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Short Communication

Characterization and Electrochemical Properties of 10 mol% Lutetium-Doped $BaCO_3$ and its Composite Electrolyte for Intermediate Temperature Fuel Cells

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In this study, $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ was prepared by a sol-gel method. Subsequently, it was combined with molten carbonates and chlorides to synthesize $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ composite electrolyte. Structural characterizations and intermediate temperature electrochemical properties of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ were investigated at 400–700 °C. X-ray diffraction showed that the main structure of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ was $BaCeO_3$ phase. The highest conductivity of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ was 6.8×10^{-2} $S\cdot cm^{-1}$ at 700 °C.

Keywords: Defects; Electrolytes; Fuel cell; Conductivity; Composite

1. INTRODUCTION

Solid oxide fuel cells (SOFCs), as an efficient and clean energy technology, have good application prospects [1–7]. The performances and applications of SOFCs are often determined by the dense electrolytes with ionic conductivities [8–13]. Iwahara et al. found that $Ba(Sr)CeO_3$-based oxides have excellent protonic conduction at high temperatures (600–1000 °C) [14]. Trivalent rare earth cation-doped $BaCeO_3$ has been widely studied [15–23]. For example, Guo et al. synthesized $BaCe_{1-x}Y_xO_{3-\alpha}$ by a microemulsion method and studied the protonic conduction at 300–600 °C [20]. Because the ionic radius of Lu^{3+} is close to that of Ce^{4+}, investigation of Lu^{3+}-doped $BaCeO_3$ is particularly necessary.

Over the past 20 years, the designs of new oxygen ion-proton and oxygen ion-inorganic salt composite electrolyte materials have been widely studied [24–31]. Meng et al. synthesized $Ce_{0.9}Gd_{0.1}O_{1.95}$-LiCl-$SrCl_2$ composite electrolyte [24]. Liu et al. studied intermediate-temperature SOFC performance of $BaCe_{0.7}In_{0.3}O_{3-\delta}$–$Gd_{0.1}Ce_{0.9}O_{2-\delta}$ composite electrolyte [26]. Huang et al. investigated conductivity, morphology and SOFC performance of $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\alpha}$- $(Na/Li)_2CO_3$ composite electrolyte [31]. Our previous reports studied Yb^{3+}-doped $BaCeO_3$-(Na/K)Cl and $BaCe_{0.9}Er_{0.1}O_{3-\alpha}$-$K_2SO_4$-$BaSO_4$ composite electrolytes [32–33]. However, up to now, there has been no report about barium cerate-compound inorganic salts.

In this study, $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ was synthesized via a sol-gel method. Then, it was combined with compound inorganic salts to prepare $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ composite electrolyte. Structural characterizations and intermediate temperature electrochemical properties of the samples were investigated.

2. EXPERIMENTAL

2.1. Materials Synthesis and Sintering

$BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ was prepared by a sol-gel method with Lu_2O_3 (0.9948 g), $Ba(CH_3COO)_2$ (12.7711 g), $Ce(NH_4)_2(NO_3)_6$ (24.6699 g) and citric acid as raw materials. Firstly, Lu_2O_3 was added to a small amount of nitric acid and heated to 90 °C for dissolution. $Ba(CH_3COO)_2$, $Ce(NH_4)_2(NO_3)_6$ and citric acid were successively added for heating and dissolving. The solution was heated until it was viscous and burnt to obtain the primary powder. The powder was sintered at 1250 °C and 1550 °C for 5 h, respectively, to obtain $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$. NaCl-KCl (1:1 mole ratio) and Li_2CO_3-K_2CO_3 (68:32 mole ratio) were mixed and heated once to form a solid solution. The mixtures of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$, NaCl-KCl and Li_2CO_3-K_2CO_3 (weight ratio 7:2:1) were heated at 750 °C for 1 h to obtain $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ (BCLu-(Na/K)Cl-$(K/Li)_2CO_3$) composite electrolyte.

2.2 Instrumentation

The structures of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ were measured by Raman spectrometer(iHR550) and X-ray diffraction (XRD, X-D-3, China). The morphologies of the samples were characterized by scanning electron microscope (SEM, Sigma 500). In order to test the AC impedances of the samples, Ag-Pd paste was coated on both sides of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$. The thickness and area of the samples were 1.0mm and 0.5 cm^2, respectively. The test temperature range was 400–700 °C with a CHI660E electrochemical analyzer (Chenhua, Shanghai). The relationship between conductivity and pO_2 was measured at 700 °C with different proportions of dry nitrogen, oxygen and hydrogen.

