

in order to study the changes in surface crystallography with greater accuracy.

Conclusion

The conductivity of the transparent electrode system is a critical factor for flat panel display performance, especially for large or high resolution panels. In this paper we have demonstrated that it is possible to plate copper onto the tin oxide electrodes of flat panel displays in a way that not only yields good conductivity but also achieves excellent adhesion. Conductivity enhancement by copper electroplating, can have wide process tolerances, facilitating ease of process control. Considering the copper film appearance, thickness, and adhesion strength, the suitable reduction and copper plating conditions are: $0.3 < Q_R < 0.5$, $31 < J_R < 93$, $0.3 < Q_{Cu} < 0.5$, and $31 < J_{Cu} < 125$. Under these conditions, the copper thickness is between 300 and 500 nm with a corresponding resistivity of $6 \mu\Omega\text{-cm}$. For 50 μm electrodes with 10 μm sidewall copper busbars in flat panel displays, this translates to an effective sheet resistivity of less than $0.5 \Omega/\square$. More detailed analysis of adhesion mechanisms are required and suitable areas of investigation have been elaborated.

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Stability of $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$ in a H_2O -Containing Atmosphere at Intermediate Temperatures

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ABSTRACT

Barium cerate-based electrolytes have been extensively studied for intermediate-temperature (600 to 800°C) solid-state ionic devices because of their high ionic conductivities at these temperatures. However, the long-term stability of these materials under the conditions of intended applications, such as in a water vapor-containing atmosphere, has been controversial in recent literature. In this study, a gadolinium-doped barium cerate, $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$, has been tested in an atmosphere containing 50 volume percent water vapor at 600 and 700°C for 1000 h. X-ray diffraction, transmission electron microscopy, differential thermal analysis, and electrochemical measurements indicate that there is no creditable evidence to suggest an observable decomposition of $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$ to $\text{Ba}(\text{OH})_2$ and CeO_2 under the testing conditions for up to 1000 h, further confirming the stability of the material under fuel cell conditions demonstrated by others.

Introduction

Barium cerate-based electrolytes have been considered good candidate materials for intermediate-temperature (600 to 800°C) solid-state ionic devices, such as solid oxide fuel cells (SOFCs), gas sensors, and stream electrolyzers, because of their high ionic conductivities and their ability of transporting both proton and oxygen ions at these temperatures.^{1,2} Furthermore, a number of dopants can be readily introduced into barium cerate to modify the ionic and electronic transport properties.³⁻⁵ To date, gadolinium-doped barium cerates exhibit the highest ionic conductivities among the doped barium cerates studied.⁶⁻¹⁰ The stability of cerate-based perovskite electrolytes in reducing atmosphere has been examined by Yokokawa *et al.*,¹¹ and it was concluded that materials are stable in the perovskite hydrogen. The stability of barium cerates in CO_2 was investigated by Scholten *et al.*^{12,13} Although it is found that BaCeO_3 may react with CO_2 to form BaCO_3 and CeO_2 at elevated temperatures when the partial pressure of CO_2 is sufficiently high, the practical stability of Gd-doped

barium cerates under the fuel cell conditions has been demonstrated experimentally to be adequate. In 1991, Bonanos *et al.*¹⁴ demonstrated the stability of a gadolinium-doped barium cerate under hydrogen-air fuel cell conditions; a fuel cell based on $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$ was tested at 800°C for over 1000 h without observable degradation in performance. Recently, Taniguchi *et al.*¹⁵ have tested another gadolinium-doped barium cerate, $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$, under fuel cell conditions (using H_2 and quasi fuel gas containing CO_2 as fuels) at 800°C for more than 2000 h and the stability was concluded to be good. These experimental results are consistent with the thermodynamic predictions using data reported by Sorokina *et al.*^{16,17} and data from other references.¹⁸ On the contrary, however, Tanner and Virkar¹⁹ have recently suggested that both doped and undoped BaCeO_3 would react with water vapor to form CeO_2 and $\text{Ba}(\text{OH})_2$ under fuel cell conditions at temperatures $\leq 800^\circ\text{C}$. More specifically, their thermodynamic calculations indicate that BaCeO_3 would decompose to $\text{Ba}(\text{OH})_2$ and CeO_2 when the partial pressure of water vapor is greater than 0.032 atm at 800°C, 3.68×10^{-3} atm at 700°C, and 2.61×10^{-4} atm at 600°C. It is noted that the equilibrium partial pressures of water vapor predicted by

