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Preparation of SOFC Anodes by Electrodeposition

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Anodes for solid oxide fuel cells (SOFCs) have been prepared by electrodeposition of either Co or Ni into a layer of porous yttria-stabilized zirconia (YSZ), 60 μm thick. The YSZ, having 65% porosity, was prepared by tape casting with graphite pore formers and was attached to the dense YSZ electrolyte. After adding 10 vol % CeO_2 by impregnation of aqueous solutions of $Ce(NO_3)_3$, followed by calcination at 723 K, the porous YSZ was made conductive by exposing it to *n*-butane at 1123 K to form a coating of carbon. As much as 40 vol % metal could be added to the porous layers, while the carbon could then be removed by exposing the anode to humidified H_2 at SOFC operating temperatures. The ohmic losses in cells containing 40 vol % Co or 30 vol % Ni were unaffected by heating to 1173 K. Finally, a cell with 15 vol % Cu and 15 vol % Co was prepared by electrodeposition of Cu onto electrodeposited Co. No carbon formation was observed on the Cu–Co anode following exposure to dry methane at 1073 K.
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Solid oxide fuel cells (SOFCs) have received a great deal of attention in recent years because they offer the promise of high efficiency and fuel flexibility.[1] These properties result primarily from the high operating temperatures that are required for diffusion of oxygen anions in the ceramic electrolyte, usually yttria-stabilized zirconia (YSZ). The best SOFC electrodes are composites of YSZ with an electronically conductive material, usually Ni at the anode and Sr-doped $LaMnO_3$ (LSM) at the cathode.[2] The YSZ in the composite electrodes plays a number of important roles, the most important being that it provides a good ion-conducting interface with the YSZ electrolyte, transporting oxygen ions into the electrodes and increasing the length of the three-phase boundary (TPB).

While electrodes based on Ni and LSM offer reasonably good performance, their widespread use is also due to the relative ease with which they can be fabricated. Because the reactivity of YSZ with both NiO and LSM is relatively low, Ni–YSZ and LSM–YSZ electrodes can be fabricated by simply mixing YSZ powder with either NiO or LSM, followed by high-temperature sintering. NiO–YSZ composites are easily reduced to form Ni–YSZ electrodes with good conductivity and porosity. Some alternatives to Ni, such as Co, cannot be produced in this way because Co cations from CoO_x diffuse into YSZ at the temperatures required for sintering the YSZ component of the electrode. Because Co has similar catalytic-reforming properties as that of Ni, a slightly higher melting temperature than Ni, and a lower affinity for sulfur than Ni,[3,4] there are potential advantages to Co–YSZ electrodes compared to that of Ni–YSZ. Finally, Co and Ni have different alloying properties with other metals, so that Co composites offer new opportunities for mixed metal electrodes. Recent studies have suggested that Cu–Co anodes exhibit good thermal stability and a high tolerance against carbon formation because Cu and Co do not form solutions and Cu tends to segregate to the surface of Cu–Co mixtures due to its lower surface energy.[5-7]

In order to produce composite electrodes with different compositions and microstructures, our laboratory has investigated an alternative fabrication method that does not require cofiring the components.[7-9] For SOFC with YSZ electrolytes, the method involves synthesizing porous YSZ layers on either side of a dense YSZ electrolyte layer, followed by addition of the conducting and catalytic components by impregnation of soluble salts into the electrode layer.[10] By sintering the porous YSZ together with the dense YSZ electrolyte, prior to the addition of the infiltrated salts, the treatment temperatures for the various components of the cermet can be different, thus avoiding the problems associated with solid-state reactions. The impregnation method has been used to make both anodes and cathodes with a wide range of compositions.[11] In addition to avoiding solid-state reactions, composites formed by impregnation have the additional advantage of forming nonrandom structures in which the impregnated phases coat the walls of the YSZ pores. This structure results in composites that have a thermal expansion match close to that of the YSZ backbone[12] and good conductivities at loadings of the conductive phase that are well below the normal percolation threshold for random media.[13]

