COPPER-PLATED STAINLESS STEEL FOR BIPOLAR PLATES IN DIRECT-OXIDATION SOFC

S.-I. Lee, S. McIntosh, J. M. Vohs and R. J. Gorte
Dept. of Chemical and Biomolecular Engineering
University of Pennsylvania
Philadelphia, Pennsylvania 19104, USA

ABSTRACT

The performance of copper-plated, stainless-steel plates, having an active area of 2.5x2.5 cm² square, was tested for use with an SOFC having a Cu-based anode for direct oxidation of n-butane at 973 K. In the absence of Cu, catastrophic carbon deposition, which rapidly caused blocking of the fuel channels, was observed due to reaction of the n-butane on the stainless steel. However, plating the fuel channels with Cu effectively prevented formation of large carbon deposits. After 24 hr operation in pure n-butane, the Cu plating effectively suppressed carbon deposition, except for the formation of tar-like substances formed by gas-phase thermal decomposition of the hydrocarbon. The tar-like substances were found to be soluble in toluene and could be analyzed by GC/MS, which showed that they were primarily poly-aromatic hydrocarbons having 2-6 aromatic rings.

INTRODUCTION

Solid oxide fuel cells (SOFC) that can operate directly with hydrocarbon fuels, without requiring those fuels to be reformed to H₂, would be extremely attractive for a large number of applications. This is particularly true for small-scale and mobile applications, where hydrocarbons other than methane are the fuels of choice. Steam reforming of higher hydrocarbons is difficult; and oxy-reforming decreases the system efficiency, adds complexity, and causes a significant dilution of the fuel by N₂, thereby limiting the ultimate fuel utilization that can be achieved. Unfortunately, Ni-cermets, the common choice for SOFC anodes because of the excellent steam-reforming properties of Ni (1, 2), deactivate rapidly in the presence of dry hydrocarbons. The reason for this is that the chemical characteristics that make Ni an excellent steam-reforming catalyst make it a catalyst for the formation of graphitic deposits.

In our laboratory, we have focused on the development of Cu-based anodes for SOFC because Cu, unlike Ni, does not catalyze the formation of graphite fibers in the presence of dry hydrocarbons (3, 4). Anodes prepared with Cu-based anodes have been shown to be stable in a wide variety of hydrocarbon fuels and to be capable of electrochemically oxidizing those hydrocarbons to CO₂ and H₂O in the absence of added steam or O₂. Because Cu is catalytically inert, it is necessary to add a catalyst, CeO₂, to the anode in order to oxidize the hydrocarbon fuel (5).
Stacks based on cells made with Cu-based cermets will need to have seals and bipolar plates that satisfy a number of chemical and mechanical properties. As with all stacks, the materials that are used must have the correct electrical conductivities, excellent gas seals, thermal expansion matches, and reasonable costs. In addition to these criteria, the materials used for a direct-oxidation SOFC must be chemically inert in the presence of dry hydrocarbons at relatively high temperatures. This criterion is particularly challenging if one is to employ cost-effective metallic interconnects, since the metal of choice is stainless steel (6, 7). Obviously, stainless steel contains Ni and Fe, both of which are catalytically active for the formation of graphite fibers.

In the present study, we demonstrate that it is possible to obtain gas-tight seals for an SOFC with a Cu-based anode in a stainless-steel bipolar plate. While stainless steel catalyzes carbon formation that blocks the gas flow when pure n-butane is fed to the anode at 973 K, carbon formation is prevented when the steel is electroplated with a thin Cu film. Following operation of cell in n-butane for 24 hrs, tar-like deposits form on the Cu films; however, these tar-like deposits are soluble in toluene and do not affect cell performance.

EXPERIMENTAL

Preparation and Testing of SOFC

The methods for preparing and testing fuel cells with Cu-cermet anodes have been discussed in other papers (3, 4, 8, 9). Briefly, an yttria-stabilized zirconia (YSZ) wafer, with one side porous and the other dense, was prepared by tape-casting methods, with graphite and poly-methyl methacrylate (PMMA) pore formers used to introduce porosity. The thickness of the dense electrolyte layer was 60 μm and this was supported by the 600-μm porous layer. The cathode material, a 50 wt% YSZ and LSM (La0.8Sr0.2MnO3, Praxair Surface Technologies) mixture, was applied as a paste onto the dense side of the wafer, then calcined to 1400 K. To prepare the anode, the porous YSZ layer was impregnated with aqueous solutions of Ce(NO3)3·6H2O and Cu(NO3)2·3H2O and calcined to 723 K to form the oxides. The final composition of the anodes was 20 wt% Cu and 10 wt% ceria.

Electrical contacts to the electrodes were formed using Pt mesh and Pt paste at the cathode and a Au mesh and Au paste at the anode. The fabricated cell having an anode area of 2.5 × 2.5 cm² and a cathode area of 1 cm², was sealed over a fuel channel recessed into a stainless steel plate using gold paste and a commercially available cement (Cerama bond 571, Aramco). The cathode was left exposed to air. Cell voltage and current were monitored and recorded with a digital multi-meter. For long performance tests, the cell potential was maintained at 0.5 volts by an electrical load and the cell potential and current density were measured as a function of time.

Copper-Plated Cell Mounts

The SOFCs were mounted in stainless-steel plates that are shown schematically in Fig. 1. The plates were made from 430 stainless steel and machined to have gas channels 300 μm in depth. The surface of fuel channel was cleaned using acetone and an acidic
solution to remove oil residue for copper plating. An aqueous Cu solution was then prepared by mixing a 0.75 M CuSO₄ solution and a 0.75 M H₂SO₄ solution. The Cu film was then plated onto flow channels using a current density of 10 mA/cm² to form a 20 μm copper film.