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Tanner and Virkar are about 3 to 4 orders of magnitude lower than the predicted values under identical conditions using Sorokina's data, as schematically shown in Fig. 1. Furthermore, Tanner and Virkar claimed that a lanthanum-doped barium cerate, $\text{La}_{0.05}\text{BaCe}_{0.95}\text{O}_{2.975}$ (note that lanthanum substitutes cerium at B-site), prepared by a coprecipitation method, had decomposed to CeO_2 and Ba(OH)_2 within 72 h when exposed to 430 Torr (~ 0.57 atm) water vapor at 500 to 800°C.¹⁹

Clearly, the stability of these materials is critical to the viability, reliability, and service life of devices or systems based on such materials. The objective of this study is to investigate the long-term stability of a gadolinium-doped barium cerate, $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$ (BCG), in a H_2O -containing atmosphere at intermediate temperatures (600 to 800°C). Thermodynamic analysis indicates that the possible decomposition products of BCG in water vapor at intermediate temperatures, if there are any, would include CeO_2 and Ba(OH)_2 . Thus, the presence of Ba(OH)_2 or CeO_2 in a BCG sample after exposure to water vapor at intermediate temperatures would suggest such decomposition. Further, decomposition of BCG to Ba(OH)_2 or CeO_2 will alter the electrical conductivities of the material, and hence the changes in electrical resistances of the sample during testing may provide additional information on the stability of the material.

Experimental

Two types of samples were used in this study. BCG powder samples were used for identification of decomposition products, while sintered BCG pellets with Pt electrodes were used for the detection of changes in electrical properties. The BCG powder was prepared using solid-state reactions. Precursors CeO_2 (Aldrich), Gd_2O_3 (Alfa), and BaCO_3 (Alfa) were mixed in the stoichiometric ratio, ball-milled, and calcined in air at 1350°C for 8 h. The calcined powder was then characterized using x-ray powder diffraction to make sure that pure perovskite phase was obtained. To prepare BCG pellets, the calcined BCG powder was pressed into pellets and sintered in air at 1550°C for 4 h to achieve sintered density greater than 95% of the theoretical value. In order to measure the electrical properties of the material during the stability test, platinum paste (Heraeus OS2) was applied to both faces of each pellet and then fired at 1250°C for 30 min to yield porous electrodes.

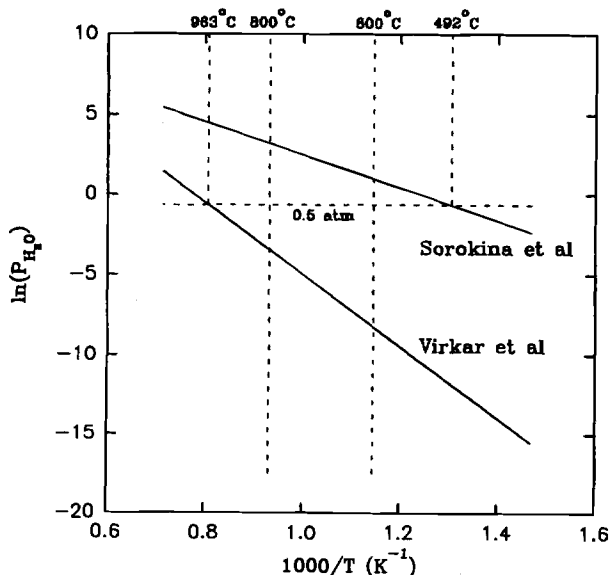


Fig. 1. Equilibrium partial pressures of water vapor for equilibrium among BaCeO_3 , H_2O , Ba(OH)_2 , and CeO_2 at temperatures $>408^\circ\text{C}$.

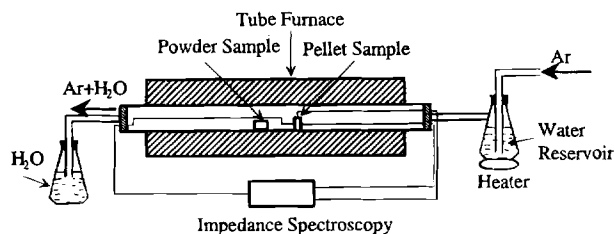
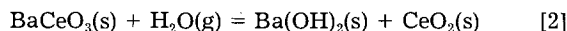


Fig. 2. Experimental arrangement for stability study.