3. RESULTS AND DISCUSSION

3.1 Characterization of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$.

Fig. 1 shows the Raman spectra of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$. The vibration peak displayed at 130 cm^{-1} may be attributed to the stretching mode of the carbonate ion [23]. The vibrations near 310–360 cm^{-1} belong to the halide vibration and the characteristic peak is 358 cm^{-1}. The bands at 471 cm^{-1} and 673 cm^{-1} belong to the Ce-O F_{2g} mode and O_h vibrational mode, respectively [34]. The results show that $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ contains barium cerate, carbonate and chloride groups.

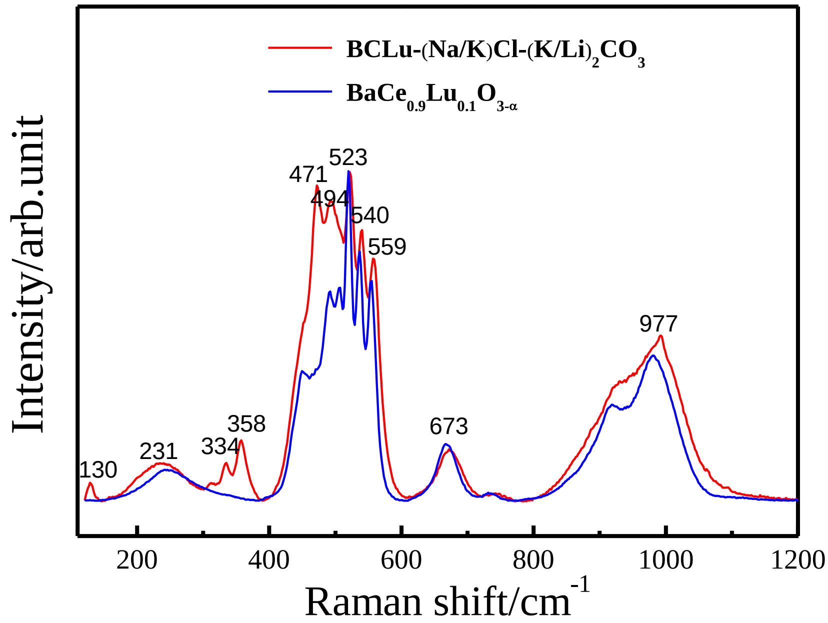

Figure 1. Raman spectra of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ (BCLu-(Na/K)Cl-$(K/Li)_2CO_3$).

Fig. 2 shows XRD patterns of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl- $(K/Li)_2CO_3$. The diffraction peaks of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ agree with Han and Guo et al. [15, 20]. For $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$, the extra peaks are obvious and come from crystalline KCl, $(Li\text{-}K)_2CO_3$ and NaCl respectively [28–29, 32]. Combined with the results of Fig. 1, there is no reaction between $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and (Na/K)Cl-$(K/Li)_2CO_3$ after being heated at 750 °C.

The external and cross-sectional SEM diagrams of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ are shown in Fig. 3. It can be seen from Fig. 3(a, b) that the grains of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ are not fully fused. It can be considered that the sintering temperature (1550 °C) did not reach the temperature for fully forming the grain boundary. There are very few non-penetrating holes in Fig. 3(b). Fig. 3(c, d) show that the molten chlorides and carbonates fill the holes between $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ particles, therefore, densifying the composite after the process of heating [28–31].

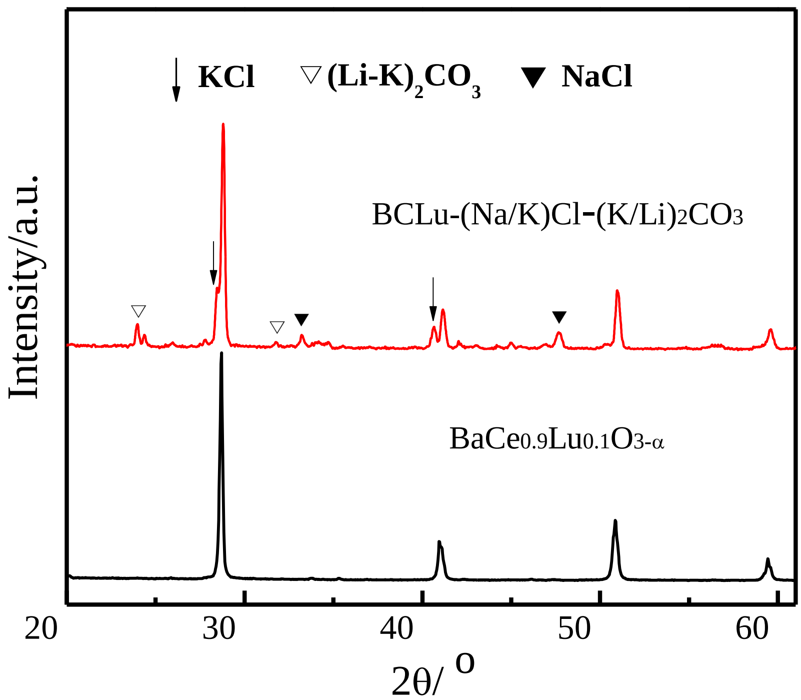

Figure 2. XRD diagrams of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ (BCLu-(Na/K)Cl-$(K/Li)_2CO_3$).

