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Synthesis and Intermediate Temperature Electrical Properties of $Zr_{0.84}Y_{0.12}Nd_{0.04}O_{2-\alpha}$-Low Melting Point Glass Powder Composite Electrolyte

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In this paper, Nd^{3+} and Y^{3+} double doped ZrO_2-low melting point glass powder (ZYN-glass) composite electrolyte was synthesized by solid-state reaction after heating at 700 °C for 6 h. XRD and SEM techniques were used to analyze the phase structures and morphologies of ZYN-glass. The (log (σT)) based on the operating temperature of ZYN-glass was studied by means of the AC impedance at 400–800 °C. The ZYN-glass showed the highest conductivity of 4.3×10^{-2} S·cm^{-1} at 800 °C. Oxygen concentration difference cell: air, Pd-Ag|ZYN-glass|Pd-Ag, O_2 was constructed at 400–700 °C. H_2/O_2 fuel cell: H_2, Pd-Ag|ZYN-glass|Pd-Ag, O_2 was also tested at 800 °C.

Keywords: Conductivity; Fuel cell; Oxide ionic; Electrolyte; Composite

1. INTRODUCTION

With the development of global industry, new clean energy sources are being widely studied. Solid oxide fuel cells (SOFCs) are investigated due to their high energy and power efficiency, excellent stability and low emissions [1–10]. 8 mol% Y_2O_3-stabilized zirconia (8YSZ) is a commercial electrolyte material used in SOFC, however, the operating temperature (800–1000 °C) is high. Over the past ten years, composite electrolytes containing inorganic materials have been found to have excellent intermediate temperature electrical properties [11–13].

It has been reported that double metal ion doped ZrO_2 has superior properties than single 8YSZ material [14–19]. Rafiuddin et al. found that MgO-CaO co-stabilized ZrO_2 has a higher conductivity than single metal ion doped ZrO_2 [14]. By mixing 3 mol% Fe_2O_3 with YSZ, Kravchyk et al. [15] demonstrated that $(ZrO_2)_{0.90}$–$(Y_2O_3)_{0.07}$–$(Fe_2O_3)_{0.03}$ increased chemical stability. These reports [14–19] showed that the introduction of a second phase influenced the intermediate temperature electrical properties in the composite electrolyte system which existed either in a crystalline or an amorphous state.

In this paper, a new $Zr_{0.84}Y_{0.12}Nd_{0.04}O_{2-\alpha}$-low melting point glass powder (ZYN-glass) composite electrolyte was prepared. The structure and morphology of ZYN-glass were analyzed by XRD and SEM. Conductivity in a nitrogen atmosphere and in an intermediate temperature H_2/O_2 fuel cell were also studied.

2. EXPERIMENTAL

8 mol%Y_2O_3 stabilized ZrO_2 (8YSZ) was prepared by a sol-gel reaction (particle size: 50 nm). 8YSZ with 4 mol% Y_2O_3 and 4 mol% Nd_2O_3 was prepared via a solid-state reaction. The mixing powder was dried and annealed at 700 °C for 6 h to obtain ZYN-glass [20].

The phase structures of 8YSZ and ZYN-glass powders were analyzed using X–ray diffraction (XRD). The microstructures of ZYN-glass were observed using scanning electron microscopy (SEM).

The (log (σT)) based on the operating temperature in a nitrogen atmosphere was tested using CHI660E electrochemical analyzer by a three-electrode system in the range from 1 Hz to 1 MHz at 400–800 °C. And the ac amplitude of electrochemical impedance spectroscopy (EIS) was 20 mV. The area and thickness of ZYN-glass were 0.5 cm^2 and 1.1 mm, respectively. A silver-palladium paste with silver wire was used as electrodes. Oxygen concentration difference cell: air, Pd-Ag|ZYN-glass|Pd-Ag, O_2 was constructed at 400–700 ^oC. H_2/O_2 fuel cell: H_2, Pd-Ag|ZYN-glass|Pd-Ag, O_2 was also fabricated at 800 ^oC.