Schematically shown in Fig. 2 is the experimental arrangement for the stability study. Powder and pellet samples were placed in the center of a quartz tube inside a tube furnace. A gas mixture, produced by bubbling argon through a water reservoir maintained at a constant temperature, was then flowed through the quartz tube to control the partial pressure of water vapor in the atmosphere in which the samples were immersed. The partial pressure of H_2O in the gas mixture is determined by²⁰

$$\log_{10} p_{\text{H}_2\text{O}} = -\frac{3075}{T} - 5.465 \log_{10} T + 2.79 \times 10^{-4} T + \frac{86^2}{T^2} + 22.19 \quad [1]$$

where T is the absolute temperature (K) of the water reservoir and $p_{\text{H}_2\text{O}}$ is the partial pressure of water vapor in atm. Thus, $p_{\text{H}_2\text{O}}$ is merely determined by the temperature of the water reservoir. According to the thermodynamic calculations of Tanner and Virkar,¹⁹ the equilibrium partial pressures of H_2O for the reaction



at 600 and 700°C are 2.61×10^{-4} atm and 3.68×10^{-3} atm, respectively. In this study, however, the water reservoir was kept at 83°C in order to maintain the $p_{\text{H}_2\text{O}}$ at about 0.5 atm (the total partial pressure of the gas mixture is assumed to be 1 atm), which is much higher than the equilibrium partial pressure of water vapor predicted by Tanner and Virkar. Stability tests were carried out at 600 and 700°C for 1000 h.

Powder samples were periodically taken out from the furnace during the test and examined using a Philips PW1800 diffractometer ($\text{Cu K}\alpha$ radiation) to detect possible phase changes. The 2θ of diffraction was varied from 15 to 85° at a scanning rate of 0.01°/s. Morphologies and electron diffraction patterns of the powder samples were further obtained using a Hitachi 200 KV FE transmission electron microscope (TEM). A Perkin-Elmer 1700 differential thermal analyzer (DTA) was used to study the thermochemical properties of standard samples containing Ba(OH)_2 and the BCG powder samples before and after the stability test. The DTA experiments were run in dry air in the temperature range from 25 to 1000°C at a heating rate of 5°C/min. Changes in resistances of the pellet samples were continuously monitored using a computerized impedance system which consists of a Schlumberger frequency response analyzer (Solartron 1255) and an electrochemical interface (Solartron 1286). The microstructures of the electrodes before and after the stability test were characterized using a Hitachi S-800 scanning electron microscope (SEM). A statistical point counting method²¹ in quantitative analysis of the microstructure was employed to estimate porosity.

Results

Identification of CeO_2 .—X-ray diffraction (XRD) was used to detect the presence of CeO_2 in the BCG powders after the stability test. In order to determine the sensitivity of detecting CeO_2 in BCG samples, three standard samples were made: (a) pure BCG, (b) 2 weight percent (w/o) CeO_2 and 98 w/o BCG, and (c) 10 w/o CeO_2 and 90 w/o

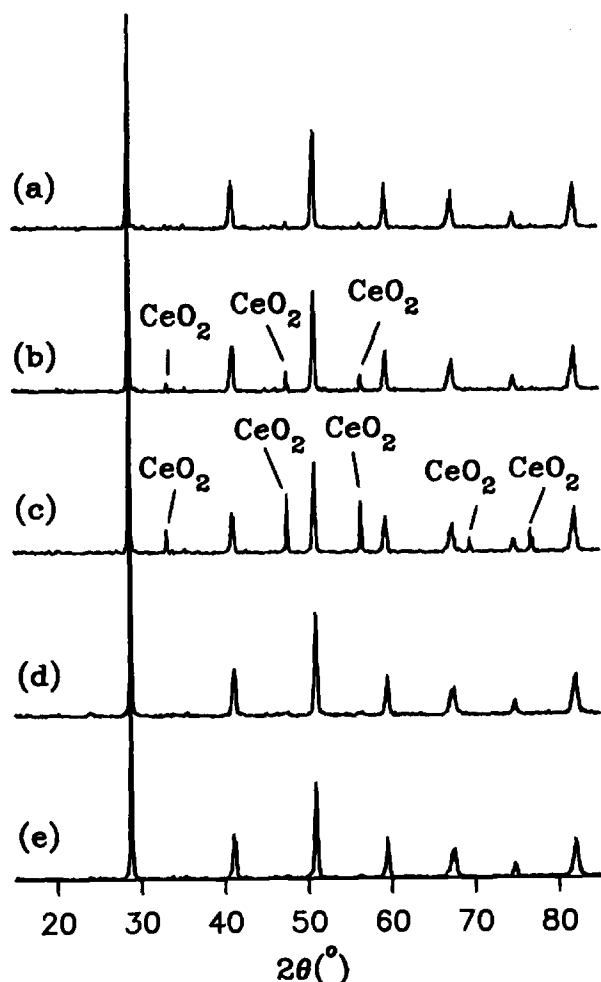


Fig. 3. X-ray diffraction patterns of standard samples: (a) pure BCG, (b) BCG with 2 w/o CeO_2 , and (c) BCG with 10 w/o CeO_2 ; and XRD diffraction patterns of BCG powder samples tested in an atmosphere containing 50 v/o water vapor for 1000 h at different temperatures: (d) 600°C and (e) 700°C.