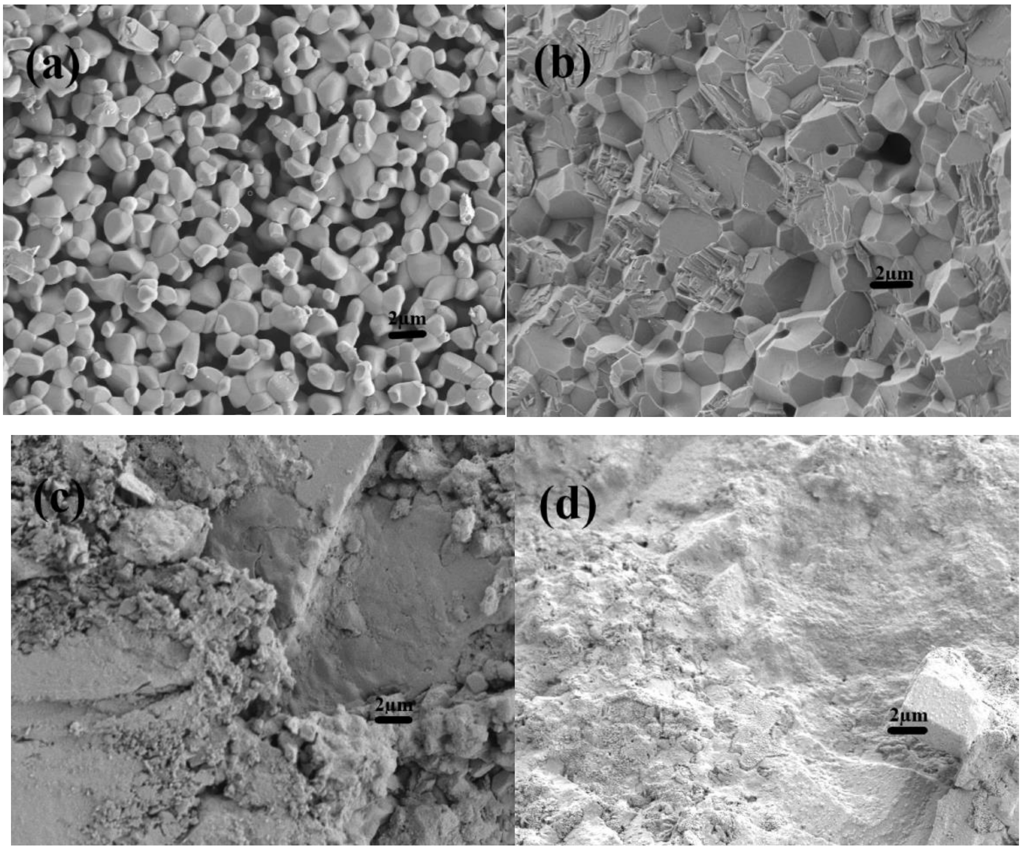

Figure 3. The external and cross-sectional SEM diagrams of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ (a,b) and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ (c,d).

3.2 Conductivity of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-(K/Li)$_2CO_3$

Fig. 4 shows the log (σT) ~ 1000 T^{-1} plots of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-(K/Li)$_2CO_3$ from 400 °C to 700 °C. From Fig. 4, it can be seen that the horizontal and vertical coordinates of the curves are basically linear. The conductivity of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ reaches the maximum value of 9.5×10^{-3} S·cm^{-1} at 700 °C. Gui et al. reported that the conductivity of $BaZr_{0.3}Ce_{0.5}Y_{0.2}O_{3-\delta}$ supplemented with 2 mol% Bi_2O_3 was 1.04×10^{-2} S·cm^{-1} at 700 °C [35]. The results show that the conductivity of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ is equivalent to the value reported in the literature. The conductivities of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-(K/Li)$_2CO_3$ are higher than that of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ in the temperature range of 400–700 °C. The maximum conductivity of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-(K/Li)$_2CO_3$ is 6.8×10^{-2} S·cm^{-1} at 700 °C. It can be considered that molten inorganic salts can further promote the long range orderly ability of conducting ions between the interface and the bulk phase of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-(K/Li)$_2CO_3$ [25].

