Preparation, Characterization and Intermediate-Temperature Electrochemical Properties of Er$^{3+}$-Doped Barium Cerate–Sulphate Composite Electrolyte

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Abstract: In this study, BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ was synthesized by a microemulsion method. Then, a BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$–K$_2$SO$_4$–BaSO$_4$ composite electrolyte was obtained by compounding it with a K$_2$SO$_4$–Li$_2$SO$_4$ solid solution. BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ and BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$–K$_2$SO$_4$–BaSO$_4$ were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectrometry. AC impedance spectroscopy was measured in a nitrogen atmosphere at 400–700 °C. The log$\sigma$–log ($p_{O_2}$) curves and fuel cell performances of BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ and BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$–K$_2$SO$_4$–BaSO$_4$ were tested at 700 °C. The maximum output power density of BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$–K$_2$SO$_4$–BaSO$_4$ was 115.9 mW·cm$^{-2}$ at 700 °C, which is ten times higher than that of BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$.

Keywords: composite; fuel cell; BaCeO$_3$; conductivity; electrolyte

1. Introduction

With the rapid development of the economy, energy problems are imminent. As one of the new energy sources, fuel cells are of great significance. Solid oxide fuel cells (SOFCs) have the advantages of high conversion efficiency, small size, no noise, reduced pollution, and so on [1–8]. However, higher operating temperatures often lead to serious performance degradation, longer start-up times and expensive interconnecting sealing materials, which are considered the main obstacles to SOFCs’ commercialization. Therefore, it is urgent to explore SOFCs operating at intermediate temperatures (400–700 °C) and at high performance at the same time. Compared with oxygen ion-conductive SOFCs, proton-conducting SOFCs can operate at lower temperatures. An exploration of electrolyte materials with high protonic conductivities at 400–700 °C is of vital importance [9–14].

It is known that BaCeO$_3$-based ceramics have good protonic conductivities at high temperatures (700–1000 °C) [15–24]. Using an electrolyte film and a composite electrolyte are two main ways to apply BaCeO$_3$-based ceramics to intermediate-temperature SOFCs [25–33]. Tong and O’Hayre fabricated five different types of H$_2$/air fuel cells using BaCe$_{0.2}$Zr$_{0.1}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ (BCZYyb), BaCe$_{0.6}$Zr$_{0.3}$Y$_{0.1}$O$_{3-\delta}$ (BCZY63) and BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ (BZY20) as electrolytes [26]. Liu et al. reported that a 30 wt.% In$^{3+}$-doped barium cerate–70 wt.% Gd$_{0.1}$Ce$_{0.9}$O$_{2-\delta}$ composite electrolyte had a high conductivity of $3.42 \times 10^{-2}$ S·cm$^{-1}$ in wet hydrogen at 700 °C [27]. The conductivities of barium cerate-ceria-type composite electrolytes are similar to those of BaCeO$_3$ doped with low-valent metal cations [27–29]. Park et al. investigated BaZr$_{0.85}$Y$_{0.15}$O$_{3-\delta}$ (BZY)-carbonate composite electrolytes, which had good...
intermediate-temperature electrochemical properties [32]. The literature has mainly focused on reporting carbonate [30–33] and chloride [34–36] composite electrolytes. Only a small number of reports on cerium dioxide–sulfate composite electrolytes have been reported [37]. It is well known that the stability of carbonate is weaker than that of sulfate. Until now, no literature has reported on the barium cerate–sulfate composite electrolyte.

In this study, we synthesized BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ by a microemulsion method. Then, a BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$–K$_2$SO$_4$–BaSO$_4$ composite electrolyte was obtained by compounding it with a K$_2$SO$_4$–Li$_2$SO$_4$ solid solution. The characterization and intermediate-temperature (400–700 °C) electrochemical properties of BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ and BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$–K$_2$SO$_4$–BaSO$_4$ were investigated.

2. Experimental

BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ was prepared by a microemulsion method. Firstly, Er$_2$O$_3$ was completely dissolved with concentrated nitric acid. Sixty milliliters of water was added to make Ba(CH$_3$COO)$_2$ and (NH$_4$)$_2$Ce(NO$_3$)$_6$ dissolve evenly. A mixture of cyclohexane, ethanol and polyvinyl alcohol (PVA) was added to the solution and stirred until it was completely emulsified to form Microemulsion A. Then, (NH$_4$)$_2$CO$_3$, NH$_4$OH, cyclohexane, ethanol and PVA were mixed evenly to form Microemulsion B [38,39]. Microemulsion B was slowly added to Microemulsion A. In the process of dropping, the number of white precipitates increased, and a large number of bubbles emerged at the same time. The precipitation was filtered and dried under an infrared lamp to obtain the precursor powder.

Finally, the precursor was calcined in a high-temperature furnace at 1250 and 1550 °C for 6 h to obtain BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$.

