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## BaCuGd<sub>2</sub>O<sub>5</sub>-BaCeO<sub>3</sub> Composite Cathodes for Barium Cerate-Based Electrolytes

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## ABSTRACT

Recent investigations into the mixed conducting properties of both copper- and gadolinium-doped barium cerates result in an interesting phase, identified as BaCuGd<sub>2</sub>O<sub>5</sub>, which exhibits substantially higher conductivity than any of the doped-barium cerate compounds studied. The predominant portion of the conduction, however, is electronic. Further, composites consisting of BaCuGd<sub>2</sub>O<sub>5</sub> and BaCe<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>3</sub> phases are studied as electrodes for barium cerate-based electrolytes. The composites are shown to have an ionic transference number of about 0.2. As electrodes, the composite material has shown excellent ambipolar transport properties and catalytic activities with interfacial resistances reduced by more than one order of magnitude compared to silver electrodes.

## Introduction

Barium cerate electrolytes are of interest due to their high ionic conductivity when compared to yttria stabilized zirconia (YSZ),<sup>1</sup> which is still the state-of-the-art electrolyte material for various solid-state ionic devices. When used for fuel cells or gas separation, the higher conductivity will translate to higher efficiency. For sensor applications, higher conductivity will allow a lower measuring temperature with a higher signal to noise ratio.

For many applications, the resistance of an electrolyte may be reduced by making the electrolyte thinner, since the resistance of an electrolyte is inversely proportional to the thickness of the sample. Thus, it may be argued that there is no reason to develop new electrolyte materials, only to produce thinner ones. This is the approach applied to most current research involving YSZ.<sup>2-6</sup> Decades of research on processing of YSZ has made it possible to prepare films of YSZ on various substrates. The performance of solid oxide fuel cells (SOFCs) based on thin-film YSZ is often limited by the interfacial resistances, not by the resistance of the electrolyte.<sup>7</sup> Extensive research to improve the electrode materials for YSZ has seen much less success.

One of the best suited materials to date for YSZ cathodes is La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> (LSM) with 0.1 ≤ x ≤ 0.5. The conductivity of LSM compounds is very high, in the range of 100 to 400 (Ω<sup>-1</sup> cm<sup>-1</sup>) at 800°C,<sup>8</sup> but this is primarily electronic conductivity due to the limited mobility of oxygen.<sup>9</sup> The oxygen ionic conductivity for La<sub>0.89</sub>Sr<sub>0.09</sub>MnO<sub>3</sub> is reported by Endo *et al.*<sup>10</sup> to be 5.9 × 10<sup>-8</sup> (Ω<sup>-1</sup> cm<sup>-1</sup>) or ten orders of magnitude smaller than the ionic conductivity. La<sub>1-x</sub>Sr<sub>x</sub>Co<sub>1-y</sub>Fe<sub>y</sub>O<sub>3-δ</sub> (LSCF) is reported to have similar total conductivities to LSM, but has an oxygen ion conductivity of 5 × 10<sup>-3</sup> (Ω<sup>-1</sup> cm<sup>-1</sup>).<sup>11</sup> LSCF compositions are not currently a viable cathode material for YSZ electrolytes due to thermal expansion incompatibilities.

Unlike the resistance of an electrolyte, the interfacial resistance of a cell is not dependent on the thickness of the electrolyte, but is determined by the nature of the two

materials in contact at the interface and the microstructure of the interface. One effective way for reducing the interfacial resistance of a given cell based on an electrolyte is to use catalytically active electrode materials. Another attractive way to reduce the electrode polarization resistance is to use electrodes of mixed ionic-electronic conductors (MIECs), which may extend the reaction sites beyond the electrode/electrolyte interface or triple-phase boundaries and to the MIEC/gas interface. An ideal electrode material would be chemically and thermally compatible with the electrolyte material during fabrication and operation of the cell, have adequate electronic or mixed ionic-electronic conductivity, and be catalytically active to assist the electrochemical reactions. The goal of this research is to investigate the transport and catalytic properties of barium cerate-based compounds and to develop compatible electrode materials for solid-state ionic devices based on doped barium cerate electrolytes.

