



Cu-Ni Cermet Anodes for Direct Oxidation of Methane in Solid-Oxide Fuel Cells

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We have examined the use of Cu-Ni alloys as anodes for the direct oxidation of methane in solid-oxide fuel cells (SOFC) at 1073 K. Ceramic-metal (cermet) composites having alloy compositions of 0, 10, 20, 50 and 100% Ni were exposed to dry methane at 1073 K for 1.5 h to demonstrate that carbon formation is greatly suppressed on the Cu-Ni alloys compared to that of pure Ni. Increased reduction temperatures also reduced the carbon formation on the alloys. The performance of a fuel cell made with a Cu(80%)-Ni(20%) cermet was tested in dry methane for 500 h and showed a significant increase in power density with time. Impedance spectra of similar fuel cells suggest that small carbon deposits are formed with time and that the increase in performance is due to enhanced electronic conductivity in the anode. Finally, the implications of the use of metal alloys for SOFC applications are discussed.

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Fuel cells are an extremely promising method for electrical power generation due to their ability to achieve very high efficiencies with low levels of pollutants in the effluent. One of the challenges to commercializing them is the fact that most fuel cells require that the fuel be H₂, which is almost always produced by reforming hydrocarbons. This adds an additional level of complexity to the overall system. However, direct oxidation of hydrocarbons is theoretically possible in solid-oxide fuel cells (SOFCs) and has been demonstrated by a number of groups.¹⁻³ The principle of operation of an SOFC involves reduction of molecular O₂ at the cathode, diffusion of the O²⁻ through a zirconia-based electrolyte, and oxidation of any combustible fuel by O²⁻ at the anode.⁴ Unfortunately, carbon deposition on the anode can be a major problem. For example, conventional designs use a Ni-based anode and Ni tends to catalyze formation of graphite from hydrocarbons.

Our group has demonstrated that carbon formation at the anode is greatly suppressed when Ni is replaced by Cu.^{4,5} Unlike Ni, Cu is a poor catalyst for C-C bond formation, a necessary reaction for coke formation. Unfortunately, Cu is also a poor catalyst for C-H and C-C bond scission. In order to obtain reasonable performance for hydrocarbon oxidation with Cu-based anodes, we found that it is essential to incorporate an oxidation catalyst, ceria in our case, with the Cu. In addition to the low catalytic activity of Cu, Cu also has a much lower melting temperature than Ni, 1083°C compared to 1453°C. This lower melting temperature is likely to limit the operating temperatures that can be used to avoid sintering.

One approach for enhancing the activity and stability of Cu-based anodes involves alloying the Cu with a second metal that is more catalytically active and has a higher melting temperature. Ni is an obvious choice for the second metal, since the melting temperature of Cu-Ni alloys increases almost linearly with Ni content. Indeed, the Cu-Ni alloys have been used for the anodes in molten carbonate fuel cells.⁶ The reactivity of Ni for alkane hydrogenolysis and dehydrogenation, reactions which are likely to be related to anode coking reactions, is greatly modified by formation of an alloy with Cu.⁷⁻⁹ For example, Sinfelt and co-workers⁷ demonstrated that the hydrogenolysis activity of a series of Cu-Ni catalysts dropped by five orders of magnitude as the Cu content increased from 0 to 60%.

In this paper, we describe results with Cu-Ni alloys for direct oxidation of methane. The results suggest that there may be advantages to using Cu-Ni alloys for this application.

