

Ba(Zr_{0.1}Ce_{0.7}Y_{0.2})O_{3-δ} as an Electrolyte for Low-Temperature Solid-Oxide Fuel Cells

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Low-temperature solid-oxide fuel cells (SOFCs) have attracted much attention worldwide because of their potential long-term stability and economical competitiveness for many (including residential and automotive) applications.^[1–11] To date, the best available electrolyte material seems to be doped ceria, which, potentially, meets most of the requirements for fuel-cell operation below 600 °C. Several critical issues still remain, however, including electronic conductivity and uncertain mechanical integrity under fuel-cell operating conditions. The discovery of a new solid electrolyte for low-temperature SOFCs is a grand challenge for the SOFC community.

Proton conductors are promising candidates as electrolytes for low-temperature SOFCs because of their low activation energy for proton conduction. Many perovskite-type oxides show high proton conductivity in a reducing atmosphere.^[12,13] One of the major challenges for this type of proton conductor is a proper compromise between conductivity and chemical stability. For example, doped BaCeO₃ has sufficiently high ionic conductivity, but the chemical stability in an atmosphere containing CO₂ and H₂O is inadequate for fuel-cell applications.^[14,15]

Because BaCeO₃ and BaZrO₃ easily form solid solutions, it is possible to replace a desired fraction of Ce in BaCeO₃ with Zr to form a solid solution that exhibits both adequate proton conductivity as well as sufficient chemical and thermal stability over a wide range of conditions relevant to fuel-cell operation.^[16–18] Here, we report a new composition, Ba(Zr_{0.1}Ce_{0.7}Y_{0.2})O_{3-δ} (BZCY7), in the barium–zirconium–cerium–yttrium (BZCY) family that, at temperatures below 550 °C, displays the highest ionic conductivity of all known electrolyte materials for SOFC applications. The performance characteristics of a single cell based on BZCY7 are very promising.

In order to investigate the chemical stability of BZCY7 and Ba(Ce_{0.8}Y_{0.2})O₃ (BCY20) in a CO₂-containing atmosphere, powder samples of both compositions were exposed to 2 %

CO₂ (balanced with H₂) at 500 °C for one week. The X-ray diffraction (XRD) patterns shown in Figure 1 suggest that BCY20 decomposed to BaCO₃, CeO₂, and Y₂O₃ during the exposure whereas BZCY7 remained unchanged, implying that BZCY7 is stable at 500 °C in an atmosphere containing 2 % CO₂. Similarly, XRD examination of BZCY7 powder samples before and after exposure to H₂ containing 15 % H₂O for one week, also shown in Figure 1, indicate that the structure of BZCY7 remained unchanged, implying that BZCY7 is stable at 500 °C in an atmosphere containing 15 % water vapor. The partial substitution of Ce by Zr indeed increased the chemical stability of the material in an atmosphere containing CO₂ and H₂O.

Figure 2 shows the ionic conductivity of BZCY7 in a humid 4 % H₂/Ar atmosphere, together with the conductivities of three conventional SOFC electrolyte materials: yttria-stabilized ZrO₂ (YSZ), La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O₃ (LSGM), and Ce_{0.8}Gd_{0.2}O₃ (GDC). The conductivity of the BZCY7 electrolyte was also carefully confirmed in a fuel-cell configuration (H₂, Ni-BZCY7|BZCY7|BCPY4, air). The composition was optimized in terms of chemical stability and proton conductivity. Clearly, BZCY7 has a higher ionic conductivity than YSZ in the entire studied temperature range. The other two oxide-ion conductors, LSGM and GDC, have higher ionic conductivities than BZCY7 at temperatures above 550 °C. At temperatures below 550 °C, however, BZCY7 showed the highest ionic

