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$_2$CO$_3$-Li$_2$CO$_3$ 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$_2$CO$_3$-Li$_2$CO$_3$ were 16.3 mW·cm$^{-2}$ and 247.5 mW·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$_{3-a}$ 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$_{3-a}$ 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)$_2$CO$_3$ 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$_2$CO$_3$-Na$_2$CO$_3$ 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$_3$-a-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$_3$-a and SrCe$_{0.6}$Zr$_{0.3}$Er$_{0.1}$O$_3$-a-Na$_2$CO$_3$-Li$_2$CO$_3$ were studied at 400-600 °C.

2. EXPERIMENTAL

SrCe$_{0.6}$Zr$_{0.3}$Er$_{0.1}$O$_3$-a 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 pH 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$_3$-a was prepared after being calcined at 1200 °C and 1540 °C for 5 h, respectively.

The molten carbonate salt (mole ratio of Li$_2$CO$_3$:Na$_2$CO$_3$ =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$_3$-a =1:4) were calcined at 620 °C for 1 h to synthesize SrCe$_{0.6}$Zr$_{0.3}$Er$_{0.1}$O$_3$-a-Na$_2$CO$_3$-Li$_2$CO$_3$.

TGA-DSC was tested using the SrCe$_{0.6}$Zr$_{0.3}$Er$_{0.1}$O$_3$-a 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$_3$-a and SrCe$_{0.6}$Zr$_{0.3}$Er$_{0.1}$O$_3$-a-Na$_2$CO$_3$-Li$_2$CO$_3$ were measured using XRD and SEM. For conductivities measurements, SrCe$_{0.6}$Zr$_{0.3}$Er$_{0.1}$O$_3$-a-Na$_2$CO$_3$-Li$_2$CO$_3$ and SrCe$_{0.6}$Zr$_{0.3}$Er$_{0.1}$O$_3$-a 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$_3$-a-Na$_2$CO$_3$-Li$_2$CO$_3$ and SrCe$_{0.6}$Zr$_{0.3}$Er$_{0.1}$O$_3$-a as electrolyte at 600 °C.
3. RESULTS AND DISCUSSION

The TGA-DSC curve of the SrCe$_{0.6}$Zr$_{0.3}$Er$_{0.1}$O$_3$-α 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 1. TGA-DSC plot of the SrCe$_{0.6}$Zr$_{0.3}$Er$_{0.1}$O$_3$-α precursor.](image)

![Figure 2. XRD patterns of SrCe$_{0.6}$Zr$_{0.3}$Er$_{0.1}$O$_3$-α and SrCe$_{0.6}$Zr$_{0.3}$Er$_{0.1}$O$_3$-α-Na$_2$CO$_3$-Li$_2$CO$_3$.](image)
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$_2$CO$_3$-Li$_2$CO$_3$ 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$_2$CO$_3$, Na$_2$CO$_3$ and ZrO$_2$ besides SrCeO$_3$ phase in the SrCe$_{0.6}$Zr$_{0.3}$Er$_{0.1}$O$_3$-$\alpha$-Na$_2$CO$_3$-Li$_2$CO$_3$ 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$_2$CO$_3$-Li$_2$CO$_3$.

**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$_2$CO$_3$-Li$_2$CO$_3$ in air from 400 °C to 600 °C.
The result illustrates that Na$_2$CO$_3$-Li$_2$CO$_3$ 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$_2$CO$_3$-Na$_2$CO$_3$ promoted a slight decomposition of Ce$_{0.5}$Yb$_{0.5}$O$_{1.75}$ [22]. And combined with previous studies [22, 23, 29], Na$_2$CO$_3$-Li$_2$CO$_3$ coexists in two forms of crystalline and amorphous phases in SrCe$_{0.6}$Zr$_{0.3}$Er$_{0.1}$O$_{3-\alpha}$-Na$_2$CO$_3$-Li$_2$CO$_3$.

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$_2$CO$_3$-Li$_2$CO$_3$ (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$_2$CO$_3$-Na$_2$CO$_3$. 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 ($\sigma$T) ~ 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$_2$CO$_3$-Li$_2$CO$_3$ 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$_2$CO$_3$-Li$_2$CO$_3$ 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$_2$CO$_3$-Li$_2$CO$_3$ 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$_2$CO$_3$-Li$_2$CO$_3$ 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$_2$CO$_3$-Li$_2$CO$_3$ indicate that the molten carbonate salt provide an additional transport function between the interfaces [17,23,30].

![Figure 5](image_url)

**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$_2$CO$_3$-Li$_2$CO$_3$ at 600 °C.
Table 1. The highest power densities of SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-α}-Na_{2}CO_{3}-Li_{2}CO_{3} and similar electrolytes in the literatures.

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Highest power densities</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-α}-Na_{2}CO_{3}-Li_{2}CO_{3} (80: 20)</td>
<td>247.5 mW·cm^{-2}, 600 °C, in this work</td>
</tr>
<tr>
<td>Ce_{0.8}Sm_{0.2}O_{1.9-} (Li/Na)<em>{2}CO</em>{3} (80: 20)</td>
<td>605 mW·cm^{-2}, 575 °C, [31]</td>
</tr>
<tr>
<td>Ce_{0.8}Sm_{0.2}O_{1.9-} (Li/Na)<em>{2}CO</em>{3} (60: 40)</td>
<td>240 mW·cm^{-2}, 575 °C, [31]</td>
</tr>
<tr>
<td>Ce_{0.9}Gd_{0.1}O_{1.95-} LiCl-SrCl_{2} (12: 5)</td>
<td>245 mW·cm^{-2}, 550 °C, 320 mW·cm^{-2}, 590 °C, [18]</td>
</tr>
</tbody>
</table>

Fig. 5 shows the $I$-$V$-$P$ curves of SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-α} and SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-α}-Na_{2}CO_{3}-Li_{2}CO_{3} at 600 °C. The highest power density obtained with using SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-α}-Na_{2}CO_{3}-Li_{2}CO_{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-α} 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)_{2}CO_{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)_{2}CO_{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-α}-molten carbonate composite electrolyte was obtained at a low synthesis temperature. The XRD patterns indicate that Na_{2}CO_{3}-Li_{2}CO_{3} coexists in two forms of crystalline and amorphous phases in SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-α}-Na_{2}CO_{3}-Li_{2}CO_{3}. The SEM photos show that the SrCe_{0.6}Zr_{0.3}Er_{0.1}O_{3-α} 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-α}-Na_{2}CO_{3}-Li_{2}CO_{3} are 247.5 mW·cm^{-2} and 1.4×10^{-1} S·cm^{-1} at 600 °C, respectively.

ACKNOWLEDGEMENTS
This work was supported by the National Natural Science Foundation (No. 51402052) of China, The Natural Science Project of Anhui Province (No. KJ2018A0337, KJ2018A0980), Excellent Youth Foundation of Anhui Educational Committee (No. gxyq2018046), Horizontal cooperation project of Fuyang municipal government and Fuyang Normal College (No. XDHX2016019, XDHXTD201704).

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