BARIUM CERATE–BASED MATERIALS FOR HYDROGEN SEPARATION MEMBRANES

R. D. Carneim, P. F. Becher, C-H. Hsueh, and T. R. Armstrong
Oak Ridge National Laboratory

1. INTRODUCTION

1.1 Chemical Stability Issues in Barium Cerate–Based Proton Conductors

It is well known that many barium-containing phases decompose into $BaCO_3$ and other phases (generally oxides, hydroxides, or carbonates, depending on the other elements present in the phase and the environment) in the presence of CO_2 in a certain temperature range. Perovskite barium cerate phases are no exception. Shima and Haile studied the effect of A-site cation stoichiometry on, among other things, the stability of doped and undoped $BaCeO_3$ compositions. It was noted that samples with Ba excess reacted with atmospheric CO_2, while stoichiometric and Ba-deficient compositions did not. It was further discovered that undoped $BaCeO_3$ could not accommodate any Ba deficiency (CeO_2 would precipitate), though the doped material could; however, a large Ba deficiency resulted in a significant decrease in total conductivity.

Another technique for improving the chemical stability of this class of materials is using additional dopants. For example, $BaZrO_3$ is extremely resistant to decomposition in CO_2-containing environments. Even acceptor-doped compositions are more stable than undoped barium cerate. Since $BaZrO_3$ and $BaCeO_3$ easily form solid solutions, it is possible to replace any desired fraction of the Ce in $BaCeO_3$ with Zr. Ryu and Haile found that Zr_{Ce} substitution did indeed improve the stability of doped and undoped $BaCeO_3$; however, at the expense of conductivity.

In this study, both approaches—A-site stoichiometry and doping—are examined. High-temperature x-ray diffraction in flowing CO_2 was used to detect the presence of $BaCO_3$ in powder sample of various compositions. Initially, the effect of A-site stoichiometry ≤ 1 was examined to determine the composition to be used for the majority of this work (i.e., synthesis, processing, and characterization). The effect of additional dopants was then studied to determine their effect on chemical stability.

1.2 Synthesis

The use of combustion synthesis (CS) [i.e., glycine nitrate process (GNP)] is an attractive powder synthesis technique due to its potential for producing high-purity nanocrystalline powders with excellent compositional homogeneity and low energy-input requirements. In this process, glycine is used as a fuel that can be encouraged to react with (burn) metal nitrates. If the fuel and oxidizer are intimately mixed, such a burn is self-sustaining requiring only a small amount of heat to ignite the mass. Theoretically, the reaction products of a stoichiometric fuel–oxidizer mixture are CO_2, H_2O, and N_2 gasses, and fine

agglomerated particles of the desired oxide composition. (Non-stoichiometric burns are not considered in this work; however, such mixtures would produce CO and/or NO_x, and produce a different reaction temperature and rate relative to the stoichiometric case.) In practice, however, lab scale reactions do not proceed perfectly resulting in noxious gasses, fuel residue, and multi-phase product (individual metal oxides, carbonates, hydroxides, even nitrates). The scaled up version commercialized by Praxair uses spray drying to dehydrate a sucrose (fuel)/metal nitrate mixture which passes from the spray drier directly into a combustion chamber for conversion into a metal oxide. The resulting powders must often be calcined to remove residual organic material and to produce the desired phase. High-temperature calcination of combustion-synthesized powders negates, at least partially, some of the advantages CS is known for: The powder may become contaminated by impurities in the calcination environment, and it will almost definitely be coarsened. Another purpose for high-temperature calcination is to coarsen the powder to make it more compatible with most fabrication processes.

With the objective of producing a powder by CS that can be used as burned (i.e., formed and sintered with minimal [or no] additional powder preparation steps), the GNP was studied in detail to determine the process parameters that produce the most useful powder. It stands to reason that the character of the powder is greatly affected by the nature of the combustion reaction: the higher the reaction temperature, the cleaner the reaction and more likely a single-phase powder will be produced. A high-velocity (explosive) reaction would result in a well-dispersed smoke-like powder, most of which would be lost to the exhaust. A slow but high-temperature reaction may produce hard (partially sintered) aggregates. There are several ways to modify the reaction including changing the burn stoichiometry and changing the initial and/or ambient temperature. The method of adjusting the reaction used in this work is changing the chemistry. By using different fuels and oxidizers the reaction can be significantly altered without producing toxic gasses or requiring environmental controls. The fuels studied are glycine, urea, carbohydrazide, and oxalic dihydrazide. The oxidizer type was changed by using different salts as the metal source. Three different combinations were used: metal nitrate sources for all three cations, substituting barium nitrite ($Ba[NO_2]_2$) as the barium source—which slightly decreases the amount of reactants relative to the all-nitrate case, and substituting cerium (IV) ammonium nitrate ($[NH_4]_2Ce[NO_3]_6$) as the cerium source—which significantly increases the amount of reactants.

