ANODE CATALYST LAYERS FOR DIRECT HYDROCARBON AND INTERNAL REFORMING SOFCs

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ABSTRACT

We describe a method to reduce coking and improve stability of Ni-based anode supported SOFCs operated with hydrocarbon fuels. The method involves placing a catalyst/barrier layer at the anode. Two separate cases are described here: operation with methane fuel or with iso-octane-H₂O-CO₂-O₂ fuel mixtures. For methane, Ni-YSZ anode supported SOFCs were tested. The barrier layer reduced the critical current density required to maintain coke-free operation by a factor >2, substantially increasing the stable operation range. Attempts to operate Ni-YSZ anode supported SOFCs with iso-octane-H₂O-CO₂-O₂ fuel mixtures resulted in performance degradation due to coking. On the other hand, the addition of an anode barrier layer containing a Ru-CeO₂ catalyst allowed stable coke-free operation. Mass spectrometer results indicated that the catalyst produced substantial H₂ and CO at temperatures above 600°C. SOFCs with thin Sm-doped ceria (SDC) electrolytes on Ni-SDC anode supports were also successfully tested with iso-octane.

INTRODUCTION

SOFCs have the advantage that they can be used with hydrocarbon fuels via either direct utilization (1) or internal reforming (2). These approaches have significant potential advantages including reduction of balance of plant (e.g., external reformers) and improvement in efficiency. In addition, direct methane SOFCs can be used for efficient co-generation of electricity and syngas (3). The problem with these approaches is coking of the anodes, which is especially prevalent for heavier hydrocarbon molecules and Ni-based anodes. While SOFCs with alternative anode materials have been developed that work stably with hydrocarbon fuels, they typically provide low power densities relative to SOFCs with conventional Ni-based anodes (4).

In the present paper, we describe an alternative approach utilizing conventional Ni-based anodes and using an anode barrier/catalyst layer to improve stability and reduce coking. Two separate cases are described here: operation with methane fuel or with iso-octane-H₂O-CO₂-O₂ fuel mixtures. The possible mechanisms behind the barrier/catalyst layer effect are discussed. Iso-octane, a high purity compound similar to gasoline, was used in these experiments to achieve a demonstration of the feasibility of SOFCs utilizing transportation fuels. This avoids a number of experimental complications with...
commercial fuels, which typically contain a number of different compounds and additives with a substantial range of compositions, as well as relatively large amounts of sulfur compounds that can seriously affect fuel cell performance. The experiments were done with conventional SOFCs at ≈ 800°C or with low temperature (<600°C) SOFCs that may be more suitable for transportation applications.

**BARRIER LAYER CONCEPT**

The barrier/catalyst layer concept is illustrated in Figure 1. Figure 1a shows the expected fuel-gas composition gradients at the anode of a conventional anode-supported SOFC during direct methane operation. Gas diffusion limitations lead to composition gradients: the hydrocarbon content decreases from the gas flow to the anode/electrolyte interface, while the product content (e.g. H₂O and CO₂) follows the opposite trend. This helps explain how coking is avoided in direct-methane SOFCs at high current density (5). However, Figure 1a shows that conditions favor coking near the free anode surface, and coking has been observed to occur preferentially at this position in direct-methane SOFCs (5).

**Figure 1.** Simplified schematic illustration of how reactant and product gas concentrations are expected to vary with position during direct methane SOFC operation without (a) and with a barrier layer (b). Part (c) shows the gas composition versus position for internal reforming with a barrier/catalyst layer.

1: Cathode
2: Electrolyte
3: Anode
4: Boundary layer
5: Fuel flow
6: Concentration of methane
7: Concentration of H₂O and CO₂
8: Barrier layer
9: Catalyst layer
10: Concentration of H₂ and CO
11: Concentration of iso-octane

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Figure 1b shows the situation with a barrier layer—a thin porous layer of inert (non-coking) material—placed in contact with the anode. The barrier yields a decrease in the methane content and an increase in the product concentration within the anode. This is expected to further decrease coking and thereby improve cell stability. Figure 1c shows the situation with a barrier/catalyst layer in an internal reforming case. It is assumed that the catalyst is less susceptible to coking than the Ni-based anode, such that the catalyst itself does not coke. The reforming reaction at the catalyst substantially reduces the hydrocarbon content of the reformate reaching the anode, thereby suppressing coking. This latter approach appears similar to cases where reforming is done at a catalyst within the stack but removed from the cells (indirect internal reforming) (6). An advantage of the present approach is the good thermal contact between the SOFCs and catalyst layers, providing good heat transfer from SOFC to catalyst for endothermic reforming reactions.

