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Structural and Electrical Characterization of a Novel Mixed Conductor: CeO₂-Sm₂O₃-ZrO₂ Solid Solution

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Solid electrolytes are key components of solid-state electrochemical devices, which are increasingly important for applications in energy conversion, chemical processing, sensing, and combustion control. 1-3 Solid electrolytes based on CeO₂ also have potential applications as structural and electronic promoters of heterogeneous catalytic reactions and oxygen membranes. 4-8

In recent years the CeO₂-ZrO₂ system has been investigated, mainly in the context of a "three-way catalyst" technology for the treatment of automobile exhausts. 9-13 It has been reported that the reducibility of ceria is greatly enhanced when it is mixed with zirconia to form a solid solution. 9-13 These results suggest that CeO₂-ZrO₂ might be an excellent mixed conductor (exhibiting both ionic and electronic conductivity). It is the numerous applications of mixed conductors as oxygen separation membranes, partial oxidation catalysts, and fuel-cell electrodes that motivated us to investigate the CeO₂-ZrO₂ solid solution as a potential mixed conductor. Recently we have shown that solid solutions of Ce₁⁻ₓ Smₓ O₂₋₅ (x = 0 to 30 mol %) solid solutions were synthesized by the hydrothermal method. The electrical properties of the solid solutions have been studied in air and under reducing conditions. Solid solutions with the fluorite structure were formed in all of the studied range of ZrO₂ substitution after calcination at 1500°C. With increasing ZrO₂ substitution up to 30 mol %, the electronic conductivity increases under a reducing atmosphere. The (Ce₀.₈₃ Sm₀.₁₇)₁₋ₓ Zrₓ O₂₋₅ solid solution has good mixed electronic and ionic conductivity; the total conductivity is 0.42 S/cm at pO₂ = 5.7 × 10⁻²¹ atm and 700°C with an estimated ionic conductivity of ca. 10⁻¹² S/cm.

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XAS measurements.—The X-ray absorption spectroscopy (XAS) measurements were made in the electron yield and fluorescence modes 15-17 on beam line X-19A at the Brookhaven National Synchrotron Light Source with double crystal [Si(111)] and monochromator. All spectra were normalized to unity step in the absorption coefficient from well below to well above the edge.

Electrical conductivity measurement.—The powder samples were pelletized and sintered at 1500°C for 24 h with a programmed heating and cooling rate of 5°C/min. The sintered samples were over 95% of the theoretical density in all cases, as determined by pycnometry.

The ionic conductivity of the materials was measured on a sintered ceramic pellet. Silver paste was painted onto two faces of the pellets, using GC Electronics paste. The sample was then dried and fired at 700°C. The ionic conductivity measurements were performed by the complex-impedance method at frequencies ranging from 0.1 Hz to 20 kHz (Solartron 1280 frequency response analyzer) on isothermal plateaus 1 h long, in air on heating and cooling every 25 to 30°C up to 800°C.

The electrical conductivity of ceria samples was measured as a function of oxygen partial pressure, pO₂, and temperature with a four-probe dc technique. A mixture of O₂, N₂, and H₂ gases passed through a water separator, set at 25 to 85°C, was used to fix different oxygen partial pressures determined from the equilibrium of the chemical reactions of the gases. The oxygen partial pressure in the gas mixture was measured by a solid-electrolyte oxygen sensor before and after the gases passed through the closed ceramic cell where the ceria solid electrolyte sample was placed for the conductivity measurements. The samples were allowed to equilibrate at the set pO₂ atmospheres for 24 h before the measurement was taken.