Experimental

Because oxides of Cu melt at temperatures lower than that required for sintering of the oxide components of the fuel cell, the ceramic-metal (cermet) composites that were used as the anodes in this study were prepared by impregnation of a porous matrix with metal salts, followed by reduction of those metal salts, as described elsewhere.⁴ Briefly, a two-layer, green tape of YSZ (yttria-stabilized zirconia, Tosoh, 8% Y₂O₃) is made by casting a tape with graphite pore formers over a green tape without pore formers. Firing the two-layer tape to 1800 K results in a YSZ wafer having a dense side, 60 μm thick in our case, supported by a porous layer, 400 μm thick. Hg porosimetry showed the porosity of the porous layer was 52%, with a fairly uniform pore-size distribution centered at ~2 μm. For those experiments requiring electrochemical measurements, a 50:50 mixture of YSZ and LSM (La_{0.8}Sr_{0.2}MnO₃, Praxair Surface Technologies) powder was applied as a paste onto the dense side of the wafer, then calcined to 1523 K to form the cathode. The porous anode layer was then impregnated with an aqueous solution of Ce(NO₃)₃·H₂O and calcined to 723 K to decompose the nitrate ions and form CeO₂. After the addition of ceria, the porous layer was impregnated with a mixed, aqueous solution of Cu(NO₃)₂·H₂O and Ni(NO₃)₂·H₂O having the desired Cu:Ni ratio. Finally, the wafer was again heated to 723 K in air to decompose the nitrates and reduced in flowing H₂ at 1173 K. Unless otherwise stated, the anodes in all of these studies were 10 wt % ceria and 20 wt % metal (Cu and Ni). The metal compositions given in this paper are based on weight percent of the metal phase.

To ensure that Cu-Ni alloys form under our synthesis conditions, X-ray diffraction (XRD) measurements were performed on a sample having a Cu-Ni ratio of 4:1. Only a single metallic phase was observed, with a lattice parameter between that of pure Cu and Ni, a result consistent with alloy formation.

For the electrochemical measurements, electronic contacts were formed using Pt mesh and Pt paste at the cathode and Au mesh and Au paste at the anode. The cell, having an anode surface area of 0.33 cm², was then sealed onto 1.2 cm alumina tubes using a zirconia-based adhesive (Aremco, Ultra-Temp 516). The electrochemical impedance spectra were measured using a Solatron 1286 electrochemical interface and Solatron 1250 frequency response analyzer. The typical frequency domain was 0.005 Hz to 65 kHz, and the measurements were performed with an open circuit.

Results and Discussion

To demonstrate the effect of alloy composition on the propensity of the anodes to form carbon, we made a series of cermets with varying Cu:Ni ratios, reduced them in H₂ at 1173 K for 3 h, and then exposed them to flowing CH₄ at 1073 K for 1.5 h. The results are

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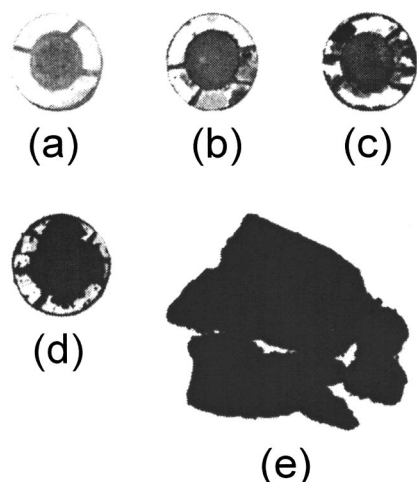


Figure 1. Photograph of cermets having 20% metal after reduction in H_2 at 1173 K for 3 h and exposure to CH_4 at 1073 K for 1.5 h. The photographs are shown for the following metal compositions: (a) 100% Cu; (b) 90% Cu, 10% Ni; (c) 80% Cu, 20% Ni; (d) 50% Cu, 50% Ni; and (e) 100% Ni.

shown in the photograph in Fig. 1. These wafers were identical to cells used in fuel cell testing, except that the cathode layer was not attached on the reverse side. The diameter of each wafer was 1.0 cm, and the white ring at the edge is YSZ used for handling samples. The cermet made with only Cu was unaffected by the treatment in CH_4 , showing no evidence for carbon formation and even maintaining its copper color. By contrast, the cermet made with only Ni formed large amounts of black carbon. The Ni cermet also fractured, probably due to the volume expansion associated with formation of Ni carbides. The Cu-Ni alloys all showed some carbon formation, as evidenced by the black powder on each sample, but the amount of carbon was clearly not proportional to the amount of Ni. For the alloy with a Cu:Ni ratio of 9:1, only small amounts of carbon formed. Even for a Cu:Ni ratio of 1:1, carbon formation appeared to be self limiting and the cermet did not fracture.

The effect of composition and pretreatment on the Cu-Ni alloy cermets is quantified in Table I. In these experiments, 0.1 g samples of YSZ powder were impregnated with mixed aqueous solutions of $Cu(NO_3)_2 \cdot H_2O$ and $Ni(NO_3)_2 \cdot H_2O$ to a loading of 10 wt % metal. After heating these powders to 750 K in air to decompose the nitrates, they were reduced in H_2 at either 1023 or 1173 K for 3 h, heated in flowing CH_4 at 973 K for the time shown, and then weighed to determine the amount of carbon that was deposited.