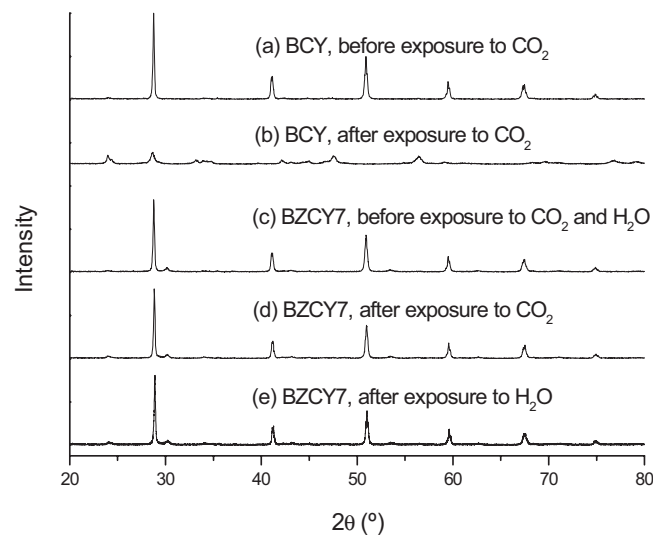


Figure 1. XRD patterns for BCY20 and BZCY7 before and after exposure to dry H₂ with 2 vol % CO₂ or H₂ with 15 % H₂O at 500 °C.

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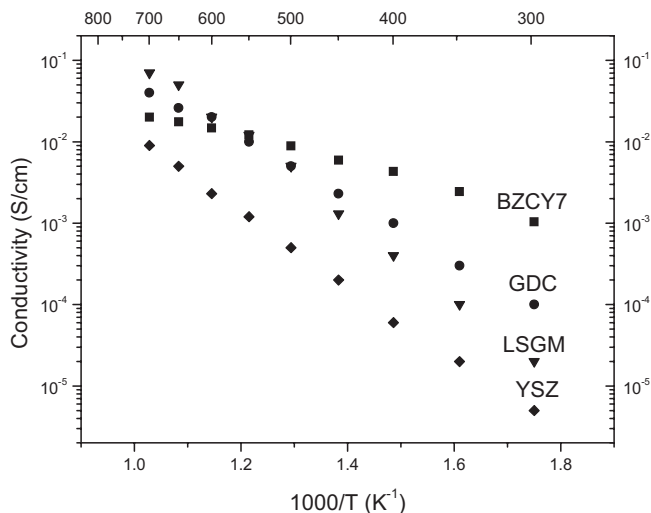


Figure 2. Comparison of the ionic conductivities of BZCY7, GDC, LSGM, and YSZ in a humid 4% H₂/Ar atmosphere at 300–700 °C (the temperature scale is given by the upper x-axis).

conductivity. At 500 °C, for example, the ionic conductivity of BZCY7 is $9 \times 10^{-3} \text{ S cm}^{-1}$, that of YSZ is $5 \times 10^{-4} \text{ S cm}^{-1}$, and the ionic conductivities of LSGM and GDC are $5 \times 10^{-3} \text{ S cm}^{-1}$. In fact, the ionic conductivity value of $9 \times 10^{-3} \text{ S cm}^{-1}$ at 500 °C represents the highest conductivity ever reported for any known SOFC electrolyte material. Figure 2 clearly shows that the activation energy for proton conduction in BZCY7 is much smaller than that for oxygen-vacancy conduction in oxygen-ion conductors such as GDC, LSGM, or YSZ. It is also noted that protons are not part of the nominal structure or stoichiometry of the metal oxide material but are present as foreign species (defects), remaining from its synthesis or from equilibrium with hydrogen or water vapor.

Preparation of dense electrolyte membranes on porous electrodes is an important step in the fabrication of high-performance SOFCs. The simple and cost-effective dry-pressing process has been successfully used to prepare ceria-based electrolyte membranes as thin as 8 μm using low filling density powders.^[3] We fabricated our BZCY7-based SOFC by a modified dry-pressing method, allowing us to fabricate crack-free films thinner than 15 μm . The membrane was uniform, and the thickness could be readily controlled by varying the amounts of powders used. The implementation of this simple and cost-effective fabrication method may enable significant cost reductions in SOFC fabrication. Furthermore, this technique is equally applicable to the fabrication of other electrochemical devices based on ceramic membranes, for example, mixed conducting composite membranes for gas separation and devices for the reformation of hydrocarbon fuels to hydrogen.

Because electrolyte/electrode interfacial polarization resistances often cause significant power losses in SOFCs, it is very important to develop catalytically active electrode materials for low-temperature operation of SOFCs. The primary function of the anode in a fuel cell based on a proton-conducting electrolyte is to facilitate fuel oxidation: $1/2 \text{ H}_2 \rightarrow \text{H}^+ + \text{e}^-$ (as-

suming H₂ as the fuel). Ni has been a particularly successful catalyst for the anode reactions in YSZ- or GDC-based SOFCs. Therefore, we used Ni-BZCY7 as the anode in our initial study. However, the development of an efficient cathode still remains a challenge. For the preliminary fuel-cell testing, we used Ba(Ce_{0.4}Pr_{0.4}Y_{0.2})O₃ (BCPY4) as the cathode material.