Electrode polarization measurement.—For the electrode polarization measurements, the ceria samples were prepressed uniaxially, then isostatically under 500 MPa. The green densities were about 55 to 58%. The green pellets were sintered at 1400°C for 1 h with a programmed heating and cooling rate of 5°C/min. The sintered samples were over 98% of the theoretical density in all cases. Platinum electrodes were attached with a commercial electrode process. First a thin Pt film was sprayed on the pellet surface and then sintered at 1200°C. Finally the Engelhard Pt paste was used to optimize the electrode properties. The sample was dried in air and fired at 900°C. The impedance measurements were performed with an impedance analyzer SI-1260 (Solartron Instruments) over 0.01 Hz to 1 MHz frequency range on isothermal plateaus 1 h long, in air on heating every 50°C up to 650°C. The inductive error associated with various components of the measurement circuit was evaluated by carrying

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out measurements in the rig on reference resistances in place of samples. All the measurements were corrected accordingly. The curve fitting was done with “Zview 2.1b” with different equivalent circuits. The solid-electrolyte conductivities as well as polarization resistances of the applied electrodes were determined directly from the impedance spectra.

**Ionic and electronic transfer numbers measurement.**—The ionic and electronic transference numbers were determined with a combination of impedance spectroscopy, open-circuit voltage measurement, and oxygen gas permeation measurements. Figure 1 shows a schematic arrangement for these measurements. Cells with Pt electrodes were attached to an alumina tube using a glass seal. The glasses were fired in situ, and the heating and cooling rates were carefully controlled to avoid cracking of the glass seal. The furnace was heated at 7°C/min to 820°C, held at that temperature for 10 min to soften the glass, and then cooled at 3°C/min to the desired temperature for testing. Impedance spectra, open-circuit potentials, and oxygen permeation rates were measured under identical conditions in an oxygen concentration cell.

Air, Pt | [Ce0.85Sm0.17]0.7Zr0.3O2-δ | Pt, Ar (or H2) 1

The oxygen concentration of the incoming and outgoing gas was monitored with an yttria-stabilized zirconia (YSZ) oxygen sensor. A computerized impedance-analysis system, consisting of a frequency response analyzer (Solartron 1255) and an electrochemical interface (Solartron 1286), was used to measure the impedance of the oxygen concentration cells in the frequency range from 1 mHz to 10 MHz at temperatures ranging from 500 to 750°C.

**Measurement of defect concentration.**—The electrical conductivity of doped ceria under reducing atmospheres is different from that under high oxygen activities because of the reduction of cerium cations from Ce4+ to Ce3+. Such reduction must at the same time increase the 2p hole and multiplet interactions can also play a complicating role.

The (Ce0.85Sm0.17)0.7Zr0.3O2-δ sample was first calcined at a high temperature, 1500°C. A thermogravimetric analyzer TGA (TA Instruments, Inc., model 2050) was used to examine the weight change under reducing atmospheres. The partial pressure of oxygen was controlled by a N2/H2 flow and measured by a YSZ oxygen sensor. A thermogravimetric analyzer (Solartron 1255) and an electrochemical interface (Solartron 1286), was used to measure the impedance of the oxygen concentration of the incoming and outgoing gases.

Despite the fact that the resulting phase is a fluorite structure (space group Fm3m) where Ce, Sm, and Zr are statistically distributed in the special position 4(a).

The unit-cell parameter for (Ce0.85Sm0.17)0.7Zr0.3O2-δ (x = 0 to 0.50) solid solution (inset in Fig. 3) calcined at 1500°C decreases linearly with the zirconia content according to Vegard’s law and as expected from effective ionic radii (rCe4+ = 0.111 nm; rSm3+ = 0.1219 nm; rZr4+ = 0.0980 nm3) considerations.

**Results and Discussion**

**Phase composition.**—X-ray diffraction (XRD) analysis (Fig. 2) indicates that the (Ce0.85Sm0.17)1-xZr0.28-x solid solutions prepared by the hydrothermal method at 260°C for x = 0.0 to 0.10 form with the cubic fluorite structure, while for x = 0.2 to 0.50 a zirconia tetragonal impurity phase is present along with the cubic fluorite phase. When the hydrothermal processing temperature is increased to 310°C, the XRD shows the zirconia tetragonal impurity phase only for x = 0.5. However, when the hydrothermally prepared solid solutions (x = 0 to 0.5; 260°C) are calcined at 1500°C for 12 h, the XRD (Fig. 3) shows no evidence of tetragonal zirconia. Figure 4 shows the phase evolution of (Ce0.85Sm0.17)1-xZr0.28-x in the range from 260 to 1300°C; the zirconia tetragonal impurity phase disappears, and the resulting diffraction peaks of the ceria fluorite phase are shifted to higher 2θ as the temperature is increased. Rietveld refinement (Fig. 5) also confirms that the resulting phase is a fluorite structure (space group Fm3m) where Ce, Sm, and Zr are statistically distributed in the special position 4(a).

