The Effects of Dopants and A:B Site Nonstoichiometry on Properties of Perovskite-Type Proton Conductors

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ABSTRACT

Investigations of perovskite-type BaCeO3 and SrCeO3, with various dopants (Y, Gd, Nd, and Ni) indicate that their microstructures and electrical properties are strongly influenced by the type and amount of dopants. Grain growth and densification of sintered samples are influenced by dopant level and A:B site nonstoichiometry. The conductivity of BaCe01Y22O3 increases with the yttrium content in hydrogen and wet Ar, and exhibits a maximum in oxygen at an yttrium content of 10 to 20%. BaCe01Y22O3 has the highest conductivity in a hydrogen atmosphere: −1.54 × 10−2 Ω−1 cm−1 at 800°C, and −4.10 × 10−2 Ω−1 cm−1 at 800°C. The effect of BaO excess depends on the concentration of dopant. Compared with BaCe01Y22O3, BaCe01Y22O3 showed a higher total conductivity in all atmospheres studied (O2, H2, and wet Ar), whereas the conductivity of BaCe01Y22O3 with excess BaO (BaO:BaCe01Y22O3 = 0.0.20Y22O3) has a higher total conductivity in all atmospheres studied (O2, H2, and wet Ar), whereas the conductivity of BaCe01Y22O3 with excess BaO (BaO:BaCe01Y22O3 = 0.0.20Y22O3) is lower than that of BaCe01Y22O3. BaCeO3 based materials have higher conductivities than those of SrCeO3 based materials, whereas SrCeO3 based materials show higher proton transference numbers.

Introduction

Mixed ionic electronic conductors (MIECs) are used in many solid-state electrochemical systems such as solid oxide fuel cells (SOFCs), solid-state gas sensors, and membranes for gas separation. Two well-known MIECs are the partially substituted perovskite oxides BaCeO3 and SrCeO3, in which substitution for Ce by trivalent cations causes the formation of oxygen vacancies and other charged defects and gives rise to mixed conduction in atmospheres containing O2, H2, and H2O vapor. Because much of the charge transport in BaCeO3 and SrCeO3 is by protons, these materials are being investigated as possible hydrogen separation membranes. To be suitable for hydrogen separation, a material must have a high selectivity for hydrogen, so its proton transference number must be much higher than its transferance number for oxygen ion conduction. To be useful in a nongalvanic mode, the transferance number for electronic conduction should be comparable to that for protonic conduction, and the protonic and electronic conductivities should be sufficiently high (>−5 × 10−2 Ω−1 cm−1). In addition, the materials must exhibit high catalytic activity for the dissociation and recombination of hydrogen at the gas/solid interfaces.

Transport properties of perovskites are strongly influenced by the ionic radii of dopants. Kilner and Brook used lattice simulation techniques to model ionic conduction in perovskites and concluded that the overall activation energy for conduction should be minimal when the host and dopant ionic radii are similar to that for protonic conduction, and the protonic and electronic transferance numbers for electronic conduction should be comparable. They reasoned that dopants with large ionic radii made oxygen ion conduction more favorable by enlarging the spacing along the a axis. Increasing dopant ionic radius. Typically, elements in group VIII, such as Fe, Co, and Ni, are appropriate dopants or a second phase must be introduced. For example, Nagamoto and Yamada have studied the effect of dopants for A and B sites on conductivity in hydrogen. Among BaCeO3 samples doped with La, Nd, Yb, Er, Tb, and Nb, Nb-doped BaCeO3 showed the highest conductivity in hydrogen. High conductivity of Nb-doped BaCeO3 in H2 was also observed by Haider and Liu. However, electrochemical studies have indicated an absence of proton conduction in Nb-doped BaCeO3. At the same time, Iwahara et al. observed that Y-, Sm-, and Nd-doped BaCeO3 had high conductivities in hydrogen, and that 20% Sm-doped BaCeO3 exhibited very high total conductivity in hydrogen, (~4 × 10−2 Ω−1 cm−1 at 800°C). However, dense samples were difficult to prepare. According to a more recent report, BaCe0.9Y0.1O2−δ may have the highest conductivity reported to date, ~3.3 × 10−2 Ω−1 cm−1 at 800°C in hydrogen.