## Experimental

The compositions of the materials investigated in this study include the standard gadolinia-doped barium cerate (BaCe<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>3</sub>), BaCuGd<sub>2</sub>O<sub>5</sub>, and a composite consisting of about 30 volume percent (v/o) BaCuGd<sub>2</sub>O<sub>5</sub> and 70 v/o BaCeO<sub>3</sub> crystallographic phases with an intended stoichiometry of the composite being BaCe<sub>0.7</sub>Gd<sub>0.2</sub>Cu<sub>0.1</sub>O<sub>x</sub>. Powders of these materials were produced by solid-state reactions and ballmilling. The gadolinia-doped barium cerate materials were produced as described elsewhere.<sup>12</sup> Both the BaCuGd<sub>2</sub>O<sub>5</sub> and the two-phase composite were formed by calcining BaCO<sub>3</sub>, CeO<sub>2</sub>, CuO, and Gd<sub>2</sub>O<sub>3</sub> at 1000°C for 8 h. X-ray diffraction was used to identify the crystallographic phases formed during processing. A Hitachi HF-2000 field emission transmission electron microscope (TEM) equipped with energy dispersive x-ray analysis (EDAX) was used to investigate the chemistry of the phases formed.

Bulk samples of various intermediate compositions, ranging from BaCe<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>3</sub> and BaCe<sub>0.8</sub>Cu<sub>0.2</sub>O<sub>3</sub> to pure BaCuGd<sub>2</sub>O<sub>5</sub> were prepared by uniaxially pressing powder of the desired phase and sintering. The BaCuGd<sub>2</sub>O<sub>5</sub> and composite samples were sintered for 8 h at 1200°C. The

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gadolinia-doped barium cerate samples were sintered at 1550°C for 8 h. The surfaces of these sintered pellets were ground, polished, and printed with silver paste (Haereus C-1000). The pellets were then fired in air at 800°C for 10 min to form porous silver electrodes. The electrical properties of the samples were characterized both in air and in an oxygen concentration cell with the configuration Ar, Ag|electrolyte|Ag, air as described elsewhere.<sup>13</sup>

The powder samples of the  $\text{BaCuGd}_2\text{O}_5$  and the composite were also made into a paste. The pastes were applied to gadolinia-doped barium cerate electrolytes in order to characterize their properties as an electrode, as shown in Fig. 1. Silver electrodes were applied to the other half of the electrolyte to form a reference cell with standard silver electrodes. Silver wires were attached to all the electrodes and the samples were placed in a test furnace. Impedance spectra of each cell were acquired under various conditions using a frequency response analyzer (Solartron 1255) and an electrochemical interface (Solartron 1286).

## Results and Discussion

**Crystal structure and stoichiometry.**—The  $\text{BaCuGd}_2\text{O}_5$  phase was initially prepared in conjunction with the barium cerate perovskite phase during attempts to introduce multiple dopants into barium cerate. The high levels of conductivity found in a two-phase material produced with an intended stoichiometry of  $\text{BaCe}_{0.7}\text{Cu}_{0.1}\text{Gd}_{0.2}\text{O}_{3-\delta}$ , led to the fabrication and study of the pure phase  $\text{BaCuGd}_2\text{O}_5$ . This phase was found to form readily by solid-state processing techniques similar to those used for barium cerate except that the pure phase  $\text{BaCuGd}_2\text{O}_5$  powders can be formed at 900°C.<sup>14</sup> Figure 2 shows the x-ray diffraction patterns attained for the  $\text{BaCuGd}_2\text{O}_5$  phase along with its reference pattern (JCPDS 39-1418). The diffraction pattern attained from the two-phase composite powder is shown in Fig. 3 with the appropriate reference patterns. The amount of  $\text{BaCuGd}_2\text{O}_5$  in the composite powder appears to be relatively small and was later quantified using TEM analysis. Using our standard processing tech-

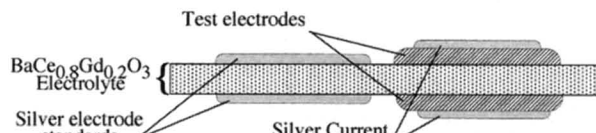


Fig. 1. A schematic diagram showing a cross-sectional view of a cell used for testing of new electrode materials.