The unit-cell parameter for (Ce0.85Sm0.17)1-xZr0.28-x (0 ≤ x ≤ 0.5) solid solution (inset in Fig. 3) calcined at 1500°C decreases linearly with the zirconia content according to Vegard’s law and as expected from effective ionic radii (rCe4+ = 0.111 nm; rSm3+ = 0.1219 nm; rZr4+ = 0.0980 nm3) considerations.

The Zr-L2,3 spectral changes between the cubic and tetragonal structures. The WL (“white line”) features at the L12 (L2) edges of 4d transition metal compounds are related to 2p3/2 (2p1/2) to 4d5/2-4d3/2 phototransitions. Consequently these WL features yield direct information on the occupancy and energy distribution of the important final 4d states (with the understanding that the final state (4d5/2) is spin and multiplet interactions can also play a complicating role).

The Zr atoms in (Ce0.85Sm0.17)1-xZr0.28-x (0 ≤ x ≤ 0.5) are in an eight-fold cubic environment for which the four-fold degenerate eg
A feature (C feature) involving the e\(_g\) (t\(_{2g}\)) final states. The mag-
bimodal structure with the less (more) intense, lower (higher) ener-
gy magnitude of the crystalline electric field (CEF) splitting is about
2.3 eV from the A-C feature splitting. Orlando et al.\(^{21}\) noted the clear
intermediate energy states of the B feature in the Zr-L\(_{2,3}\) spectra of
ZrO\(_2\). Their projected DOS figure exhibits a roughly 2 eV splitting
between the band centroids which, without a full photoabsorption
calculation, is in adequate agreement with the Zr-L\(_{2,3}\) results pre-

dented here.

The Zr-L\(_{2,3}\) spectra for tetragonally distorted fluorite ZrO\(_2\)-\(_{\beta}\) in
Fig. 6 manifest a similar two peak A-C structure. The additional
spectral intensity of the A and C peaks of ZrO\(_2\)-\(_{\beta}\) in compari-
going to (Ce\(_{0.83}\)Sm\(_{0.17}\)\(_{0.5}\)Zr\(_{0.5}\)O\(_2\)-\(_{\beta}\) spectrum. Moreover, in the
XAS of ZrO\(_2\)-\(_{\beta}\) an additional unresolved intermediate B feature (or
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calculation, is in adequate agreement with the Zr-L\(_{2,3}\) results pre-

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ate electronic charge carriers according to the reaction

\[ \text{Ce}^4 + \text{V}^6_\text{O} \rightarrow \text{Ce}^{4+} + \text{V}^{6+}_\text{O} \]

and \( \text{V}_\text{O} \) solid solution for the (Ce 0.83 Sm 0.17 ) 1−x Zr x O 2−δ region.

Fig. 6. The Zr-L 3 and L 2 spectra for cubic-fluorite (Ce 0.83 Sm 0.17 ) 0.5 Zr 0.5 O 2 and for ZrO 2 with a tetragonally distorted fluorite structure. Note the A and C features of the cubic material that are associated with the four-fold \( \varepsilon_3 \) and six-folds \( \varepsilon_2 \) orbitals, respectively, with the CEF splitting, \( \Delta \), being ca. 2.3 eV.