SrCeO3 doped with Yb and Y have also been studied as proton conductors. Compared to BaCeO3 based materials, SrCeO3 based materials have lower total conductivities but higher proton transference numbers. Their higher proton transference numbers may make these materials desirable for hydrogen separation due to increased hydrogen selectivity. However, the electronic transference number of Y-doped SrCeO3 (and BaCeO3) was <0.2 at 800°C, based on open-circuit voltage measurements on hydrogen concentration cells. Also, the materials exhibited high interfacial polarization during hydrogen permeation tests. In order to improve catalytic properties and electronic conductivity, appropriate dopants or a second phase must be introduced. Typically, elements in group VIII, such as Fe, Co, and Ni, are good catalysts, and Ni-oxide cermet has already been used as anode material in SOFCs because of its good catalytic properties and high electronic conductivity. In addition to stoichiometric alkaline earth cerates, BaCeO3 containing excess BaO and complex perovskites with the formula of A2B4Nb5O19 have been studied. After water uptake measurements and conductivity analysis, Kreuer et al. concluded that excess BaO formed a grain boundary phase. Recently, Shima and Haile reported that excess BaO aids in densification and enhances the conductivity of 15% Gd-doped BaCeO3 in wet Ar at 500°C, but samples with 4% BaO excess eventually lost mechanical integrity due to reaction with atmospheric CO2.
In this study, stoichiometric and nonstoichiometric BaCeO₃ and SrCeO₃ were doped with various materials (Gd, Nd, Y, and Ni) at different dopant levels (5, 10, and 20%), and the effects of these composition variations on sinterability, microstructure, and conductivity were characterized.

**Experimental**

**Sample preparation.**—BaCeO₃ and SrCeO₃ based materials were prepared by using solid-state reactions.²⁹ All powders in this study had a perovskite structure except SrCe₆₋ₓ/(Niₓ, Yₓ)O₃₋₉, in which CeO₂ was detected by X-ray diffraction (Scintag, XDS 2000). Pellets of doped BaCeO₃ were sintered in air at 1550°C for 10 h. SrCeO₃ based materials without Ni dopant were sintered in air at 1500°C for 10 h, whereas, materials with Ni dopant were sintered in air at 1300°C for 5 h. Both sides of each pellet were then polished with 600 grit SiC polishing paper. Platinum (Hereraus CL11-5100) or silver (Hereraus C1000) paste was painted on the polished surfaces and dried in air at 150°C for 5 h and subsequently fired in air for 12 min at 1200°C (for Pt paste) or at 850°C (for Ag paste) to form porous electrodes for electrochemical measurements.

**Microstructure.**—Microstructures of materials were studied by scanning electron microscopy (SEM; JEOL JSM-5400) on as-sintered surfaces, fracture surfaces, and etched surfaces. To prepare an etched surface, the pellet was first polished with 600 grit SiC polishing paper, then immersed in 1 N HNO₃ solution for 2 mm, and finally cleaned in isopropyl alcohol.

**Impedance spectroscopy.**—An impedance analyzer (HP4192A LF) was used to acquire impedance spectra in the frequency range from 5 Hz to 13 MHz at temperatures between 550 and 800°C. Before the impedance measurements, each cell was first equilibrated at 800°C for 5 h and subsequently cooled to 550°C in the desired atmosphere (O₂, H₂, or wet Ar). Water vapor was obtained by bubbling Ar through deionized water at room temperature (~22°C).

H⁺/O²⁻ transference number.—The ratios of proton and oxygen ion transference numbers to the total ionic transference numbers were obtained by discharging a fuel cell

\[ \frac{t_{\text{H}⁺}}{t_{\text{ion}}} = \frac{w_e}{w_i} \]  

and

\[ t_{\text{ion}} = t_{\text{H}⁺} + t_{\text{O}²⁻} \]

where \( w_e \) and \( w_i \) are the rates of water vapor evolution from the cathode side and anode side, respectively, and \( w_i \) is the total rate of water vapor evolution from both sides or calculated from the short-circuit currents (using Faraday's law). The rates of water vapor evolution due to electrochemical process were calculated from the flow rates of carrier gas and humidity measurements by a hygrometer (Fisher Scientific) in both sides of the cell under both open-circuit and short-circuit conditions. This procedure provides relative transference numbers only. To measure the absolute transference numbers, a separate experiment would be needed to determine the electronic contribution.