Figure 3a shows a typical scanning electron microscopy (SEM) image of the electrolyte/electrode bilayer fabricated by a modified dry-pressing and co-sintering process. The SEM image indicates that the BZCY7 electrolyte film is about 15 μm thick and appears fully dense, without any noticeable connected pores, before fuel-cell testing. The SEM image shown in Figure 3b reveals that the electrolyte film is well-adhered to the anode substrate, without any cracking or delamination after fuel-cell testing.

Shown in Figure 4 are the current–voltage characteristics and corresponding power densities for a fuel cell based on a BZCY7 electrolyte membrane of 65 μm thickness at different temperatures. Each data point was recorded about 2 h after

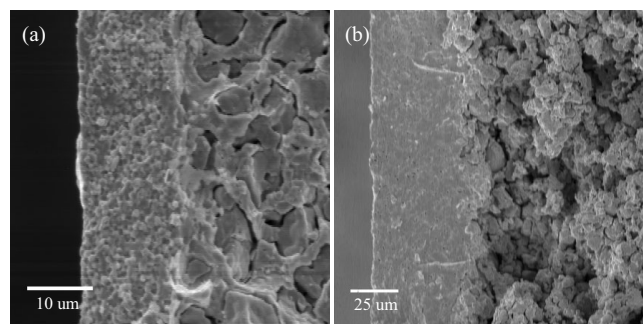


Figure 3. Cross-sectional SEM images of BZCY7 electrolyte films supported by a NiO-BZCY7 anode. a) A bilayer with a 15 μm BZCY7 electrolyte film before fuel-cell testing (as-prepared). b) A bilayer with a 60 μm BZCY7 electrolyte film after fuel-cell testing.

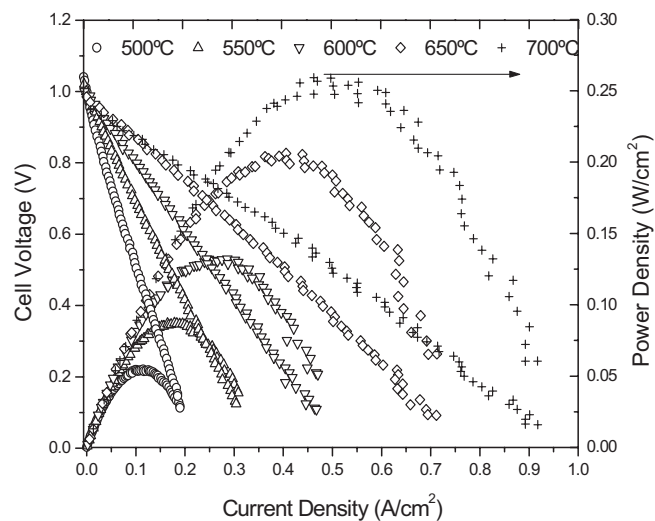


Figure 4. Typical current–voltage characteristics and corresponding power densities measured at different temperatures for a fuel cell with a BZCY7 electrolyte membrane 65 μm thick.

the cell reached a steady state. The open-circuit voltages (OCV) of 1.01 V at 600 °C and 1.05 V at 500 °C indicate that the electrolyte membrane, prepared by the modified dry-pressing and co-firing process, is sufficiently dense. Peak power densities were 270, 148, and 56 mW cm⁻² at 700, 600, and 500 °C, respectively. Although the performance characteristics of BZCY7-based fuel cells are still not as high as we hoped, the high conductivity and chemical stability of BZCY7 are very encouraging and imply that a new generation of low-temperature SOFCs may become possible.