One drawback of the impregnation method is the difficulty of fabrication. While porous-dense, YSZ structures can be produced by inexpensive tape-casting methods,[10] the impregnation procedure is tedious due to the requirement of using multiple steps. For example, to achieve sufficient conductivity and stability for LSM–YSZ composites by impregnation, it is necessary to fill a minimum of 15% of the pore volume with LSM.[14] Based on studies of Cu anodes,[15] even higher loadings appear to be required for metals. However, the maximum amount of the electronic conductor that can be added in a single impregnation step is limited by the cation content of the solution volume that fills the pores. In the case of LSM prepared using nitrate salts,[16] it was necessary to use multiple impregnation steps, even when using molten salts with essentially no water, due to the large volume of the nitrate anions. A higher concentration of metal could be obtained using solutions with less bulky anions, such as Cl^-, but removal of these anions during subsequent calcinations would be difficult. The use of nanoparticle solutions avoids the need for charge-neutralizing anions, but the concentrations of metal ions in nanoparticle solutions tend to be low compared to salt solutions.[16]

A potentially simple method for adding large amounts of metal to the porous electrode in a single step involves electrodeposition. In past work from our laboratory, bimetallic composites have been prepared by electrodeposition of Cu into highly porous, 1.2 mm thick Ni–YSZ cermets[8] and both Cr and Co into thin Cu–YSZ composites.[7-9] Because electrodeposition requires that the substrate onto which the metals are to be deposited be conductive, past work from our laboratory required a pre-existing ceramic–metallic (cermet) composite. Because it would be desirable to electrodeposit directly into the porous ceramic, we set out to determine whether the substrate could be made conductive through the use of carbon coatings.[17-19]

In this paper, we demonstrate the synthesis of Ni and Co cermets by electrodeposition into carbon-coated, porous YSZ. While we found it difficult to electroplate Cu in this way, we show that Cu can be plated onto an electroplated-Co layer so as to produce a composite that is stable against the formation of carbon when exposed to hydrocarbon fuels at high temperatures.

Experimental

Cell fabrication.— The initial step in fabricating cells for this study involved producing YSZ wafers with a 300 μm thick dense

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Table I. Carbon content and conductivity of YSZ layer as a function of time exposed to *n*-butane at 1123 K.

Deposition time (min)	Wt % carbon	Vol % carbon	Resistance
5	2	3	Not conductive
7	4	6	Conductive
10	7	11	Conductive
30	16	29	Conductive

layer attached to a 60 μm porous layer. The diameter of the YSZ wafer after firing was 1 cm but the diameter of the porous layer that would become the electrode was only 0.65 cm. These wafers were synthesized by laminating two green tapes that had been prepared by tape-casting methods, with one tape containing graphite pore formers in order to achieve 65% porosity after sintering. The tapes were prepared using aqueous-based slurries of YSZ (Tosoh, 8 mol % Y_2O_3) as described elsewhere.[10] After sintering the YSZ wafer to 1823 K, the cathode, a 50 wt % mixture of YSZ and LSM ($La_{0.8}Sr_{0.2}MnO_3$, Praxair), 50 μm thick, was painted onto the dense side of the wafer and the calcined to 1523 K. The area of the cathode was the same as that of the porous layer that would become the anode. After applying the LSM–YSZ cathode, 10 vol % ceria was introduced into the porous YSZ layer by sequentially impregnating aqueous solutions of $Ce(NO_3)_3 6H_2O$ (Alfa Aesar) and calcining to 723 K in air.

After introducing the ceria, a carbon layer was deposited onto the porous YSZ to make the porous layer electronically conductive for electrodeposition. The carbon was deposited by exposing the porous layer to *n*-butane at elevated temperatures. To ensure that the LSM cathode was not affected in this process, the cells were sealed onto an alumina tube so that only the porous layer was exposed to the hydrocarbon. For noncatalytic surfaces, pyrolysis of *n*-butane to polyaromatic species occurs in the gas phase,[20,21] followed by condensation of electronically conductive polyaromatics onto the surface of the porous layer. Because the formation rate of polyaromatics depends strongly on the flow geometry and the time with which the *n*-butane remains at high temperatures,[20] we only studied the carbon deposition rate qualitatively. At 1073 K, we found that it was necessary to expose the porous layer to *n*-butane for several hours to make the anode substrate conductive; at 1173 K, the layer became conductive within minutes, making it difficult to control the amount of carbon deposited. Therefore, in this study, carbon was deposited at 1123 K as a compromise between the two temperature extremes. Table I shows the wt % and vol % of carbon in the porous layers as a function of deposition time (the vol % carbon was calculated from the weight change, assuming that the density of the deposits was that of graphite). A rough estimate of the conductivity of the carbon film was determined at room temperature using a handheld ohmmeter.