**Results and Discussion**

**Material sintering.**—Initially, green pellets were placed directly on an Al₂O₃ setter for sintering. After sintering, the surface areas in contact with alumina were yellowish, while the uncontacted surface areas were brown or dark green, depending on the initial material composition. The large difference in color suggested a reaction with the setter. As expected, the X-ray diffraction analysis of the contacted surface areas revealed the presence of CeO₂ as the major phase and BaCeO₃ as a minor phase (Fig. 1a). An X-ray diffraction analysis of the uncontacted surface areas (the so-called free surface) showed the perovskite structure of BaCeO₃, and possibly a trace amount of CeO₂, due to BaO loss at high temperature (Fig. 1b). Cross-sectional views (Fig. 2a) showed clearly the formation of a reacted layer.
layer 10 to 15 μm thick, whereas no such layer was evident in materials that did not contact Al₂O₃ (Fig. 2b). Energy dispersive X-ray (EDX) analysis showed that the molar ratio of Ba over Ce in the reacted layer was ~1:9. Similar reactions were evident after sintering other doped BaCeO₃ and SrCeO₃ on Al₂O₃ setters, suggesting a reaction such as:

$$\text{Ba(Sr)CeO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{CeO}_2 + \text{Ba(Sr)Al}_1\text{O}_4 \quad [4]$$

Such a reaction between Ba(Sr)CeO₃ and Al₂O₃ must be considered in fabricating thin films of Ba(Sr)CeO₃ on alumina substrates.²⁵²⁶ To prevent the reaction in the present study, powders with the same composition as the green pellets were used as a buffer layer between the green pellets and the setter.

Microstructure.—Photomicrographs of as-sintered surfaces of SrCeO₃ based materials (Fig. 3) show that both stoichiometric and nonstoichiometric (i.e., with excess SrO) SrCeO₃ can be densified at 1500°C. Increasing the temperature to 1550°C caused extra grain growth. Undoped SrCeO₃ showed a rough surface with honeycomblike structure (Fig. 3a). A similar structure was observed by Du and Nowick on a thermally etched Ba₃Ca₁₅Nb₁₅O₃₉₄ surface.²⁷ Under identical sintering conditions (temperature and dwell time), grain growth increased as dopant level increased (Fig. 3a, b, and c).

Photomicrographs of BaCeO₃ based materials sintered at 1550°C are shown in Fig. 4. In this study, stoichiometric 5% Y-doped BaCeO₃ did not densify well (~89 % dense; Fig. 4a), whereas a sample with 5% excess BaO (BaO-0.90CeO₂-0.025Y₂O₃) had a very dense fracture surface (~94 %; Fig. 4b). This suggests that the proper amount of excess BaO promotes sintering for this dopant level (5% Y). At higher dopant concentration (10% Y), however, the stoichiometric material was very dense (~98 %; Fig. 4c), whereas, the sample with 5% excess BaO (BaO-0.85CeO₂-0.05Y₂O₃) was not very dense (~91 % dense) and had finer grains (Fig. 4d). The observation of
Kulscar28 that 2 mol % excess BaO in BaTiO3, as a grain size refiner suggests that the excess BaO may inhibit grain growth in the 10% Y-doped sample.

Excess BaO may incorporate into the perovskite up to the solubility limit according to defect reactions:

$$\text{BaO} = \text{Ba}^{2+} + \text{O}^{2-} + \text{V}_{\text{Ce}} + 2\text{V}_{\text{O}}^* \quad [5a]$$

and

$$2\text{BaO} = \text{Ba}^{2+} + \text{Ba}_{\text{0.5}}^{0} + 2\text{O}^{2-} + \text{V}_{\text{O}}^* \quad [5b]$$

At low dopant concentrations, the forward reactions may be favored because the concentration of oxygen vacancies introduced by the dopant is relatively small. As a result, excess BaO can be easily incorporated into the structure to create additional oxygen vacancies, which improve vacancy diffusion and thereby promote sintering. Higher dopant concentrations, however, may saturate the material with oxygen vacancies, in which case the forward reactions in 5a and 5b become less favorable. As a result, Ba-rich phases may segregate at grain boundaries, thus impeding sintering.