As a comparison, the fundamentally different synthesis method of homogeneous coprecipitation (CP) was examined. Homogeneous coprecipitation also has the potential for producing homogeneous nanocrystalline powders. With this process, however, a high-temperature calcination step is unavoidable. A commercially synthesized powder procured from Praxiar Specialty Materials was also examined.

2. SYNTHESIS

2.1 Composition Selection

Based on available literature data and the non-sensitivity of the composition, $BaCe_{0.80}Y_{0.20}O_{3-\delta}$ was chosen for this study. Yttrium-doped barium cerate has one of the highest conductivities of oxide materials, and a relatively wide usable temperature range (Fig. 1). As a reference a 1 kg lot of powder was obtained from Praxair with this composition. Since many barium-containing compounds tend to decompose into $BaCO_3$ and other oxides (in this case, $Ce_{1-x}Y_xO_{2-x2}$) at moderately high temperatures in the presence of CO_2, the final composition chosen for this study was the slightly barium-deficient composition $Ba_{0.98}Ce_{0.80}Y_{0.20}O_{3-\delta}$ (BCY88) in order to improve its stability under these conditions (Sect. 3).

2.2 Stock Solution Preparation

In preparation for both synthesis processes, the metal sources with variable (i.e., not precisely known) water contents were dissolved in deionized water, filtered, and the resulting solutions characterized. Cerium (III) nitrate ($Ce[NO_3]_3 \bullet xH_2O$, source) and yttrium nitrate ($Y[NO_3]_3 \bullet xH_2O$, source) solutions were prepared for this reason. Barium nitrate ($Ba[NO_3]_2 \bullet H_2O$, source) was also prepared in this manner due to its low and slow solubility, and a barium nitrite solution was prepared mainly to allow filtering prior to use (barium carbonate was found on dissolving the solid). Cerium (IV) ammonium nitrate was used in powder form. The solutions were characterized by gravimetric analysis of the oxide after calcination or by complexometric titration with ethylendiaminetetraacetic acid disodium salt (EDTA•2Na). Solutions were prepared to have metal ion concentrations of approximately 1 mol·kg or greater, with the exception of $Ba[NO_3]_2$ which has a much lower solubility than the other materials. This process allows precise compositional control during the preparation of the precursor solutions for CS and CP which is required for multi-cation mixed metal oxides.

2.3 Combustion Synthesis I—Solid Intermediate

2.3.1 Solid-Intermediate Combustion Synthesis

Initially, all twelve precursor compositions were tested under “best-case-scenario” conditions as a screening process to eliminate poorly-behaved metal source–fuel combinations. The twelve compositions were the three combinations of metal sources, each of which were used with each of the four fuels (Table 1). Appropriate masses to produce 15 grams of BCY88 of each component were combined in a beaker (glass) and stirred in the manner outlined in Table Mixing. After all components were completely dissolved, the solution was heated, with continued agitation, to allow water to evaporate. Prior to the solution becoming an unwieldy sticky mass in the bottom of the beaker, the material was transferred to a

Table 1. Compositions and Characteristics of Materials Prepared Using Solid-Intermediate GNP-CS