BCG. The first three XRD patterns shown in Fig. 3 are the patterns of these three standard samples. Clearly, 2 w/o CeO_2 in BCG can be unequivocally identified using XRD. Thus, XRD is sufficiently sensitive to a small amount of CeO_2 in BCG powder. Also shown in Fig. 3 are the XRD patterns of BCG powder samples tested in the H_2O -containing atmosphere for 1000 h at two temperatures: (d) 600°C and (e) 700°C. The XRD patterns for the BCG powder samples after the stability test perfectly match the XRD pattern of the BCG powder before the test. All peaks in these diffraction patterns are corresponding to the peaks in the standard pattern of BaCeO_3 (PDF 22-74), indicating that there are no observable peaks corresponding to CeO_2 in the BCG samples after the stability test. Thus, no observable amount of CeO_2 can be found in the BCG powder samples after the stability test.

Identification of Ba(OH)_2 .—Unlike CeO_2 , Ba(OH)_2 is not sensitive to x-ray diffraction; there was no observable difference between the XRD pattern of a pure BCG sample and that of a standard sample consisting of 95 w/o BCG and 5 w/o Ba(OH)_2 . Further, measuring the pH of deionized water containing BCG powder that has undergone the stability test does not determine whether any BCG decomposed to Ba(OH)_2 during the test, because BCG reacts directly with water to form Ba(OH)_2 during immersion, as discussed later. Accordingly, other techniques have to be used in order to identify Ba(OH)_2 .

TEM examinations of these samples indicate that the morphology of Ba(OH)_2 powder (a) is quite different from

that of BCG ceramic powder (b), as shown in Fig. 4. The morphology of a mixture of 95 w/o BCG and 5 w/o Ba(OH)_2 is shown in Fig. 4c. Clearly, Ba(OH)_2 particles appear to be very different from those of BCG. However, the appearance of the BCG powder samples before and after the test at 600°C, as shown in Fig. 4b and d, are almost indistinguishable except for some differences in particle size, which may result from the variation in preparation of the TEM samples. No similar morphology of Ba(OH)_2 , as shown in Fig. 4a and c, can be found in Fig. 4d. In addition, electron diffraction patterns were also obtained from both Ba(OH)_2 and BCG particles in the standard samples and they are quite different. Because of the polymorphism and noncrystallinity of Ba(OH)_2 , it was very difficult to obtain any meaningful diffraction pattern from the Ba(OH)_2 particles; however, expected diffraction patterns were readily obtained from the BCG particles. Thus, TEM studies clearly suggest that there is no observable amount of Ba(OH)_2 in BCG powder samples after the stability test.

DTA was also used to identify the presence of Ba(OH)_2 in the samples. Since Ba(OH)_2 is highly hygroscopic and the removal of water and desorption of gases (such as CO_2) are endothermal processes, it is possible to use DTA to identify Ba(OH)_2 from endothermal peaks associated with the removal of H_2O and desorption of gas(es) from Ba(OH)_2 in the samples. Figure 5a is a DTA curve of a standard Ba(OH)_2 sample. Peaks associated with removal of water and desorption of gas(es) from Ba(OH)_2 can be clearly seen. While these peaks can be readily identified from the DTA curve of a mixture sample consisting of 95 w/o BCG and 5 w/o Ba(OH)_2 , as shown in Fig. 5b, traces of similar peaks are observable in the DTA curve of a mixture sample consisting of 98 w/o BCG and 2 w/o Ba(OH)_2 . The DTA curves for BCG before and after the test at 600°C for 1000 h in the H_2O -containing atmosphere are almost indistinguishable and no observable traces of peaks corresponding to Ba(OH)_2 can be identified, as seen in Fig. 5c and d. The peaks at low temperatures seen in the DTA curves for all samples (including the ones before and after the stability test) are due probably to the weak adsorption of gases by powder samples at room temperature. Therefore, the DTA analysis also suggests that there is no detectable amount of Ba(OH)_2 in the BCG samples after the stability test.