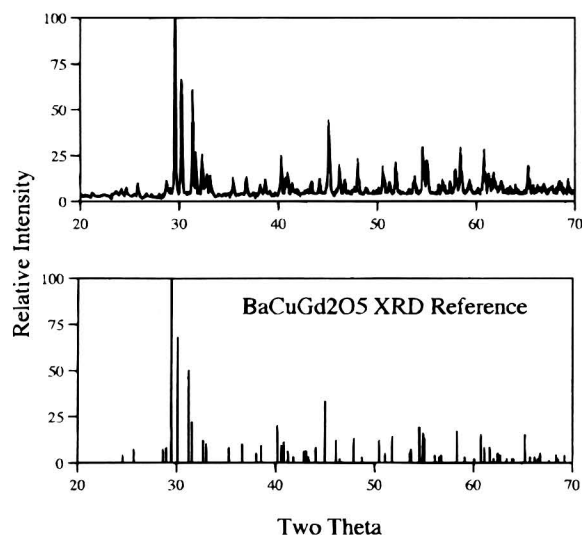


Fig. 2. An x-ray diffraction pattern obtained from a powder sample of  $\text{BaCuGd}_2\text{O}_5$  and a reference pattern.

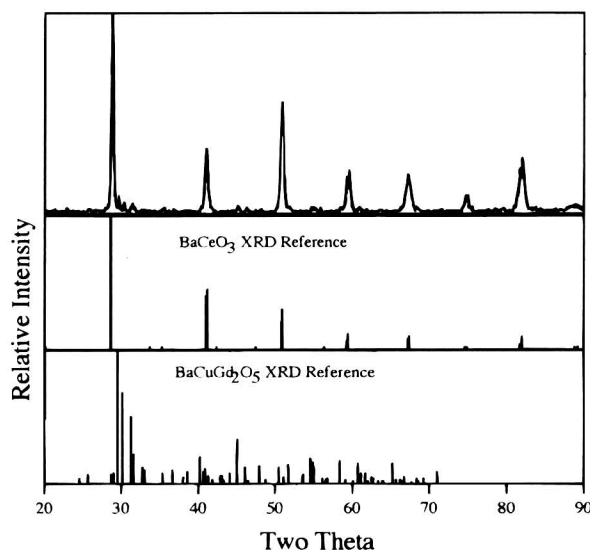


Fig. 3. An x-ray diffraction pattern from a two-phase composite material and the corresponding reference patterns.

niques, all compositions which contained copper oxide, gadolinia, and baria formed some of the  $\text{BaCuGd}_2\text{O}_5$  phase. The addition of ceria to the mixture generally produced some barium cerate perovskite phase. The  $\text{BaCuGd}_2\text{O}_5$  and barium cerate easily formed together under identical processing conditions, suggesting good compatibility of the two materials.

Under the TEM, EDAX analysis of the two-phase composite powder shows the chemistry to vary substantially in the  $\text{BaCeO}_3$  phase from the intended stoichiometry of  $\text{BaCe}_{0.7}\text{Cu}_{0.1}\text{Gd}_{0.2}\text{O}_{3-\delta}$ . The approximate chemistry became  $\text{Ba}_{0.9}\text{Cu}_{0.1}\text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{3-\delta}$  with the formation of a small amount of the  $\text{BaCuGd}_2\text{O}_5$  phase. The  $\text{BaCuGd}_2\text{O}_5$  phase accounts for about 10% of the particles analyzed. It is found that this second phase also contains ceria and has an approximate stoichiometry of  $\text{BaCu}_{(1-x)}\text{Gd}_{(2-y)}\text{Ce}_{(x+y)}\text{O}_{5-\delta}$ , with  $x$  and  $y$  having average values of 0.15 and 0.2, respectively. The substitution of copper into the baria site in the perovskite structure is unexpected due to their large difference in ionic radius and the fact that copper was found to dope in place of ceria when gadolinia was not present.<sup>15</sup>

The pure gadolinia-doped barium cerate required sintering at 1550°C for 8 h to attain high densities, whereas compositions containing even small amounts of copper could be densified by sintering at 1150°C for 8 h. A scanning electron microscope (SEM) micrograph of the surface of the two-phase composite is seen in Fig. 4. The sample retained both the barium cerate and the  $\text{BaCuGd}_2\text{O}_5$  crystallographic phases. Using the SEM and x-ray dot mapping techniques (Fig. 5), the two phases could be identified as forming distinct grains uniformly dispersed throughout the sintered sample. Analysis of these images using statistical counting techniques indicates that the volume fraction of the  $\text{BaCuGd}_2\text{O}_5$  crystallographic phase was about 30% and that of the  $\text{BaCeO}_3$  crystallographic phase was 70% in the sample with intended stoichiometry of  $\text{BaCe}_{0.7}\text{Gd}_{0.2}\text{Cu}_{0.1}\text{O}_x$  after sintering. This indicates that the amount of  $\text{BaCuGd}_2\text{O}_5$  phase increased from about 10% (according to TEM/EDAX analysis) to about 30% during the sintering process.