Ba Source	Ce Source	Fuel	Drying and Product Characteristics	T_{ig}/°C	Burn Characteristics	Sintered Density/ g·cm^{-3}
Nitrate	Nitrate	glycine	hard, hygroscopic, colorless glassy	322	self-sustaining, moderate speed, fluffy product	3.99
Nitrate	Nitrate	urea			results in low-density flakes; color differences	
Nitrate	Nitrate	carbazide	hard, hygroscopic, pink glassy	322	vigorous reaction, not self-sustaining; many fine ejected particles	
Nitrate	Nitrate	oxalic dihydrazide	chalky, bright yellow	312	vigorous reaction; moderate speed; appears self-sustaining; no shape change (product contained)	4.31
Nitrate	Amm. Nitrate	glycine	brownish, gooey	302	self-sustaining, moderate speed, fluffy product	4.18
Nitrate	Amm. Nitrate	urea	yellow, pasty		results in flakes (higher density than 2); color differences; some char	1.99
Nitrate	Amm. Nitrate	carbazide		338	vigorous but slow reaction, not self-sustaining; many fine ejected particles	
Nitrate	Amm. Nitrate	oxalic dihydrazide	chalky, bright yellow	312	vigorous reaction; slower than 4; appears self-sustaining; no shape change (product contained)	4.53
Nitrite	Nitrate	glycine	light brown, glassy	332	ignition delay with larger pieces, low speed; fluffy product (though less so than 1)	2.98
Nitrite	Nitrate	urea	light brown, pasty		results in flakes (higher density than 6); color differences	
Nitrite	Nitrate	carbazide	dirty pink, glassy	270	rapid burn, not self-sustaining; color differences; nice powder	
Nitrite	Nitrate	oxalic dihydrazide	bright yellow, low-density, chalky	338	long ignition delay; not self-sustaining; nice powder and yield	3.74

flat glass plate with its surface temperature controlled at approximately 150°C on a hot plate and dried to completion. [An earlier cursory test determined that the ignition temperature of most of these compositions was higher than 300°C. The surface temperature was frequently checked (type K thermocouple surface temperature probe) to ensure 150°C was not exceeded.] During this final drying stage, the material was manually agitated with a metal spatula. The dried precursors were placed in unsealed glass sample jars that were placed in a desiccator with calcium sulfate (DriRite) desiccant.

The bulk of the samples were then reacted to produce powder for testing. Each composition was reacted by placing pieces of it under a metal crucible on a metal pan on a hot plate at above 400°C—well above the ignition temperature (T_{ig}) of the compositions that ignite. The crucible was in place to prevent the material from wandering during burning and to contain as much product as possible. The materials that did not ignite were reacted by placing them in a furnace at 500°C for 10 min in an alumina sagger. These powders were then analyzed by x-ray diffraction (XRD) for phase determination. The as-burned

powders were also pressed into pellets (≈1 g powder pressed uniaxially at 70 MPa in a 12.7 mm diameter cylindrical steel die) and sintered for 600 min at 1450°C, 1550°C, and 1650°C in air (heating at 5°C·min^{-1}, cooling at 10°C·min^{-1}). Densities were determined of the intact sintered pellets by the Archimedes method in ethanol. X-ray diffraction was also performed on the sintered pellets to determine the final phase.

2.4 Combustion Synthesis II—Conventional GNP-Type

Based on the characteristics of the initial twelve samples, four compositions were selected for further testing. Precursor solutions were prepared as above to produce approximately 50 g of powder. These compositions were then burned as in conventional GNP-CS: rather than drying the solutions, each composition is taken in 50 mL to 200 mL batches, poured into a 4 L stainless steel beaker and heated on a hot plate at its maximum setting until the solution dried sufficiently and ignited. A 100 mesh stainless steel sieve covered the beaker to contain the product. The resulting powders were collected and sieved (using a second 100 mesh stainless steel sieve). Powders produced in this manner required some sort of heat treatment to remove residual organic material from incomplete combustion. These powders were divided into thirds and each portion calcined at a different temperature. The powder was placed in an alumina sagger and placed in a hot furnace for 20 min. The calcination temperatures were 600°C, to burn off the residual organics without affecting the phase composition of the powder, 1000°C, to partially react the powder to produce a specific mixture of phases, and 1200°C, to completely transform the powder to single-phase BCY88. Phase identification was performed on the calcined powders with XRD, and pellets were pressed, sintered, and analyzed as above (except pressing pressure was 105 MPa).

2.5 Homogenous Coprecipitation

Powders were produced by drop-wise adding the appropriate metal nitrate solution to the heated and agitated ammonium oxalate ($[NH_4]_2C_2O_4$) solution, then washing, drying, and calcining the precipitate. The metal nitrate solution was prepared by mixing the appropriate amounts of the Ba-, Ce-, and Y-nitrate stock solutions and diluting the result with deionized water to the desired concentration. For example, to produce 500 mL of solution with a metal ion concentration of 0.1 mol·L^{-1}, the appropriate amounts of the stock solutions were used to produce 25 mmol BCY88 and this mixture diluted to a total volume of 500 mL. Ammonium oxalate solutions were prepared by dissolving the $(NH_4)_2C_2O_4$•H_2O powder in the appropriate amount of deionized water with heat and agitation. For example, the $(NH_4)_2C_2O_4$ solution used with the above metal nitrate solution was a 0.1 mol·L^{-1} solution with an total oxalate ion to metal ion ratio of 3; 0.15 mol of $(NH_4)_2C_2O_4$•H_2O was dissolved in heated deionized water to make 1.5 L of

solution. Metal nitrate solutions, at room temperature, were added drop-wise—but rapidly—to $(NH_4)_2C_2O_4$ solutions at 70°C.

