

The influence of sintering additive on the structure and intermediate-temperature electrochemical properties of Gd^{3+} and Er^{3+} co-doped ceria electrolyte

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In this study, $\text{Er}_{0.1}\text{Gd}_{0.1}\text{Ce}_{0.8}\text{O}_{2-\alpha}$ (EGDC) was synthesized at different temperatures by a nitrate-citric acid combustion method. $\text{Er}_{0.1}\text{Gd}_{0.1}\text{Ce}_{0.8}\text{O}_{2-\alpha}$ -4 mol% NiO (EGDC-NiO) was also prepared by adding 4 mol% NiO as a sintering additive. The morphologies and structures of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO were investigated using scanning electron microscopy (SEM) and X-ray diffraction (XRD). Intermediate-temperature electrochemical properties were also studied using AC impedance, gas concentration cell and fuel cell. SEM results showed that adding sintering additive NiO or increasing sintering temperature can improve the densities of electrolytes. The $\log(\sigma T)$ vs. $1000/T$ results showed that 1350-EGDC-NiO had the highest conductivity of $5.3 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at 750 °C. The maximum output power densities of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO were $34.8 \text{ mW} \cdot \text{cm}^{-2}$, $56.8 \text{ mW} \cdot \text{cm}^{-2}$ and $63.6 \text{ mW} \cdot \text{cm}^{-2}$ at 750 °C, respectively.

Keywords: Electrolyte; Fuel cell; CeO_2 ; Conductivity

1. INTRODUCTION

Fuel cells use the chemical energy of the fuel, which is stored in electrochemical cells to generate electricity. For fuel cells with solid electrolytes as the main support, the oxide ion diffusivity and conductivity of the electrolyte materials determine the electrochemical performance of the fuel cells to a large extent [1-6]. Zirconia-based solid electrolytes are used at high temperature (800–1000 °C) [7]. In order to reduce energy consumption, solid electrolytes with good electrochemical properties at medium temperature have been developed [8-9]. Among the metal oxides, CeO_2 is an important rare earth oxide, which has attracted extensive attention for catalysis, fuel cells, sensors, oxygen storage capacitors and biological applications [10-12]. Liu *et al.* used $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.95}$ electrolyte to test acetone content [11]. I. Diaz-Aburto *et al.* synthesized Mo-doped ceria by a combustion method which had good catalytic

activity for carbon gasification [12]. CeO₂-based electrolytes have high conductivities at medium temperature (600–800 °C).

It is well known that ceria has a face-centered cubic fluorite structure. The crystal structure with a larger radius of Ce⁴⁺ provides a wider space for oxide ion migration. Reports have shown that the doping effect of rare earth oxides is better than that of alkaline earth oxides. Kumar *et al.* reported that the conductivity of Ce_{0.8}Sm_{0.1}Gd_{0.1}O_{2-δ} was higher than that of Ce_{0.8}Ca_{0.1}Gd_{0.1}O_{2-δ} and close to Ce_{0.8}Sr_{0.1}Gd_{0.1}O_{2-δ} under the same conditions [13]. Anwar *et al.* investigated how the dopant content influenced the conduction properties. Conductivities increased in the order: $\sigma(\text{Ce}_{0.80}\text{Sr}_{0.075}\text{Er}_{0.125}\text{O}_{2-\delta}) < \sigma(\text{Ce}_{0.80}\text{Sr}_{0.05}\text{Er}_{0.15}\text{O}_{2-\delta}) < \sigma(\text{Ce}_{0.80}\text{Sr}_{0.025}\text{Er}_{0.175}\text{O}_{2-\delta}) < \sigma(\text{Ce}_{0.80}\text{Er}_{0.20}\text{O}_{2-\delta})$ [6]. However, Ce⁴⁺ is partially reduced to Ce³⁺ in a reducing environment of the anode during the operation of SOFCs. Reports have shown that rare earth oxides co-doped CeO₂-based electrolytes greatly reduce the enthalpy of association between oxygen vacancy and doped ions, therefore, the activation energy decreases and the ionic conductivity increases [14-17]. Soepriyanto *et al.* prepared La, Y, Nd and Gd co-doped ceria solid electrolytes using a high temperature solid state method, and Nd, Gd co-doped with 20 mol% doping concentration sample had the highest intermediate-temperature electrochemical property [18]. CeO₂-based electrolytes need to be densified at high temperature (1400–1600 °C). Adding a sintering additive is a common method to improve the density of refractory material. However, the influence of sintering additives on the electrical properties of electrolytes remains unclear, with no consensus reached [19-24].