In this experiment, molten K$_2$SO$_4$–Li$_2$SO$_4$ (1:1 mole ratio) was prepared in a muffle oven at 750 °C for 2 h [40]. Our previous studies indicated that the stability of 70 wt.% SrCe$_{0.9}$Yb$_{0.1}$O$_{3-\alpha}$–30 wt.% (Na/K)Cl was lower, though its conductivities were higher than 80 wt.% SrCe$_{0.9}$Yb$_{0.1}$O$_{3-\alpha}$–20 wt.% (Na/K)Cl [41]. Therefore, the BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ powders were evenly mixed with molten K$_2$SO$_4$–Li$_2$SO$_4$ powders in a weight proportion of 80%:20%. After being sieved and pressed, the disks were put into the muffle furnace heated at 750 °C for 2 h to obtain BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$–K$_2$SO$_4$–BaSO$_4$.

BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ and BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$–K$_2$SO$_4$–BaSO$_4$ were characterized by an X-ray diffractometer (XRD, X’pert Pro MPD, Holland’s company, Amsterdam, Netherlands), a confocal-micro Raman spectrometer (invia, Renishaw, Gloucestershire, United Kingdom), a scanning electron microscope (SEM, S-4700, Hitachi, Tokyo, Japan). The Ba, Ce, Er, O, K and S elements in BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$–K$_2$SO$_4$–BaSO$_4$ were measured by the energy-dispersive X-ray spectroscopy.

For intermediate-temperature electrochemical properties, BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ and BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$–K$_2$SO$_4$–BaSO$_4$ were polished to a thickness of 1.0 mm. Circles 8 mm in diameter were drawn in the center of both sides of the discs with a pencil, and a 20%Pd–80%Ag paste was coated on the circles (area: 0.5 cm$^2$). AC impedance spectroscopy was measured in a nitrogen atmosphere at 400–700 °C. The frequency ranged from 1 to $10^5$ Hz, and the signal voltage was 0.05 V. The log$\rho$~log(\$p_{O_2}$) curves of BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ and BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$–K$_2$SO$_4$–BaSO$_4$ were tested by adjusting different proportions of air, nitrogen, oxygen and hydrogen at room temperature ($p_{H_2O} = 2.3 \times 10^3$ – 3.1 $\times 10^3$ Pa). The two sides of BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ and BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$–K$_2$SO$_4$–BaSO$_4$ were in hydrogen and oxygen atmospheres, respectively, which constituted the following fuel cells: H$_2$, Pd–Ag | sample | Pd–Ag, O$_2$. We then measured their $I$–$V$–$P$ curves.

3. Results and Discussion

Figure 1 is the XRD spectra of BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ (1250 and 1550 °C) and BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$–K$_2$SO$_4$–BaSO$_4$. The diffraction peaks of BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ (1250 and 1550 °C) correspond to the standard diagram of BaCeO$_3$ (JCPDS 85-2155). Neither of the two samples detected Er$_2$O$_3$, which indicates that they had entered the lattice of perovskite phase. In BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ (1250 °C), in addition to the perovskite phase, there was a very small amount of the CeO$_2$ phase, indicating the initial calcination temperature should be raised to 1300 or 1350 °C [22]. The weak alkali
salt Li₂SO₄ reacted with the strong base BaO to form BaSO₄ when BaCe₀.₉Er₀.₁O₃−α powders were mixed with molten sulphate, as indicated by the equation: BaO + Li₂SO₄ = BaSO₄ + Li₂O. CeO₂ may be separated from the perovskite structure when sulphate and BaCe₀.₉Er₀.₁O₃−α form a composite electrolyte. This is why CeO₂ also appears in BaCe₀.₉Er₀.₁O₃−α–K₂SO₄–BaSO₄.

![XRD patterns](image)

**Figure 1.** XRD patterns of BaCe₀.₉Er₀.₁O₃−α (1250 and 1550 °C) and BaCe₀.₉Er₀.₁O₃−α–K₂SO₄–BaSO₄.

Figure 2a,b shows SEM photos of the external and cross-sectional surfaces of the BaCe₀.₉Er₀.₁O₃−α (1550 °C) ceramic prepared by the microemulsion method. It can be seen that BaCe₀.₉Er₀.₁O₃−α (1550 °C) had a compact structure, complete grain growth, clear grain boundaries, and very few holes. The density of the BaCe₀.₉Er₀.₁O₃−α (1550 °C) ceramic prepared by the microemulsion method was higher than that by the high-temperature solid-state method at the same sintering temperature. After adding sulphate, the boundaries between grains became not particularly distinct. There were different degrees of adhesion between grains [32,33]. This is due to the BaCe₀.₉Er₀.₁O₃−α grains being wrapped in molten sulfate.

