

Short Communication

Gadolinium Doped Strontium Cerate Prepared by Citric-Nitrate Auto-Combustion Process and Intermediate Temperature Electrical Properties of Its Composite Electrolyte

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In this work, $\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}$ electrolyte was prepared by a citric-nitrate auto-combustion (CNA) method using Gd_2O_3 , HNO_3 , $\text{Sr}(\text{NO}_3)_2$, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and citric acid as raw materials and subsequently compounded with NaCl/KCl. The XRD results have shown that no reactions between $\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}$ and NaCl/KCl have taken place. The SEM examinations reveal that the particle size of $\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}$ is uniform, and the surface is uniformly covered by NaCl/KCl that acts as the $\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}$ particle binder. The ionic and protonic conduction of $\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}$ (SCGd-CNA) was studied by using gas concentration cells. The fuel cell based on $\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}$ -NaCl-KCl (SCGd-CNA-NK) exhibits excellent cell performance with a maximum power output density of $215 \text{ mW}\cdot\text{cm}^{-2}$ at 700°C , which is much higher than for single cerium strontium material, SCGd-CNA, *i.e.* $20.7 \text{ mW}\cdot\text{cm}^{-2}$ at 700°C .

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

1. INTRODUCTION

Electrolytes with excellent ionic conduction have drawn considerable research attention owing to their wide application in fuel cells, sensors, etc. [1–5]. In recent years, novel composite electrolytes such as ceria-carbonates or ceria-chlorides have been widely studied, usually at an intermediate temperature range ($400\text{--}700^\circ\text{C}$) [1–10]. Gulgun et al. found that the softened Na_2CO_3 phase could significantly enhance the ionic conductivity, which serves as a glue in the nanocomposite electrolyte of $\text{CeO}_2\text{-Na}_2\text{CO}_3$ [1]. Mao et al. studied doped barium cerate-carbonate [4], doped ceria-carbonate [6] and

$\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}\text{-(Li/Na)}_2\text{CO}_3$ composite electrolytes [7] and found they had high conductivities and excellent fuel cell performance at intermediate temperatures.

Rare earth doped perovskite-type materials exhibit fairly protonic conduction at high temperatures in a hydrogen-containing atmosphere [11–16]. And protonic conduction in SrCeO_3 is affected by many factors, such as cation radius of rare earth dopants, concentration of defects, temperature and density, etc. The traditional synthesis of SrCeO_3 -based electrolytes is usually performed by a solid-state reaction method with a relative high temperature that exceeds 1500 °C. In the past few decades, wet chemical synthesis methods have been developed for preparing SrCeO_3 -based electrolytes at lower temperatures [15,16]. For instance, Amsif et al. [17] found Gd^{3+} doped BaCeO_3 had the highest proton conductivity while investigating various rare earth dopants in BaCeO_3 . The search for high conductivity solid electrolyte is a popular yet challenging research topic. The citric-nitrate auto-combustion (CNA) method is widely used to synthesize functional materials due to its significant advantages in producing fine and uniform powders. Herein, we focus our investigation on $\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}$. To the best of our knowledge, so far, there is no report about the intermediate temperature electric properties of $\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}\text{-NaCl-KCl}$ composite electrolyte.

In this work, the citric-nitrate auto-combustion (CNA) method was used to synthesize $\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}$ (SCGd-CNA) at the relatively low temperature of 1100 °C. Furthermore, a $\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}\text{-NaCl-KCl}$ (SCGd-CNA-NK) composite electrolyte was also prepared. The structure and micrographics of the electrolytes were characterized by using X-ray diffraction (XRD) and scanning electron microscope (SEM). The oxide ionic and protonic conduction of SCGd-CNA under different conditions were investigated by using hydrogen, oxygen and water vapor concentration cells.

2. EXPERIMENTAL SET-UP

$\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}$ electrolyte was prepared via the CNA method. Gd_2O_3 was firstly dissolved in concentrated nitric acid. The stoichiometric amounts of $\text{Sr}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ were mixed in distilled water. The molar ratio of total metal nitrates to citric acid was 1: 3. Subsequently, the ammonia solution was added dropwise to the above solution and the pH of the solution was adjusted to be in the range of 8-9. The solution was evaporated at 90 °C for 5 h until a viscous gel was formed. After heating to 200 °C on the plate, expansion and decomposition occurred and grey green ash was obtained. The obtained ash was calcined at 1100 °C for 5 h [18]. For comparison with the composite electrolyte, the $\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}$ (SCGd-CNA) pellet was synthesized at 1500 °C for 5 h.

The molar ratio of NaCl (0.158 g) and KCl (0.202 g) = 1:1 [19], and was heated at 720 °C twice. Then, 80 wt% $\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}$ (1100 °C)(1.44 g)-20 wt% (Na/K)Cl (0.36 g) powder was mixed and ground [20]. The resultant powder was uniaxially pressed into disks under 200 MPa and heated at 750 °C for 1 h to obtain $\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}\text{-NaCl-KCl}$ (SCGd-CNA-NK) composite electrolyte.

