Silver-BaCe$_{0.8}$Gd$_{0.2}$O$_3$ Composites as Cathode Materials for SOFCs Using BaCeO$_3$-Based Electrolytes

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ABSTRACT

Composites of silver and BaCe$_{0.8}$Gd$_{0.2}$O$_3$ ceramics have been studied as cathode materials for intermediate-temperature solid oxide fuel cells using BaCeO$_3$-based electrolytes. Results indicate that the electrochemical properties of these composites are quite sensitive to the composition and microstructure of the electrodes. The optimal silver content of the composites seems to fall within the range of 50 to 70 volume percent, depending on the particular microstructure of the electrode. As compared to pure silver electrodes, the composite electrodes show better adhesion to the electrolyte, higher exchange current densities, and lower cathodic overpotentials under various conditions. The observed high performance of the composite electrodes is attributed primarily to the fine-grained microstructure and high porosity of the composites, as the BaCe$_{0.8}$Gd$_{0.2}$O$_3$ phase inhibits grain growth of the silver phase in the composites.

Introduction

The overall performance of a solid oxide fuel cell (SOFC) is determined by the electrochemical characteristics of each and every cell component, including the electrolyte, the cathode, and the anode.[1-7] For a given electrolyte material, the selection of suitable electrodes, *i.e.*, the cathode and the anode, becomes a key issue. Barium cerate (BaCeO$_3$) based electrolytes are considered to be promising electrolytes for SOFCs to be operated at intermediate temperatures (600 to 800°C).[8] Compared to high-temperature SOFCs based on yttria-stabilized zirconia electrolytes, the performance of intermediate-temperature SOFCs depends more on the electrode-electrolyte interfaces, since the interfacial polarization of solid-state cells increases rapidly with the decrease of temperature.[5-7] Accordingly, the development of catalytically active electrode materials is crucial to achieving high performance for intermediate-temperature SOFCs using BaCeO$_3$-based electrolytes.

The electrodes for SOFCs should have high electrical conductivities, high catalytic activities, adequate porosity for gas transport, good compatibility with the electrolyte, and long-term stability. In order to achieve high catalytic activities, it is preferred that the electrodes be highly porous so that they retain a large number of active sites for electrochemical reactions, *i.e.*, the triple-phase points or triple-phase boundaries. For SOFCs using BaCeO$_3$-based electrolytes, silver (Ag) has been studied as a cathode material since silver is known to have high catalytic activity for oxygen reduction and evolution. At temperatures below 800°C, the evaporation of Ag seems not to be a problem (the evaporation loss of Ag was reported to be only 0.3 μm/year at 750°C in the literature[9]). However, two major problems remain when Ag is used as cathodes for BaCeO$_3$-based electrolytes. First, Ag electrodes readily densify at relatively low temperatures (such as 850°C or even below 800°C, at which the electrodes are processed and operated) resulting in a dense electrode with little porosity. This significantly deteriorates the performance of the electrodes because the number of the triple-phase points or boundaries is reduced and the impedance to gas transport through the electrodes is increased. Second, pure Ag electrodes have poor adhesion to the BaCeO$_3$-based electrolytes due to a large mismatch in thermal expansion coefficients between the two materials.

In order to overcome these problems, we have studied Ag-ceramic composite electrodes. In the composites, the densification of the Ag phase is inhibited by the ceramic phases. The electrodes then retain a porous microstructure while the SOFC undergoes thermal tensions during processing and operation. Clearly, the retained porous microstructure will significantly enhance the performance

of the electrodes. In addition, electrodes of this kind should have better adhesion to the electrolytes, since the stress arising from thermal expansion mismatch is minimized not only by the porous, heterogeneous microstructure of the electrodes but also by tailoring the thermal expansion coefficient of the composites. Further, there is still another potential advantage with using the composite electrodes. If the ceramic phases added are ionic conductors or mixed electronic-ionic conductors, the composite electrodes as a whole may turn out to be a mixed conductor, which allows ambipolar transport within the solid phase which is generally favored for catalytic electrodes.[3]

Composites of Ag- and BaCeO$_3$-based ceramics are logical candidate cathode materials for BaCeO$_3$-based electrolytes, for three obvious reasons. First, BaCeO$_3$ containing electrode materials are compatible both chemically and physically with BaCeO$_3$-based electrolytes, and there will be minimum reactions at the interface between the electrolyte and the electrode. Second, the problem of thermal expansion mismatch will be minimized, and the adhesion of the electrodes to the electrolytes will be improved. Third, BaCeO$_3$-based ceramics have high melting points, and the added ceramic phase inhibits the grain growth of the Ag phase. In this study, composites of Ag and BaCe$_{0.8}$Gd$_{0.2}$O$_3$ were evaluated as cathode materials. Electrochemical properties of these cathodes were investigated and correlated with the compositions and microstructures.