Therefore, Gd³⁺ and Er³⁺ co-doped CeO₂ (Er_{0.1}Gd_{0.1}Ce_{0.8}O_{2-α}) was synthesized at different temperatures by a nitrate-citric acid combustion method in this study. Er_{0.1}Gd_{0.1}Ce_{0.8}O_{2-α}-4 mol% NiO was also prepared by adding 4 mol% NiO as a sintering additive. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to study their structures and morphologies. Their conductivities, and gas concentration cell and fuel cell performance were also investigated.

2. EXPERIMENTAL

Firstly, Gd³⁺ and Er³⁺ co-doped CeO₂ was synthesized by a nitrate citric acid combustion method. According to the molar ratio in the formula of Er_{0.1}Gd_{0.1}Ce_{0.8}O_{2-α} (EGDC), the mixed solution of Ce⁴⁺, Gd³⁺ and Er³⁺ was prepared by dissolving ammonium ceric nitrate in water and Gd₂O₃ and Er₂O₃ in nitric acid. Citric acid with a molar ratio of 2 to metal ions was added. NH₄OH was dropped to adjust the pH value of the mixed solution to 7. After evaporation and concentration, the primary powder was obtained by heating and spontaneous combustion. The powder was pressed at 200 MPa and EGDC was obtained by calcining at 800 °C for 5h. EGDC powder was fully mixed with NiO in the molar ratio of 100: 4. The EGDC and Er_{0.1}Gd_{0.1}Ce_{0.8}O_{2-α}-4 mol% NiO (EGDC-NiO) were obtained by calcining at 1350 °C or 1450 °C for 5h and labelled as 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO, respectively.

The structures of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO were determined by X-ray diffraction (XRD). For comparison, Er_{0.1}Ce_{0.9}O_{2-α}-4 mol% NiO (1350-EDC-NiO) was prepared by calcining at 1350 °C for 5h. The morphologies of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO were observed by scanning electron microscopy (SEM). Their conductivities were measured on a CHI660E

electrochemical workstation using AC impedance analysis at 500-750 °C in a dry nitrogen atmosphere (thickness: 1.0-1.1 mm, electrode area: 0.5 cm²). The relationships between conductivity and oxygen partial pressure were studied. The hydrogen concentration discharge cell: H₂, Pd-Ag|electrolyte|Pd-Ag, 30% H₂ and H₂/O₂ fuel cell performance of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO at 750 °C were also investigated. A 20% palladium-80% silver paste with silver wires was used to fabricate the electrodes for the fuel cell tests.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of Er_{0.1}Gd_{0.1}Ce_{0.8}O_{2-α} and Er_{0.1}Gd_{0.1}Ce_{0.8}O_{2-α}-4 mol% NiO calcined at 800 °C, 1350 °C and 1450 °C, respectively. From Fig. 1, CeO₂ solid solution with a cubic fluorite structure was basically formed after sintering at 800 °C for 5 h, which is consistent with the standard spectrum (JCPDS, 00-046-0507) [19]. The half peak width indicates that the synthesized powder was of nanometer scale. The half peak width becomes narrower after being calcined at 1350 °C or 1450 °C, which indicates that Gd³⁺ and Er³⁺ replaced Ce⁴⁺ in the lattice and form CeO₂ crystal phase completely [20-21]. In addition to the diffraction peaks of CeO₂, there were very few Er₂O₃ phases in 1350-EGDC-NiO. This shows that NiO entered the lattice of CeO₂ phase. The ionic radii of six coordinate Ni²⁺, Ce⁴⁺, Gd³⁺ and Er³⁺ were 0.069 nm, 0.087 nm, 0.093 nm and 0.089 nm, respectively. The ionic radii of Gd³⁺ and Er³⁺ were larger than that of Ce⁴⁺ which makes the lattice structure unstable. Therefore, Ni²⁺ could also replace Er³⁺ at Ce⁴⁺ site to form a more stable lattice structure.