Electrical conductivity in the low oxygen partial pressure (p O 2 ) region.—The electrical conductivity of the (Ce 0.83 Sm 0.17 ) 1−x Zr x O 2−δ solid solution for \( x = 0, 0.02, 0.08, 0.2, \) and 0.3 in the low p O 2 region is shown in Fig. 8. The electrical conductivity tends to increase with decreasing p O 2 . The increased electrical conductivity in the low p O 2 region can be attributed to the partial reduction of the Ce 4+ to generate electronic charge carriers according to the reaction

\[ 2\text{Ce}^{4+} + \text{O}_2 \rightarrow 2\text{Ce}^{3+} + \text{V}_\text{O}^{6+} + \frac{1}{2}\text{O}_2 \]

where \( \text{Ce}^{4+} \) is a Ce 4+ on a Ce 4+ lattice site and \( \text{Ce}^{3+} \) is a Ce 3+ on a Ce 4+ lattice. For a stoichiometric reaction, it can be assumed that

\[ [\text{Ce}^{4+}] = 2[V_\text{O}^{6+}], \quad [\text{Ce}^{3+}] = [V_\text{O}^{6+}] \]

and 

\[ [\text{Ce}^{4+}] = K^{1/2}[[\text{Ce}^{4+}]][\text{O}_2]^{1/2} [\text{V}_\text{O}^{6+}]^{-1/2} p_{\text{O}_2}^{-1/4} \]

Fig. 7. Temperature dependence of the ionic conductivity of the (Ce 0.83 Sm 0.17 ) 1−x Zr x O 2−δ solid solutions (\( x = 0.0 \) to 0.50). Inset: composition dependence of activation energy of the (Ce 0.83 Sm 0.17 ) 1−x Zr x O 2−δ solid solutions (\( x = 0.0 \) to 0.50).
estimation that the ionic conductivity of (Ce
0.83 Sm
0.17 )
0.7 Zr
0.3 O
2 solid solutions (e > 100 S/cm) is not satisfied, indicating that the higher the electrical conductivity, the larger the ZrO
2 content, the higher the electrical conductivity. The total electrical conductivity of (Ce
0.83 Sm
0.17 )
0.7 Zr
0.3 O
2 is 0.42 S/cm at P
O2 = 5.7 × 10
−21 atm and 700°C. Thermogravimetric measurements suggest that δ = 0.047 under the same condition, which is equivalent to doping ceria with 22% Sm
3+.

Table I. Variation of stoichiometry of Ce
0.83 Sm
0.17 −δ Zr0.3O2−δ under reducing atmospheres.

<table>
<thead>
<tr>
<th>Log (P(O2)) (atm)</th>
<th>δ</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>−17.3</td>
<td>0.0274</td>
<td>Ce4+Ce3+Ce2+Ce0.5Ce0.5Sm0.019Sm0.981Zr0.3O1.913</td>
</tr>
<tr>
<td>−17.9</td>
<td>0.0312</td>
<td>Ce4+Ce3+Ce0.5Ce0.5Sm0.019Sm0.981Zr0.3O1.919</td>
</tr>
<tr>
<td>−19.0</td>
<td>0.0372</td>
<td>Ce4+Ce3+Ce0.5Ce0.5Sm0.019Sm0.981Zr0.3O1.903</td>
</tr>
<tr>
<td>−19.4</td>
<td>0.0393</td>
<td>Ce4+Ce3+Ce0.5Ce0.5Sm0.019Sm0.981Zr0.3O1.901</td>
</tr>
<tr>
<td>−20.1</td>
<td>0.0467</td>
<td>Ce3+Ce2+Ce0.5Ce0.5Sm0.019Sm0.981Zr0.3O1.893</td>
</tr>
<tr>
<td>−20.3</td>
<td>0.0494</td>
<td>Ce3+Ce2+Ce0.5Ce0.5Sm0.019Sm0.981Zr0.3O1.891</td>
</tr>
<tr>
<td>−21.3</td>
<td>0.0536</td>
<td>Ce3+Ce2+Ce0.5Ce0.5Sm0.019Sm0.981Zr0.3O1.886</td>
</tr>
</tbody>
</table>

Figure 8. Total electrical conductivity of the (Ce
0.83 Sm
0.17 )
0.7 Zr
0.3 O
2 solid solutions (x = 0.0 to 0.50) under reducing atmospheres and at 700°C.

