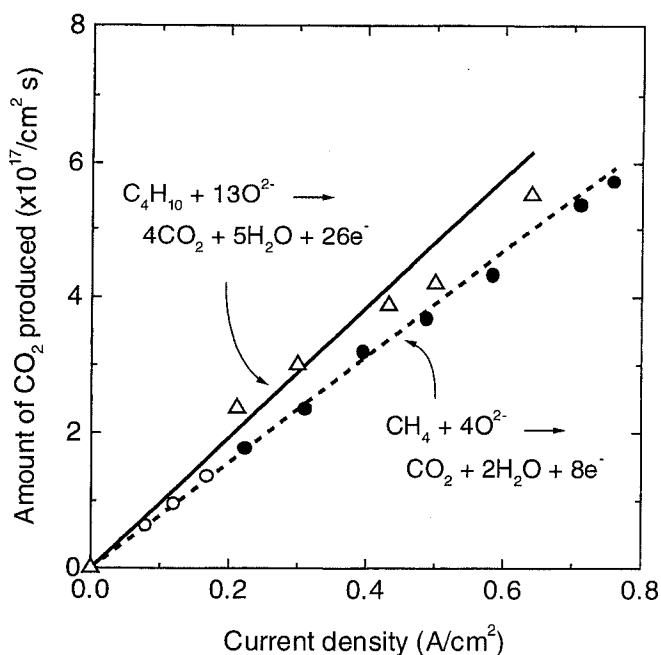


Figure 2. Rate of CO₂ production versus current density for an SOFC with a Cu/CeO₂/YSZ anode while operating with dry CH₄ and dry C₄H₁₀ at 750°C

In addition to gaseous hydrocarbon fuels, the performance of the Cu/CeO₂/YSZ anodes while operating on pure hydrocarbons and complex hydrocarbon mixtures that are liquids at room temperature were measured. Specific fuels that have been used include hexane, toluene, decane, and a synthetic diesel. The current density and power density versus voltage characteristics for a fuel cell with a Cu/CeO₂/YSZ anode operating at 700°C on a synthetic diesel fuel are displayed in Figure 3. The electrolyte layer in this cell was 60 μm thick and the YSZ anode matrix was 50% porous prior to being impregnated with Cu and CeO₂. After impregnation the anode contained 30 wt.% Cu/CeO₂. The diesel fuel was injected directly into the anode side of the fuel cell using a syringe pump. A N₂ carrier gas was also flowed through the anode side of the cell. The N₂ flowrate was such that the volume % of hydrocarbons in the gas exposed to the anode was 20%. The open circuit voltage for this cell is 0.87 V and the power density at 0.5 V is 0.08 W/cm². The performance of the cell was stable over time with no evidence of carbon deposition on the anode. This is illustrated in Figure 4, which displays the current and voltage density as a function of time while using diesel fuel and operating at 700°C with a constant load. Note that the current density is essentially constant over the entire 12 hr duration of the experiment.

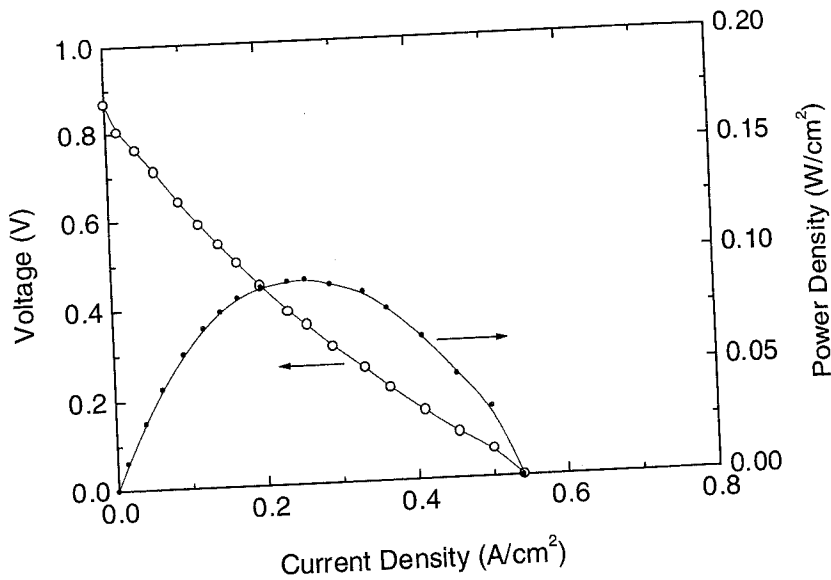


Figure 3. Voltage and power density versus current density for an SOFC operating at 700°C on a synthetic diesel fuel. This fuel cell had a Cu/CeO₂/YSZ anode and a 60 μm thick YSZ electrolyte layer.

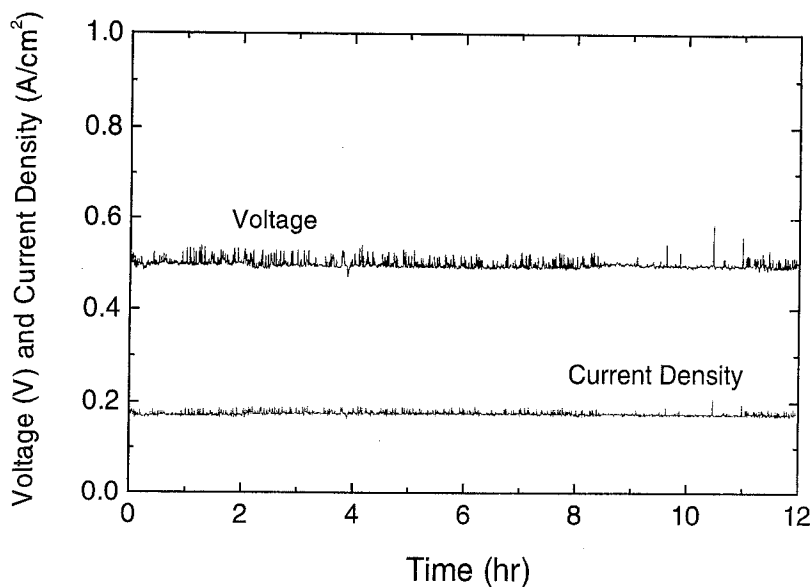


Figure 4. Voltage and current versus time for an SOFC operating at 700°C on a synthetic diesel fuel. This fuel cell had a Cu/CeO₂/YSZ anode and a 60 μm thick YSZ electrolyte layer.

The results of this study are very encouraging since they demonstrate that Cu/CeO₂/YSZ anodes are active for the direct electrochemical oxidation of a wide range of hydrocarbon fuels. Unlike conventional Ni/YSZ anodes, Cu/CeO₂/YSZ anodes are highly resistant to deactivation due to carbon deposition and exhibit long-term, stable operation on dry hydrocarbons. Thus, the operation of SOFCs directly on dry hydrocarbon fuels is clearly feasible. This development has the potential to significantly reduce the complexity of SOFC power generation systems that run on common hydrocarbon fuels such as gasoline and diesel.

CONCLUSIONS

We have demonstrated that anodes composed of mixtures of Cu, CeO₂, and YSZ are active for the direct electrochemical oxidation of a wide range of hydrocarbon fuels including methane, butane, decane, and synthetic diesel. The results of this study have significant implications for the widespread use of SOFCs in transportation and distributed-power applications.

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