After the metal nitrate solution was consumed, the heat was turned off and the mixture allowed to cool to room temperature overnight with continued stirring. Stirring was then discontinued and the precipitate allowed to settle. After 20 min to 60 min, the liquid was poured off and deionized water added to wash the precipitate. The new mixture was stirred for a few minutes and then allowed to settle again. This washing procedure was repeated four or more times. After the final wash cycle, the precipitate was transferred into a glass pan (Pyrex™) and completely dried in a drying oven at 50°C to 100°C. After producing the first such composition, high-temperature XRD (HTXRD) was performed on the precipitate to determine the necessary calcination temperature. Diffraction patterns were obtained from room temperature to 1300°C at 100°C intervals. Based on the HTXRD results, calcination of the precipitates was performed by placing the precipitate, in an alumina sagger, into a furnace at 1100°C for 30 min.

3. POWDER CHARACTERIZATION AND SINTERING

Initially, powders were pressed into pellets and sintered with a minimum of intermediate processing to determined the synthesis parameters that would produce a powder with the simplest processing requirements. Powders resulting from solid-intermediate combustion synthesis were processed as-burned, powders from conventional GNP-CS were calcined at three different temperatures as described above, and powders from coprecipitation were used after the 1100°C calcination step.

Based on the initial experiments using solid-intermediate combustion synthesis, four compositions clearly produced superior sintered pellets; those using either all standard nitrate metal sources or $(NH_4)_2Ce(NO_3)_6$ with $Ba(NO_3)_2$ and $Y(NO_3)_3$, and either glycine or ODH as the fuel (Fig. 2). Table 1 also lists reaction characteristics as observed and sintered pellet densities (1550°C for 10 h). Powders were then produced using these parameters with the conventional GNP-CS process. Though this process was expected to not produce as high quality a powder as the solid-intermediate version, it has the advantage—at the laboratory scale—of demanding significantly less painstaking preparation and having fewer safety concerns. The best results (sintered samples) were obtained using standard nitrate metal sources and ODH or glycine fuel (Fig. 3). The choice of fuel had a significant effect on the behavior of the process and character of the powder. The ODH-fueled powder was more compact and easier to handle than the glycine-fueled powder, and resulted in a better sintered pellet. Using glycine as the fuel resulted in a very loose, low-density powder; however, due to the greater solubility of glycine, preparation for, and execution of the combustion process was more straightforward. Powders produced by coprecipitation also produced acceptable sintered pellets. Though this powder was also fairly dense (similar to the ODH-fueled combustion synthesized powder), it had a paste-like consistency which resulted in poor flowability.

Figure 2 also shows the results of sintering powders synthesized using $Ba(NO_2)_2$ and/or urea and carbazide. Those samples prepared with urea did not densify, though most of these pellets remained intact. This is in contrast to the pellets prepared with the carbazide-fueled powders, which densified somewhat but developed different phases in the interior and exterior regions of the pellets and eventually disintegrated with time at ambient conditions.

Those samples prepared with $Ba(NO_2)_2$ as the barium source followed this pattern; it was eliminated due to inferior densification of even the glycine- and ODH-fueled compositions. Further study may be warranted to determine the fundamental causes of the poor behavior of powders prepared with these fuels and barium source.

Some particle size and size distribution measurements have been done to determine the fundamental powder characteristics responsible for the some of the differences in behavior. Further data in this area is currently being collected, as well as specific surface area measurements. From the currently available data (Figs. 4 and 5) it is possible to make a few qualitative conclusions. First of all, there is no significant difference (i.e., order of magnitude) in the median particle sizes of the various powders examined (the four conventional GNP-CS–produced powders and the CP-produced powder). From the micrographs, it is clear that the glycine-fueled powder is composed of particles which have a porous, web-like morphology; the ODH-fueled powder has particles composed of a relatively dense arrangement of nanometer-scale primary particles; and the coprecipitated powder is composed of large, brick-shaped agglomerates (a relic of the oxalate crystallization process) with an intermediate density.