![SEM photos](image)

**Figure 2.** The external (a,c) and cross-sectional (b,d) SEM photos of BaCe₀.₉Er₀.₁O₃−α (1550 °C) and BaCe₀.₉Er₀.₁O₃−α–K₂SO₄–BaSO₄.
The energy-dispersive X-ray spectroscopy result of BaCe$_{0.9}$Er$_{0.1}$O$_3$–K$_2$SO$_4$–BaSO$_4$ is shown in Figure 3. The spectrum had major peaks assigned to the Ba, Ce, Er, O, K and S elements. The atomic ratios of Ba/Ce, Ba/Er and S/K are 0.87, 9.21 and 1.54. The low content of the Ba element may be due to the formation of BaSO$_4$ by the reaction: BaO + Li$_2$SO$_4$ = BaSO$_4$ + Li$_2$O, resulting in segregation. The elements mapping images indicated that the spatial distribution of sulphate was uniform.

Figure 3. The energy-dispersive X-ray spectroscopy and elements mapping images in BaCe$_{0.9}$Er$_{0.1}$O$_3$–K$_2$SO$_4$–BaSO$_4$.

Figure 4 shows the Raman spectra of BaCe$_{0.9}$Er$_{0.1}$O$_3$–α (1550 °C) and BaCe$_{0.9}$Er$_{0.1}$O$_3$–K$_2$SO$_4$–BaSO$_4$. In BaCe$_{0.9}$Er$_{0.1}$O$_3$–α (1550 °C), Raman activity peaked around 653 and 723 cm$^{-1}$, corresponding to the $O_h$ vibrational mode and Ce–O vertical bending vibration in the $A_{1g}$ mode, respectively. In BaCe$_{0.9}$Er$_{0.1}$O$_3$–K$_2$SO$_4$–BaSO$_4$, the Raman peaks near 353, 520, 987 and 1120 cm$^{-1}$ were attributed to S–O bending, bending deformation, symmetrical stretching and antisymmetric telescopic vibration, respectively [38,42–44].
was higher than that of BaCe0.7 (1550 °C). This may be related to its high density, as shown in Figure 3.

The conductivity of BaCe0.9Er0.1O3−α (1550 °C) and BaCe0.9Er0.1O3−α–K2SO4–BaSO4 achieved were 9.4 × 10−3 and 1.8 × 10−1 S·cm−1 at 700 °C. Under the same conditions, the conductivity of BaCe0.9Er0.1O3−α–K2SO4–BaSO4 was higher than that of BaCe0.7In0.3−δ–Gd0.1Ce0.9O2−δ [27] and comparable to values of BaCe0.83Y0.17O3−δ–Sm0.15Ce0.85O2−δ [29]. This indicated that the sulphate was conducive to the conduction of ion defects through the interface region in the BaCe0.9Er0.1O3−α–K2SO4–BaSO4 composite electrolyte. The conductivity of BaCe0.9Er0.1O3−α was equivalent to that of BaCe0.7In0.15 Ta0.05 Y0.1 O3−δ [22] and BaCe0.5 Zr0.3 Y0.2−x Yb0.1 O3−δ in wet H2 (~3% H2O) [18]. This may be related to its high density, as shown in Figure 3.

Figure 4. Raman spectra of BaCe0.9Er0.1O3−α (1550 °C) and BaCe0.9Er0.1O3−α–K2SO4–BaSO4.

Figure 5 shows the conductivities of BaCe0.9Er0.1O3−α (1550 °C) and BaCe0.9Er0.1O3−α–K2SO4–BaSO4 in nitrogen measured from 400 to 700 °C. It can be seen from Figure 5 that the BaCe0.9Er0.1O3−α–K2SO4–BaSO4 had a beneficial effect on conductivity. With the addition of sulphate, the conductivity was significantly improved. This is because the sulphate distributed at the grain boundary and formed a continuous phase, so both the main phase and the grain boundary phase could conduct ions. The highest conductivities of BaCe0.9Er0.1O3−α (1550 °C) and BaCe0.9Er0.1O3−α–K2SO4–BaSO4 were 9.4 × 10−3 and 1.8 × 10−1 S·cm−1 at 700 °C.