Effects of excess BaO on microstructure were also studied by examining 5% Y-doped BaCeO3 with and without excess BaO after acid etching. After acid etching for 2 min in HNO3, the sample with 5% excess BaO (BaO-0.90CeO2-0.025Y2O3) showed clearly distinguished grains (Fig. 5a), but the stoichiometric doped BaCeO3 (BaCe0.95Y0.05O3) was randomly corroded (Fig. 5b) with finer grains. Although excess BaO acted as a grain size refiner in BaO-0.85CeO2-0.05Y2O3 (Fig. 4d), the observation of coarser grains in BaO-0.90CeO2-0.025Y2O3, rather than in BaCe0.90Y0.05O3, is exactly opposite. It is possible that most of excess BaO in the sample with low dopant concentration (BaO-0.90CeO2-0.025Y2O3) had already become incorporated into the matrix according to Eq. 5. This incorporation could create more vacancies and thus promote grain growth and densification.29 In the sample with the high dopant concentration (BaO-0.85CeO2-0.05Y2O3), however, most of the excess BaO may exist as grain boundary phases due to oxygen vacancy saturation in the matrix. The existence of excess BaO at grain boundaries in BaO-0.85CeO2-0.05Y2O3, however, could act as a grain-size refiner and impede sintering.28

As for stability, samples with compositions of SrO-0.90CeO2-0.025Y2O3, SrO-0.85CeO2-0.05Y2O3, and 1.05SrO-CeO2 appeared to be acceptable immediately after sintering, but crumbled into pieces after exposure to air for several days. After exposure to air for many weeks, as-sintered BaO-0.90CeO2-0.025Y2O3 and BaO-0.85CeO2-0.05Y2O3 pellets, however, retained good mechanical integrity. However, if the as-sintered pellets were broken into two pieces and then exposed to air, BaO-0.90CeO2-0.025Y2O3 maintained good integrity while BaO-0.85CeO2-0.05Y2O3 crumbled. The lower stability in air of BaO-0.85CeO2-0.05Y2O3 than that of BaO-0.90CeO2-0.025Y2O3 suggested that the former may have more Ba-rich phases at grain boundaries than the latter. Scanning electron microscopy (SEM) examination on fracture surfaces of BaO-0.90CeO2-0.025Y2O3 showed that the entire fracture surface is dense, as shown in Fig. 4b, and that there was no observable change after the fracture surface was exposed to air for four weeks. However, after exposure of sintered BaO-0.85CeO2-0.05Y2O3 to air for two weeks, examination of the center portion of the fracture surface revealed a Ba-rich phase in the grain boundaries (Fig. 6). EDX analysis showed that the molar ratio of Ba over Ce is ~9:1 in the Ba-rich phase, while neighboring grains had a molar ratio of Ba:Ce:Y ~49:44:7, close to the molar ratio of Ba:Ce:Y = 100:85:10 when the material was prepared. The observation of a Ba-rich phase in BaO-0.85CeO2-0.05Y2O3 confirmed our assumption that the excess BaO likely exists in the grain boundary area of the sample with high dopant concentration due to the possible saturation of oxygen vacancies. Such a Ba-rich phase was not observed in the surface layer of the sintered pellet because BaO was probably vaporized at high temperature during sintering. As such, the stable surface layer prevented the Ba-rich phase in the center of the sintered body from further reacting with atmospheric CO2, thereby maintaining the good integrity of the as-sintered pellets. However, after the pellet was broken, the Ba-rich phase inside the sintered body was readily accessed by atmospheric CO2, forming BaCO3 and consequently causing the crumbling of the pellet.