Both Ni and Co were electroplated onto conductive-carbon substrates (11 vol % carbon) from aqueous solutions. Electrical connection for electrolytic deposition was achieved using a Ag wire that had been attached to the porous electrodes with Ag paste. The LSM cathode and the Ag wire were sealed with wax to keep them from being exposed to the plating bath. Both Co and Ni were plated onto carbon layers with a Gamry potentiostat (model 1286A). In order to achieve uniform plating of the metals inside the porous electrodes, it was necessary to avoid both concentration gradients and potential gradients in the plating solution within the YSZ pores.[8] Concentration gradients were minimized by using low plating currents and relatively high concentrations of metal salts in the plating solution. Potential gradients in the solution were minimized by maximizing the solution conductivity.

The Co electrolyte solution contained 0.5 M in $CoCl_2 \cdot 6H_2O$, with 60 g/L H_3BO_3. A Co foil was used as the counter electrode. For Ni, the solution was similar except a 1.5 M solution of $NiCl_2$ was substituted for the Co salt and a Ni wire was used as the counter electrode. The electrodeposition current was maintained at 1.5 mA in both cases. (Note: the use of metal-chloride salts in electrodeposition did not lead to chloride contamination.) The temperature of the electrolyte solution was 323 K; upon completion of the plating process, the electrode was thoroughly rinsed with deionized water. The total amounts of added metal were determined by measuring the weight changes in the sample but these values were identical to the amounts determined coulometrically.

As discussed in previous publications,[8,22-25] uniform plating of Cu requires the use of dilute solutions and low current densities. While we were unable to prepare uniform Cu deposits directly on the carbon substrate, we were able to synthesize Cu–Co bimetallic composites by electroplating Cu onto Co. This was accomplished using an electrolyte bath made up of 0.02 M $CuSO_4$ and 0.25 M sodium citrate ($Na_3C_6H_5O_7$) and a deposition current of 0.2 mA. The pH of the bath was adjusted to a value of 2 by the addition of H_2SO_4.

Characterization procedures.— To test the performance of the metal composites as SOFC anodes, the cells were attached to an alumina tube with a ceramic adhesive (Aremco, Ceramabond 552). Most of the tests were in humidified H_2 (3% H_2O) at the anode with the cathode simply exposed to air, although higher steam concentrations were used in some experiments to ensure that carbon had been removed.[21] Impedance spectra were measured in the frequency range of 0.1 Hz to 100 KHz using a Gamry Instruments potentiostat. In all cases, Ag paste and wire were used as the current collector under both air and fuel conditions.

The samples were also examined using scanning electron microscopy (SEM, JEOL-6400) and energy dispersive X-ray spectroscopy (EDS) to determine the distributions of Ni and Co in the composites. Because Cu and Co are immiscible and because Cu layers on Co are effective in preventing the carbon formation that would normally occur on Co during exposures to methane at high temperatures,[7] the Cu–Co composites were simply exposed to dry methane at 1073 K in order to determine whether Co remained exposed.

Results and Discussion

Figure 1 shows SEM images in the region near the electrolyte interface for the porous YSZ, before and after incorporation of 10 vol % ceria and either 20 vol % Ni or 30 vol % Co. In the case of the Ni and Co composites, the SEM images were taken after the electrodes were heated in air at 1073 K to remove carbon and then treated in H_2 at 1073 K to reduce the metals. As discussed elsewhere,[26] the structure and porosity of the YSZ matrix is determined by the size, shape, and quantity of the pore formers. For this case, Fig. 1a indicates that the YSZ matrix has the appearance of a sponge, with pores roughly 2 μm in diameter making up 65% of the total volume. After the addition of ceria and either Co (Fig. 1b) or Ni (Fig. 1c), a significant fraction of the pore volume has been filled. The inner surfaces of the metal-containing composites were also much rougher in appearance.