Figure 5. The conductivities of BaCe0.9Er0.1O3−α (1550 °C) and BaCe0.9Er0.1O3−α–K2SO4–BaSO4 in nitrogen from 400 to 700 °C.
The conduction characteristics of $\text{BaCe}_0.9\text{Er}_{0.1}\text{O}_{3-\alpha}$ and $\text{BaCe}_{0.9}\text{Er}_{0.1}\text{O}_{3-\alpha}$–$\text{K}_2\text{SO}_4$–$\text{BaSO}_4$ were tested by adjusting different proportions of gases. As seen in Figure 6, the conductivities of the samples in a reductive atmosphere are very close to those in an oxidizing atmosphere. The log$\sigma$–log $(p_{O_2})$ curves of $\text{BaCe}_{0.9}\text{Er}_{0.1}\text{O}_{3-\alpha}$ and $\text{BaCe}_{0.9}\text{Er}_{0.1}\text{O}_{3-\alpha}$–$\text{K}_2\text{SO}_4$–$\text{BaSO}_4$ were almost horizontal straight lines. When the temperature exceeded the melting point of sulphate salts, the mobility of various ions (Ba$^{2+}$, Li$^+$, K$^+$, H$^+$) was greatly enhanced, which led to a low activation energy for ion transport in the interface regions. The proton was the smallest cation, and the mobility of protons was greater than other ions (Li$^+$, K$^+$), resulting in an increased conductivity. Therefore, ion conduction appeared to become dominant [34].

![Figure 6](image.png)

**Figure 6.** The log$\sigma$–log $(p_{O_2})$ curves of $\text{BaCe}_{0.9}\text{Er}_{0.1}\text{O}_{3-\alpha}$ and $\text{BaCe}_{0.9}\text{Er}_{0.1}\text{O}_{3-\alpha}$–$\text{K}_2\text{SO}_4$–$\text{BaSO}_4$ at 700 °C.

Hydrogen/oxygen fuel cells were assembled with $\text{BaCe}_{0.9}\text{Er}_{0.1}\text{O}_{3-\alpha}$ and $\text{BaCe}_{0.9}\text{Er}_{0.1}\text{O}_{3-\alpha}$–$\text{K}_2\text{SO}_4$–$\text{BaSO}_4$ as supporting electrolytes and Pd–Ag as electrodes. The current–voltage characteristic curves are shown in Figure 7. The resistance directed from current–voltage characteristic curve of $\text{BaCe}_{0.9}\text{Er}_{0.1}\text{O}_{3-\alpha}$–$\text{K}_2\text{SO}_4$–$\text{BaSO}_4$ (2.76 Ω) was lower than that of the value (5.54 Ω) from AC impedance at 700 °C, implying that the protonic conduction was dominant under the fuel cell condition [45]. The maximum power density of $\text{BaCe}_{0.9}\text{Er}_{0.1}\text{O}_{3-\alpha}$ was 10.9 mW·cm$^{-2}$ at 700 °C. Because the fuel cell was supported by the electrolyte and the electrolyte was thicker (1.0 mm), the current and power density were relatively low. When the voltage was 0.6 V, the maximum output power density of $\text{BaCe}_{0.9}\text{Er}_{0.1}\text{O}_{3-\alpha}$–$\text{K}_2\text{SO}_4$–$\text{BaSO}_4$ was 115.9 mW·cm$^{-2}$ at 700 °C, which is ten times higher than that of $\text{BaCe}_{0.9}\text{Er}_{0.1}\text{O}_{3-\alpha}$. The results show that $\text{BaCe}_{0.9}\text{Er}_{0.1}\text{O}_{3-\alpha}$–$\text{K}_2\text{SO}_4$–$\text{BaSO}_4$ is an excellent electrolyte material for medium-temperature fuel cells.

![Figure 7](image.png)

**Figure 7.** Hydrogen/oxygen fuel cells assembled with $\text{BaCe}_{0.9}\text{Er}_{0.1}\text{O}_{3-\alpha}$ and $\text{BaCe}_{0.9}\text{Er}_{0.1}\text{O}_{3-\alpha}$–$\text{K}_2\text{SO}_4$–$\text{BaSO}_4$ as supporting electrolytes at 700 °C.
4. Conclusions

In this study, a BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$-$\text{K}_2\text{SO}_4$-$\text{BaSO}_4$ composite electrolyte was obtained by compounding it with a K$_2$SO$_4$-Li$_2$SO$_4$ solid solution. The XRD diffraction peaks of BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ (1550 °C) corresponded to the standard diagram of BaCeO$_3$, which indicated that Er$_2$O$_3$ had entered the lattice of perovskite phase. SEM photos showed the BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ grains were wrapped in molten sulfate. The highest conductivities of BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ and BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$-$\text{K}_2\text{SO}_4$-$\text{BaSO}_4$ were 9.4 × 10$^{-3}$ and 1.8 × 10$^{-1}$ S·cm$^{-1}$ at 700 °C, respectively. The log$\sigma$–log (p$p_{\text{O}_2}$) curves of BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$ and BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$-$\text{K}_2\text{SO}_4$-$\text{BaSO}_4$ are almost horizontal straight lines, which indicated that ionic conductivity was dominant. The maximum output power density of BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$-$\text{K}_2\text{SO}_4$-$\text{BaSO}_4$ was 115.9 mW·cm$^{-2}$ at 700 °C, which is ten times higher than that of BaCe$_{0.9}$Er$_{0.1}$O$_{3-\alpha}$.

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