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Short Communication

Synthesis and Electrochemical Properties of Intermediate Temperature $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-molten Carbonate Composite Electrolyte

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An erbium-doped $SrCeO_3/SrZrO_3$ electrolyte was synthesized via a sol-gel method using zirconium nitrate, cerium nitrate, strontium nitrate, nitric acid, citric acid and erbium oxide as raw materials. And $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-molten carbonate composite electrolyte was obtained at a low synthesis temperature. The thermal gravimetry analysis-differential scanning calorimetry (TGA-DSC) was tested to determine the formation temperature of $SrCeO_3/SrZrO_3$ solid solution phase. The structure (X–ray diffractometer, XRD), morphology (scanning electron microscope, SEM), conductivities and H_2/O_2 fuel cells of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ were studied at 400-600 °C. The highest power densities of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ were 16.3 $mW{\cdot}cm^{-2}$ and 247.5 $mW{\cdot}cm^{-2}$ at 600 °C, respectively.

Keywords: Composite; $SrCeO_3$; Electrolyte; Conductivity; Fuel cell

1. INTRODUCTION

Inorganic $SrCeO_3$-based solid electrolytes have excellent protonic conduction in water-saturated hydrogen atmospheres at 600-1000 °C. They are extensively used in fuel cells, solid sensors, organic reactors and hydrogen pumps etc. [1–10]. Normally, Ce^{4+} was doped with the trivalent elements such as Y^{3+}, Eu^{3+}, Yb^{3+} and Tm^{3+} can improve the conductivities of $SrCeO_3$ [11–16]. Tsuji et al. synthesized $SrCe_{0.9}Eu_{0.1}O_{3-\alpha}$ by using the solid-state reaction after calcining at 1550 °C for 10 h, respectively [11]. Li et al. studied an $SrCe_{0.9}Eu_{0.1}O_{3-\alpha}$ protonic solid electrolytes to assemble a organic reactor for H_2 production [12]. However, the chemical stabilities of $SrCeO_3$-based solid electrolytes are poor. In contrast, $SrZrO_3$-based solid electrolytes are stable. Therefore, $SrCeO_3/SrZrO_3$ solid solutions

which have high chemical stabilities and conductivities were investigated [13–16]. For example, Bredesen et al. [13] studied thulium or ytterbium doped $SrCeO_3/SrZrO_3$ solid solution which applied to hydrogen permeability. The electro-negativity and the ionic radii of Er^{3+} are 1.24 and 0.89 Å, which are much closer in electro-negativity and ionic radius to Y^{3+} (1.22, 0.90 Å), Yb^{3+} (1.3, 0.87 Å) and Tm^{3+} (1.25, 0.88 Å). In our opinion, if these trivalent elements have almost the same electro-negativity and ionic radius, it is logical to assume that the Er^{3+}-doped $SrCeO_3$ should also exhibit high proton conductivity. Therefore, erbium-doped $SrCeO_3/SrZrO_3$ is the object in the study.

Over the past decade, composite electrolytes such as $BaCeO_3$, $LaGaO_3$, CeO_2-based solid ceramic-carbonates, have been extensively investigated for intermediate temperature (400–600 °C) fuel cells [17–23]. Wang et al. synthesized a $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$-$(Li/Na)_2CO_3$ and it had a stable conductivity of 7-9×10^{-2} S·cm^{-1} at 600 °C [20]. Marques et al. found that the conductivities of $Ce_{0.5}Yb_{0.5}O_{1.75}$-Li_2CO_3-Na_2CO_3 composite electrolyte exceeded 0.1 S·cm^{-1} above 500 °C [22]. Our previous studies have shown that $SrCeO_3$-NaCl-KCl composite electrolytes had excellent intermediate temperature electrochemical properties [24–25]. However, there are few studies about $SrCeO_3/SrZrO_3$ solid solution-carbonate composite electrolytes.

In this study, an erbium-doped $SrCeO_3/SrZrO_3$ electrolyte was synthesized via a sol-gel method. And $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-molten carbonate composite electrolyte was obtained at a low temperature. The structure (XRD), morphology (SEM), conductivities and H_2/O_2 fuel cells of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ were studied at 400-600 °C.

2. EXPERIMENTAL

$SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ was synthesized via a sol-gel method using zirconium nitrate, cerium nitrate, strontium nitrate, nitric acid, citric acid and erbium oxide as raw materials. Firstly, erbium oxide was dissolved in nitric acid and zirconium nitrate, cerium nitrate and strontium nitrate were mixed in distilled water. Then, the *p*H was adjusted to 8-9 with an ammonia solution using citric acid as complexing agent. Finally, $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ was prepared after being calcined at 1200 °C and 1540 °C for 5 h, respectively.