For the Cu-YSZ, sample, no weight change was observed upon exposure to CH_4 at 973 K. This confirms the earlier reports that Cu is inert under these conditions.⁵ Significant weight gains were observed with the 9:1 and 4:1 Cu-Ni alloys and the gains were larger on the sample having more Ni. What is more interesting is the fact

Table I. The effect of reduction temperature on carbon formation of Cu-Ni alloys. Samples having 10% metal on YSZ powder were reduced in H_2 for 3 h at the temperature shown and then exposed to flowing CH_4 at 973 K for the time shown.

Sample	Reduction temperature (K)	Exposure time (h)	Weight gain (g/g)
Cu	1023	12	<0.01
Cu-Ni(9:1)	1023	12	0.14
	1173	12	0.01
	1173	36	0.02
Cu-Ni(4:1)	1023	12	0.50
	1173	12	0.08
	1173	36	0.10

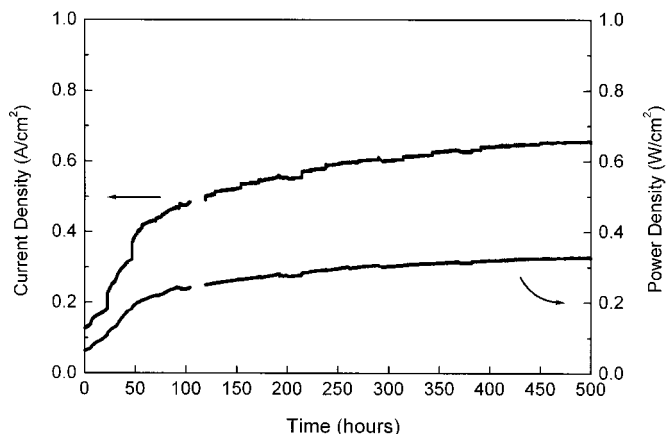


Figure 2. Plots of current density and power density as a function of time at 1073 K for a cell made with an alloy anode having 80% Cu and 20% Ni. The fuel was 100% CH_4 , and the cell potential was maintained at 0.5 V.

that significantly less carbon formed on the samples after they had been reduced in H_2 at 1173 K compared to when they were reduced at 1023 K. Since it has been suggested that the surface of Cu-Ni alloys tends to be enriched with Cu¹⁰ and since carbon formation on Ni likely requires a minimum Ni ensemble size,⁷ we suggest that the higher reduction temperatures lead to increased Cu enrichment. Notice that the surface concentration must not approach equilibrium rapidly at 973 K, the temperature at which carbon deposition was measured, or else the initial reduction temperature would not matter. Finally, the amount of carbon deposited on the alloys did not increase linearly with time, but seemed to approach a constant value after long times.

To determine whether the Cu-Ni alloys might be useful as anodes for direct-oxidation fuel cells, we made a model fuel cell with an alloy anode having a Cu:Ni ratio of 4:1. After ramping the cell to 1073 K in H_2 , the feed to the anode was changed to flowing CH_4 . Because of the small anode size, the conversion of the fuel was less than 1% for reasonable flow rates, implying that the $H_2O:CH_4$ ratio in the anode compartment was negligible. The cell potential was then fixed at 0.5 V and the current and power densities measured as a function of time, with the data shown in Fig. 2. The data demonstrate that, even at 500 h of operation, fouling due to carbon deposition is negligible. Rather, we observed a large increase in the performance with time, with the power density increasing by more than a factor of five.