Conductivity of BaCeO3 based materials—Temperature dependence of stoichiometric doped BaCeO3—Shown in Fig. 7a are the total conductivities of doped BaCeO3 in 1 atm oxygen as determined by impedance spectroscopy. The total conductivity of Y-doped BaCeO3 increased with temperature. The conductivity of BaCe0.90Gd0.05O3−δ was slightly higher than that of BaCe0.90Y0.05O3−δ and BaCe0.90Sr0.05O3−δ in this work at temperatures <700°C, but was almost the same at >700°C.
Shown in Fig. 7b is the temperature dependence of conductivity in 4% H_2. The conductivities of samples with 5, 10, and 20% Y increased with dopant concentration. For BaCeO_3 doped with 20% Y, Nd, and Gd, the conductivity increased in the order of Nd, Gd, and Y at a given temperature. Contrary to expectation, the conductivity of 20% Nd-doped BaCeO_3 was not very high. Moreover, 20% Y-doped BaCeO_3 had the highest conductivity in this work, —1.54 × 10^{-2} \text{S cm}^{-1} at 600°C and —4.16 × 10^{-3} \text{S cm}^{-1} at 800°C. Compared to the results of Iwahara et al.\(^2\) for 20% Y-doped BaCeO_3 in H_2, the conductivities in this work are lower, partially because measurements in the present study were made in 4% H_2 instead of 100% pure hydrogen.

Shown in Fig. 7c is the temperature dependence of conductivity in wet Ar. The conductivity of Y-doped BaCeO_3 increased with dopant concentration. Among the samples with 20% dopants, conductivity increased in the order of Nd-, Y-, and Gd-doped BaCeO_3 in the temperature range of 550 to 800°C. The 20% Gd-doped BaCeO_3 had the highest conductivity with the lowest activation energy (~0.31 eV) in wet Ar,\(^4\) whereas the activation energies for other materials were very close to one another, —0.4 eV.

**Composition dependence of stoichiometric doped BaCeO_3.**—For Y-doped BaCeO_3, at a given temperature, conductivity measured in wet Ar (Fig. 7c) and 4% H_2 (Fig. 8a) which is dominated by ionic conduction, increased monotonically with dopant concentration from 5 to 20%. In O_2, however, there is a significant contribution from electron hole conduction; conductivity increased with dopant concentration from 5 to 10%, and then decreased slightly with dopant concentration up to 20%. The smooth curve in Fig. 8b implies a possible maximum between 10 and 20%. The increase in conductivity with dopant concentration could be related to an increase in charge carrier concentration through the reaction

$$\text{BaO + Y_2O_3 \rightarrow 2YO + 3 O}^\text{2-} + \text{V}_{\text{Ce}}^\text{+}$$\[^6\]

However, sintered density and defect structure may also affect total conductivities.

**Effects of A:B site nonstoichiometry.**—As shown in Fig. 9, samples with BaO excess had higher conductivity than the stoichiometric doped samples with 5% Y as the dopant. However, at a higher dopant concentration (10% Y), excess BaO reduced the total conductivity, except at a lower temperature (<600°C), in H_2. This variation of conductivity with BaO excess could be correlated to the density change with BaO excess. At a 5% dopant level, BaO:0.90CeO_2:0.05Y2O_3 had a greater density (~94% dense) than BaCe_0.85Y_0.15O_2 (~89% dense), whereas, at the 10% level, BaO:0.85CeO_2:0.05Y_2O_3 had a lesser density (~91%) than BaCe_0.80Y_0.20O_2 (~98% dense; Fig. 4). However, Shima et al. found that 4% excess BaO reduced the conductivity of 15% Gd-doped BaCeO_3 in wet Ar at lower temperatures (250 to 400°C) and enhanced it at higher temperatures (500°C), even though the sample with excess BaO had increased density. They attributed the reduced conductivity at low temperature to defect association.\(^21\)

This variation of conductivity with excess BaO may also
be related to defect structure. At a low dopant concentration (5% Y), incorporation of excess BaO into the pervoskite matrix induces high vacancy concentration and increases conductivity, whereas at a high dopant concentration (10% Y), excess BaO tends to reside in grain boundary phases that may inhibit conduction in the temperature range studied.