**Total conductivity.**—The bulk samples were tested in air, argon, and in oxygen concentration cells. The prepared  $\text{BaCuGd}_2\text{O}_5$  was found to be unstable in hydrogen, limiting its usefulness to cathode applications. In air, the conductivities of the  $\text{BaCuGd}_2\text{O}_5$  and the composite material containing both barium cerate and  $\text{BaCuGd}_2\text{O}_5$ , are significantly higher than those of the standard  $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_5$ . The results shown in Fig. 6 also indicate that the activation energy for conduction in  $\text{BaCuGd}_2\text{O}_5$  is much smaller



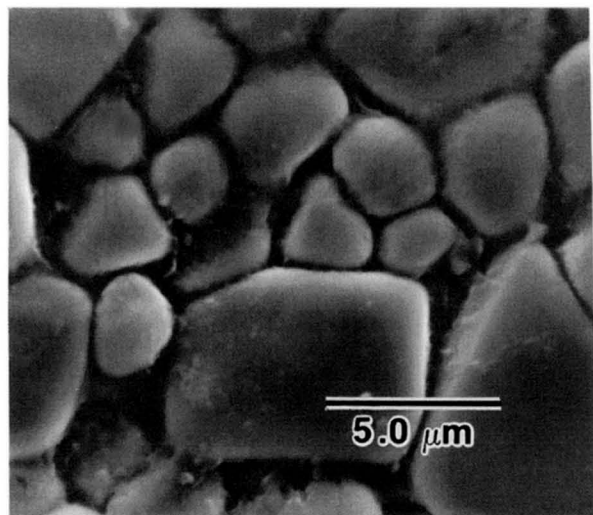


Fig. 4. An SEM micrograph of a composite consisting of 70 v/o  $\text{BaCeO}_3$  and 30 v/o  $\text{BaCuGd}_2\text{O}_5$  sintered at  $1200^\circ\text{C}$  for 12 h.

than that in other barium cerate-based compounds studied. The conductivities of the composite sample were, as expected, between those of the two pure phases. The impedance spectra for the  $\text{BaCuGd}_2\text{O}_5$  showed negligible interfacial loop, suggesting that it may have a significant

component of electronic conductivity and may be well suited to electrode applications.

**Ionic transference number.**—Both the  $\text{BaCuGd}_2\text{O}_5$  and the composite samples were studied using oxygen concentration cells in order to determine the ionic or electronic transference numbers. These results indicate that the  $\text{BaCuGd}_2\text{O}_5$  exhibits predominantly electronic conduction. In an oxygen concentration cell with a configuration of  $\text{air}/\text{Ag}/\text{BaCuGd}_2\text{O}_5/\text{Ag}/\text{Ar}$ , the observed cell voltage is negligible. Under similar test conditions, the barium cerate- $\text{BaCuGd}_2\text{O}_5$  composite attained an open-cell voltage of about 12 mV, or about 8% of the Nernst potential. This indicates mixed ionic-electronic conductivity for the composite material. Using the open-cell voltage ( $V_{\text{oc}}$ ) measurements of the cell, the Nernst potential ( $E_N$ ) calculated from the oxygen partial pressures across the cell, and ac impedance data taken *in situ*, the ionic transference number can be determined through the use of the following equation<sup>14</sup>

$$t_i = 1 - \frac{R_b}{R_T} \left( 1 - \frac{V_{\text{oc}}}{E_N} \right) \quad [1]$$

Where  $R_b$  and  $R_T$  are the bulk electrolyte and total cell resistance, respectively. The ionic transference number for the composite material was found to vary with temperature, ranging from 0.24 at  $630^\circ\text{C}$  to 0.17 at  $780^\circ\text{C}$ . The ionic conductivity of the mixed conducting barium cerate- $\text{BaCuGd}_2\text{O}_5$  composite as calculated from the total conductivity and ionic transference number is nearly equal to