Plots of the cell potential as a function of current density for H_2 and CH_4 on the Cu-Ni anode at 1073 K, performed at the conclusion of the 500 h test, are shown in Fig. 3. First, the open-circuit voltages (OCV) for both H_2 and CH_4 were approximately 1.0 V, slightly below the theoretical OCVs at this temperature. While a number of factors can cause a decreased OCV, it is important to point out that leaks in this cell were negligible. As in previous work which demonstrated direct oxidation of methane on Cu-cermet anodes,⁵ the conversion of methane to CO_2 and H_2O was low and corresponded to the ion flux through the electrolyte. Second, the potential vs. current lines remain straight to high current densities. If diffusional limitations were important, one would expect the slope to change more dramatically as the current density increased. The picture in Fig. 1 clearly implies that some carbon forms on anodes with a Cu:Ni ratio of 4:1, but the data in Fig. 3 demonstrate that this carbon must not block a substantial fraction of the pore volume in the anode. Finally, as reported in earlier work on direct oxidation of hydrocarbon fuels,^{5,11} the performance of the cells with H_2 was better than with CH_4 . In this particular example, the maximum power density was 0.44 W/cm^2 for H_2 and 0.33 W/cm^2 for CH_4 .

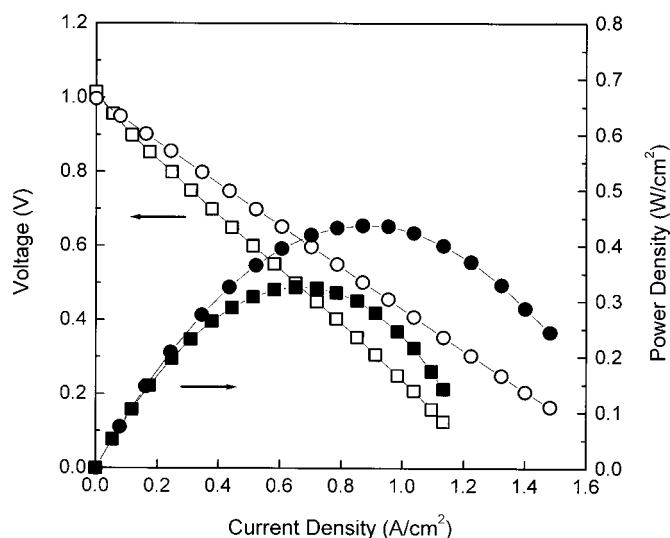


Figure 3. Plots of cell potential (open symbols) and power density (filled symbols) as a function of current density for the cell in Fig. 2 at 1073 K. The data were taken after completion of the 500 h test. The circles are for H_2 and the squares for CH_4 .

In an attempt to determine the reason for the increase in power density with time in Fig. 2, we measured electrochemical impedance spectra on a cell prepared in the same manner as that shown in Fig. 2 and 3. The power densities measured on this cell were somewhat lower than those obtained on the first cell; however, we again observed a dramatic increase in the performance with time on stream at 1073 K in pure CH_4 . The cell potential was again maintained at 0.5 V during the aging process. The electrochemical impedance spectra for this cell are shown in Fig. 4 after 32, 102, and 168 h. The total cell resistance, r_t , is the real-axis intercept at low frequency. Consistent with the increase in performance with time, r_t decreases from $\sim 16.5 \Omega \text{ cm}^2$ at 32 h in Fig. 4a to $1.6 \Omega \text{ cm}^2$ at 168 h in Fig. 4c. The impedance spectra also provide additional information on the cell performance. r_t is the sum of the ohmic resistance, r_R , and the interfacial resistance, r_i , which includes both reaction and transport resistances. Because r_R does not have an imaginary component, it is determined from the high-frequency intercept with the real axis. Each component of r_i will contribute an arc in the impedance spectrum so long as the characteristic response times for the processes are different.

What is most interesting about the data in Fig. 4 is the fact that both r_R and r_i decrease with time exposed to CH_4 , along with the total resistance of the cell. While it is difficult to determine r_R in Fig. 4a, r_R is $0.9 \Omega \text{ cm}^2$ after 102 h and $0.6 \Omega \text{ cm}^2$ after 168 h. Furthermore, there is evidence for at least two rate processes making up r_i after 32 h with resistances of $4 \Omega \text{ cm}^2$ (from 12 to $16 \Omega \text{ cm}^2$ in Fig. 4a) and $8 \Omega \text{ cm}^2$ (from 4 to $12 \Omega \text{ cm}^2$). Assuming these can be identified with similar processes at 168 h, the sum of the interfacial resistances have dropped to less than $1.0 \Omega \text{ cm}^2$. Finally, to make sure that the only changes in the fuel cell were occurring at the anode, the cell used for collection of the data in Fig. 4 was subjected to a mixed-gas treatment (5% CO , 95% CO_2) for 3 h to remove some of the carbon that had deposited after 168 h. Dry CH_4 was then reintroduced to the composite anode, and the spectra were measured, after 32 h in flowing CH_4 . The impedance spectra obtained after this procedure were very similar to the results shown in Fig. 4a, suggesting that changes in the cathode and electrolyte are not likely to have caused the changes in the resistances with time on stream.