**EXPERIMENTAL**

Ni-YSZ anode-supported fuel cells were prepared as follows. Ni-YSZ anode supports were made by mixing NiO (Baker) and 8-YSZ (Tosoh), in a weight ratio of 1:1, and ball milling in ethanol for about 20 hours. 10 wt% of starch was then added to the mixture and the ball milling was continued for another two hours. The milled powder mixture was dried and pressed into pellets with diameter of 19 mm and thickness of about 0.7 mm. The pellets were bisque fired at 1000°C for 4 hours. A YSZ electrolyte layer was coated on the anode support by colloidal deposition and then was co-sintered at 1400°C for 4 hours. Cathodes consisting of a layer of 70 wt% La0.6Sr0.4Fe0.2Co0.8O3 (LSCF, Praxair) and 30 wt% Gd-doped Ceria (GDC, NexTech), followed by pure LSCF layer, were applied by screen printing on the YSZ electrolyte and fired at 900°C for 4 hours.

For the SDC cells, anode powders of SDC (NexTech) and NiO (J. T. Baker) in a weight ratio of 60:40 were ball-milled for 20 h with ethanol as the medium, then 10% starch was added and ball-milled for 4 h. The powders were dried at 80°C, screened with 120-mesh sieve and pressed into pellets, which were bisque fired at 800°C for 4 h. Then an active NiO-SDC anode layer and a thin SDC electrolyte layer were coated by colloidal deposition technique, respectively. After co-sintering of the anode/electrolyte at 1400°C, La0.6Sr0.4Co0.2Fe0.8O3 (LSCF) - Ce0.85Sm0.15O1.925 (SDC) cathode layers were applied. LSCF-SDC cathodes were prepared by mixing LSCF powder (Praxair) with SDC powder (NexTech) in a weight ratio of 7:3. A screen-printing vehicle (Heraeus) was added to the mixed powder to make a slurry. The slurry was applied onto the SDC electrolyte and fired at 1100°C for 4 h. A second layer of pure LSCF slurry was applied and fired at 900°C for 4 h.

Barrier layer pellets were composed of partially stabilized zirconia (PSZ), or PSZ mixed with CeO2 in a weight ratio of 1:1. The powders were mixed with 20 wt% starch filler in ethanol for 20h. Dried powders were pressed into pellets ≈ 0.4 mm thick and fired at 1400°C for 4 hrs. In some cases, a catalyst layers consisting of RuO2 powder (Aldrich) with CeO2 powder (Aldrich) in a weight ratio of 1:10 were applied on both sides of PSZ-CeO2 pellets by colloidal deposition and fired at 900°C for 4 h.

For fuel cell tests, the PSZ-CeO2 supported catalyst layer and the anode side of the cell were sealed to alumina tubes using Ag ink. Current collector grids were painted on the
electrodes using Ag ink. SOFCs tests were carried out using a standard single-cell testing geometry. In some cases, barrier layers were placed direct against the SOFC anode. The Ni-based anode was fully reduced in humidified H₂ at 700°C or 600°C for YSZ or SDC electrolyte SOFCs, respectively. Cells were first tested with the cathode exposed to ambient air and the anode to humidified (3% H₂O) hydrogen. The cells were then tested with either humidified methane or iso-octane/H₂O/CO₂/O₂ mixtures. The current-voltage curves were obtained using an Electrochemical Workstation (IM6, ZAHNER).

RESULTS AND DISCUSSION

Direct Methane Operation

The effect of a barrier layer on the SOFC stability region was determined using the following protocol. After achieving stable operation in hydrogen, the fuel was switched to methane with the cell maintained near maximum power. After the switch to methane, the voltage \( V \) at constant current \( J \) dropped by \( \approx 20\% \) to a new steady state value. \( J \) was then maintained constant near the maximum power point for >3h, long enough to observe whether \( V \) was stable. \( J \) was then reduced and maintained constant for >3h. This latter step was repeated until \( V \) became unstable. In prior studies, it was shown that the transition from stable to unstable was associated with coking of the anode (5). Figure 2 shows an example of the methane results, taken at 800°C. Without the barrier layer (Figure 2a), stable operation was maintained only for \( J > 1.8 \text{ A/cm}^2 \). With the barrier layer, the cell was stable for \( J > 0.6 \text{ A/cm}^2 \) (Figure 2b). Similar results were obtained at 750°C, with the critical current density \( J_c \) decreasing from 1.2 A/cm² to 0.2 A/cm² with the barrier. At 700°C and below, \( J_c \) was small enough that it was experimentally difficult to observe the effect of the barrier layer. Overall, these results imply that stable operation can be maintained over a much wider operating parameter range with the barrier layer.

Figure 2. Cell voltage versus time at constant current \( J \) for SOFCs operated in humidified methane at 800°C without (a) and with (b) barrier layer. The cells were operated at different \( J \) values for 6h in each step, starting at high \( J \) and reducing \( J \) in steps.