Experimental

A series of Ag-BaCe$_{0.8}$Gd$_{0.2}$O$_3$ composite pastes with different Ag contents were prepared by mixing a powder of BaCe$_{0.8}$Gd$_{0.2}$O$_3$ (abbreviated to BCG) and unfritted Ag paste (Heraeus: C4400UF) in different ratios. Porous composite electrodes were obtained by screen-printing the composite pastes onto pellets of BaCe$_{0.8}$Gd$_{0.2}$O$_3$ electrolytes and firing at 900°C for 10 min. For comparison, pure Ag electrodes were also prepared by screen printing and firing under the same conditions and were studied in parallel with the composite electrodes.

The microstructures of the fired electrodes were studied using a Hitachi S-800 scanning electron microscope (SEM). A statistical "point counting" method in quantitative stereology[10] was employed to estimate the porosity and the volume fraction of the BCG phase (and hence the Ag phase) in the composite electrodes. In estimating porosity, a transparent grid consisting of seven horizontal and nine vertical lines, thus forming a mesh with 63 nodes (points), was placed on SEM images of appropriate magnifications (4000 times to 6000 times), and the number of points that lie in the pores was counted. This number divided by the total number of test points (63) yielded a fraction of points in the pores. The counting was repeated at least ten times on different SEM views, thus obtaining

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an average value of the point fraction, which directly approximates the porosity.[10] Apparent volume fraction of the BCG phase or the Ag phase was similarly estimated. To specify the composition of a composite, this apparent volume fraction was adjusted to a volume fraction relative to the volume of the solid phases, i.e., excluding the porosity. The volume fractions of Ag in the solid phase estimated using this method were in good agreement with the values calculated from the compositions of the composite pastes.

Both three-electrode and four-electrode configurations were used for the electrochemical characterization of the cells.[5] A computerized impedance analysis system, consisting of a Schlumberger frequency response analyzer (SI 1255) and an electrochemical interface (SI 1286), was used to measure the impedance of the cells at temperatures ranging from 660 to 740°C in open air in the frequency range from mHz to MHz. From the impedance spectra acquired, exchange current densities of the electrode-electrolyte interfaces were calculated as the key kinetic parameter characterizing the electrochemical activity of the electrodes for oxygen reduction and evolution.

Cathodic overpotentials of the symmetrical cells in dry air, wet air, and oxygen were determined using four-probe impedance and polarization techniques.[11] In addition, cathodic overpotentials under fuel cell conditions were studied using the following cell configuration

H_2 + 3 v/o H_2O (1 atm), Pt | $BaCe_{0.8}Gd_{0.2}O_3$ | Ag
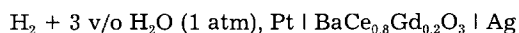
or Ag-BCG, air (1 atm)

The wet air and wet hydrogen were produced by flowing air or hydrogen through a water bubbler at room temperature. The wet gases thus contained about 3 volume percent (v/o) of water vapor. All the overpotential measurements were made at temperatures between 600 and 750°C, which is the preferred operation temperature range of the $BaCeO_3$-based SOFCs.

Results and Discussion

Adhesion.—Since $BaCe_{0.8}Gd_{0.2}O_3$ typically sinters at temperatures above 1500°C, the $BaCe_{0.8}Gd_{0.2}O_3$ phase in the composite did not sinter with the electrolyte when a Ag-BCG composite electrode was fired at 900°C for 10 min. However, the Ag-BCG composite electrodes as a whole attained a much better adhesion to the electrolyte in comparison to pure Ag electrodes. While the adhesion of Ag electrodes to $BaCe_{0.8}Gd_{0.2}O_3$ electrolytes was seemingly improved slightly by increasing the firing temperature of the electrodes, it is impractical to increase the firing temperature above 900°C due to rapid densification and significant evaporation of Ag at these temperatures. Firing Ag electrodes at 900°C for 10 min resulted in a weak bonding between the Ag layer and the BCG electrolyte due to a large mismatch in thermal expansion coefficients between Ag and the electrolyte (the thermal expansion coefficient of BCG was found in the neighborhood of 9×10^{-6}/°C while the thermal expansion coefficient of Ag is about 19×10^{-6}/°C). The bonding could not withstand repeated heating-cooling cycles (from ambient temperature to 800°C); the Ag layer usually delaminated from the electrolyte after the second heating-cooling cycle. In practice, it is very difficult to use pure Ag as electrode for BCG electrolytes due to the poor bonding. In contrast, the Ag-BCG composite electrodes retained good adhesion to the BCG electrolyte after repeated heating-cooling cycles. This is because the ceramic phase in the composite interrupts the Ag phase, and the mismatch in thermal expansion coefficients between the composite electrode and the electrolyte is reduced. The stresses caused by thermal expansion mismatch between the Ag phase in the composite and the electrolyte are further relieved by the porous microstructure of the composite layer.