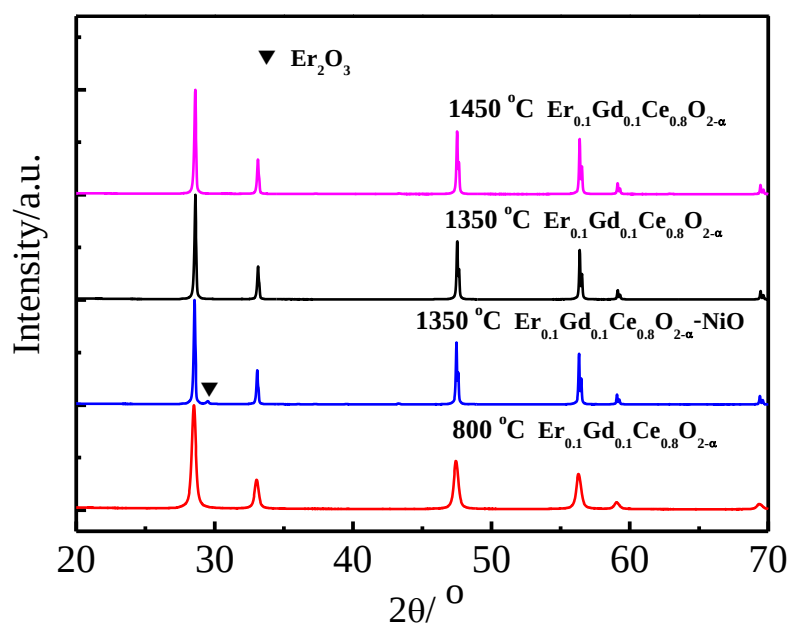


Figure 1 XRD patterns of 800 °C Er_{0.1}Gd_{0.1}Ce_{0.8}O_{2-α} (EGDC), 1350-EGDC, 1450-EGDC, 1350-EGDC-NiO and 1350-EGDC-NiO, respectively.

Fig. 2 shows the SEM morphologies of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO. In addition to a higher porosity of 1350-EGDC, the other samples (1450-EGDC and 1350-EGDC-NiO)

were more compact. The SEM difference between 1350-EGDC and 1450-EGDC shows that increasing the sintering temperature can significantly improve the grain growth of the samples. Compared with 1350-EGDC, 1350-EGDC-NiO had a denser structure under the same sintering conditions. The average grain sizes of 1450-EGDC and 1350-EGDC-NiO were approximately 1 μm and 0.7 μm , respectively.