Electrical properties.—Impedance spectra of Pt|BCG|Pt cells exposed to the water-containing atmosphere at 700°C were periodically acquired during the stability test. The resistances of the BCG pellets in the cells were obtained from the intercepts of the impedance loops with the real axis at high frequencies. Interfacial resistances were approximately determined from the difference between the intercept at low frequencies and the intercept at high frequencies with the real-axis. The bulk resistances of the Pt|BCG|Pt cells tested at 600 and 700°C are shown in Fig. 6a as a function of the test time. Initially, the resistance changed quite a lot and it took some time for the electrical properties to stabilize. A gradual increase in bulk resistance was observed in both cases. However, the observed resistance change at 600°C for 1000 h is much smaller than that at 700°C for 1000 h. This directly contradicts the thermodynamic predictions, which would suggest that at lower temperatures the material would be less stable and the change in resistance would be expected to be larger if the material is indeed unstable in such a temperature range. Therefore, the observed gradual increase in resistance cannot be attributed to the decomposition of BCG. Such an increase is due probably to the deterioration in adhesion of Pt electrodes onto BCG electrolyte and some interfacial aging. Shown in Fig. 6b are the interfacial resistances of Pt|BCG|Pt cells during the stability test. The gradual increase in interfacial resistance can be explained by examination of the microstructures of the electrodes before and after the test at 700°C (Fig. 7). Although porosity of the electrode before and after the test is almost the same (about 28%), the average pore size increased from 3.6

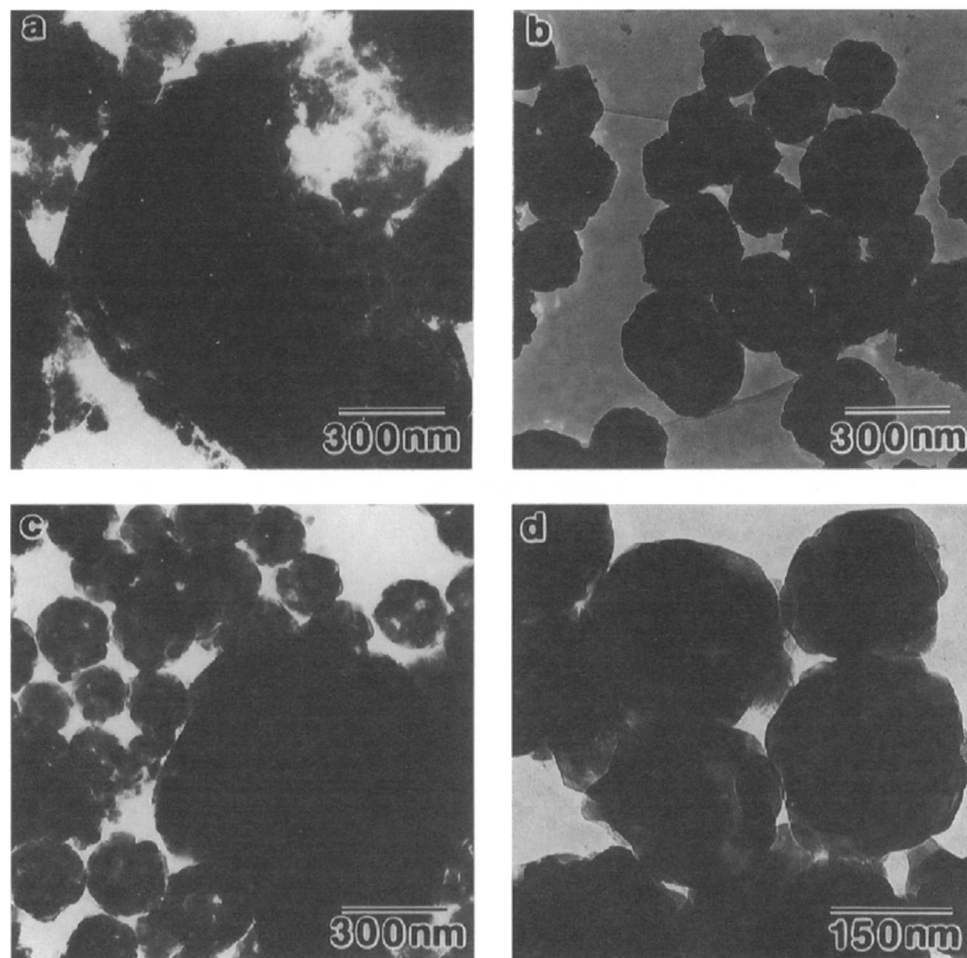


Fig. 4. TEM micrographs of (a) Ba(OH)_2 , (b) BCG before the stability test, (c) BCG with 5 w/o Ba(OH)_2 , and (d) BCG after the stability test at 600°C .

to $6.5\ \mu\text{m}$. This means that less active sites are available for the electrochemical reaction and thus higher interfacial resistances.