Microstructure.—Figure 1 shows SEM photographs of some typical surface views of the Ag-BCG composite electrodes and the pure Ag electrodes. The microstructure of the composite electrodes is completely different from that of pure Ag electrodes. The microstructure of the fired Ag electrodes appears to be dense, even before being subjected to any measurement at high temperatures, as shown in Fig. 1a. The Ag electrode is nearly pore-free and consists of densely packed large grains. The grain size ranges from 6 to 20 μm. Clearly, this type of microstructure is highly undesirable since the resistance to gas transport through the electrode is high and the triple-phase points and boundaries among Ag, electrolyte, and gas are minimal. However, the microstructure showed little change with time at high temperatures during measurements or operation; the long-term stability of the electrode may be expected to be good.

The microstructure of Ag-BCG composite electrodes, on the other hand, is highly porous. The freshly fired composite electrodes look like an aggregate of loosely packed fine-grained particles (Fig. 1b). Compared to the pure Ag electrodes, the grain size of the Ag phase (darker particles) in the composite electrode is much smaller, ranging from 1 to 3 μm. The BCG phase (brighter particles) is in the form of fine grains (ranging from 1 to 3 μm) and is well dispersed in the composite. The porosity of the shown microstructure was estimated to be about 23% using the method of quantitative stereology. High catalytic activity of such electrodes is expected since the combination of fine-grained microstructure and high porosity gives rise to high specific area and plentiful triple-phase points and boundaries, thus facilitating both charge-transfer and mass transport across electrode-electrolyte interfaces.[3,5] In addition, such a composite can be a good mixed ionic-electronic conductor when the volume fraction of Ag is properly chosen which further improves the catalytic properties of the electrodes.

After the samples with the composite electrodes were subjected to elevated temperatures for an extended period of time (first at 800 to 860°C for about 2 h, then at 740°C for about 180 h), some coarsening of the Ag grains was observed, while the BCG phase still retained its fine-grained microstructure (Fig. 1c). It is noted, however, that the porosity of the composite after long-term test remained nearly unchanged (23%) as compared to the fresh sample, although the pores coalesced into larger ones along with the coarsening of the Ag grains. This means that the coarsening of the Ag grains did not result in appreciable densification of the composite electrode.

Shown in Fig. 2 are the cross-sectional views of the corresponding samples of the composite electrodes. These cross-sectional views further showed that the samples before and after long-term testing had similar thicknesses (about 10 μm) and similar porosities. Clearly, the BCG grains acted as a grain-growth inhibitor, and in the meantime, hardened the skeleton frame of the composite. Nevertheless, the coarsening of the Ag phase and the coalescence of the pores reduced the specific surface area and the numbers of triple-phase points and boundaries of the composite electrodes. Accordingly, it is expected that the composite electrodes would experience some degradation in performance at operation temperatures. The stabilized properties, however, should be still far better than those of pure Ag electrodes.

Electrochemical properties.—Effect of volume fraction of silver on interfacial resistance.—Shown in Fig. 3 are a series of impedance spectra for cells having Ag-BCG composite electrodes with different volume fractions of Ag. The impedance spectra were measured at 740°C in air and the Ag volume fractions ranged from 50 to 100 volume percent (v/o) (i.e., pure Ag). At least two depressed semicircles are observed in each spectrum. Since the same type of electrolytes were used and the shape of the semicircles changed with the composition of the electrodes, it is clear that the intercept of the impedance locus with the real axis at high frequencies corresponds to the bulk resistance of the electrolyte, and the two depressed semicircles are related to the electrochemical processes occurring at the electrode-electrolyte interfaces.
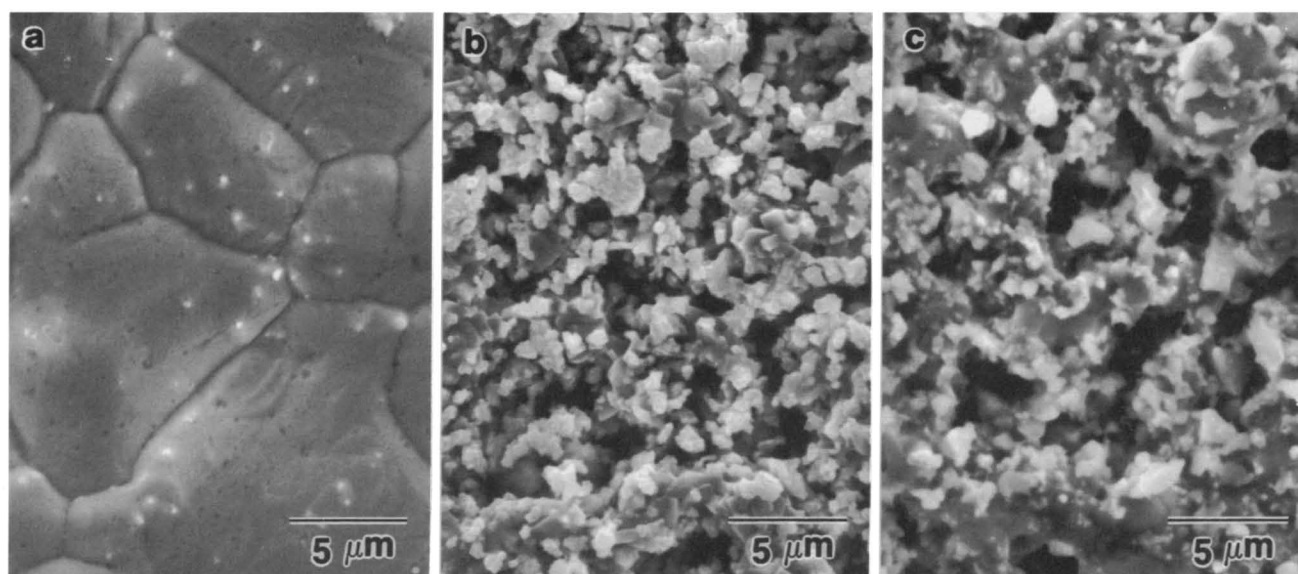
Fig. 1. SEM surface views for (a) a pure Ag electrode before impedance measurement, (b) a composite electrode of 78 v/o Ag-22 v/o BCG before impedance measurement, and (c) a composite electrode of 78 v/o Ag-22 v/o BCG after being tested at 800 to 860°C for about 2 h and at 740°C for 180 h.