Figure 3 shows typical stable cell performance in methane at different temperatures with the barrier layer. Open circuit voltages increased from 1.02 to 1.15 V with increasing temperature. The maximum power densities ranged from 0.16 W/cm² at 650°C to 0.82 W/cm² at 800°C. For low to moderate current densities and cell temperatures <750°C,
the current-voltage curves showed neutral or positive curvature, suggesting that activation polarization and ohmic resistance were the main losses. There was evidence of a limiting current behavior at higher temperatures and at current densities approaching \( \approx 1.8 \text{ A/cm}^2 \), resulting from the reduction in the rate at which fuel can diffuse to the anode due to the presence of the barrier layer.

Visual observation after cell tests showed no evidence of coking or anode structure changes when the barrier layers were used under stable conditions. For cells tested without the barrier, severe coking and anode destruction can be seen after performance degradation at the same current densities. As discussed with Figure 1 above, stable SOFC operation with methane has been explained by the decreased methane content and increased cell reaction products, e.g. CO\(_2\) and H\(_2\)O, in the anode. The barrier layer further decreases the methane content and increases the concentration of reaction products within the Ni-based anode. Thus, a lower current density is sufficient to prevent coking. While the gas composition in the barrier layer favors coking more, coking is nonetheless unlikely there because there is no catalyst (e.g. Ni).

**Iso-Octane Internal Reforming**

Heavy hydrocarbons such as iso-octane will cause coking much more readily than methane, especially with Ni-based anodes. There has been some work reported on SOFC operation with heavy hydrocarbons by using Cu-based anodes. However, with Ni-based anodes there has been little work done. Even when used in reforming mixtures where coking is not expected based on equilibrium considerations, there can still be coking on Ni (7). Internal reforming is nonetheless desirable since it can improve fuel efficiency by utilizing excess fuel cell heat for the endothermic reforming reaction.

Indeed, attempts to run anode-supported SOFCs directly on 6% iso-octane balanced by air without the catalyst layer were unsuccessful. The cell performance was initially good but decayed rather rapidly, as shown for the example of an SDC-electrolyte cell in Figure 4. Subsequent observation indicated the degradation was due to severe coke buildup on the Ni-SDC anode. With the addition of a porous catalyst layer between the fuel stream and the anode, stable operation was achieved; as shown in Figure 4, performance was stable with a constant power output of \( \approx 0.46 \text{ W/cm}^2 \) over 60 h at 590°C. Power densities >0.6 W/cm\(^2\) were achieved at 590°C (note that these temperatures reflect an \( \approx 40°C \) increase above the furnace temperature due to the exothermic partial oxidation reaction). Although the formation of carbon is expected
over temperature from 300°C to 800°C from the thermodynamic prediction for this gas composition (8), no carbon was observed on the catalyst layer during the experiments. The coking was presumably kinetically limited at these relative low temperatures.

Anode-supported SOFCs without catalyst layers were also unstable when used with iso-octane-CO₂- H₂O fuel streams. Figure 5 shows examples of the decrease in YSZ-electrolyte cell voltage for constant current operation at 770°C with three different fuel compositions: 6% iso-octane-94% CO₂, 3% iso-octane-72% CO₂-25% steam, or 5% iso-octane-76% CO₂-19% air. The degradation was due to severe coke buildup on the Ni-YSZ anode, which was visible to the eye in many cases. SEM-EDX spectra taken from the SOFC anodes after degradation showed a clear carbon peak along with the expected Ni, Zr, and Y peaks.

Two modifications were required to achieve stable SOFC operation with iso-octane fuel mixtures. First, the porous catalyst layer was placed against the anode side of the SOFC. The effect of the catalyst layer can be seen by comparing curves 1 and 4 in Figure 5, that were both obtained with 6% iso-octane balanced by CO₂. The cell was much more stable with the catalyst than without, showing a nearly constant voltage, although subsequent observation indicated very slight carbon deposition on the catalyst layer. Second, the addition of a small amount of air to the fuel yielded fully stable performance (curve 5 in Figure 5) with no carbon detected on the catalyst layer or the fuel cell by SEM-EDX.

Mass spectrometer measurements showed that the catalyst layer effectively produced hydrogen for the SOFC anode. Figure 6 is a typical mass spectrum showing the exhaust gas composition versus temperature after flowing a 5% iso-octane-9% air ~86% CO₂ mixture at 100 sccm over a Ru-CeO₂ catalysis layer. CO and H₂ began to increase.
substantially at temperature above $\approx 550^\circ$C. Above $700^\circ$C, a small amount of methane was observed. The $O_2$ peak decreased with increasing temperature from $\approx 280^\circ$C to $550^\circ$C, indicating that oxidation occurred at relatively low temperatures.