3.1 Stability in CO_2

3.1.1 BCY88 Compositions

A series of $Ba_xCe_{0.80}Y_{0.20}O_{3-\delta}$ powders was synthesized with x = 0.90, 0.95, 0.98, and 1.00 (BCY08, BCY58, BCY88, and BCY108, respectively) to study the effect of A-site deficiency on the stability of this composition in CO_2. These powders were produced by the traditional GNP-CS method using yttrium nitrate, cerium ammonium nitrate, and barium acetate as the cation sources and glycine as the fuel. Each of the powders was characterized using high-temperature XRD (HTXRD, instrument) in 101.3 kPa (1 atm) flowing CO_2 as follows. A sample of the powder was placed on the platinum-rhodium heater strip of the instrument and the sample chamber sealed. The temperature was raised to 1200°C in air or flowing helium and held for 20 min. An XRD scan under these conditions confirmed the sample was single-phase perovskite. At this point the gas in the sample chamber was switched to flowing CO_2. The following steps were then repeated until no perovskite phase remained: hold for 5 min, perform XRD scan, lower temperature by 50°C (Fig. 6).

Results of this study are shown in Fig. 7. Note that the temperature was controlled at even 50°C increments by a thermocouple welded to the opposite side of the heater strip, but a more accurate measure of the sample temperature for each scan was determined by optical pyrometry. In the stoichiometric case (BCY108), $BaCO_3$ peaks are apparent in the scan at ≈1120°C. The barium-deficient compositions, however, do not form $BaCO_3$ until ≤1060°C. This measurable difference, though modest, indicated that a barium-deficiency could be accommodated and improved the stability of the phase. Since no significant difference was noted between the three barium deficient compositions, the highest barium-content composition, BCY88, was chosen as the focus of this study. The reduction in A-site occupancy is sufficient to reduce the possibility of decomposition and small enough that it should not significantly affect electrical properties.

3.1.2 Effect of Zr, Mg, and V Additions

The substitution or addition of these cations into the basic $BaCeO_3$ composition was examined in an effort to improve stability and/or ease processing requirements. Ryu and Haile studied the effect of partially substituting Zr for Ce in undoped and Gd- and Nd-doped $BaCeO_3$. It was found that a large amount of Zr substitution in doped samples (0.20 to 0.40 of the B-site depending on the acceptor dopant species) resulted in the composition being nearly completely immune to $BaCO_3$ formation. Unfortunately, conductivity decreased by as much as an order of magnitude with Zr addition relative to the doped, Zr-free compositions. The current study attempted to combine the stability-enhancing effects of partial Zr_{Ce} substitution and using a Ba-deficient composition to improve the stability in CO_2-containing environments with a lower Zr content than the previous study; thereby avoiding the dramatic conductivity reduction. Both undoped and Y-doped compositions were investigated.

Samples were prepared by the conventional GNP-CS process and characterized by HTXRD in flowing CO_2 as described above. Higher initial temperatures for the analysis were required as $BaCO_3$ formed in some of these compositions at temperatures ≥1200°C. Figure 8 shows the results for the Zr-containing samples: $Ba_{0.98}Ce_{0.85}Zr_{0.15}O_{3-\delta}$ and $Ba_{0.98}Ce_{0.95}Zr_{0.05}O_{3-\delta}$ (BCZ885 and BCZ895, respectively). Of the undoped samples, the two lower Zr-content compositions contained $BaCO_3$ at temperatures as high as ≈1300°C. The final sample (BCZ885), however, was considerably more stable, remaining single-phase perovskite throughout the entire temperature range tested (down to ≈750°C). The standard Y doping was added to the stable BCZ885 composition resulting in the following behavior: This composition is single-phase perovskite at ≥900°C. This is a significant improvement over the corresponding Zr-free composition (BCY88); however it is not as good as the compositions reported by Ryu and Haile, and the effect of this amount of Zr in this composition on conductivity has not been determined. All Mg-doped

compositions ($Ba_{0.98}Ce_{0.85}Mg_{0.15}O_{3-\delta}$ and $Ba_{0.98}Ce_{0.95}Mg_{0.05}O_{3-\delta}$ [BCM885 and BCM895]) and the Mg- and V-doped composition ($Ba_{0.98}Ce_{0.82}Mg_{0.15}V_{0.03}O_{3-\delta}$ [BCMV8/15/3]) contained $BaCO_3$ at temperatures up to ≈1350°C.