As determined from the impedance spectra, the interfacial resistances of all composite electrodes (ranging from 0.33 $\Omega \cdot cm^2$ to 1.56 $\Omega \cdot cm^2$ at 740°C) were much smaller than those of pure Ag electrodes (greater than 2.56 $\Omega \cdot cm^2$ at 740°C). As expected, the interfacial resistance of the composite electrodes is a strong function of the composition, *i.e.*, the volume fraction of each constituent phase. The effect of composition of composite electrodes on exchange current density can be more clearly seen from the plots shown in Fig. 4. For the temperature range studied (650 to 750°C), the exchange current densities of the composite electrodes changed considerably with volume fraction of Ag in the composite electrodes. While all composite electrodes showed higher exchange current densities than the pure Ag electrode, the electrode with composition of 62 v/o Ag and 38 v/o BCG showed the highest exchange current densities, which is about six times those

of the pure Ag electrode. The exchange current densities at 700°C were plotted in Fig. 5 as a function of the volume percentage of Ag. In the range of 62 to 100 v/o of Ag, the exchange current density continuously increased with the decrease in Ag content. Further decreasing Ag content to 50 v/o resulted in a slight downturn in the exchange current density. The optimal Ag content seems to fall within the range of 50 to 70 v/o. This is in rough agreement with what the percolation theory predicts,[12] noting that the interfacial resistance is influenced by ambipolar transport properties, catalytic properties, and gas transport through electrodes, while the percolation theory predicts only the ambipolar transport properties of the solid phase.

Time-dependence of electrochemical properties.—As mentioned earlier, one major concern for using Ag-based electrodes is the reduction in porosity and specific surface
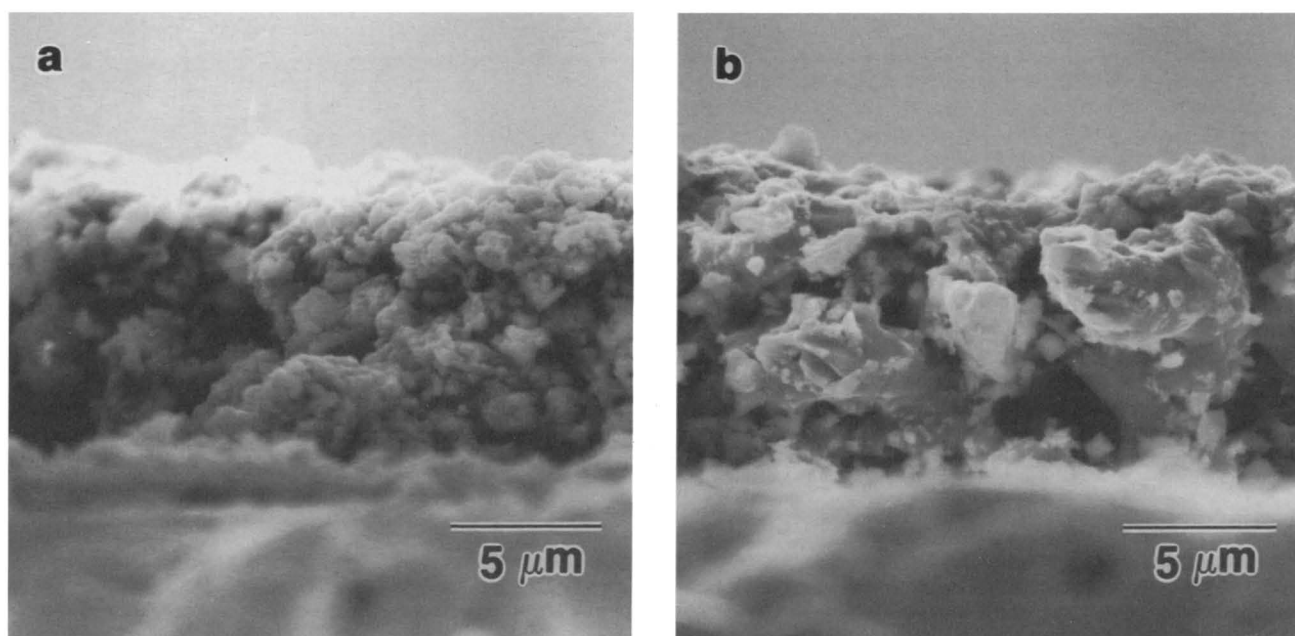