To ensure that the metals were deposited down to the electrolyte interface, we examined the composites from Fig. 1 using EDS. The EDS results were obtained while averaging a spot roughly 10 μm in diameter. The data (not shown) indicated that the compositions of both the Ni and Co composites are uniform down to the electrolyte interface, within the experimental accuracy of the technique. Indeed, there was no evidence for preferential metal deposition near the composite-fluid interface for loadings below 40 vol %. It was easy to detect when metal deposition occurred on the external surface of the composite at loadings above 40 vol %, because the metal film would grow out from the porous electrode layer, over the electrolyte surface. This did not occur in the samples shown here.

Additional proof for metal depositing within the pore structure came from observing the results of oxidizing Ni cermets with different Ni contents. When a composite with 30 vol % Ni was oxidized at 1073 K in air, there was no noticeable damage to the electrode layer. Complete oxidation of the Ni in this case would result in

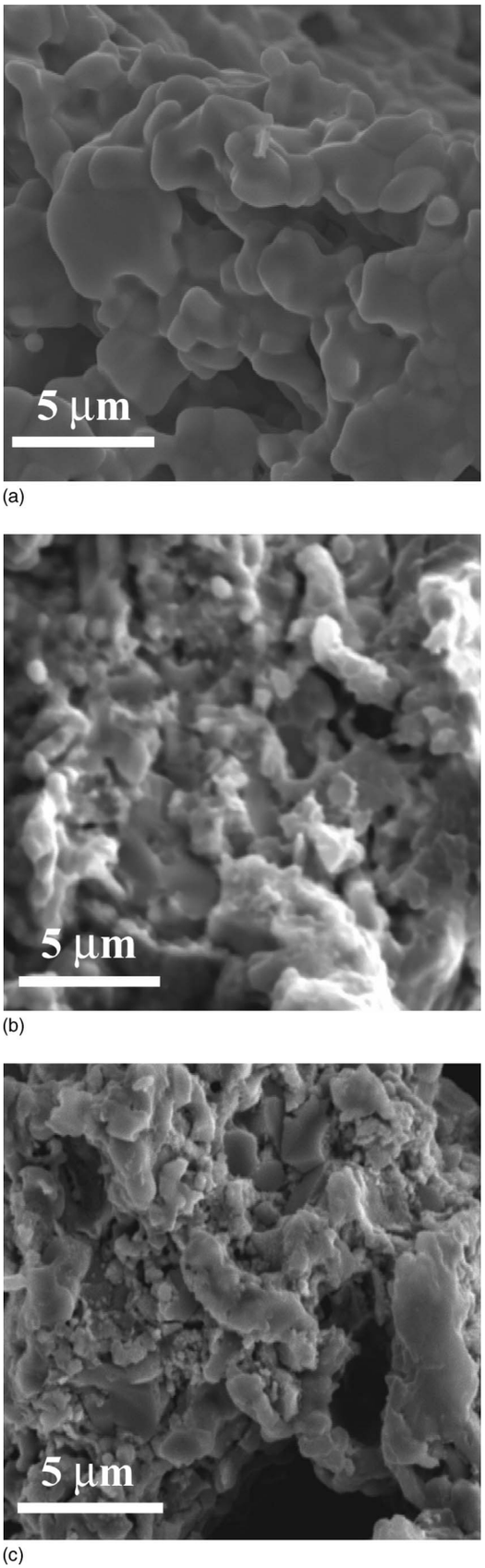

Figure 1. SEM images of a porous YSZ matrix (a) before and (b) after incorporation of 10 vol % ceria and 20 vol % Ni or (c) 30 vol % Co.