4. CONCLUSIONS

4.1 Synthesis

The synthesis study is nearly complete, though more powder will be synthesized as needed for further characterization. It was determined that several synthesis routes are available depending on the processing or product requirements. Conventional GNP-CS using glycine as the fuel is the most straightforward and forgiving synthesis method; however, the resulting powder has an extremely low density and is therefore more difficult to store and process than other options. With slightly more effort, this process utilizing ODH as the fuel is attractive: the resulting powder is easier to work with, though precursor preparation requires more time and energy (the precursor solution must be heated). The best quality powder appears to have been produced using the solid-intermediate precursor combustion synthesis method with ODH as the fuel. The advantages of this method are better homogeneity and more complete combustion. However, precursor preparation and processing requires care and much time. These problems might be alleviated by integrating the drying and combustion stages into a one-step, two-zone spray pyrolysis process which should, conceivably produce better results even than those obtained with the laboratory-scale process used in this work.

4.2 Properties

Significant work will still be done in the area of powder characterization and sintered part properties. As mentioned above, detailed powder characterization is currently in progress. Finally, several sintered test specimens will be prepared for determination of conductivity and hydrogen permeation, and further stability and sintering studies described below.

4.3 Chemical Stability

Significant work has been done in determining the stability of this class of materials in powder form at high temperatures in a pure CO_2 environment. It was known that the presence of barium in compounds often results in decomposition into a $BaCO_3$ and other phases. It was found that a slight barium deficiency in the composition inhibited this process and this was exploited. Further results showed that significant substitution of Zr for Ce resulted in a sizable improvement in stability. This effect may warrant future study.

The characterization done thus far has been under “worst-case-scenario” conditions: a high surface area powder was subjected to pure, flowing CO_2. In actual application, the material is a dense body subjected to conditions with a lower partial pressure of CO_2. Further stability studies of this material will be done under more representative conditions including behavior in an H_2O environment.

4.4 Constrained Sintering

The final major section of this study involves the constrained sintering of this material. Specifically, producing a thin, dense membrane of BCY88 on a thick, porous support of the same material. A model and analytical procedure by Hsueh is available for modeling the stress distribution in this type of geometry that takes into account the sintering of both the film and the substrate. Experimental techniques for determining the elastic and viscous properties of the materials being modeled during sintering are, to a great extent, established. The uniaxial viscosity of the sintering body can be determined with a minimum of experimental runs utilizing a cyclic loading technique during isotheral sintering in a dilatometer. This is based on a method suggested by Cai et al. during constant heating rate sintering and has been successfully applied to the isothermal case. The most promising method for determining the elastic tensor as a function of density during sintering is resonant ultrasound spectroscopy (RUS). With this technique, a disk-shaped sample is supported by three ultrasonic transducers and inserted into the hot zone of a furnace. Resonance spectra can be obtained at various times during the sintering cycle, which can be used to determine the relevant elastic constants (isotropic symmetry is assumed for polycrystalline ceramics). This technique has produced useful information for test samples at room temperature. However, this technique is sensitive to various parameters, particularly the precise sample size and shape. Irregularities that are initially present or emerge during sintering can cause resonant peak shifts, extinction, and/or splitting which complicate the analysis.

5. BIBLIOGRAPHY

P. Z. Cai, D. J. Green, and G. L. Messing, *J. Am. Ceram. Soc.*, **80,** 1940 (1997).

P. Z. Cai, G. L. Messing, and D. J. Green, *J. Am. Ceram. Soc.*, **80,** 445 (1997).

F. Chen, P. Wang, et al., *J. Mater. Chem.*, **7,** 1533 (1997).

C. H. Hsueh, *Scrip. Metall.*, **19,** 1213 (1985).

K. Katahira, Y. Kohchi, T. Shimura, and H. Iwahara, *Solid State Ionics*, **138,** 91 (2000).

T. Norby, *Solid State Ionics*, **125,** 1 (1999).

K. J. Ryu and S. M. Haile, *Solid State Ionics*, **125,** 355 (1999).

D. Shima and S. M. Haile, *Solid State Ionics*, **97,** 443 (1997).

K. Takeuchi, C.-K. Loong, et al., *Solid State Ionics*, **138,** 63 (2000).