Discussion

Uncertainty of thermodynamic data.—As seen in Fig. 1, the equilibrium partial pressures of water vapor ($p_{\text{H}_2\text{O}}$) for the co-existence of Ba(OH)_2 , CeO_2 , and BaCeO_3 at temperatures $>408^\circ\text{C}$ can be quite different when different sets of thermodynamic data were used. Clearly, if the data reported by Tanner and Virkar¹⁹ are accurate, BaCeO_3 would be thermodynamically unstable at temperatures $\leq 800^\circ\text{C}$ in an atmosphere containing $p_{\text{H}_2\text{O}} \geq 0.032\ \text{atm}$. In other words, BaCeO_3 would be unstable under fuel cell conditions at temperatures $\leq 800^\circ\text{C}$. In stark contrast, however, if the data reported by Sorokina *et al.*^{16,17} are used, the equilibrium partial pressures of water vapor are about 3 to 4 orders of magnitude higher than those predicted by Tanner and Virkar.¹⁹ Accordingly, BaCeO_3 would be stable at temperatures $\geq 492^\circ\text{C}$ in an atmosphere containing $p_{\text{H}_2\text{O}} \leq 0.5\ \text{atm}$. This means that BaCeO_3 is thermodynamically stable under fuel cell conditions at temperatures $\geq 492^\circ\text{C}$. Therefore, the uncertainty of the available thermodynamic data is too large to draw any meaningful conclusion on the thermodynamic stability of BaCeO_3 at intermediate temperatures. Further, even if BaCeO_3 is unstable thermodynamically, the material may still be practically useful if it is kinetically stable under the service conditions.

Effect of dopant.—To date, there is no creditable evidence, either thermodynamic calculation or experimental observation, to support the conclusion that gadolinium-doped BaCeO_3 would decompose to Ba(OH)_2 and CeO_2 under hydrogen-air fuel cell conditions at intermediate temperatures. If undoped BaCeO_3 and La-doped barium

cerates (such as $\text{La}_{0.05}\text{BaCe}_{0.95}\text{O}_{2.975}$) were indeed unstable in atmospheres containing $p_{\text{H}_2\text{O}} > 0.032\ \text{atm}$ ($\sim 24.3\ \text{Torr}$) at temperature $\leq 800^\circ\text{C}$,¹⁹ the experimental results in this

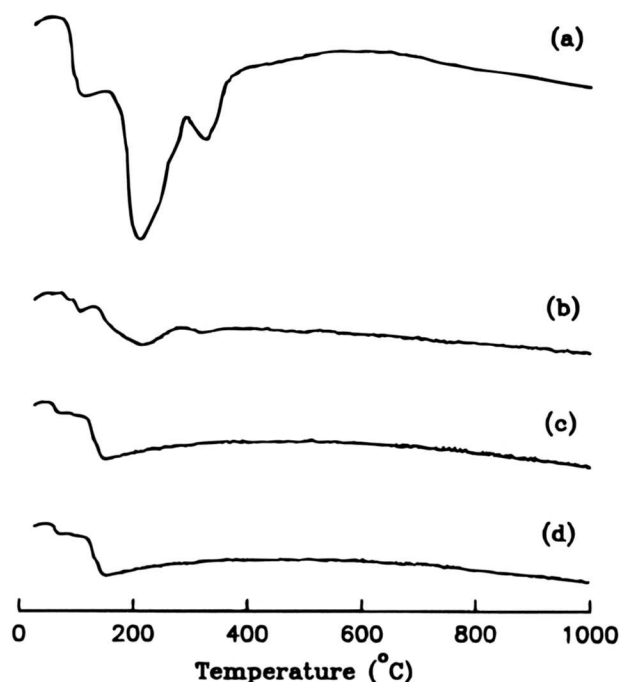


Fig. 5. DTA curves of (a) Ba(OH)_2 , (b) BCG with 5 w/o Ba(OH)_2 , (c) BCG before the stability test, and (d) BCG after the stability test at 600°C , at a heating rate 5°C/s in dry air.