**Conductivity of doped SrCeO$_3$**—Shown in Fig. 10 are the total conductivities of doped SrCeO$_3$ in oxygen and hydrogen. The conductivities for BaCe$_{1-x}$Y$_x$O$_3$ under comparable conditions are reproduced from Fig. 7 for reference. Obviously, doped SrCeO$_3$ had lower conductivities in O$_2$ and H$_2$ than those of BaCeO$_3$ based materials. As with BaCeO$_3$, conductivity increased as dopant concentration increased from 5 to 10% in both O$_2$ and H$_2$. The activation energy for conduction in H$_2$ was lower than that in O$_2$. Conductivity of SrCe$_{0.85}$Y$_{0.05}$O$_3$ was surprisingly low (~$10^{-7}$ Ω$^{-1}$ cm$^{-1}$ at 650°C). The Ni was probably not a good dopant in terms of conductivity, although Ni-oxide cermets were reported to have good catalytic properties in SOFC applications.

$H^+/O^-$ conduction.—Figure 11 shows the relative ionic transference numbers of SrCe$_{0.95}$Y$_{0.05}$O$_{3-t}$ in this work, as well as those of the 10% Y- and 10% Gd-doped BaCeO$_3$ that were reported by Iwahara et al. Compared to the results of BaCeO$_3$ based materials, SrCeO$_3$ based materials have higher proton transference numbers and lower oxygen ion transference numbers. In SrCe$_{0.95}$Y$_{0.05}$O$_{3-t}$, more than 85% of the ionic conductivity was carried by protons in the testing temperature range (600-800°C) and oxygen ions contributed to only ~15% of the ionic conductivity. Ionic conduction was completely protonic below 600°C.

**Conclusions**

Dopant species and concentration strongly affected the microstructures and electrical properties of BaCeO$_3$ and SrCeO$_3$. Grain growth and densification of sintered samples were influenced by dopant level and nonstoichiometry on A and B sites. The conductivity of BaCe$_{1-x}$Y$_x$O$_3$ ($x = 0.05$, 0.1, and 0.2) increased in hydrogen and wet Ar with Y content. Of the doped BaCeO$_3$, BaCe$_{0.9}Y_{0.1}O_{3-t}$ showed the highest conductivity in hydrogen (~$1.54 \times 10^{-2}$ Ω$^{-1}$ cm$^{-1}$ at 600°C and ~$4.16 \times 10^{-3}$ Ω$^{-1}$ cm$^{-1}$ at 800°C). Although SrCeO$_3$ based materials had lower conductivities than those of BaCeO$_3$ based materials, they exhibited higher proton and lower oxygen ion transference numbers than BaCeO$_3$, which may be useful for improving their selectivity for hydrogen separation.

**Acknowledgments**

This work was supported, and this manuscript created, under Contract W-31-109-Eng-38, of the U.S. Department of Energy, Federal Energy Technology Center.
Determination of the Trap Density in Amorphous Silicon by Quasi-Static Capacitance-Voltage Measurements

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ABSTRACT

A special metal-oxide-semiconductor structure based on hydrogenated amorphous silicon has been fabricated. The quasi-static capacitance-voltage (CV) curves of this device are calculated for various trap densities of the amorphous silicon. Due to the occurrence of punch-through, Poisson's equation cannot be solved analytically. Thus, a finite elements approach has been used to compute the potential distribution and the charge density in the semiconductor. Differentiation of the quasi-static capacitance-voltage (CV) curves of this device are calculated for various trap densities of the amorphous sil-

In this method a specially designed metal-oxide-a-Si structure is used and its CV curve is recorded. CV techniques are known from monocrystalline silicon MOS capacitance measurements where they are among the major diagnostic tools used to investigate trap properties. There is a big difference, however, between monocrystalline and amorphous metal-oxide-semiconductor (MOS) structures in the monocrystalline case, the CV characteristics are controlled by surface states (the bulk states being negligible), while for amorphous silicon, the CV characteristics are controlled by the bulk states (the surface states being negligible). Among the first to report on this observation were

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