The molten carbonate salt (mole ratio of Li_2CO_3:Na_2CO_3 =1:1) was obtained after being heated at 580 °C [26]. The mixtures (weight ratio of the molten carbonate salt and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ =1:4) were calcined at 620 °C for 1 h to synthesize $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$.

TGA-DSC was tested using the $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ precursor in nitrogen from 25 °C to 1000 °C with a heating rate of 15 °C·min^{-1}. The electrolyte structures and morphologies of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ were measured using XRD and SEM. For conductivities measurements, $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ were processed into thin wafers (electrode area = 0.50 cm^2, thickness = 1.0-1.1 mm). The resistance values were obtained using an electrochemical analyzer (CHI660E, made in China) in the frequency range of 1 Hz–1 MHz from 400 °C to 600 °C in air. H_2/O_2 fuel cells were also tested using $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ as electrolyte at 600 °C.

3. RESULTS AND DISCUSSION

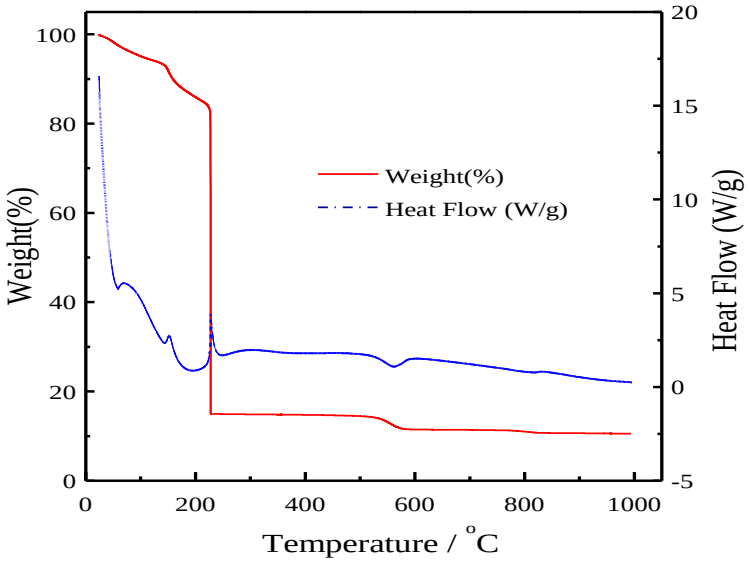

Figure 1. TGA-DSC plot of the $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ precursor.

The TGA-DSC curve of the $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ precursor is shown in Fig. 1. The plot shows a 16.5% weight loss from 25 °C to 225 °C which is attributed to the evaporation of water and ammonia from the dry gel. There was a severe weight loss accompanied by an exothermic peak in a very narrow temperature range from 225 to 230 °C which is ascribed to the decomposition of ammonium salt and citric acid. A gentle declining weight loss was found from 530 to 580 °C which is attributed to the incomplete nitrate [27–28]. TGA and DSC plots are almost horizontal after 980 °C which means that the temperature is close to the formation of $SrCeO_3/SrZrO_3$ solid solution phase. Therefore, the first calcined temperature is 1200 °C.

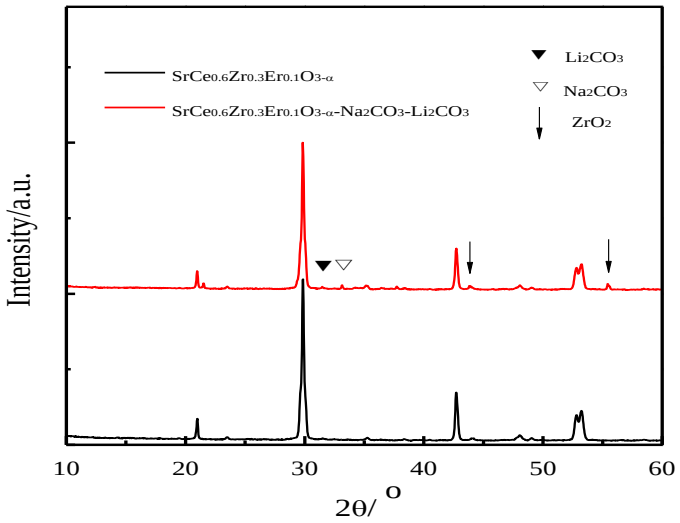

Figure 2. XRD patterns of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$.

The XRD patterns of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ are shown in Fig. 2. The diffraction peaks confirm that $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ is consistent with the standard $SrCeO_3$ crystal plane. There are diffraction peaks of Li_2CO_3, Na_2CO_3 and ZrO_2 besides $SrCeO_3$ phase in the $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ pattern.