An important question is how all of these resistances can decrease simultaneously? Furthermore, the data from Table I and Fig. 1, as well as the reversibility of the impedance spectra, would sug-

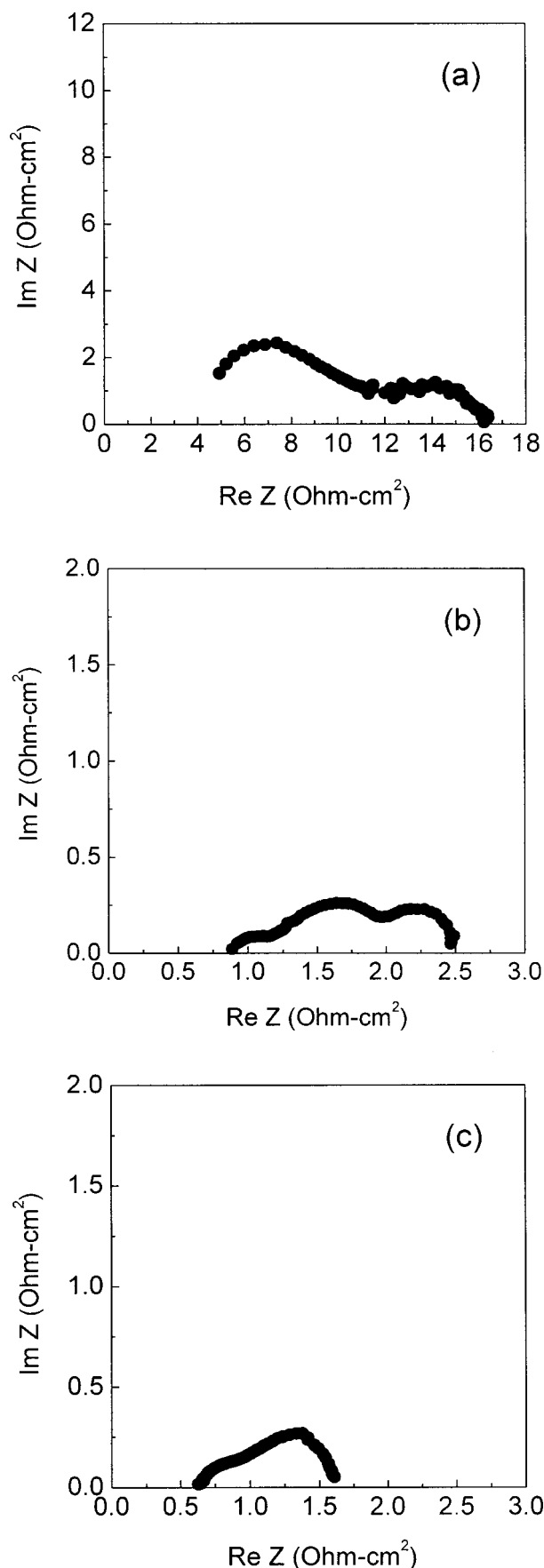


Figure 4. Impedance spectra for a Cu-Ni cermet anode (80% Cu, 20% Ni) at 1073 K with CH_4 fuel. The data were taken after (a) 32 h, (b) 102 h, and (c) 168 h.