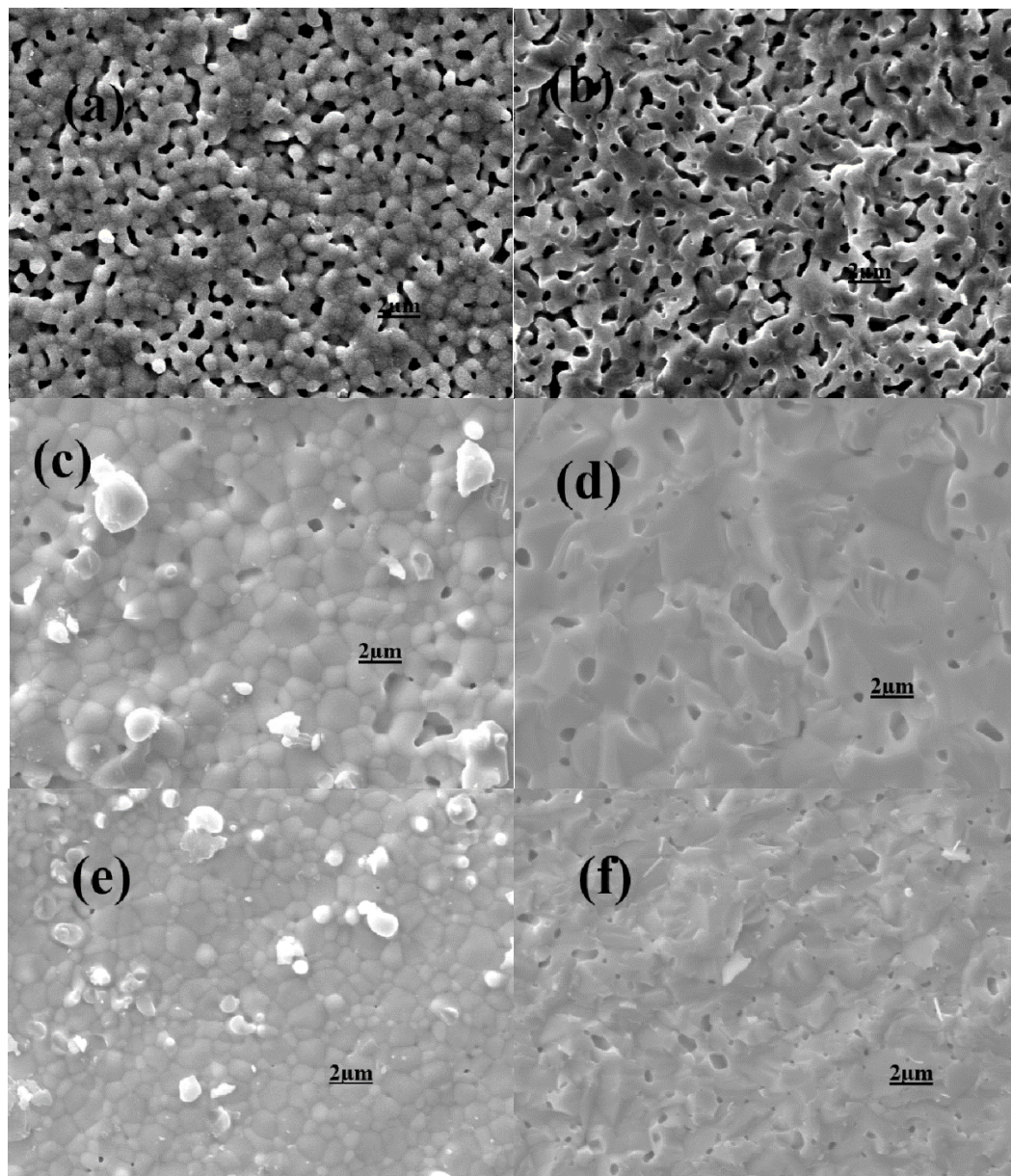


Figure 2 SEM images of (a, c, e) the surface photos of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO, (b, d, f) the cross section photos of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO.

These phenomena indicate that NiO can promote the grain boundary migration of EGDC ceramics [22]. Fig. 3 is the energy-dispersive X-ray spectroscopy result for $\text{Er}_{0.1}\text{Gd}_{0.1}\text{Ce}_{0.8}\text{O}_{2-\alpha}$ -4 mol% NiO (1350-EGDC-NiO). The spectrum has major peaks assigned to Gd, Ce, Er, Ni and O elements. The atomic ratios of Ce/Er, Er/Gd, Ce/Ni and Gd/Ni were 7.69, 1.04, 22.41 and 2.81, respectively. The molar

ratios of elements were basically consistent with 1350-EGDC-NiO. The elements mapping images indicated that spatial distributions of Gd, Ce, Er and Ni were uniform.