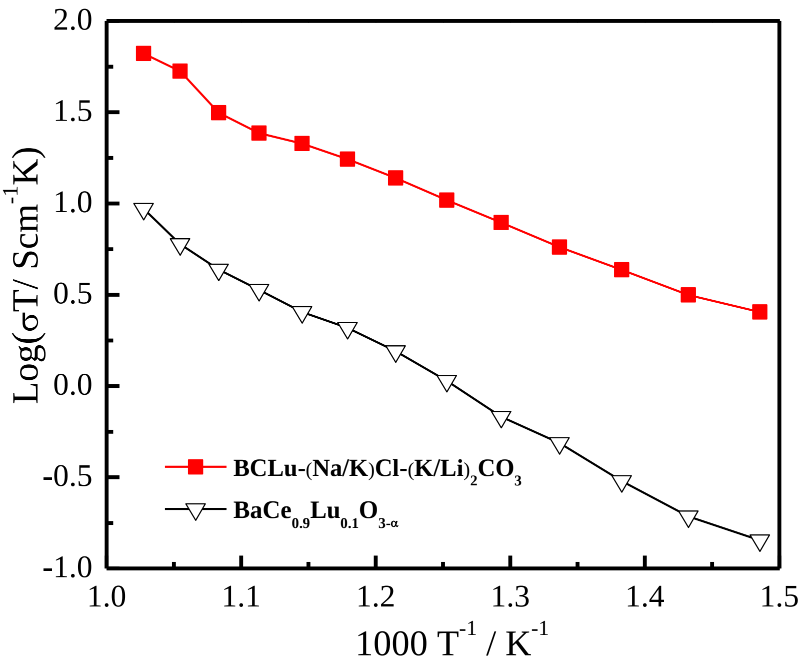

Figure 4. log (σT) ~ 1000 T^{-1} plots of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-(K/Li)$_2CO_3$ (BCLu-(Na/K)Cl-(K/Li)$_2CO_3$) at 400–700 °C.

Fig. 5 shows the relationship between conductivity and pO_2 of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-(K/Li)$_2CO_3$ at 700 °C. The relationship between conductivity and pO_2 is usually measured to study the sample's ionic conduction. Lyagaeva et al. found that $BaCe_{0.5}Zr_{0.3}Y_{0.2-x}Yb_xO_{3-\alpha}$ was a pure ionic conductor at 600 °C [18]. In Fig. 5, the conductivities in nitrogen, oxygen and hydrogen under different pO_2 are almost the same, which shows that $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-(K/Li)$_2CO_3$ show ionic conduction at 700 °C.

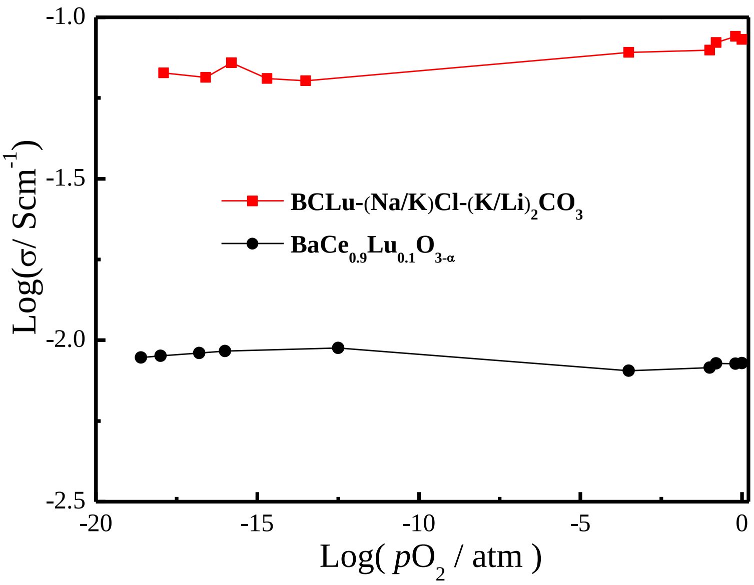

Figure 5. The log $\sigma \sim$ log (pO_2) plots of $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ (BCLu-(Na/K)Cl-$(K/Li)_2CO_3$) at 700 °C.

4. CONCLUSIONS

In this study, molten carbonates and chlorides were combined with $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ to synthesize a new composite electrolyte, $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$. The Raman spectrometer results showed that $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ contained barium cerate, carbonate and chloride groups. The SEM diagrams showed that the molten chlorides and carbonates filled and densified the composite. The relationship between conductivity and pO_2 showed that $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$ and $BaCe_{0.9}Lu_{0.1}O_{3-\alpha}$-(Na/K)Cl-$(K/Li)_2CO_3$ were ionic conductors at 700 °C.

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CONFLICTS OF INTEREST
None

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