3. RESULTS AND DISCUSSION

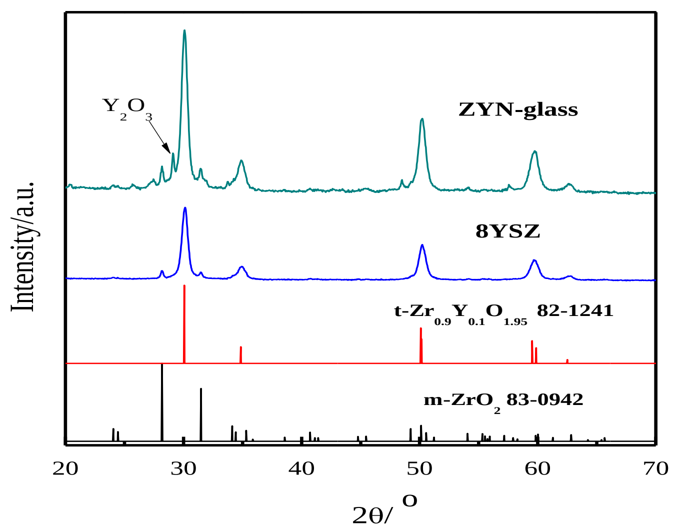


Figure 1. XRD patterns of the 8YSZ and ZYN-glass.

Fig. 1 shows XRD patterns of the 8YSZ and ZYN-glass. 8YSZ possesses a major t-$Zr_{0.9}Y_{0.1}O_{1.95}$ (JCPDS 82-1241) phase with a minor m-ZrO_2 (JCPDS 83-0942) structure. ZYN-glass occurs as a mixture of tetragonal, monoclinic and Y_2O_3 phases. In the double metal ion (M^{n+}) doped ZrO_2 system, ZrO_2 is fully stabilized when the M^{n+} content is below 13 mol% [21]. The Y_2O_3 phase is observed when the total M^{n+} content is 16 mol% [22].

Fig. 2 shows the surface (a) and cross-sectional (b) SEM photos of the ZYN-glass. Obviously, the low melting point glass powder has a vital influence on the micromorphology of the ZYN-glass. There are no pores in the surface and cross-sectional SEM photos of the ZYN-glass which indicates the composite electrolyte is dense.

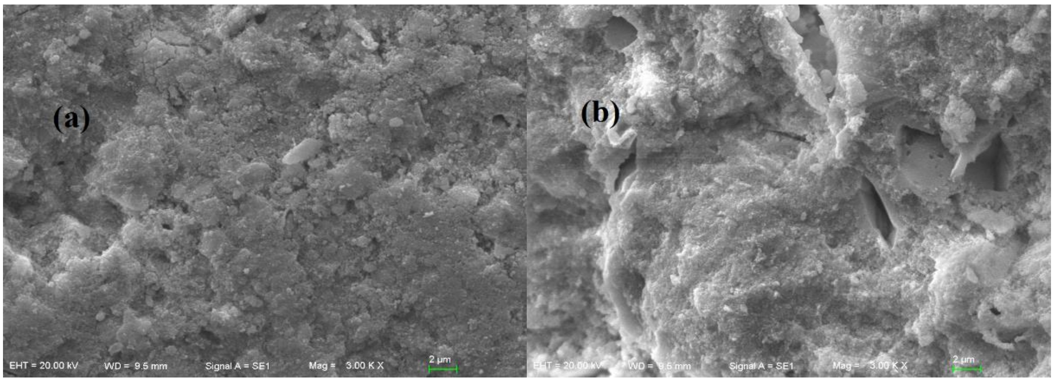
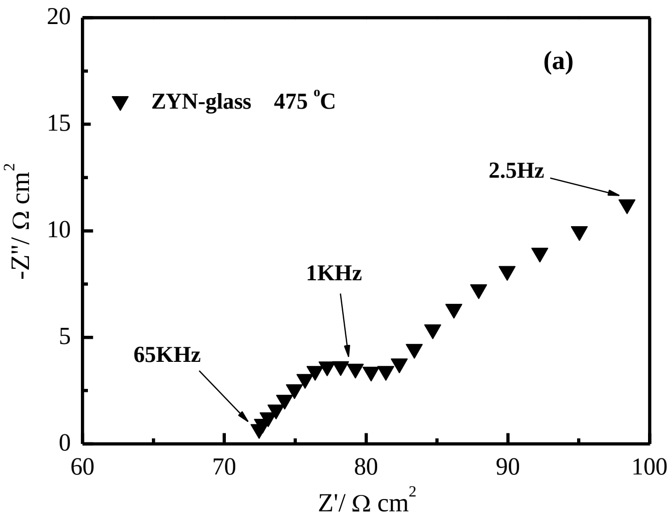


Figure 2. Surface (a) and cross-sectional (b) SEM photos of the ZYN-glass.