Fig. 2. SEM cross-sectional views for (a) a composite electrode of 78 v/o Ag-22 v/o BCG before impedance measurement and (b) a composite electrode of 78 v/o Ag-22 v/o BCG after being tested at 800 to 860°C for about 2 h and at 740°C for 180 h.
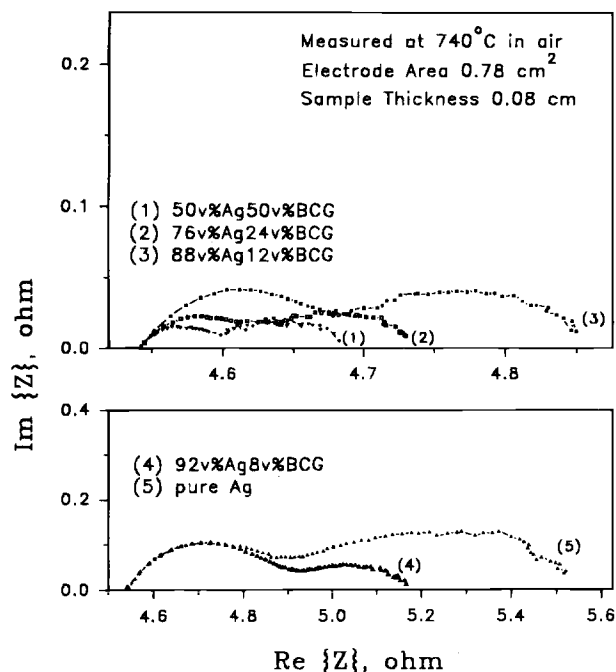
Fig. 3. Impedance spectra measured at 740°C in air for cells with Ag-BaCe$_{0.8}$Gd$_{0.2}$O$_3$ composite electrodes of different compositions.

Fig. 4. Temperature dependence of exchange current density measured in air for cells with Ag-BaCe$_{0.8}$Gd$_{0.2}$O$_3$ composite electrodes of different compositions, in comparison with that for a cell with pure Ag electrodes.

area due to the densification of the Ag phase. It is seen in the above section that specific surface area may also be reduced merely by a coarsening of the Ag grains (without appreciable densification). If considerable densification or coarsening takes place during the course of operation, degradation of the electrode performance is expected. Since the densification and coarsening will eventually come to a stop, the electrochemical properties of the electrodes will tend to be stabilized after some time. Therefore, it is more meaningful to compare the stabilized properties between different electrodes. Shown in Fig. 6 are changes in exchange current density with time for a composite electrode and a pure Ag electrode while the temperature was kept constant at 740°C. The pure Ag electrode changed little in catalytic activity over a long time, while the composite electrode showed a considerable degradation up to about 250 h. However, after about 280 h continuous operation, the composite electrode still showed much higher exchange current density than the Ag electrode.

These observations can be well correlated with the microstructures of the electrodes as delineated earlier. The Ag electrodes were initially rather dense, and there was little room for continuous densification during operation. Accordingly, the time-dependent degradation is small. The composite electrodes were initially fine-grained and very porous, and there was coarsening of the Ag grains and coalescence of the pores during operation. Therefore, the time-dependent degradation is large. Also, as expected, the stabilized catalytic activity of the composite electrodes is still much better than that of Ag electrodes since the stabilized composite electrodes are still much more porous than Ag electrodes. In addition to the effect of microstructure, the mixed-conducting nature of the composite electrodes may also have contributed to the observed catalytic effect.[3] It is believed that there remains much room for improving the electrochemical properties of the composite electrodes through optimization of the processing, composition, and microstructure.

