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High-performance intermediate temperature fuel cells of new $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$-inorganic salt composite electrolytes

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ABSTRACT

In this study, novel dense $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$-(Na/K)Cl (SCY-NK), $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$-$(Li/K)_2CO_3$ (SCY-LK) and $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$—NaCl—$CaCl_2$ (SCY-NC) composite electrolytes were synthesized at lower temperature. The result of SEM images indicates that the composites are sufficiently dense. The highest conductivities are observed to be 1.2×10^{-1} S cm^{-1} for SCY-NK at 700 °C, 1.0×10^{-1} S cm^{-1} for SCY-LK at 600 °C and 3.3×10^{-2} S cm^{-1} for SCY-NC at 600 °C, respectively. The log σ ~ log (pO_2) plots result indicates that the composites are almost pure ionic conductors under hydrogen-containing atmosphere. The H_2/O_2 fuel cells using the SCY-NK, SCY-LK and SCY-NC as electrolytes generate the maximum power densities of 425 mW cm^{-2} at 700 °C, 256 mW cm^{-2} at 600 °C and 133 mW cm^{-2} at 600 °C, correspondingly.

1. Introduction

$SrCeO_3$-based materials doped with some rare earth as an acceptor show proton conduction under hydrogen-containing atmosphere at high temperatures, which make them be used in various electrochemical systems such as hydrogen pumps, steam electrolytes and hydrogen sensors. The partial substitution of trivalent element for Ce^{4+} is the conventional way to improve proton conductivity of $SrCeO_3$ [1–3]. It is well known that $SrCeO_3$ electrolyte doped with Yb has the best performance and the conductivity of 10 mol% Yb doped $SrCeO_3$ electrolyte is 10^{-4}–10^{-3} S cm^{-1} at 600–800 °C in the presence of water vapor [4].

During the past decades, there are increasing interest to reduce the operating temperature of fuel cells to intermediate temperature range (400–700 °C). Therefore, considerable efforts have been devoted for searching and developing appropriate ionic conducting electrolytes in the temperature range of 400–700 °C [5–9]. Zhu proposed doped cerium oxide-carbonate composites which have greatly enhanced ionic conductivity and excellent cell performance in intermediate temperature fuel cells (ITFCs) [10,11]. And the ionic conductor-inorganic salts composite electrolyte materials have been widely studied [12–15]. However, there is no information about intermediate temperature electrical properties of Yb^{3+} doped $SrCeO_3$-inorganic salt composite electrolyte.

In this study, we prepared dense $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$-(Na/K)Cl (SCY-NK), $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$-$(Li/K)_2CO_3$ (SCY-LK) and $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$—NaCl—$CaCl_2$ (SCY-NC) composite electrolytes which have never been reported and the intermediate temperature (400–700 °C) conduction behaviors were investigated using some electrochemical methods. The performance of H_2/O_2 fuel cells were also tested using them as electrolytes.

2. Experimental

$SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$ was prepared by high-temperature solid state reaction. All the used reagents of CeO_2 (Sinopharm Chemical Reagent Co., Ltd, 99.95%, 6.6811 g), Yb_2O_3 (Sinopharm Chemical Reagent Co., Ltd, 99.99%, 0.8498 g) and $SrCO_3$ (Sinopharm Chemical Reagent Co., Ltd, 99.0%, 6.4315 g) are analytical-grade and stoichiometric amounts of them were first mixed in ethanol for 1 h with an agate mortar and dried by an infrared lamp. The mixed powder was calcined at 1300 °C for 5 h. The resulting powder was ground and sintered at 1500 °C in air for 5 h which labelled as SCY. For comparison with the composite electrolytes, the SCY pellet was

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also synthesized.