**GC/MS Analysis**

As discussed below, a carbonaceous film formed on the Cu plate following a 24 hr exposure to n-butane. To determine the composition of this material, it was first dissolved in liquid toluene and then analyzed using a Shimadzu Gas Chromatograph equipped with a MS detection system. A fused silica capillary column (DB-5MS, 30 m x 0.25 mm, J&W Scientific Inc.) was used with a temperature programmed from 60 to 310°C at rate of 5 K/min.

**RESULTS AND DISCUSSION**

The cell potential and power densities are plotted in Fig. 2 as a function of current density for a cell operating on H₂ and n-butane at 973 K. The open-circuit voltages (OCV) were 1.1 V for H₂ and 0.96 V for n-butane, demonstrating that there were no substantial leaks in the seals. As reported in previous studies, the cell potentials and power densities were better when H₂ was the fuel than when n-butane. The V-I curve was nearly linear for H₂ but concave for n-butane, probably due to some catalytic limitations for the oxidation of n-butane. These results are very similar to what has been reported previously by our laboratory.

In this study, the maximum power density was only 0.16 W/cm² for H₂ and 0.09 W/cm² for butane, about 20% lower than we have reported previously for small button cells. Based on impedance spectra, it appears that the use of high-resistance leads was responsible for this decrease in performance. The impedance spectra showed that the total electrode resistance in H₂ was 1.2 ohm-cm², similar to what we have seen with button cells (10); but we observed an increased ohmic resistance that appears to be responsible for the decreased performance.

As a demonstration of cell stability, Fig. 3 shows the potential and current density as a function of time for the SOFC with pure n-butane as fuel for a period of 24 hour. The data show that the current and potential did not change during the run.

Figure 4 shows the cell mount before and after the 24-hr exposure to n-butane shown in Fig. 3. After removing the cell from the stainless-steel mount, it was discovered that the Cu-plated mount was covered by a thin, carbonaceous layer. This carbonaceous layer was easily removed by washing in toluene, revealing that the copper plating remained intact.

To gain insight into the mechanism for carbon formation on the Cu-coated plates, the tar-like substances were analyzed by GC-MS after they were dissolved in toluene. The GC trace and an identification of major compounds are shown in Fig. 5 and Table 1. It was found that the deposits consist primarily of poly-aromatic hydrocarbons having between two and six aromatic rings. These compounds are probably formed as a result of gas-phase, free-radical reactions (10-12).
While the poly-aromatic compounds shown in Table 1 might be considered precursors to graphite, it is important to note that these deposits are very different from what is formed in the presence of a metal catalyst such as Ni or Fe. First, most of the compounds in Table 1 have vapor pressures that are high enough at 973 K to suggest that there is probably a steady state between deposition and vaporization of these compounds. Certainly, we did not observe a decrease in cell performance with time. Second, in earlier experiments in which bare stainless steel was exposed to n-butane, large graphitic deposits were observed that essentially filled the fluid channels. These carbon deposits could only be removed by physical grinding. Removing these carbon deposits revealed pitting of the stainless steel, suggesting that components from the stainless steel were incorporated into the deposits.

CONCLUSIONS

The results of this study show that copper plating can be used to effectively suppress catalytic carbon deposition in the fuel channel of stainless steel bipolar plates that might be used for direct-oxidation SOFC.

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Figure 1. Schematic diagram of the SOFC mount used in this study.

1: Stainless steel stack
2: Cu-cermet anode
3: Electrolyte
4: Cathode
5: Pt current collector
6: Ceramic seal

Figure 2. Cell potential and power density vs. current density while running on H₂ and n-butane at 973 K. The squares are for H₂ and the circles for n-butane.
Figure 3. Cell performance in n-butane as a function of time at 973 K while holding the cell potential at 0.5 V.

Figure 4. Photograph of cell mount before and after exposure to n-butane at 973 K for 24 hrs.
Figure 5. The GC trace obtained from the carbonaceous deposits formed on Cu-plated stainless steel following exposure to n-butane at 973 K for 24 hours. The structures of selected species are given, along with numbers corresponding to the compounds in Table 1.

Table 1. Names and molecular weights for selected products that are shown in Figure 5.

| Peak no. | Name                                           | MW   |
|---------|------------------------------------------------|------|
| 1       | Ethyl methyl benzene, Propenyl benzene etc.    | 118  |
| 2       | 1,4-Dihydronaphthalene                         | 130  |
| 3       | Naphthalene: C_{10}H_{8}                        | 128  |
| 4       | Acenaphthene: C_{12}H_{10}                      | 154  |
| 5       | Acenaphthylene: C_{12}H_{8}                     | 152  |
| 6       | Phenanthrene, Anthracene : C_{14}H_{10}        | 178  |
| 7       | 2-methyl-phenanthrene, 1-methyl-anthracene: C_{15}H_{12} | 192  |
| 8       | 2-Phenylnaphthalene: C_{16}H_{12}              | 204  |
| 9       | Pyrene: C_{16}H_{10}                            | 202  |
| 10      | Benzo[a]fluorine, Benzo[b]fluorine: C_{17}H_{12} | 216  |
| 11      | Benzo[a]anthracene, Chrysene, Triphenylene: C_{19}H_{12} | 228  |
| 12      | Benzo-fluoranthene, Benzo-pyrene, Perylene: C_{20}H_{12} | 252  |
| 13      | Benzo[ghi]pyrphenene, Anthanthrene : C_{22}H_{12} | 276  |