Cathodic polarization.—Shown in Fig. 7 are the cathodic polarization curves measured in dry air, wet air (3% H$_2$O), and oxygen at 740°C for a 62 v/o Ag-38 v/o BCG electrode and a pure Ag electrode in symmetrical cells. At this temperature, the cathodic overpotentials for the composite
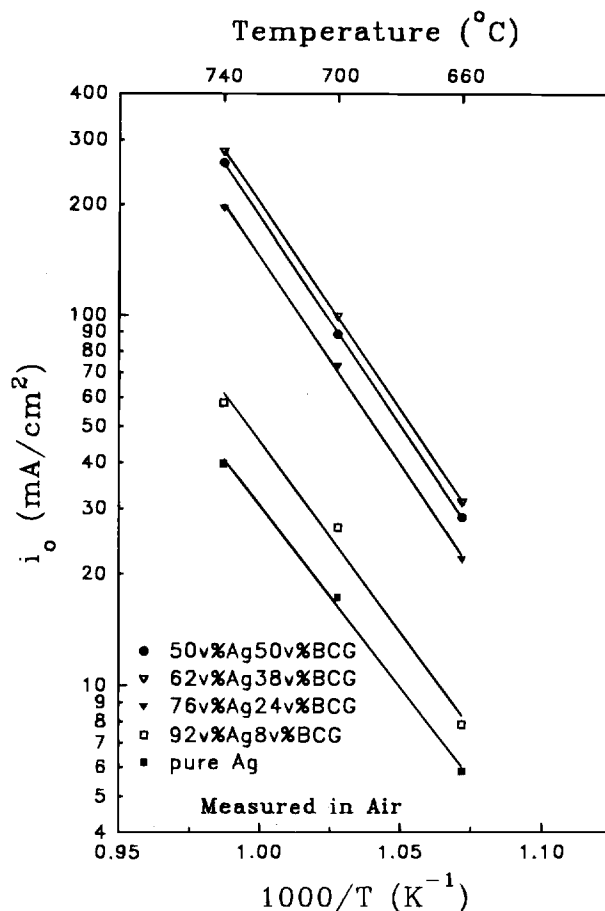
electrode in any of the three atmospheres were substantially lower than those for the pure Ag electrode under the same conditions. As compared to the pure Ag electrode, the cathodic overpotentials at a current density of 40 mA/cm^2 for the composite electrode showed about 50% reduction in
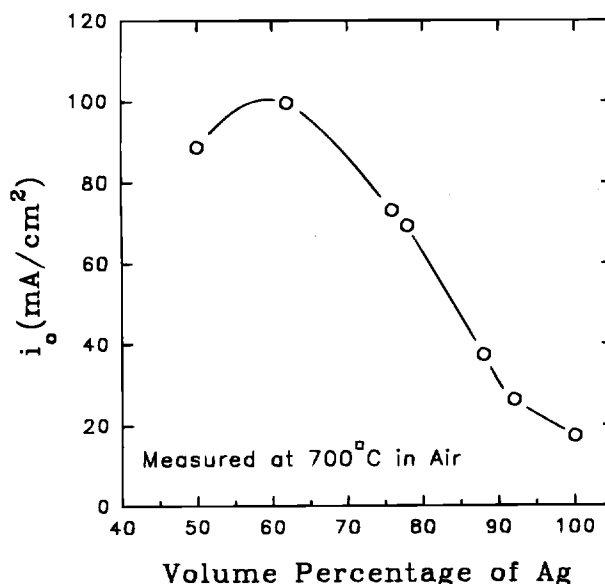

Fig. 5. Composition dependence of the exchange current densities of the Ag-BaCe$_{0.8}$Gd$_{0.2}$O$_3$ composite electrodes, measured in air.
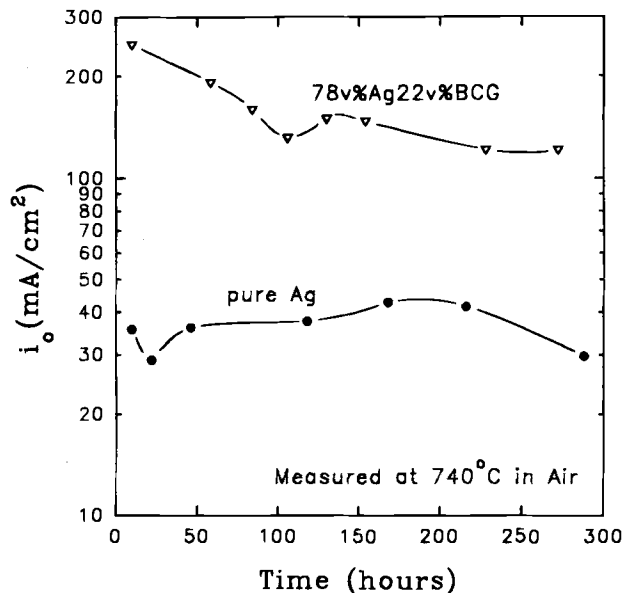
Fig. 6. Changes of exchange current density over time measured in air for a sample with 78 v/o Ag-22 v/o BCG electrodes and for a sample with pure Ag electrodes, while the temperature was kept constant at 740°C.

Fig. 8. Changes of cathodic overpotentials with temperature for a composite electrode of 62 v/o Ag-38 v/o BCG and a pure Ag electrode at a current density of 40 mA/cm² in (a) dry air and (b) oxygen, measured in symmetrical cells.

dry air, about 65% reduction in oxygen, and about 40% reduction in wet air. Shown in Fig. 8 are changes of cathodic overpotentials with temperature for both the composite electrode and the pure Ag electrode at a current density of 40 mA/cm² in dry air and in oxygen. The composite cathode consistently showed significantly lower overpotentials than the Ag cathode in both atmospheres.