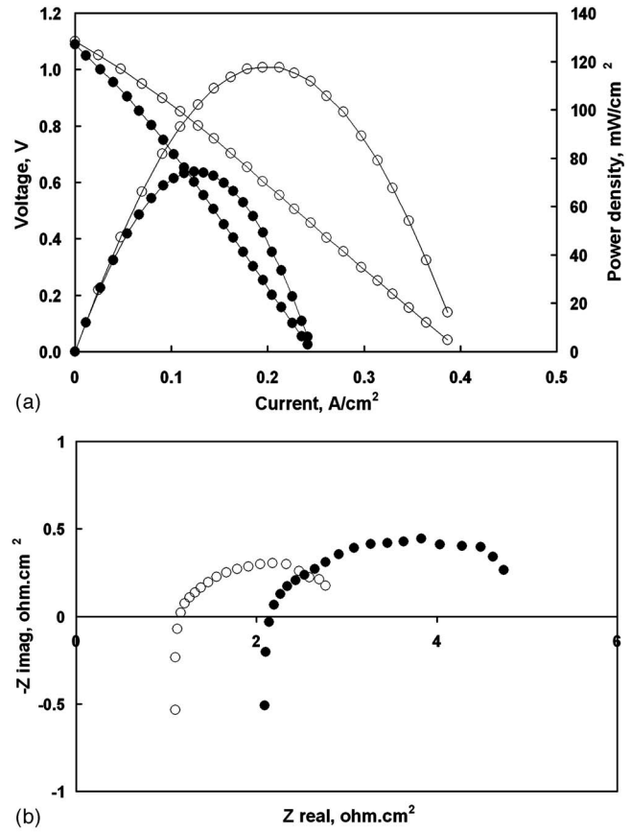

Figure 2. (a) *V-i* polarization and (b) impedance spectra for an SOFC with an anode containing 10 vol % ceria and 29 vol % carbon operating on humidified H_2 at 1073 K. Data are shown (○) before and (●) after treatment in H_2 with 30 vol % H_2O at 1073 K for 2 h.

a NiO phase that should fill 52% of the pore volume. (Notice that we do not suggest that the composite with 30 vol % Ni would be stable with repeated oxidation and reduction cycles.) When a composite with 40 vol % Ni was oxidized under the same conditions, the composite turned into a powder that flaked off the electrolyte layer. The calculated volume of the NiO in this case, which would be 71%, exceeded the available pore volume of the structure.

Before testing the electrochemical activity of the metal composites, a cell having 10 vol % ceria and 29 vol % carbon was tested in humidified H_2 (3% H_2O) at 1073 K, because previous work had shown carbon-ceria composites could exhibit reasonable performance as SOFC anodes.[27] Voltage-current density (*V-i*) polarization curves and impedance spectra for this cell are shown in Fig. 2. Figure 2a indicates that the cell exhibited an open-circuit voltage (OCV) close to the Nernst potential of 1.07 V and an initial maximum power density of 118 mW/cm^2; however, the maximum power density dropped to 74 mW/cm^2 after the anode was treated in H_2 with 30 vol % H_2O at 1073 K for 2 h. The impedance spectra in Fig. 2b demonstrate that the loss in performance was due to an increase in the ohmic resistance of the cell, which changed from approximately 1.1 to 2.2 Ω cm^2 following treatment in steam. At 1073 K, the 300 μm electrolyte is expected to contribute 0.7 Ω cm^2 to the ohmic resistance, so that the electrical resistance of the lead wires and resistance of the carbon film can explain the initial ohmic resistance of 1.1 Ω cm^2. Because carbon deposits on ceria are easily oxidized by steam at 1073 K,[21] the higher resistance following treatment in steam is almost certainly due to removal of the carbon, with the remaining residual conductivity likely due to the ceria film within the porous YSZ. Using the increase in the ohmic resistance to