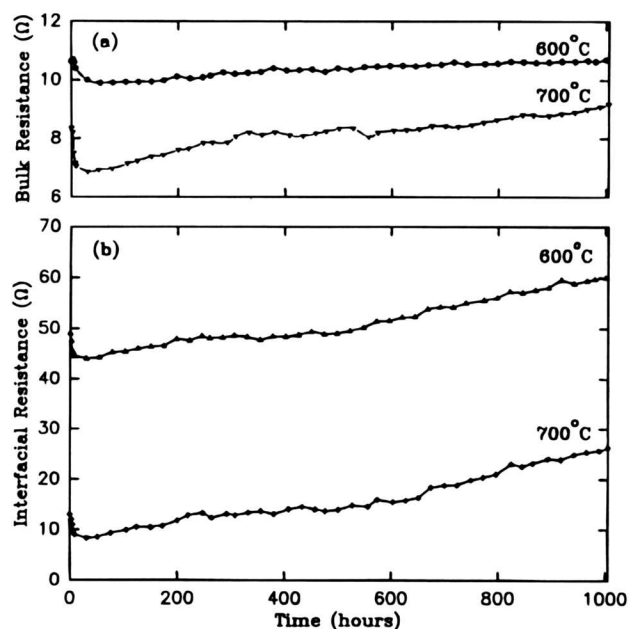


Fig. 6. Resistances of (a) the bulk electrolyte and (b) the electrolyte-electrode interfaces of Pt|BCG|Pt cells as a function of immersion time in an atmosphere containing 50 v/o water vapor and 50 v/o argon at 600 and 700°C (the electrode area was 0.78 cm² and the sample thickness was 0.124 cm).

study would strongly suggest that the addition of gadolinium to BaCeO₃ not only enhances the conductivity but also improves stability, either thermodynamically or kinetically or both. Thus, dopants may play an important role in determining the stability of the material. In fact, addition of appropriate dopants to improve the stability of materials has been a common practice in materials design.

Stability at low temperatures.—It is noted, however, that BCG is indeed unstable in water. Shown in Fig. 8 is an XRD pattern of BCG powder after being immersed in water at 85°C for 10 days, clearly indicating that the decomposition products include BaCO₃ and CeO₂. In addition, the pH of deionized water containing BCG powder continuously increased with time, indicating a continuous formation of Ba(OH)₂ during immersion (or instability of BCG in water). These observations seem to be consistent with the thermodynamic data of Sorokina *et al.*¹⁶⁻¹⁸ Accordingly, measuring the pH values of deionized water containing BCG powder having undergone the stability test cannot conclusively prove or disprove the presence of Ba(OH)₂ in such BCG powder before immersion in water.

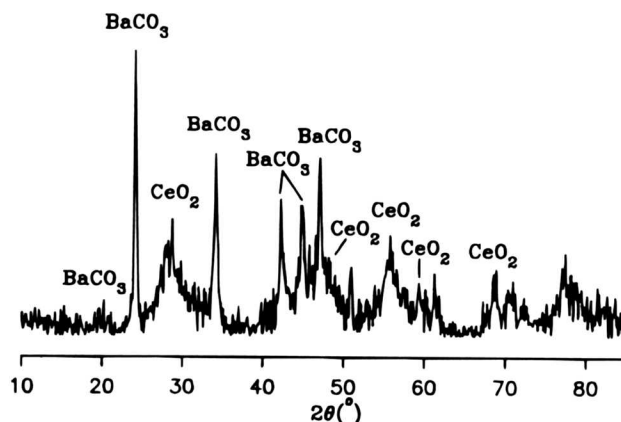


Fig. 8. X-ray diffraction pattern of a BCG powder sample after being immersed in hot water (85°C) for 240 h.

Conclusion

X-ray diffraction analyses of BaCe_{0.8}Gd_{0.2}O₃ tested in an atmosphere containing about 50 volume percent (v/o) (0.5 atm) water vapor at 600 and 700°C for 1000 h indicates that there is no observable amount of CeO₂ formed in the sample. Similarly, TEM and DTA analyses suggest that there is no detectable amount of Ba(OH)₂ formed in the sample after the stability test. Further, changes in electrical resistances during the test contradict the thermodynamic prediction. Therefore, experimental results indicate that there is no creditable evidence to suggest an observable decomposition of BaCe_{0.8}Gd_{0.2}O₃ to Ba(OH)₂ and CeO₂ in an atmosphere containing 50 v/o water vapor at 600 and 700°C for up to 1000 h.

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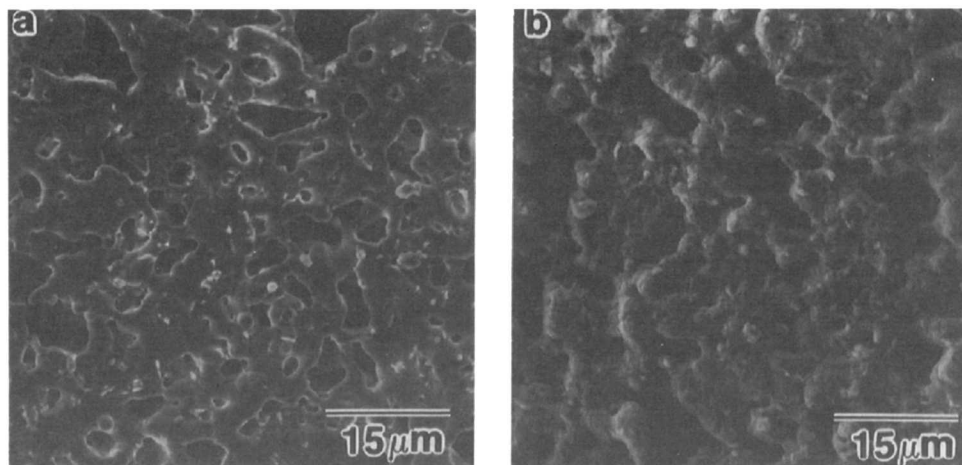


Fig. 7. SEM micrographs of electrode surfaces before and after testing at 700°C.