Impedance analysis of the single cells indicated that, at low temperatures, the performance of the BZCY7-based cells was primarily limited by the relatively high polarization resistance of the electrodes. Two typical impedance spectra, measured at 500 and 600 °C, are shown in Figure 5. The intercept with the real axis at high frequencies represents the resistance of the electrolyte and lead wires, whereas the difference between the high-frequency and low-frequency intercepts with the real axis represents the sum of the electrode polarization resistances of the cell. At 500 °C, the polarization resistance of the electrodes is about 3.2 Ω cm² whereas the resistance of the electrolyte is only about 2 Ω cm². It is noted that this electrode polarization resistance is far greater than those of other well-known cathode materials for SOFCs, such as Sm_{0.5}Sr_{0.5}CoO₃ (SSC)-GDC^[19,20] or samarium-doped ceria (SDC)-SSC,^[21] at 500 °C. However, the suitability of using SSC and Sr-doped LaCoO₃ (LSC) as cathodes for BZCY7 electrolyte-based fuel cells is yet to be determined, because SSC and LSC are mixed conductors with significant oxygen-ion conductivities while BZCY7 is a proton conductor. Clearly, the development of proper cathode materials for BZCY7 electrolytes remains a challenge.

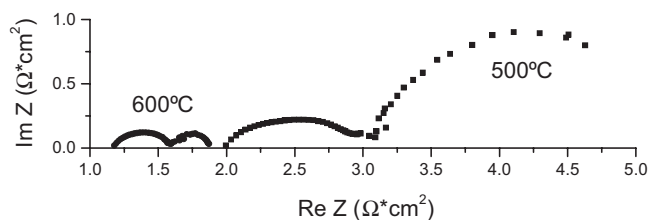


Figure 5. Impedance spectra of a single cell measured under open-circuit conditions at different temperatures.

Experimental

Preparation of BZCY7 Powders: BZCY7 was prepared by a solid-state reaction method. Stoichiometric amounts of high-purity barium carbonate, zirconium oxide, cerium oxide, and yttrium oxide powders (all from Aldrich Chemicals) were mixed by ball-milling for 48 h. The resultant mixtures were then dried and calcined at 1100 °C in air for 10 h to form the perovskite phase. The calcined oxides were ball-milled for 24 h and calcined again at 1150 °C for another 10 h. The ball-millings and calcinations were repeated until a pure phase was obtained.

Conductivity Measurements: After confirming a single phase by XRD, the ceramic powders were uniaxially pressed into pellets and sintered at 1550 °C in air for 10 h. Then, both sides of the sintered disks were grounded and polished to obtain the desired thickness and to produce faces that were flat and parallel to one another. Pt paste

was applied as electrode and fired at 900 °C for 1 h to form porous Pt electrodes. Conductivity was measured using an impedance system that consisted of a Solartron 1255 HF frequency response analyzer and a Solartron 1286 electrochemical interface.

Chemical Stability Measurements: BZCY7 and BCY20 powder samples were kept at 500 °C for one week in H₂ containing 2% CO₂ or 15% H₂O. To obtain 15% water vapor, H₂ gas was bubbled through deionized water at 50 °C. The XRD patterns were taken for powder samples before and after exposure to the CO₂ or H₂O-containing atmosphere.

Fabrication and Testing of Single SOFCs: Dense BZCY7 electrolyte membranes were fabricated onto Ni-BZCY7 anode substrates using a modified dry-pressing and co-firing process, which achieved crack-free dense BZCY7 membranes, 15 μm thick, by using readily available micro-size BZCY7 powders. The powders of BZCY7 and NiO were weighed at a ratio of 1:1.92 (w/w) (50:50 v/v) and mixed with flour, acting as the pore former, to form an anode precursor. The precursor was pressed in a stainless steel module to form an anode substrate with a flat surface and a certain mechanical strength. The BZCY7 powders were added and evenly distributed onto the substrates with a sieve. Then the BZCY7 powder layer was pressed together with the anode substrate and subsequently co-fired at 1350 °C for 6 h. Subsequently a porous cathode of BCPY4 paste was screen-printed on the BZCY7 electrolyte film and sintered at 1200 °C for 2 h to form a single cell, consisting of a Ni-BZCY7 anode, a BZCY7 electrolyte film, and a BCPY4 cathode. The thickness of the BCPY4 cathode was around 20 μm, and the thickness of the Ni-BZCY7 anode was about 0.8 mm. The electrode active area was 0.182 cm². Two silver wires were connected to each electrode as current leads. The cell was mounted on an alumina supporting tube for fuel-cell testing at 500–700 °C with humidified hydrogen (3 vol% H₂O) as fuel and stationary air as oxidant. The fuel-cell performances were measured using an EG&G Potentiostat/Galvanostat (Model 273A) interfaced with a computer.

The microstructure and morphology of the tested cells were examined using a Hitachi S-570 scanning electron microscope.

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