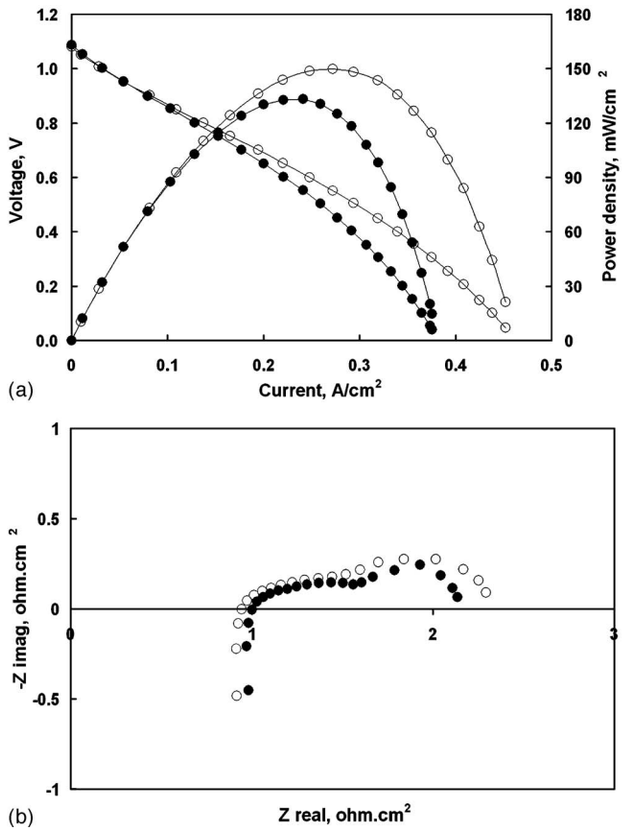

Figure 3. (a) *V-i* polarization and (b) impedance spectra for an SOFC with an anode containing 10 vol % ceria and 30 vol % electroplated Ni operating on humidified H_2 at 1073 K (○) before and (●) after heating to 1173 K for 2 h in a 70% H_2–30% H_2O mixture.

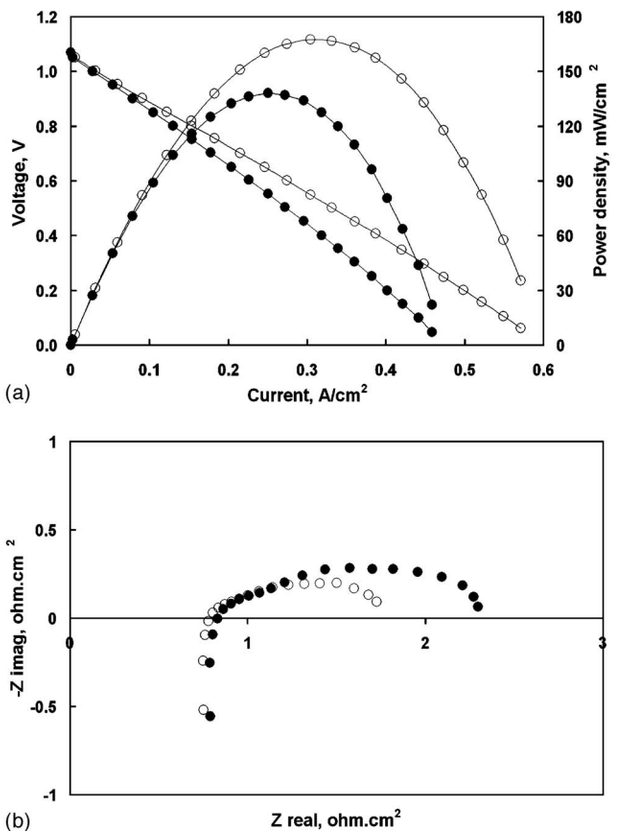

Figure 4. (a) *V-i* polarization and (b) impedance spectra for an SOFC with an anode containing 10 vol % ceria and 40 vol % electroplated Co operating on humidified H_2 at 1073 K (○) before and (●) after treatment with a 50% H_2–50% H_2O mixture at 1073 K for 2 h and heating to 1173 K in a 97% H_2–3% H_2O overnight.

calculate the conductivity of the 60 μm anode after carbon removal, we obtain a value of 0.005 S/cm. This is in good agreement with earlier measurements that porous YSZ with 10 vol % ceria has a conductivity of approximately 0.01 S/cm in the anode environment.[15]