Figure 6. Mass spectroscopy measurement from the exhaust gas versus $T$ for 5% iso-octane-9% air-86% CO$_2$ fuel mixtures after flowing over a Ru- CeO$_2$ catalyst layer at 100 sccm.

![Mass spectroscopy measurement](image)

Figure 7. Voltage and power density versus current density for the cell NiO-YSZ|YSZ|LSCF-GDC, LSCF, with a catalyst layer, Ru- CeO$_2$|PSZ|Ru- CeO$_2$ tested in 5% iso-octane-9% air-86% CO$_2$ at 100 sccm in the anode and ambient air in the cathode at different cell temperatures.

![Voltage and power density](image)

The above results showed that the catalyst layer was crucial for allowing stable cell operation without coking. Based on the thermodynamic analysis shown in Figure 8, the present fuel compositions were stable against coking at temperatures $> 720^\circ$C, but were within the coking regime for the lower-temperature cells. Note that coking can still occur on Ni catalysts even under thermodynamically non-coking conditions (7). Recent studies have shown that Ni is especially well suited for growing carbon fibers (9). It is nonetheless desirable to use Ni in SOFC anodes because it is very good electrochemically (10).

The present cells had conventional Ni-based anodes to achieve good power densities, using the catalyst layer to prevent coking. The lack of coking at the Ni-based anode can be explained by reforming at the Ru-Ceria catalyst layer, which eliminated most of the hydrocarbon species before the fuel reached the Ni anode. A key element of this strategy was the choice of a catalyst metal, Ru, that promotes hydrocarbon reforming but does not itself cause coking (11).
There are three minor drawbacks to the catalyst layer. First, it is expected to reduce the rate at which fuel can diffuse to the anode, thereby decreasing cell power density. Indeed, test results at 770°C typically showed lower power densities of \( \approx 0.6 \) W/cm\(^2\) with the catalyst layer compared to initial values (prior to degradation) of \( 0.8 \sim 1 \) W/cm\(^2\) without the layer. Second, since the catalyst layer was electrically insulating in the present experiments, electrical current collection could be an issue. However, a slight modification of a typical interconnect design, where the catalyst layer is present only in the interconnect gas flow channels as shown schematically in Figure 9, could be used to provide good current collection. Third, Ru is much more expensive than Ni, but the cost is not a problem since the amount of Ru used is very small.

The other factor required for stable cell operation was having at least 10% air in the fuel mixture. This represents a 2% oxygen addition to the fuel, and it is not clear what role this plays in preventing coking. One possibility is that the oxygen helps remove carbon on the catalyst. While the addition of oxygen amounts to burning some of the fuel, the amount of air is too small to substantially reduce the efficiency, or to substantially dilute the fuel with nitrogen.

The present results compare favourably with other recently reported methods for using heavy hydrocarbon fuels in SOFCs. SOFCs have recently been reported to operate successfully on \( N_2 \)-diluted \((7)\) and other heavy hydrocarbon fuels \((12)\). However, the power densities were substantially lower \((0.1 \text{W/cm}^2)\) than in the present results. Prototype SOFC systems have recently been developed for vehicle auxiliary electrical power utilizing external partial oxidation reforming of gasoline to produce a hydrogen-rich fuel \((13)\). However, partial oxidation reforming has substantially lower efficiency than is possible with \( \text{H}_2\text{O}\text{-CO}_2 \) reforming.

Figure 8. Calculated equilibrium product distribution as a function of temperature for a 5% iso-octane-9% air-86% \text{CO}_2\) inlet fuel mixture.

Figure 9. Schematic view of a possible planar SOFC stack configuration with catalyst layers between the fuel stream and the anodes.
In cases where reforming is done within the stack but away from the cells, or in an external reformer, heat transfer will not be as good and additional hardware is required. One disadvantage of direct internal reforming is that the endothermic reaction may be too rapid, causing substantial SOFC or catalyst cooling near the fuel inlet. The present catalyst layer may have an advantage in this regard, since the catalyst material can be varied to suitably adjust the rate of the reforming reaction. The addition of oxygen to the fuel also helps mitigate this cooling because of the exothermic partial oxidation reaction.

**SUMMARY AND CONCLUSIONS**

Operation of Ni-YSZ anode supported SOFCs directly on methane with/without barrier layers was studied, and the results show that barrier layers significantly improve stability of direct methane operation. The probable mechanism is the change in fuel composition within anode.

The present results also show the feasibility of direct internal reforming SOFCs using hydrocarbon fuels such as iso-octane. Both partial oxidation and steam/dry reforming were successfully used. Steam/dry reforming has the advantage of potentially allowing high system efficiency. However, more work needs to be done to prove that this approach is practical with real fuels such as gasoline, diesel, and aircraft fuels; recently developed techniques for reducing sulfur contamination to low levels may be especially useful.

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