Effect of water vapor.—The large difference in the cathodic overpotentials in dry air and in wet air for both cathode materials shown in Fig. 7 clearly indicates that moisture has a significant effect on the catalytic activities of the cathodes, in addition to the effect of oxygen partial pressure. These results indicate that both oxygen partial pres-
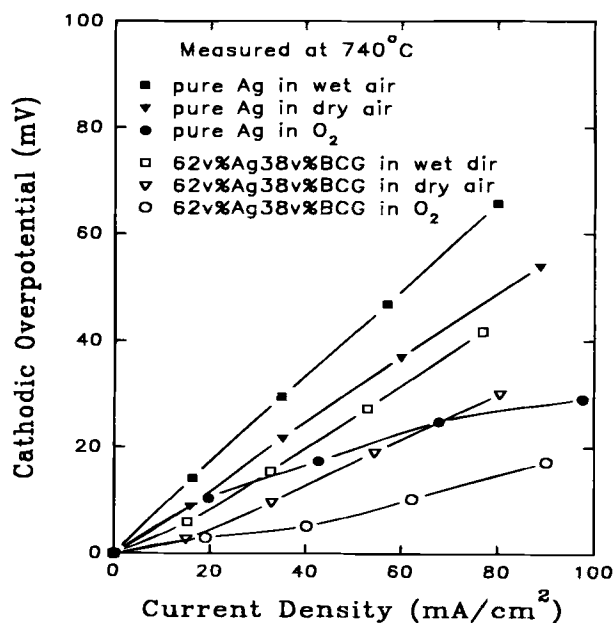

Fig. 7. Cathodic polarization curves in dry air, wet air (3% H₂O), and oxygen at 740°C for cells with composite electrodes of 62 v/o Ag-38 v/o BCG and with pure Ag electrodes, measured in symmetrical cells.
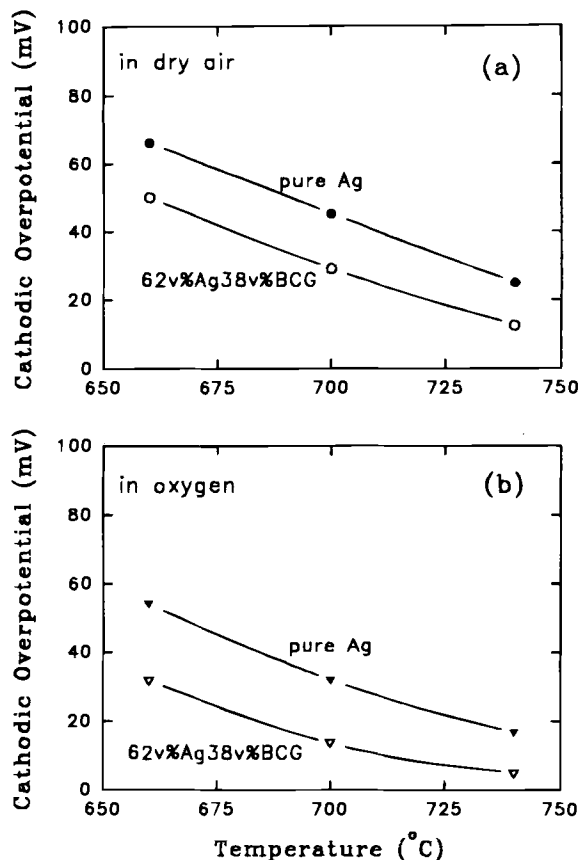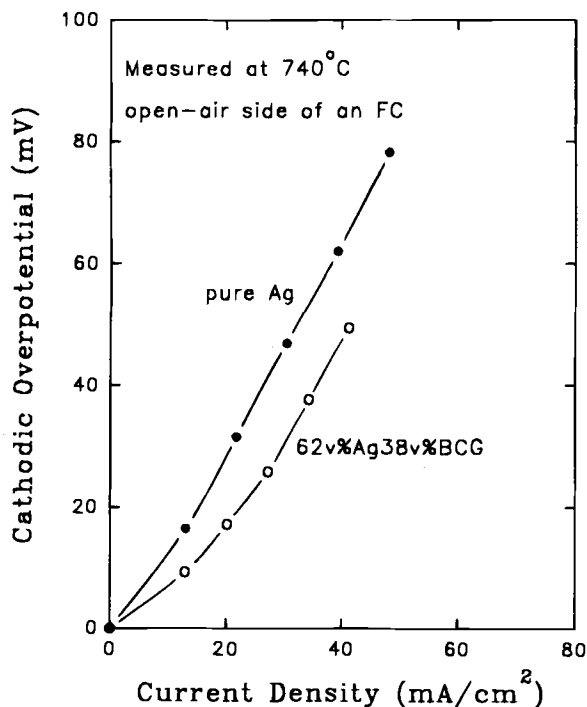