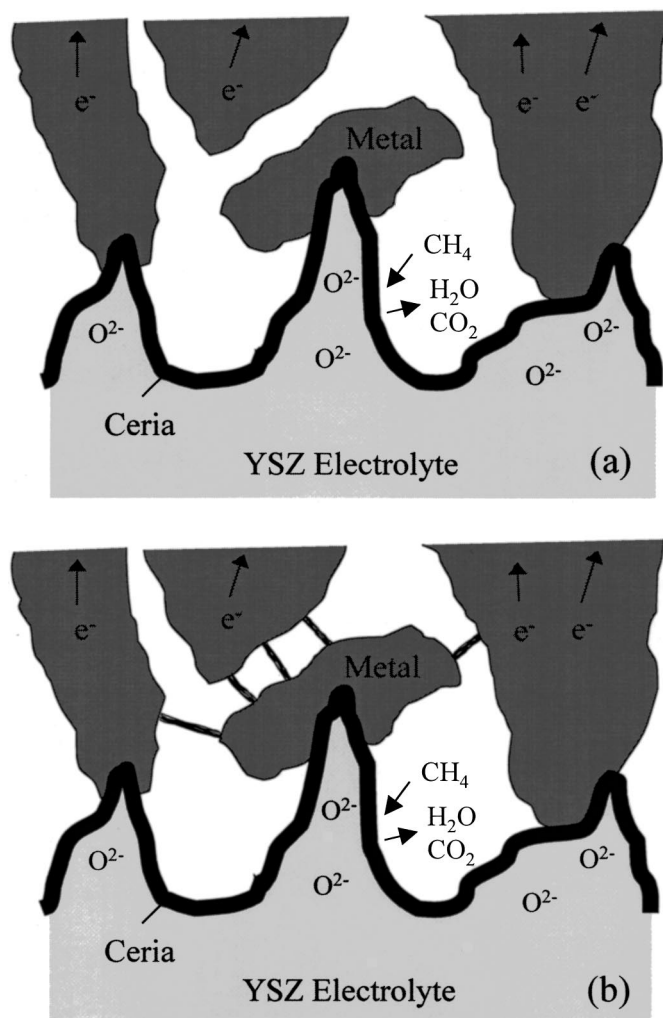


Figure 5. Model of the composite of the three-phase boundary (a) before and (b) after operation with CH_4 .

gest that the changes in the data are due to carbon deposition in the anode. Since one of the arcs in the impedance spectra is usually associated with diffusion, how can the diffusional resistance decrease with carbon deposition?

One possible model for understanding the results is shown in Fig. 5, which is a schematic of the three-phase boundary region at the anode. In previous papers describing Cu-based anodes,^{2,4} we have shown that Cu acts primarily as an electronic conductor, while ceria is a catalyst for oxidation of the fuel and may also assist in charge transfer at the interface. We assume that the Cu-Ni alloy is also mainly an electronic conductor. Following the lead of Virkar and co-workers,¹² we assume that “fingers” of YSZ from the electrolyte extend into the anode region to increase the transfer of O^{2-} ions. As shown in Fig. 5a, we suggest that some metal particles are

not connected to the outside circuit and cannot assist in the removal of electrons. Therefore, the entire region under the isolated metal particle is ineffective for the electrochemical reaction. With the addition of moderate levels of carbon, these isolated metal particles could become electronically connected to the outside circuit, as shown in Fig. 5b. Because more of the anode surface is now involved in the electrochemical reaction, the effect of using a higher fraction of the surface will be an apparent decrease in all of the resistances.

The experimental results in this paper have a number of implications for anode development in SOFCs. First, the fact that small amounts of carbon can apparently lead to such significant improvements in the fuel-cell performance has obvious implications for the Cu-based anodes prepared by impregnation of a porous matrix with Cu-containing salts.⁴ Presumably, the structure of these cermets will be similar to that of the Cu-Ni alloys, so that there may be isolated regions in the anodes of the Cu cermets as well. If this is the case, performance improvements might be possible by better engineering of the anode microstructures. For example, increased porosities for the YSZ component of the anode, as well as higher metal contents, should decrease the need for carbon to provide connectivity in the electronic component of the anode.

Second, it is clear that SOFC anodes based on Cu-Ni alloys have properties very different from that of either Ni-based cermets or Cu-based cermets. The catalytic properties of the alloys are not simply the sum of the properties of the two individual metals. While there have been some investigations of alloys in molten-carbonate fuel cells,⁶ relatively little has been done with alloys in SOFC. Clearly, this opens the door for the investigation of a large variety of materials which could have advantageous properties for fuel cells.

Conclusions

We have demonstrated that carbon formation is greatly suppressed on SOFC anodes based on Cu-Ni alloys compared to Ni-based anodes. It appears that direct-oxidation fuel cells made of Cu-Ni alloy cermets are feasible at 1073 K for CH_4 .

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