The performance in humidified H_2 at 1073 K of a cell with an anode containing 30 vol % Ni and 10 vol % ceria is reported in Fig. 3. Data are given for the initial performance and after heating to 1173 K for 2 h in a 70% H_2–30% H_2O mixture. The higher temperature used for steaming the anode in this case was to ensure that all carbon was removed without oxidizing the Ni. (Note: separate experiments were performed using temperature programmed oxidation to demonstrate that these conditions were sufficient to remove carbon.[21]) As indicated in Fig. 3a, the maximum power density again decreased following the treatment in steam, from 149 to 133 mW/cm^2. However, the impedance spectra in Fig. 3b indicate that the ohmic resistance increases only slightly after the high-temperature steam treatment, from 0.95 to 1.0 Ω cm^2, showing that the Ni maintains conductivity in the composite. Unfortunately, the non-ohmic losses are large, nearly 1.4 Ω cm^2. Because earlier work showed that similar LSM–YSZ cathodes exhibited a polarization loss of 0.4 Ω cm^2 at 973 K,[14] the anode losses of the Ni-ceria-cermet in this study must be greater than 1.0 Ω cm^2.

We suggest that there are two reasons for the low performance of this Ni–ceria anode. First, high-performance Ni–YSZ anodes have a finer pore structure near the electrolyte interface.[28] Second, while the addition of ceria with the metal can significantly improve the performance of the anode, the properties of the ceria are strongly dependent on the pretreatment conditions that it receives.[29-31] We reproduced this result in the present study by testing two fuel cells that were identical except for having the ceria layer calcined to 723 K in one case and 1123 K in the other. The Co in these two cells was added by impregnation of the nitrate salts to avoid the need to add carbon, as earlier work has shown electrodes prepared in this way can exhibit good performance.[12] The cathode was again a 50:50 mixture of LSM, prepared in exactly the same way as when the Co was added by electrodeposition. The total electrode polarization losses for the cell with ceria calcined to 723 K were 0.5 Ω cm^2 at 1073 K in humidified H_2, while the total electrode losses for the 1123 K cell were 1.0 Ω cm^2. While the electrode losses on the 1123 K cell were lower than we observed on the cells prepared by electrodeposition, the treatment under the reducing conditions required for carbon deposition has been shown to have a much larger affect on ceria surface area and reducibility.[32]

Results for a cell with an anode having 40 vol % Co are shown in Fig. 5. Data are again reported for the initial performance and after treatment to remove carbon. In this case, the anode was treated with a 50% H_2–50% H_2O mixture at 1073 K for 2 h, after which it was heated in 97% H_2–3% H_2O to 1173 K overnight. Figure 4a indicates that the maximum power density in humidified H_2 at 1073 K was initially 175 mW/cm^2 and that this decreased to 135 mW/cm^2 after the treatment to remove carbon. Impedance spectra in Fig. 4b show that the ohmic resistance of the cell was between 0.7 and 0.8 Ω cm^2 and was again unaffected by the anode treatments.

Finally, we examined Cu–Co–ceria composites prepared with 15 vol % Cu electroplated onto 15 vol % Co. To show that Cu completely covered the Co layer, we first heated two samples, one with and one without the Cu, in dry CH_4 for 4 h at 1073 K. While Co