(p
O2 = 5 × 10
−18 to 5 × 10
−22 atm) is the same as the oxygen-vacancy concentration generated by doping pure ceria with 17.4 to 22.8 mol % Sm
3+ in air. Although direct measurement of ionic conductivity has not been possible under reducing atmospheres, it is reasonable to estimate that the ionic conductivity of (Ce
0.83 Sm
0.17 )
0.7 Zr
0.3 O
2 under reducing atmospheres (P
O2 = 5 × 10
−18 atm) is ca. 0.01 S/cm, as observed in the sample Ce
0.8 Sm
0.2 O2 at 700°C in air.

Figure 8 also shows that at a fixed P
O2, the larger the ZrO
2 content, the higher the electrical conductivity. The total electrical conductivity of (Ce
0.83 Sm
0.17 )
0.7 Zr
0.3 O
2 is 0.42 S/cm at P
O2 = 5.7 × 10
−21 atm and 700°C. Thermogravimetric measurements suggest that δ = 0.047 under the same condition, which is equivalent to doping ceria with 22% Sm
3+. Therefore, it is estimated that the ionic conductivity under the same condition should be close to ca. 0.009 S/cm. Subtraction on the ionic conductivity yields the n-type electronic conductivity of ca. 0.41 S/cm. A dilemma for the traditional substituted ceria is that on the one hand the ionic conductivity is increased by orders of magnitude when oxygen vacancies are formed as a consequence of substitution with lower valent cations, on the other hand such substitution generally leads to a considerable decrease in the electronic conductivity. The (Ce
0.83 Sm
0.17 )
0.7 Zr0.3O2−δ solid solution appears to have a relatively good combined electronic and ionic conductivity typically required for solid oxide fuel cell (SOFC) anode materials. Even though the desirable electronic conductivity requirement for anode materials for SOFC (e.g., 100 S/cm) is not satisfied, (Ce
0.83 Sm
0.17 )
0.7 Zr0.3O2−δ solid solution together with a current collector might be a good choice for the anode material in SOFC.

The increase of electrical conductivity with increased ZrO
2 doping can be attributed to the enhancement of the reducibility of the (Ce
0.83 Sm
0.17 )
0.7 Zr0.3O2−δ solid solutions induced by the addition of the Zr into the CeO
2 lattice. According to Balducci et al., the Ce4+/Ce3+ reduction energy is significantly reduced even by a small amount of zirconia for CeO
2−ZrO
2 solid solution. The high mobility of oxygen vacancies through the bulk and the surface will assist the Ce4+/Ce3+ redox cycle. All these factors will contribute to the enhancement of electronic conductivity.

Ionic and electronic transference numbers.—The Nernst potential and open-circuit voltage of the air-H
2 and air-Ar oxygen concentration cells as a function of temperature are shown in Fig. 9. The bulk and total resistances of the concentration cells were determined from the intercepts of the impedance spectra with the real-axis at high and low frequencies, respectively.

The average oxide ionic transference numbers, t
i, of (Ce
0.83 Sm
0.17 )
0.7 Zr0.3O2 were determined from the combination of impedance spectroscopy and open-circuit potential measurement using the equation

\[ t_i = 1 - \frac{R_b}{R_t} \left(1 - \frac{V_{oc}}{E_N}\right) \]

where R
b and R
i are the bulk and total resistance, respectively, of the air-H
2 and air-Ar cells as determined from the impedance spectroscopy measurement, and V
oc and E
N are the open-circuit potential and Nernst potential across the cells, respectively. Furthermore, the average ionic transference numbers, t
i, were calculated from the combination of oxygen permeation and impedance measurements using the following equation

\[ \frac{t_i}{V_{oc}} = \int_{E_N}^{E_{oc}} \frac{E(N)}{E_{oc} - E(N)} dE \]

Figure 9. Nernst potential and open-circuit potential of oxygen concentration cell with the configuration of (a, top) air, Pt | (Ce
0.83 Sm
0.17 )
0.7 Zr0.3O2−δ | Pt, H
2 and (b, bottom) air, Pt | (Ce
0.83 Sm
0.17 )
0.7 Zr0.3O2−δ | Pt, Ar measured at different temperatures.
The ionic current due to the permeation of oxygen through the oxygen concentration cell, \( I_{O^2^-} \), can be calculated as \[ I_{O^2^-} = \frac{85.59(V_2X_2 - V_1X_1)}{T} \] where \( V_2 \) and \( V_1 \) are the flow rate (mL/min) of the outgoing and incoming gas, respectively, and \( X_2 \) and \( X_1 \) are the oxygen partial pressures (atm) of the outgoing and incoming gas, respectively. \( T \) is the absolute temperature at which the gas flow rate was measured.