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Fast Protonic Conductors of Water-Containing P₂O₅-ZrO₂-SiO₂ Glasses

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ABSTRACT

Fast protonic conductors were prepared in the P₂O₅-containing silicate glasses using the sol-gel method. The 5P₂O₅ · 5ZrO₂ · 90SiO₂ glasses, obtained by heating at 200 to 800°C, were crack-free and chemically stable and exhibited room temperature conductivities of 10⁻³ S/cm, which were higher by ~5 orders of magnitude than that of the dried gel or porous silica glass. These high conductivities were regarded as the fast proton mobility accelerated by molecular water which was chemically bonded with POH groups.

Introduction

Fast proton-conducting solids have attracted much attention, because they have a large potential for use in clean energy fields, such as hydrogen gas sensors and hydrogen fuel cells. Although some hydrated crystalline compounds, H₃(PMo₁₂O₄₀) · 30H₂O, H₃(PW₁₂O₄₀) · 30 H₂O, and H₂UO₂PO₄ · 4H₂O, have been known to show high proton conductivity,^{1,2} they are not appropriate for industrial applications. These materials are unstable to humidity and not easily shaped into a film. Fast proton-conducting glasses, if developed, extend beyond the limitation of the above-mentioned compounds and have potential ability for various applications. Glasses are more suitable because of their high transparency and easy formation of films and plates.

We have proved that protons are very mobile when they are strongly hydrogen-bonded in glasses, and a magnitude of proton conductivity is primarily determined by the degree of hydrogen bonding and the concentration of mobile protons in glass structure.³⁻⁶ We prepared alkaline-earth phosphate glasses by melting at low temperatures ~700°C so that the amount of protons remained as large as possible. The conductivity of these glasses was ~10⁻⁵ S/cm at around 100°C, which is highest among the melt-quenched glasses.⁷ Generally, the content of protons in glasses is apt to decrease with increasing the temperature of glass melting. Thus, it is desirable to prepare the glass with a large amount of protons at low temperature, *e.g.*, by using a sol-gel method. More recently, using a sol-gel method we successfully prepared the P₂O₅-ZrO₂ dried-gels which have room temperature conductivities of approximately 10⁻² S/cm.⁷ These high conductivities are considered to be achieved by the fast proton mobility under the

coexistence of molecular water in glass. In this view, the sol-gel technique can be used in the preparation of fast protonic conducting glasses containing a large amount of water.

Generally the phosphate materials are lacking in chemical durability; the water lowers mechanical strength and chemical stability. In fact, it was found that the prepared P₂O₅-ZrO₂ gels are fragile and are broken into pieces upon heating above 200°C, although chemical durability is improved by the addition of ZrO₂.⁷ Such disadvantages limit the use of glasses to practical applications.

In this paper, we report the preparation of crack-free and chemically stable P₂O₅-ZrO₂-SiO₂ glasses using the sol-gel technique and fast protonic conductivities of these glasses. Transparent and high electrical conducting glasses are possible for application in hydrogen-related fields. The high conductivity of the glasses obtained is discussed in relation to the water in glass.

Experimental

A clear solution was synthesized by hydrolysis of Zr(OC₂H₅)₄, PO(OC₂H₅)_{3-x}(OH)_x, and Si(OC₂H₅)₄. Zr(OC₂H₅)₄ and Si(OC₂H₅)₄ were commercially available and used as received. PO(OC₂H₅)_{3-x}(OH)_x was obtained by distilling P₂O₅ in 2-C₃H₇OH at a weight concentration of 10% at 150°C. After cooling at room temperature, a mixture of Zr(OC₂H₅)₄ and 2-C₃H₇OH was added to react with PO(OC₂H₅)_{3-x}, followed by adding 2 g HCONH₂. Si(OC₂H₅)₄ was separately hydrolyzed in the proportion of Si(OC₂H₅)₄/H₂O = 1 in moles for 1 h at room temperature and then added to the solution of zirconium phosphate precursor compound, followed by stirring for 1 h at room temperature. The resulting homogeneous solution was