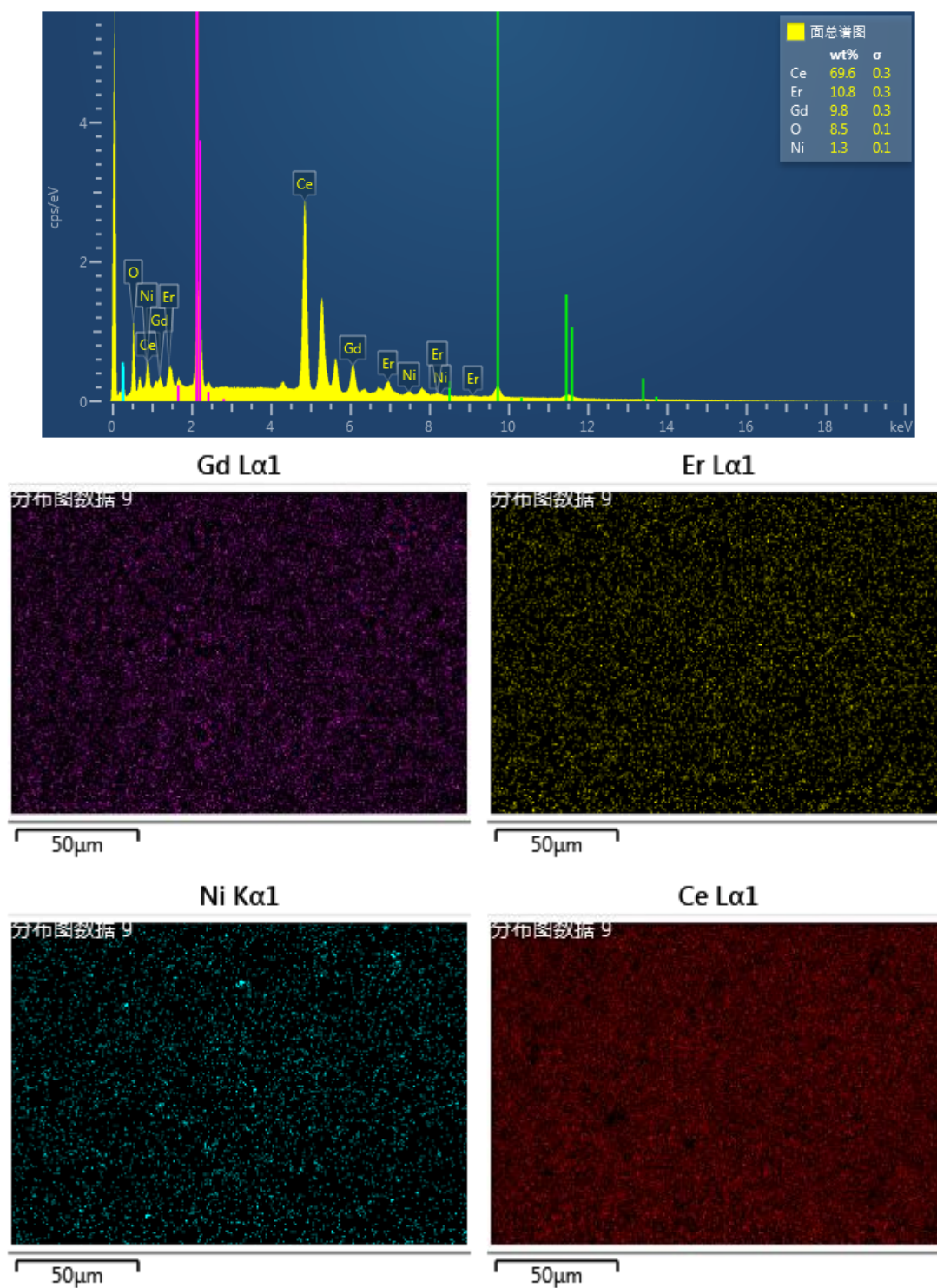


Figure 3 The energy-dispersive X-ray spectroscopy and elements mapping images in $\text{Er}_{0.1}\text{Gd}_{0.1}\text{Ce}_{0.8}\text{O}_{2-x}$ -4 mol% NiO (1350-EGDC-NiO).