Fig.3 shows the AC impedance spectra of ZYN-glass at 475 °C, 550 °C and 600 °C, respectively. The diagrams consist of a semicircle and a straight line. A semicircle at high frequencies is ascribed to the contribution of the ionic charge carriers into the grains of ZYN-glass.



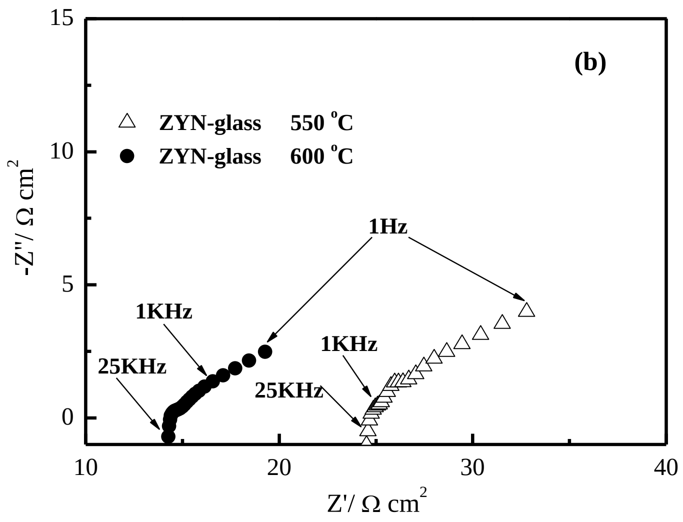


Figure 3. The AC impedance spectra of ZYN-glass at (a)475 °C, (b)550 °C and 600 °C.

The semicircle gradually disappears as the temperature rises above 600 °C which means the transfer ability of the ionic charge carriers is thermally improved. A straight line at low frequencies can be explained by polarization at the electrode/electrolyte interface [15].

Fig. 4 shows the (log (σT)) based on the operating temperature of ZYN-glass in a nitrogen atmosphere from 400 to 800 °C. The (log (σT)) ~ 1000 T^{-1} plot of the ZYN-glass is in conformity with the Arrhenius law and the activation energy is 75.5 ± 1 kJ·mol^{-1}. It can be observed from Fig. 4 that the conductivities of ZYN-glass are higher than in our previous report of ZYE-glass [22] and in the Kravchyk et al. [15] study of $(ZrO_2)_{0.90}$–$(Y_2O_3)_{0.07}$–$(Fe_2O_3)_{0.03}$ meaning that the double metal ion doped ZrO_2 is effective. The ZYN-glass shows the highest conductivity of 4.3×10^{-2} S·cm^{-1}, whereas the ZYE-glass [22] achieves 3.0×10^{-2} S·cm^{-1} at 800 °C.

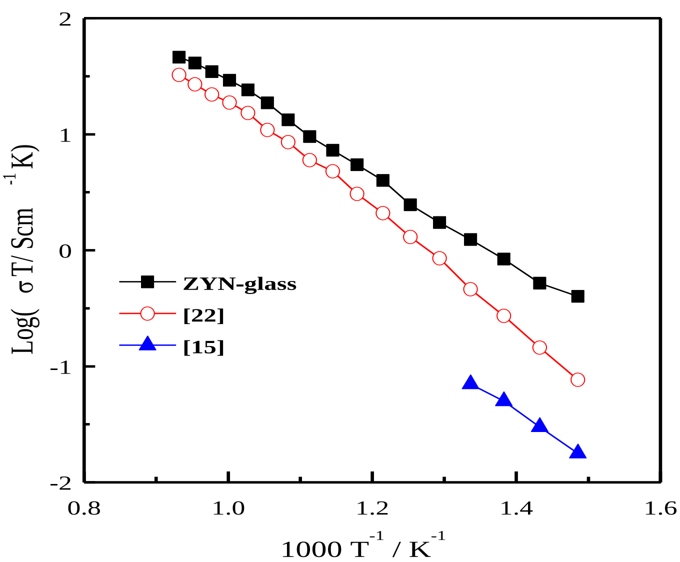


Figure 4. The (log (σT)) based on the operating temperature of ZYN-glass in nitrogen atmosphere at 400–800 °C.