The mole ratio of NaCl (0.158 g)/KCl (0.202 g), Li_2CO_3 (0.126)/K_2CO_3 (0.234 g) and NaCl (0.121 g)/$CaCl_2$ (0.239 g) was controlled to be 1:1 and heated at 720 °C, 580 °C and 580 °C, respectively. Then, 80 wt% SCY powder (1.44 g) was mixed with 20 wt% NaCl/KCl, Li_2CO_3/K_2CO_3 and NaCl/$CaCl_2$. The mixtures were ground, followed by sieving (100 mesh) and pressed into pellet by a pressure of 200 MPa. Finally, they were heated at 750 °C, 600 °C and 600 °C for 1 h to obtain $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$-(Na/K)Cl (SCY-NK), $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$-(Li/K)$_2CO_3$ (SCY-LK) and $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$—NaCl—$CaCl_2$ (SCY-NC) composite electrolytes.

The crystalline structures of the SCY, SCY-NK, SCY-LK and SCY-NC were determined at room temperature by X—ray diffraction (XRD) analysis. The microstructures of them were observed by a scanning electron microscope (SEM).

For the electrochemical determinations, round plates roughly 18 mm in diameter with thickness of 1.0—1.2 mm were produced. 20%Pd—80%Ag paste were smeared on both sides (area: 0.5 cm^2) of them which acted as electrodes. Ag mesh was attached to 20% Pd—80%Ag paste and Ag wire was served as the output terminal and the electrical collector, respectively. The impedance spectra were recorded over the frequency range from 1 Hz to 1 MHz with an electrochemical analyzer (CHI660E made in China). The conductivity measurement as a function of temperature in dry N_2 was performed. For the experimental atmospheres, dry gases were obtained by drying through P_2O_5. The conductivity as the function of oxygen partial pressure (pO_2) was measured in the pO_2 range of 1—10^{-20} atm. The pO_2 was accommodated by commixing O_2, air, N_2 and H_2 in proper ratio and measured using an oxygen sensor on line. The H_2/O_2 fuel cell was also constructed.

3. Results and discussion

Fig. 1 shows the X—ray diffraction (XRD) patterns of the SCY, SCY-NK, SCY-LK and SCY-NC. It can be seen from Fig. 1 that only diffractions for $SrCeO_3$ phase in JCPDS (01-082-2370) are found in the as-prepared SCY. It indicates that pure $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$ powder is prepared successfully after calcining at 1500 °C for 5 h. The composite SCY-NK, SCY-LK and SCY-NC samples show the same diffractions which are identified for $SrCeO_3$ phase, meanwhile, there are some additional peaks of NaCl in JCPDS (01-072-1668), $(Li_{0.5}K_{0.5})_2CO_3$ in JCPDS (01-087-0731) and KCl in JCPDS (01-073-0380) for the three composite samples. It is assumed that there has no reaction between SCY and inorganic salts after grinding and heat-treatment [13—16].

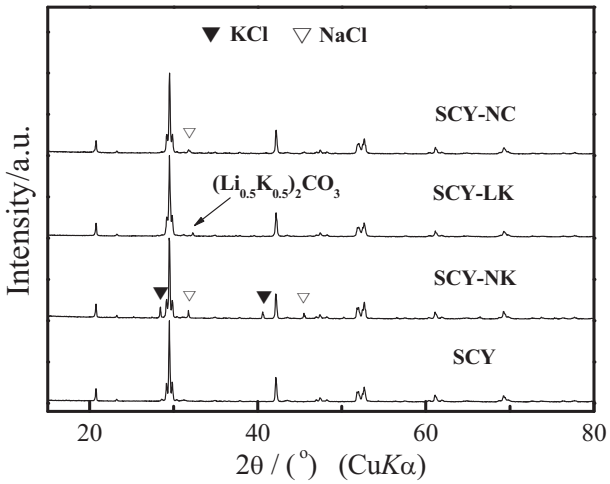

Fig. 1. XRD patterns of the SCY, SCY-NK, SCY-LK and SCY-NC.

Fig. 2 displays SEM images of external and cross-sectional surface of SCY and the three composite samples. As seen from Fig. 2(a,b), the SCY sample is very dense and the molten NaCl/KCl, Li_2CO_3/K_2CO_3 and NaCl/$CaCl_2$ cover the $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$ particle surfaces uniformly from Fig. 2(c—h). The molten inorganic salts appear to serve as the glue for the $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$ particles. This is similar to the observation of ceria-carbonates composite electrolytes prepared through similar heat treatments [12,13].