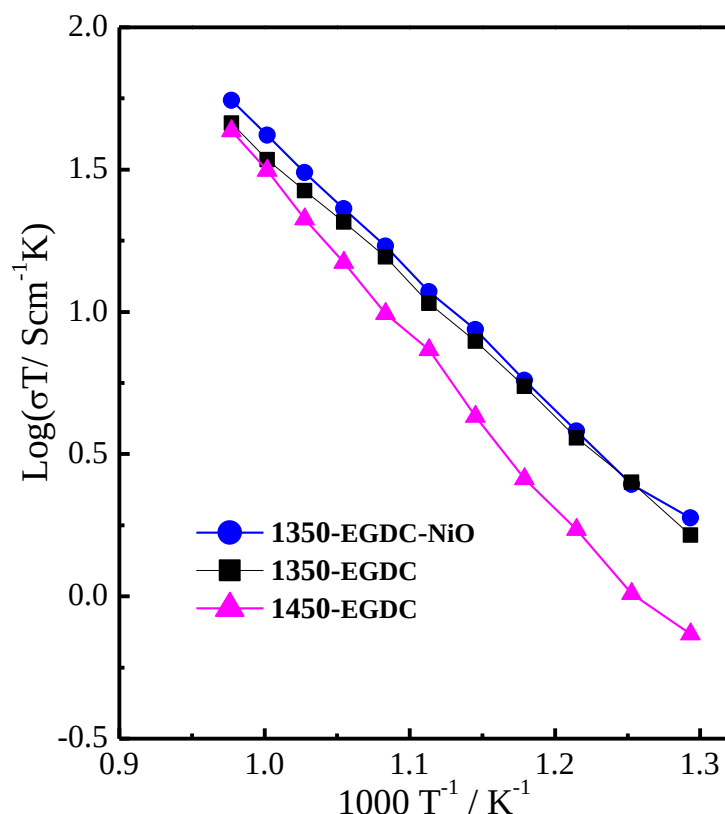


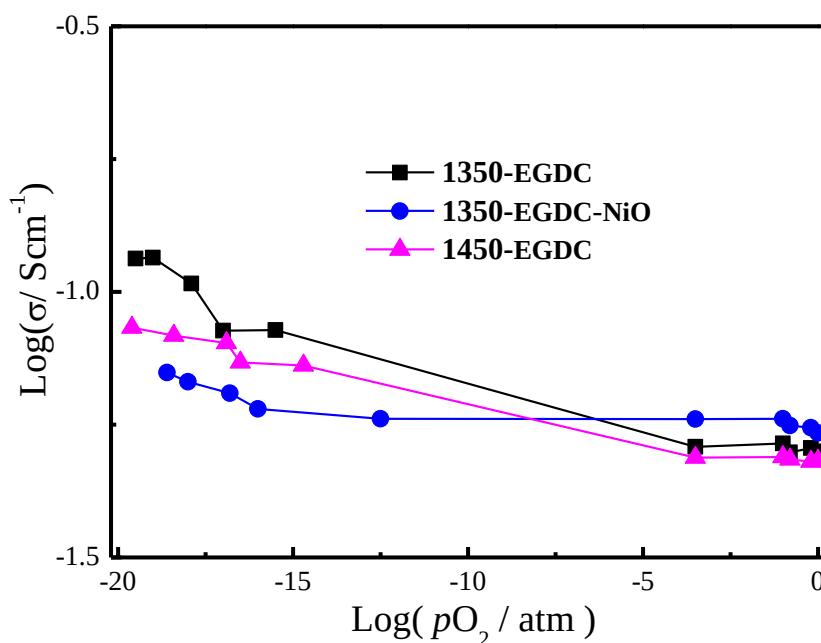
Figure 4 The $\log(\sigma T) \sim 1000 T^{-1}$ plots of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO at 500-750 °C in a dry nitrogen atmosphere.

The relationships between conductivity and temperatures of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO at 500-750 °C in a dry nitrogen atmosphere are shown in Fig. 4. It is well known that the total conductivity is composed of grain conductivity and grain boundary conductivity. Combined with Fig. 2, the conductivity in 1350-EGDC was mainly contributed to by grain size. The grain boundary conductivity increases with the increased of sintering temperature and addition of sintering additive NiO. And the larger the grain boundary size, the lower the conductivity. Therefore, the conductivity of 1350-EGDC was higher than that of 1450-EGDC. Fig. 4 shows that the increase of electrolyte density contributed to the conductivity. 1350-EGDC-NiO had the highest conductivity of $5.3 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at 750 °C.