The average oxygen ion transference numbers of \((Ce_{0.83}Sm_{0.17})_{0.7}Zr_{0.3}O_2-d\) as determined from the air-H₂ and air-Ar oxygen concentration cells using Eq. 11 and 12 are shown in Fig. 10.

In the air-H₂ cell, the average ionic transference numbers obtained from the combination of gas permeation and impedance spectra are more reliable than those from the combination of open-circuit potential and impedance spectra, since the open-circuit potentials are relatively small. While in the air-Ar cell, the average ionic transference numbers obtained from the combination of gas permeation and impedance spectra and those from the combination of open-circuit potential and impedance spectra agree quite well. It can be seen that in the air-H₂ cell, \((Ce_{0.83}Sm_{0.17})_{0.7}Zr_{0.3}O_2-d\) exhibits mixed ionic-electronic conduction with mainly electronic conduction in the temperature range of 600 to 750°C. On the other hand, in the air-Ar cell, \((Ce_{0.83}Sm_{0.17})_{0.7}Zr_{0.3}O_2-d\) shows mixed conduction with predominantly ionic character.

Electrode polarization resistance.—In Fig. 11 and 12 two series of impedance diagrams recorded at higher (650°C) and lower (500°C) temperatures for \((Ce_{0.83}Sm_{0.17})_{0.7}Zr_{0.3}O_2-d\) are presented. In both cases, the diagrams exhibit two well-defined semicircles representing the properties of the solid electrolyte at higher frequencies and those of the electrodes at low frequencies. The solid-electrolyte resistance and the total resistance of the electrochemical cell, Air, Pt \| (Ce_{0.83}Sm_{0.17})_{0.7}Zr_{0.3}O_2-d \| Pt, H₂, Pt were determined from the intercepts of the impedance loops with the real axis at high (ca. 0.1 MHz) and low (10⁻² to 1 Hz) frequencies, respectively. As can be seen in Fig. 11, a wide variation in electrode polarization resistance (5 to 50 Ω-cm² at 650°C, as calculated from the three cells consisting of electrolyte materials with different thicknesses in Fig. 11) is observed. The electrode polarization resistances for both the reference electrode and the working electrode are plotted in Fig. 13. The polarization resistances of the electrodes show different slopes indicating different mechanisms of electrode polarizations (in the reference electrode, R₁, Pt-mesh collector was incorporated) and increase by four orders of magnitude when the temperature is decreased by 200°C (from 650 to 450°C).

Conclusion

\((Ce_{0.83}Sm_{0.17})_{x}Zr_{x}O_2-d\) (\( x = 0 \) to 0.5) solid solutions were prepared by the hydrothermal method at 260°C. When these samples are calcined at 1500°C, the XRD exhibit a fluorite pattern. The electronic
conductivity increases dramatically for the (Ce$_{0.83}$Sm$_{0.17}$)$_{0.7}$Zr$_{0.3}$O$_{2-\delta}$ composition in reducing atmospheres. The (Ce$_{0.83}$Sm$_{0.17}$)$_{0.7}$Zr$_{0.3}$O$_{2-\delta}$ solid solution appears to have a relatively good combined electronic and ionic conductivity; the total conductivity is 0.42 S/cm at $p_{O_2} = 5.7 \times 10^{-21}$ atm and 700°C; the ionic conductivity is estimated to be close to ca. $10^{-2}$ S/cm.

Figure. 13. Temperature dependence of electrode polarization resistance in the cell, air, Pt | (Ce$_{0.83}$Sm$_{0.17}$)$_{0.7}$Zr$_{0.3}$O$_{2-\delta}$ | Pt, air.

References