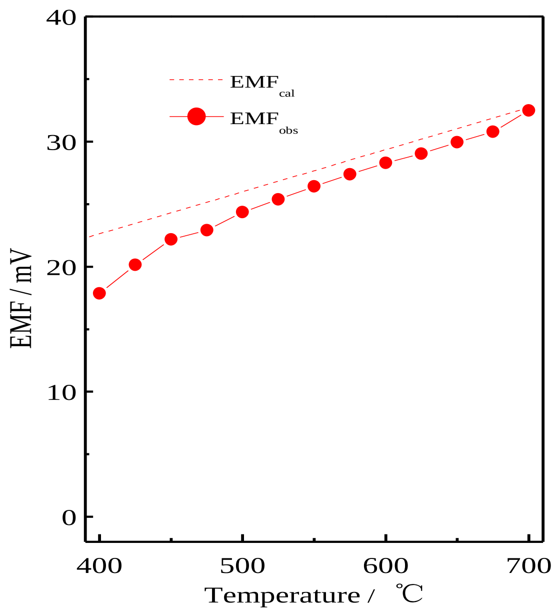


Figure 5. Oxygen concentration difference cell: air, Pd-Ag|ZYN-glass|Pd-Ag, O_2 at 400–700 °C.

The oxygen concentration difference cell: air, Pd-Ag|ZYN-glass|Pd-Ag, O_2 at 400–700 °C is given in Fig. 5. The theoretical electromotive forces (EMF_{cal}) are calculated as: $EMF_{cal} = \frac{RT}{4F} t_o \ln[p_{O_2 (A)} / p_{O_2 (B)}]$ when $p_{H_2O (A)} = p_{H_2O (B)}$ and $t_o = 1$ [23-24]. The observed (EMF_{obs}) electromotive forces are read out according to a potentiometer. The transport number of $t_o = EMF_{obs} / EMF_{cal} = 0.79\text{-}0.99$ can be obtained from Fig. 5. The t_o gradually increases as the temperature rises from 400 °C to 700 °C, which means the transfer ability of O^{2-} is thermally improved. The result demonstrates that ZYN-glass is a good oxide ionic conductor.

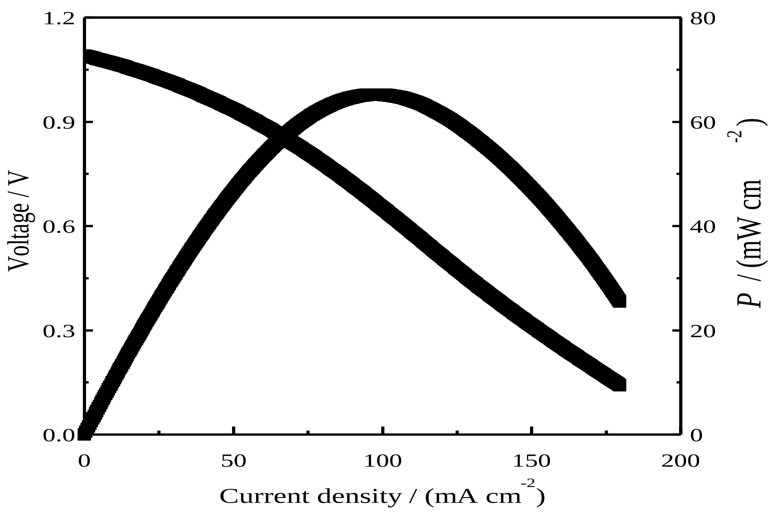


Figure 6. Performance of the H_2/O_2 fuel cell of the ZYN-glass at 800 °C.

Fig. 6 shows the H_2/O_2 fuel cell performance of the ZYN-glass with the open circuit voltage of 1.09 V at 800°C. The highest power density (P_h) is 65.2 mW·cm^{-2}, while our previous report of ZYE-glass [22] gives the P_h of 60.6 mW·cm^{-2} at 800°C meaning that the double metal ion doped ZrO_2 is effective. The P_h of the YSZ membrane fuel cell with NiO-YSZ anode is 160 mW·cm^{-2} at 850 °C [25] which is higher than that of our result. The enormous improvement in P_h is ascribed to the reduction of the electrolyte thickness.

4. CONCLUSIONS

In this study, a new $Zr_{0.84}Y_{0.12}Nd_{0.04}O_{2-\alpha}$-low melting point glass (ZYN-glass) composite electrolyte was prepared. The activation energy of ZYN-glass is 75.5 ± 1 kJ·mol^{-1} and the highest conductivity is 4.3×10^{-2} S·cm^{-1} at 800 °C. The t_o transport number is 0.79-0.99 and the result demonstrates that ZYN-glass is a good oxide ionic conductor. Finally, the highest power density (P_h) of ZYN-glass (thickness = 1.1 mm) is 65.2 mW·cm^{-2} at 800°C.

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