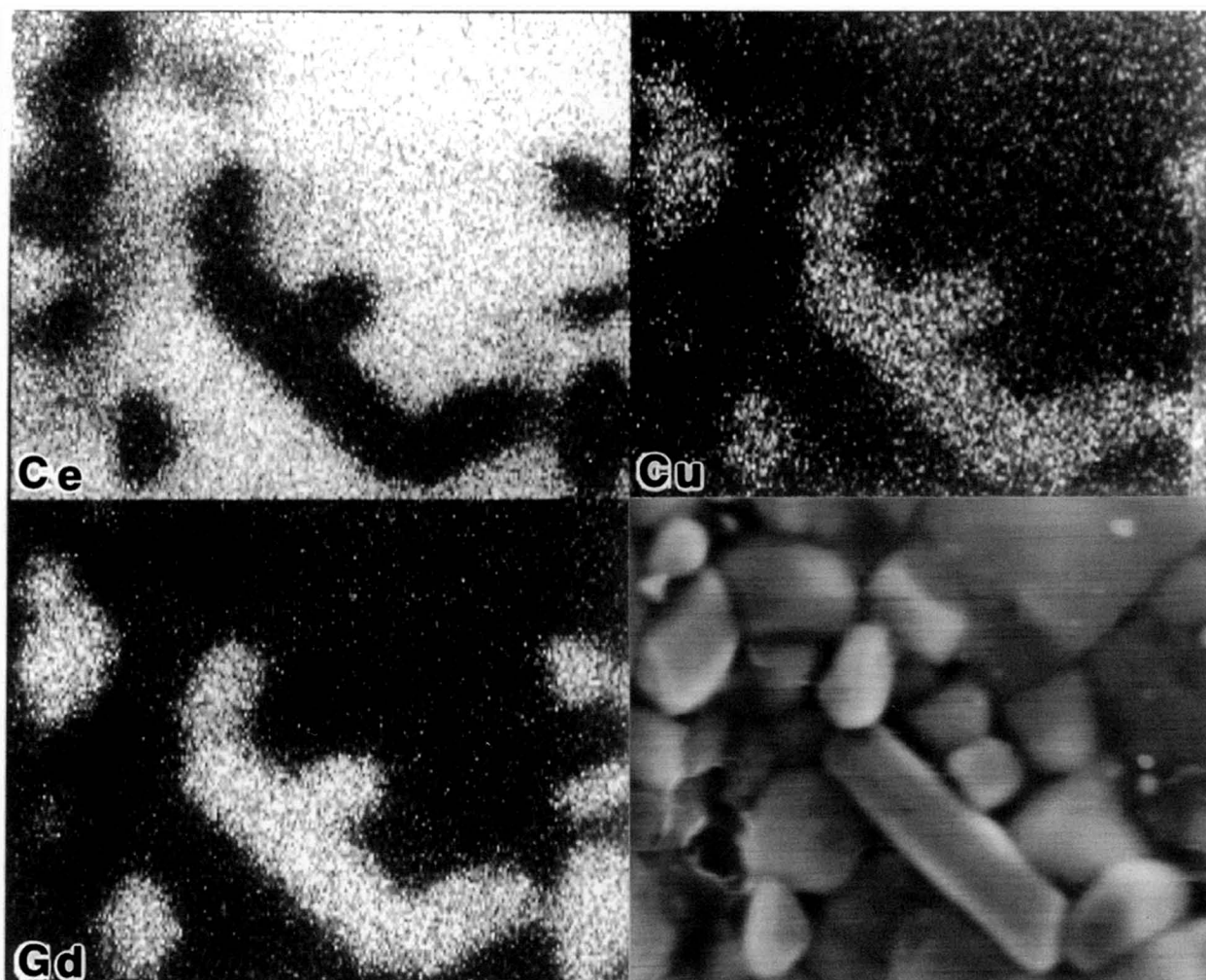


Fig. 5. X-ray dot mapping for cerium, copper, and gadolinium showing the distribution of the  $\text{BaCeO}_3$  and  $\text{BaCuGd}_2\text{O}_5$  phases in a sintered bulk composite sample.