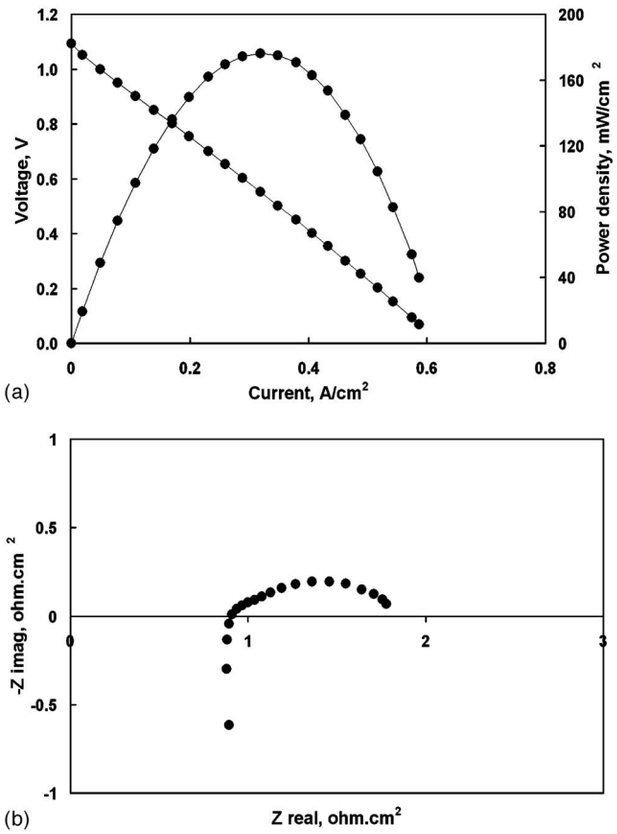

Figure 5. (a) *V-i* polarization and (b) impedance spectra for an SOFC with an anode containing 10 vol % ceria, 15 vol % electroplated Cu, and 15 vol % Co operating on humidified H_2 at 1073 K after treatment in a 50% H_2–50% H_2O mixture at 1073 K for 3 h.

does not form carbon fibers as severely as does Ni,[7] there were significant deposits of carbon on the electrode that did not have Cu and one edge of the porous layer broke off from the electrolyte due to the stresses associated with the carbon formation. By contrast, there was no evidence for any carbon formation on the Cu-containing cell, similar to what has been reported previously for Cu–Co composites exposed to methane.[7]

The *V-i* polarization and the corresponding impedance data are reported in Fig. 5 for a cell with a Cu–Co anode operating in humidified H_2 at 1073 K. The anode had been treated in a 50% H_2–50% H_2O mixture at 1073 K for 3 h to remove carbon. This cell exhibited the best performance of all the cells we tested, exhibiting a maximum power density of 175 mW/cm^2. The ohmic resistance remained good for the 300 μm electrolyte, 0.9 Ω cm^2, and the nonohmic losses were less than 1.0 Ω cm^2. We had anticipated that the Cu-containing anode would perform much worse than those with only Co or Ni, because Cu is a much poorer oxidation catalyst than either Co or Ni. Furthermore, the metal surface in the Cu–Co-ceria anode is almost certainly pure Cu, both because Cu was deposited onto the Co and because of the thermodynamic driving force for Cu remaining at the surface.[7] The fact that the performance of the electrodes is similar with all the metals and that anode losses are strongly affected by how the ceria layer is treated suggests that ceria is playing the main catalytic role in these cells, with the metals primarily providing electronic conductivity.

We did not attempt to optimize the performance of electrodes made by electroplating the metals. The goal of the present study was simply to demonstrate that high loadings of metals could be incorporated using inexpensive and relatively simple electroplating methods. It is likely that tailoring of the microstructure and the catalytic properties of the ceria (e.g., by using a ceria–zirconia mixed oxide[30]) would lead to better performance.

In addition to providing an easy and scalable method for adding metals, the electroplating approach to electrode fabrication also allows preparation of novel electrode structures, such as the layered structures in the Cu–Co case. With the Cu–Co-ceria electrodes, this layered structure provides electrodes with the carbon tolerance of Cu and the thermal stability of Co, but there may be other advantages to layered structures. For example, coatings of chromia on Ni cermets might enhance the tolerance of the electrodes to redox tolerance if chromia layers can suppress Ni oxidation.

Clearly, additional work would be needed to make these composite electrodes prepared by electrodeposition practical. However, we believe that the principles outlined in this study can be used for preparing electrodes with potentially useful structures.

Conclusion

It is demonstrated that metal–ceramic (cermet) composites with high metal loadings can be prepared by electroplating Ni or Co onto carbon films prepared by pyrolyzing hydrocarbons onto porous oxide substrates. Electroplating can also be used to prepare cermets with different metal layers, such as Cu-covered Co, to achieve unique properties that would not be possible with an electrode made from a single metal.

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