The conductivities of 1350-EGDC-NiO were higher than those of $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Ba}_{0.05}\text{Er}_{0.05}\text{O}_{2-\alpha}$ [25] and composite electrolyte $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\alpha}$ -30% Al_2O_3 [26], however, it was equivalent to $\text{Ce}_{0.8}\text{Pr}_{0.10}\text{Gd}_{0.10}\text{O}_{1.90}$ [27] under the same temperatures (Table 1). It may be that a part of NiO entered $\text{Er}_{0.1}\text{Gd}_{0.1}\text{Ce}_{0.8}\text{O}_{2-\alpha}$ lattice and replaced Er^{3+} which would have increased the vacancy concentration. The increased vacancy concentration may have promoted the migration of conducting ions.

Table 1. The conductivities of 1350-EGDC-NiO and M^{n+} -doped CeO_2 in the literatures.

solid electrolytes	conductivities ($10^{-2} \text{ S}\cdot\text{cm}^{-1}$)
1350-EGDC-NiO	0.99 600 °C, 1.8 650 °C, 3.2 700 °C, 5.3 750 °C
$\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Ba}_{0.05}\text{Er}_{0.05}\text{O}_{2-\alpha}$	0.38 650 °C, 0.64 700 °C, 1.2 750 °C [25]
$\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\alpha}$ -30% Al_2O_3	0.32 600 °C, 0.67 650 °C [26]
$\text{Ce}_{0.8}\text{Pr}_{0.10}\text{Gd}_{0.10}\text{O}_{1.90}$	4.2 700 °C, 5.1 750 °C [27]

**Figure 5.** The $\log\sigma$ vs. $\log(p\text{O}_2)$ curves of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO at 750 °C.

The relationships between conductivities and oxygen partial pressure of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO at 750 °C were studied, as shown in Fig. 5. The conductivities did not change with the oxygen partial pressure in the range of $p\text{O}_2 = 10^{-4} \sim 1$ atm, which indicates that 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO are excellent oxygen ion conductors because of their good oxide ionic conductivities in an oxidizing atmosphere. This result is consistent with the relevant reports [15, 23]. Taub *et al.* reported that the electronic conductivity of Gd^{3+} and Co^{3+} co-doped CeO_2 is $-1/6$ relationship with $p\text{O}_2$ under a reductive condition [15]. The conductivities increased with the decrease of oxygen partial pressures, which indicates that there was a small amount of electron conduction in the reduction range of $p\text{O}_2 = 10^{-19} \sim 10^{-12}$ atm.

Fig. 6 shows the hydrogen concentration discharge curves of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO at 750 °C. It can be seen from Fig. 6 that there were stable discharge curves, which indicates that the directional migration of metal ions is impossible. Only protons or oxide ions can migrate directionally. According to the hydrogen concentration discharge cell, H_2 , Pd-Ag|electrolyte|Pd-Ag, 30% H_2 , only protons can migrate in the cell. The calculated electromotive force (EMF_{cal}) at 750 °C of the cell was calculated according to the Nernst equation when the electrolyte is a pure proton

conductor. Fig. 6 shows that the actual open circuit voltages were lower than the EMF_{cal} value (53 mV). This indicates that 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO have small amounts of electron conduction, which is consistent with the conclusion in Fig. 5. The electron conduction may be avoided by using other fuels rather than H_2 , for example, biomass, plastics, food waste etc. [28-29].