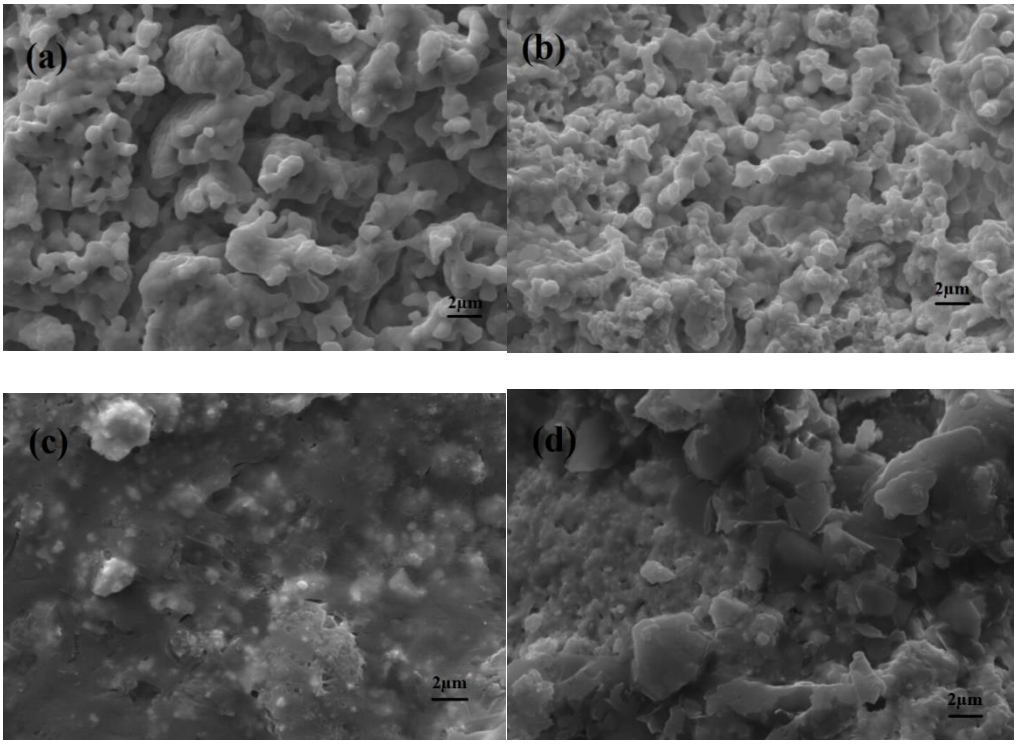

Figure 3. (a,b) SEM photos of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ pellet calcined at 1540 °C for 5 h; (c,d) external and cross-sectional surfaces of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$.

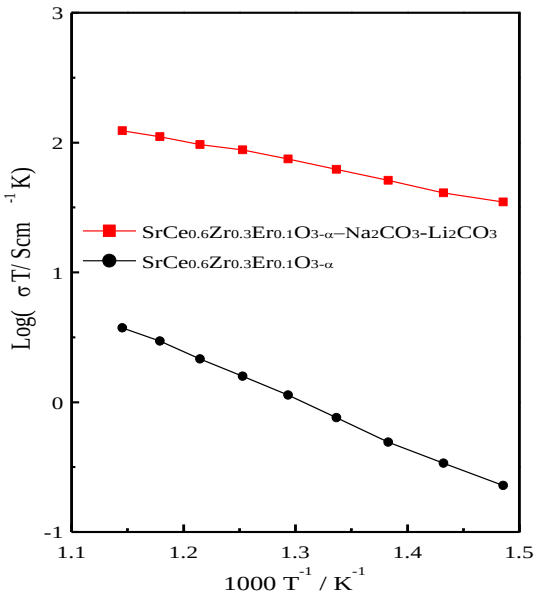

Figure 4. The log (σT) ~ 1000 T^{-1} plots of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ in air from 400 °C to 600 °C.

The result illustrates that Na_2CO_3-Li_2CO_3 melts entry into $SrCeO_3$/$SrZrO_3$ solid solution to reduce the limitation of ZrO_2. Marques et al. revealed that the introduction of Li_2CO_3-Na_2CO_3 promoted a slight decomposition of $Ce_{0.5}Yb_{0.5}O_{1.75}$ [22]. And combined with previous studies [22, 23, 29], Na_2CO_3-Li_2CO_3 coexists in two forms of crystalline and amorphous phases in $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$.

The SEM photos of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ (a,b) and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ (c,d) are shown in Fig. 3. From Fig. 3(a,b), the sintered $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ has clear agglomeration with a grain size is 2-6 μm. From Fig. 3(c,d), there is an interlacing composition between $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ and Li_2CO_3-Na_2CO_3. It can be observed that the $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ particles are nestled inside molten carbonate salt which makes the composite electrolyte into a continuous 3-D reticulated structure [17].