Fig. 3 shows Arrhenius plots of the conductivities of SCY and the three composite electrolytes in dry N_2 atmosphere at 400—700 °C. The impedance spectra are recorded over the frequency range from 1 Hz to 1 MHz. As can be seen from Fig. 3, the conductivities of the three composite electrolytes are higher than that of SCY and the highest conductivities are observed to be 1.2×10^{-1} S cm^{-1} for SCY-NK at 700 °C, 1.0×10^{-1} S cm^{-1} for SCY-LK at 600 °C and 3.3×10^{-2} S cm^{-1} for SCY-NC at 600 °C, respectively. It is concluded that the enhanced conductivity of the composite electrolytes may be attributed to the molten inorganic salts and the interfaces between the $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$ particles and amorphous salts which provide another fast ionic transport way [11—18]. In the conductivity curve of SCY-NK, a sharp discontinuity is seen at 650 °C which can be explained by a superionic phase transition occurred with the melting point of the NaCl—KCl eutectic [12,17,18]. There is also the same in the other two composite electrolytes. The activation energy in SCY is measured to be 148 ± 2 kJ mol^{-1} and that for SCY-NK is 115 ± 2.7 kJ mol^{-1} at 500—650 °C [19]. However, SCY-NK shows very low activation energy of 23.1 ± 1.2 kJ mol^{-1} above 650 °C. Similar trends are found in the SCY-LK and SCY-NC. This could be due to the mobile ions especial hydroxyd ion$H^{\cdot}$ become less tightly bound to the molten inorganic salts matrix [11,13].

In order to investigate ionic conduction of the three composite electrolytes, the dependence of the conductivity on the partial pressure of oxygen ($pO_2 = 10^{-20} \sim 1$ atm) is investigated. Fig. 4 shows the plots of log σ ~ log (pO_2) in dry atmospheres. There is no variation of the conductivity with pO_2 under hydrogen-containing atmosphere which indicates that the three composite electrolytes show pure conductors of ion. It is well known that $SrCeO_3$-based materials show excellent proton conduction under hydrogen-containing atmosphere [20—23]. When the temperature exceeds the melting point of inorganic salts, the mobility of various ions (Na^+, K^+, Li^+, Ca^{2+}, $H^{\cdot}$, CO_3^{2-} and Cl^-) greatly enhances which leads to a low activation energy for ion transport in the interface regions between the SCY and molten inorganic salts phases [11—18]. Therefore, ion conduction appears to become dominant and the conductivity is not dependent on oxygen partial pressures. It can also be seen from Fig. 4 that conductivities decrease with the increasing pO_2 under oxidizing conditions. It is assumed that the oxide ions and electronic holes produced from the $SrCe_{0.9}Yb_{0.1}O_{3-\alpha}$ in the composites cannot move easily through the molten inorganic salts eutectic at high oxygen partial pressure [16].

Fig. 5 exhibits the impedance spectra of the H_2/O_2 fuel cells under open circuit condition. The impedance spectra show only one depressed arc which may be ascribed mainly to the interface resistance of electrode—electrolyte. The intercepts of the arc with the real axis at low frequency (LF) and high frequency (HF) represent the total cell resistance (R_t) and ohmic resistance (R_o), respectively, while the difference between R_t and R_o corresponds to interfacial polarization resistance (R_p). And the R_t, R_p and R_o, are 1.71 Ω cm^2, 0.73 Ω cm^2 and 0.98 Ω cm^2 at 700 °C for SCY-NK, 2.28 Ω cm^2, 0.95 Ω cm^2 and 1.33 Ω cm^2 at 600 °C for SCY-LK and 4.74 Ω cm^2, 3.22 Ω cm^2 and 1.52 Ω cm^2 at 600 °C for SCY-NC, correspondingly [13].

Fig. 6 illustrates the I—V and I—P curves of the H_2/O_2 fuel cells of the three composite electrolytes. As seen from Fig. 6, the open