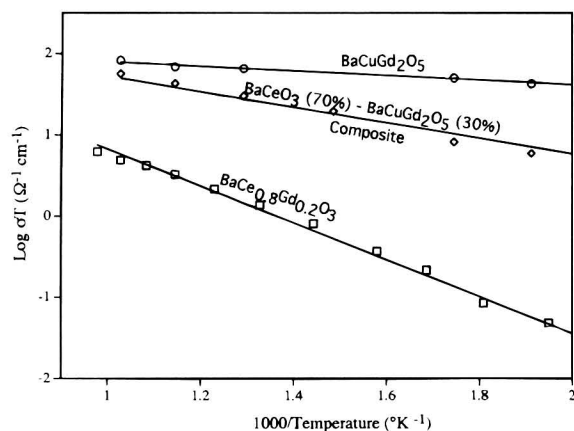


Fig. 6. Total conductivities of a pure phase  $\text{BaCuGd}_2\text{O}_5$ , a composite consisting of 70 v/o  $\text{BaCeO}_3$  and 30 v/o of  $\text{BaCuGd}_2\text{O}_5$  and of  $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$ . All conductivities were measured in air using impedance spectroscopy.

that of the gadolinia-doped barium cerate measured in a similar concentration cell. Figure 7 shows the total and ionic conductivities for the barium cerate- $\text{BaCuGd}_2\text{O}_5$  composite tested here in comparison to those for  $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$ .

**Electrode applications.**—To determine the usefulness of the  $\text{BaCuGd}_2\text{O}_5$  and the composite as cathode materials on barium cerate electrolytes, test cells using these materials as electrodes were constructed to determine the interfacial resistances. In order to eliminate any bias introduced by the electrolyte, the standard silver electrode and the test electrodes were constructed on the same electrolyte, as seen in Fig. 8. The electrodes produced from the ceramic powders were somewhat crude, being thicker than ultimately desired with noticeable cracks in the film after sintering. Silver paste was applied over the ceramic electrodes to act as a current collector for the possibly discontinuous cracked ceramic cathodes.

The cells were tested using impedance spectroscopy in air at temperatures from 200 to 800°C. Typical impedance spectra obtained from the two pairs of electrodes of a test cell are shown in Fig. 9. The area of each electrode was produced as consistently as possible to allow easy comparison between the new electrodes and the standard silver electrodes. This direct comparison method which utilizes the same electrolyte for both the test electrode and the

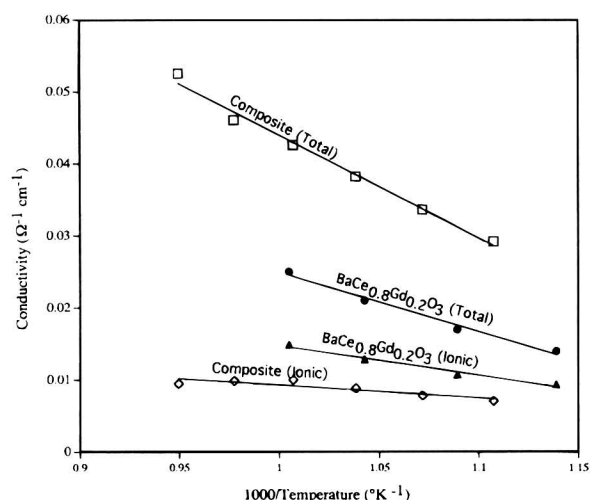


Fig. 7. Total and ionic conductivities for a barium cerate- $\text{BaCuGd}_2\text{O}_5$  composite and a  $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$  electrolytes measured in an oxygen concentration cell with a configuration of  $\text{Ar}/\text{Ag}|\text{electrolyte}|\text{Ag}$ , air.

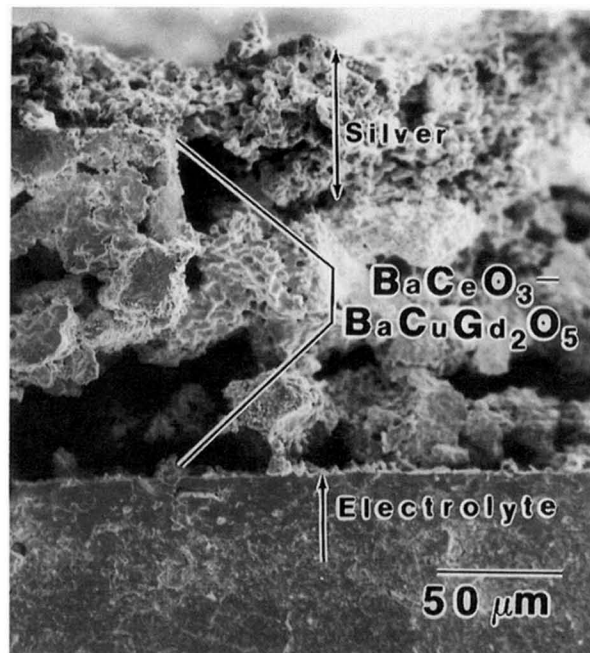


Fig. 8. An SEM micrograph of the cross section of a symmetrical cell with the composite electrodes and Ag current collectors.