Fig. 4 shows the log (σT) ~ 1000 T^{-1} plots of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ in air from 400 °C to 600 °C. From Fig. 4, the slope of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ is lower than that of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ which means the conduction ion migration ability of the former is strong. The activation energies of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ are 31.6 ± 0.7 kJ·mol^{-1} and 69.8 ± 0.8 kJ·mol^{-1}, respectively. The conductivities of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ vary from 3.4×10^{-4} S·cm^{-1} to 4.1×10^{-3} S·cm^{-1} and 5.2×10^{-2} S·cm^{-1} to 1.4×10^{-1} S·cm^{-1} at 400–600 °C, correspondingly. The lower activation energy and higher conductivities of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ indicate that the molten carbonate salt provide an additional transport function between the interfaces [17,23,30].

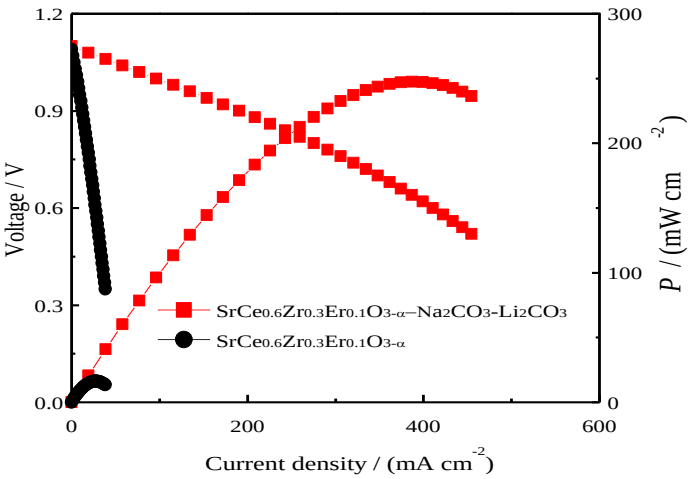

Figure 5. The *I-V-P* curves of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ at 600 °C.

Table 1. The highest power densities of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ and similar electrolytes in the literatures.

Electrolytes	Highest power densities
$SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ (80: 20)	247.5 mW·cm^{-2}, 600 °C, in this work
$Ce_{0.8}Sm_{0.2}O_{1.9}$- $(Li/Na)_2CO_3$ (80: 20)	605 mW·cm^{-2}, 575 °C, [31]
$Ce_{0.8}Sm_{0.2}O_{1.9}$- $(Li/Na)_2CO_3$ (60: 40)	240 mW·cm^{-2}, 575 °C, [31]
$Ce_{0.9}Gd_{0.1}O_{1.95}$- LiCl-$SrCl_2$ (12: 5)	245 mW·cm^{-2}, 550 °C, 320 mW·cm^{-2}, 590 °C, [18]

Fig. 5 shows the *I-V-P* curves of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ at 600 °C. The highest power density obtained with using $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ as the electrolyte is 247.5 mW·cm^{-2}, which was estimated to be about 15 times higher than that of the $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ with 16.3 mW·cm^{-2}. This may be attributed to the homogeneous 3-D reticulated structure of the composite electrolyte. The P_h value of our result is close to the fuel cell performance of 60 wt% $Ce_{0.8}Sm_{0.2}O_{1.9}$-40 wt% $(Li/Na)_2CO_3$ (575 °C) and $Ce_{0.9}Gd_{0.1}O_{1.95}$- LiCl-$SrCl_2$ (550 °C), however, lower than 80 wt% $Ce_{0.8}Sm_{0.2}O_{1.9}$-20 wt% $(Li/Na)_2CO_3$ (575 °C) and $Ce_{0.9}Gd_{0.1}O_{1.95}$- LiCl-$SrCl_2$ (590 °C) as shown in Table 1 [18, 31]. This may be due to the different electrolyte types and fuel cell construction.

4. CONCLUSIONS

An erbium-doped $SrCeO_3/SrZrO_3$ electrolyte was synthesized via a sol-gel method and $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-molten carbonate composite electrolyte was obtained at a low synthesis temperature. The XRD patterns indicate that Na_2CO_3-Li_2CO_3 coexists in two forms of crystalline and amorphous phases in $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$. The SEM photos show that the $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$ particles are nestled inside molten carbonate salt to form a continuous 3-D reticulated structure. The highest power density and conductivity of $SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-\alpha}$-$Na_2CO_3$-$Li_2CO_3$ are 247.5 mW·cm^{-2} and 1.4×10^{-1} S·cm^{-1} at 600 °C, respectively.

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