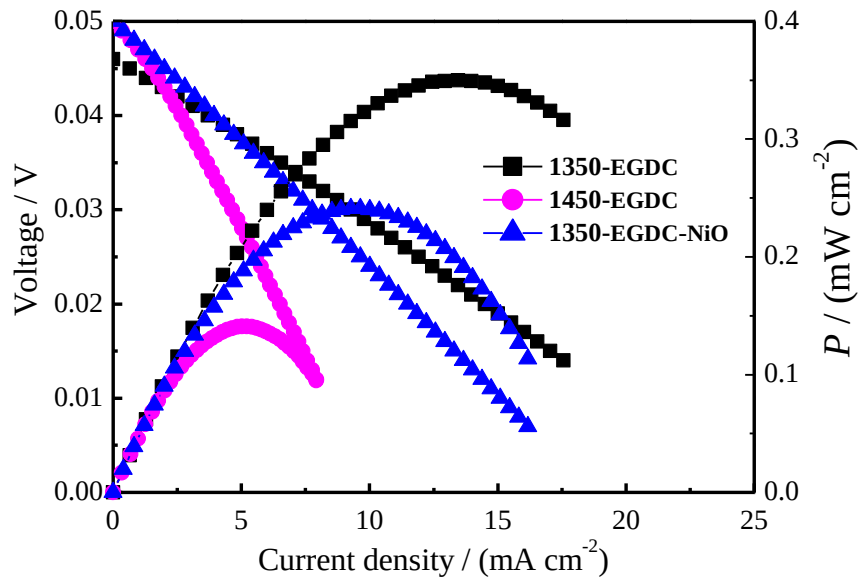


Figure 6. The hydrogen concentration discharge cell: H_2 , Pd-Ag|electrolyte|Pd-Ag, 30% H_2 of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO at 750 °C.

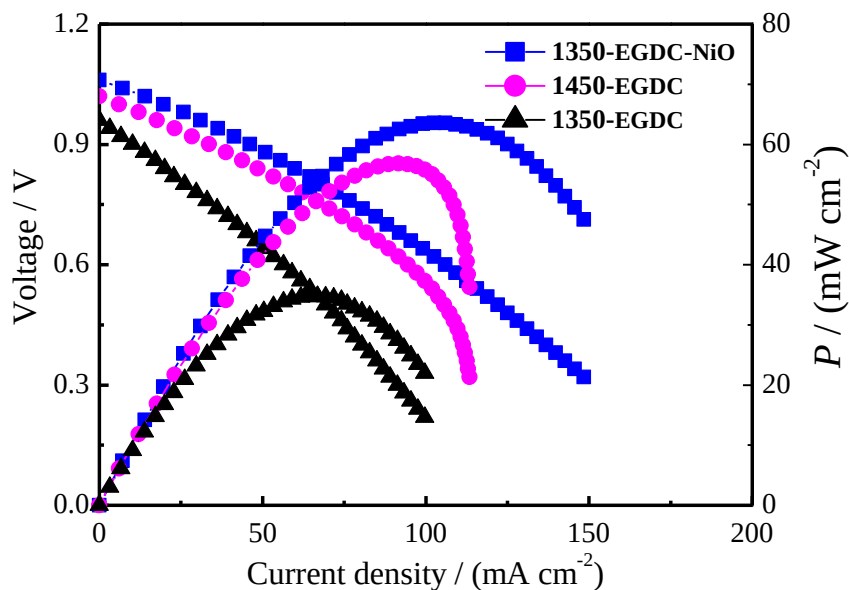


Figure 7. The H_2/O_2 fuel cell I - V - P curves of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO at 750 °C.

Fig. 7 shows H₂/O₂ fuel cell output performances of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO at 750 °C. The open circuit voltages of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO were 0.96 V, 1.02 V and 1.06 V respectively. The open circuit voltages were lower than the theoretical value, which indicates that there was a certain degree of electronic conduction [24]. The output power densities increased with the increase of current densities. The maximum output power densities of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO were 34.8 mW·cm⁻², 56.8 mW·cm⁻² and 63.6 mW·cm⁻² at 750 °C, respectively. The results show that the compact sample with sintering additive NiO at lower sintering temperature (1350 °C) had a better electrical property.

4. CONCLUSIONS

In this study, Er_{0.1}Gd_{0.1}Ce_{0.8}O_{2-α} (EGDC) and Er_{0.1}Gd_{0.1}Ce_{0.8}O_{2-α}-4 mol% NiO (EGDC-NiO) were synthesized at different temperatures. XRD analysis indicated that CeO₂ structure was formed after sintering at 800 °C for 5 h. SEM results showed that 1450-EGDC and 1350-EGDC-NiO had dense structures. The conductivities of 1350-EGDC-NiO were higher than those of 1450-EGDC. The hydrogen concentration discharge cell and logσ vs. log(pO₂) curves indicated that 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO had small amounts of electron conduction under reductive conditions. The maximum output power densities of 1350-EGDC, 1450-EGDC and 1350-EGDC-NiO were 34.8 mW·cm⁻², 56.8 mW·cm⁻² and 63.6 mW·cm⁻² at 750 °C, respectively. 1350-EGDC-NiO had a better intermediate-temperature electrochemical property.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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