standard, quickly shows the differences in interfacial resistance between the two. Comparison of the two spectra clearly shows the advantages of using the new electrode materials over silver. The interfacial resistance,  $R_p$ , can be calculated from impedance data and the ionic transference number,  $t_i$ , as

$$R_p = \frac{R_T - R_b}{t_i \left[ 1 - \frac{R_T}{R_b} (1 - t_i) \right]} \quad [2]$$

where  $R_T$  and  $R_b$  are the total and bulk resistance as determined from impedance spectroscopy.<sup>16</sup> Estimates of the ionic transference number have been reported<sup>14</sup> to be on the order of  $t_i \approx 0.6$  for  $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$  in air. The interfacial resistances of the  $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$  cells using different electrode materials are shown in Fig. 10. All of the materials have a similar slope; however, the interfacial resistances of the cell using silver electrodes are ten to fifteen times greater than those of the cell using the  $\text{BaCuGd}_2\text{O}_5$ - $\text{BaCeO}_3$  composite electrodes.

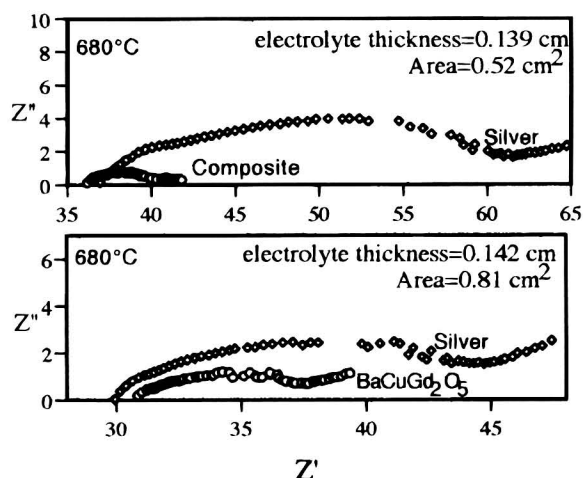


Fig. 9. Impedance spectra of symmetrical cells with different electrodes: silver,  $\text{BaCuGd}_2\text{O}_5$ , and a composite.

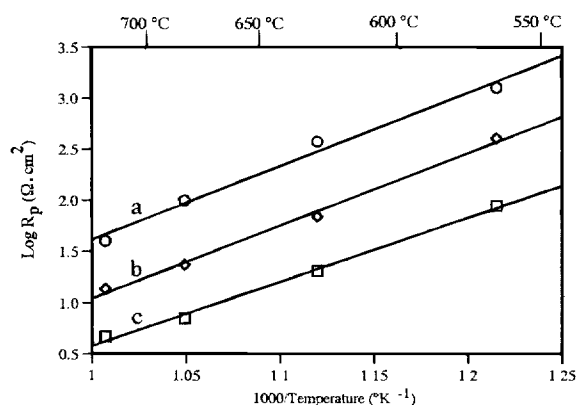


Fig. 10. Interfacial resistances of symmetric cells using different electrodes: (a) silver, (b)  $\text{BaCuGd}_2\text{O}_5$ , and (c)  $\text{BaCuGd}_2\text{O}_5$ - $\text{BaCeO}_3$  composites.

### Conclusions

$\text{BaCuGd}_2\text{O}_5$  has been identified as a viable electrode material for  $\text{BaCeO}_3$ -based electrolytes because of its high total conductivities with a substantial amount of electronic conductivity and excellent compatibility with barium cerate compounds. The  $\text{BaCuGd}_2\text{O}_5$  readily coexists with barium cerate to form a two-phase composite. The composite exhibits high ambipolar transport properties under gas permeation conditions and has an ionic transference number of about 0.2. When used as electrodes on  $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$  electrolyte, the interfacial resistance of the cell is reduced more than ten times in comparison to a cell using platinum or silver electrodes.

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