Fig. 9. Cathodic polarization curves for cells with a composite electrode of 62 v/o Ag-38 v/o BCG and with a pure Ag electrode. The cells were tested at 740°C under a fuel cell condition: H_2 + 3 v/o H_2O (1 atm), Pt | $BaCe_{0.8}Gd_{0.2}O_3$ | Ag or Ag-BCG, air (1 atm).
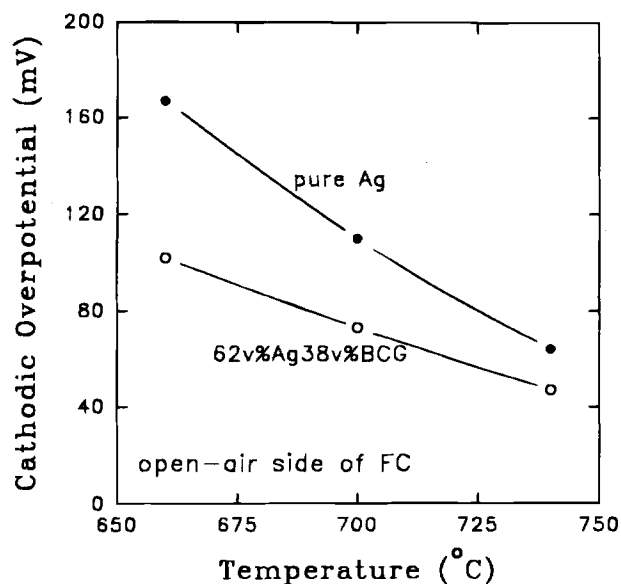
Fig. 10. Changes of cathodic overpotentials with temperature for a composite electrode of 62 v/o Ag-38 v/o BCG and a pure Ag electrode at a current density of 40 mA/cm², while the cells were under a fuel cell condition: H_2 + 3 v/o H_2O (1 atm), Pt I $BaCe_{0.8}Gd_{0.2}O_3$ I Ag or Ag-BCG, air (1 atm).

sure and moisture are important factors influencing kinetics of the cathode. This issue is important because water evolution can take place on both cathode and anode for fuel cells using $BaCe_{0.8}Gd_{0.2}O_3$ electrolyte, which is a mixed-ionic conductor transporting both oxygen ion and proton. Detailed study on the kinetics of these cathodes will be discussed in subsequent communications.

Figure 9 shows cathodic polarization curves for a 62 v/o Ag-38 v/o BCG electrode and a pure Ag electrode at 740°C, measured from the air side of a fuel cell with a configuration of

$$H_2 + 3 \text{ v/o } H_2O \text{ (1 atm), Pt I } BaCe_{0.8}Gd_{0.2}O_3 \text{ I Ag}$$

or Ag-BCG, air (1 atm)

Again, the cathodic overpotentials for the composite electrode were substantially lower than those for the pure Ag electrode. This is also seen from the temperature dependence of cathodic overpotential for the two electrodes at a current density of 40 mA/cm², measured under the same condition (Fig. 10). A comparison between Fig. 9 and Fig. 7 indicates that the cathodic overpotentials measured under the fuel cell condition are relatively close to, but still larger than, those measured using a symmetrical cell in wet air. This is understandable because the cathode of the fuel cell was exposed to open air which is humid, and also because there was significant water evolution at the cathode due to protonic transport through the electrolyte. Water evolution may exert considerable influence on the kinetics to the cathode. For a symmetrical cell in wet air, on the other hand, the cathode essentially involves only oxygen reduction. Another possible reason for the discrep-

ancy between the data measured under the two conditions is the variations in the microstructures and electrical properties of the cell components, including the electrolyte and the electrode. It has been found that the properties of both the electrolyte and the electrode are quite sensitive to processing and that any slight variations in preparation of either component may cause significant change in the interfacial properties. This again indicates that the performance of electrodes can be further improved through processing.

Conclusion

Composites of Ag-$BaCe_{0.8}Gd_{0.2}O_3$ are very promising cathode materials for $BaCeO_3$-based electrolytes. The composite electrodes attain a highly porous microstructure as the $BaCe_{0.8}Gd_{0.2}O_3$ phase inhibits the grain growth of the Ag phase in the composites. As compared to a pure Ag electrode, the composite electrodes show better adhesion to the electrolyte, higher exchange current densities, and lower cathodic overpotentials under various conditions. The optimal Ag content of the composites seems to fall within the range of 50 to 70 v/o, depending on the specific microstructure of the electrode. Water vapor seems to have a significant effect on the kinetics of the cathode. Further study will focus on understanding the mechanisms of the electrochemical reactions at the interfaces and improving the performance of the Ag-$BaCe_{0.8}Gd_{0.2}O_3$ composite electrodes through optimization of processing, composition, and microstructure.

Acknowledgments

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