The crystalline phase of SCGd-CNA and SCGd-CNA-NK was determined by using powder X-ray diffraction (XRD). The micrographics of the samples were observed by SEM.

In order to explore the oxide ionic and protonic conduction of SCGd-CNA under different conditions, the values of observed electromotive force (EMF_{obs}) for the hydrogen, oxygen and water vapor concentration cells were determined at 500-700 °C, as shown below [21].

$$EMF_{obs} = \frac{RT}{2F} \{ -t_{ion} \ln[p_{H_2(A)} / p_{H_2(B)}] + t_O \ln [p_{H_2O(A)} / p_{H_2O(B)}] \} \quad (1)$$

$$EMF_{obs} = \frac{RT}{4F} \{ t_{ion} \ln[p_{O_2(A)} / p_{O_2(B)}] - 2 t_H \ln [p_{H_2O(A)} / p_{H_2O(B)}] \} \quad (2)$$

The conductivities of SCGd-CNA and SCGd-CNA-NK in dehumidified air were measured at 500-700 °C. The H_2/O_2 fuel cells of SCGd-CNA and SCGd-CNA-NK were also constructed.

3. RESULTS AND DISCUSSION

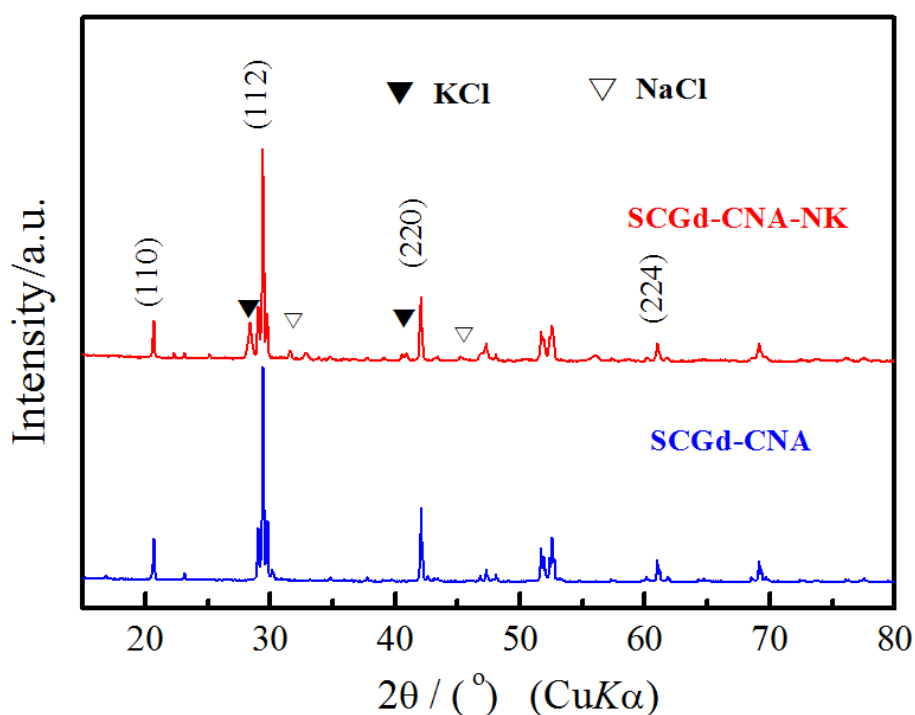


Figure 1. XRD patterns of SCGd-CNA and SCGd-CNA-NK samples.

Fig. 1 shows the XRD patterns for the SCGd-CNA (1500 °C) and SCGd-CNA-NK. The XRD pattern of SCGd-CNA confirms that the diffraction peaks are indexed to the perovskite structure of $SrCeO_3$. The XRD angles at 20.75, 29.48, 42.18 and 61.13° belong to the (110), (112), (220) and (224) crystal planes of $SrCeO_3$, respectively. The presence of NaCl and KCl in the SCGd-CNA-NK composite electrolyte was detected, which suggests that no reactions between $SrCe_{0.9}Gd_{0.1}O_{3-\alpha}$ and NaCl/KCl took place [20].

The micrographics of SCGd-CNA and SCGd-CNA-NK are displayed in Fig. 2. Fig. 2(a,b) shows the external and cross-sectional micrographics of SCGd-CNA (1500 °C) which has a dense and crack-free microstructure with a few closed pores after being calcined at 1500 °C for 5 h [11–15]. In

comparison to SCGd-CNA of Fig. 2(a,b), the average grain sizes of SCGd-CNA-NK of Fig. 2(c,d) is uniform and smaller than in previous reports [10,20].

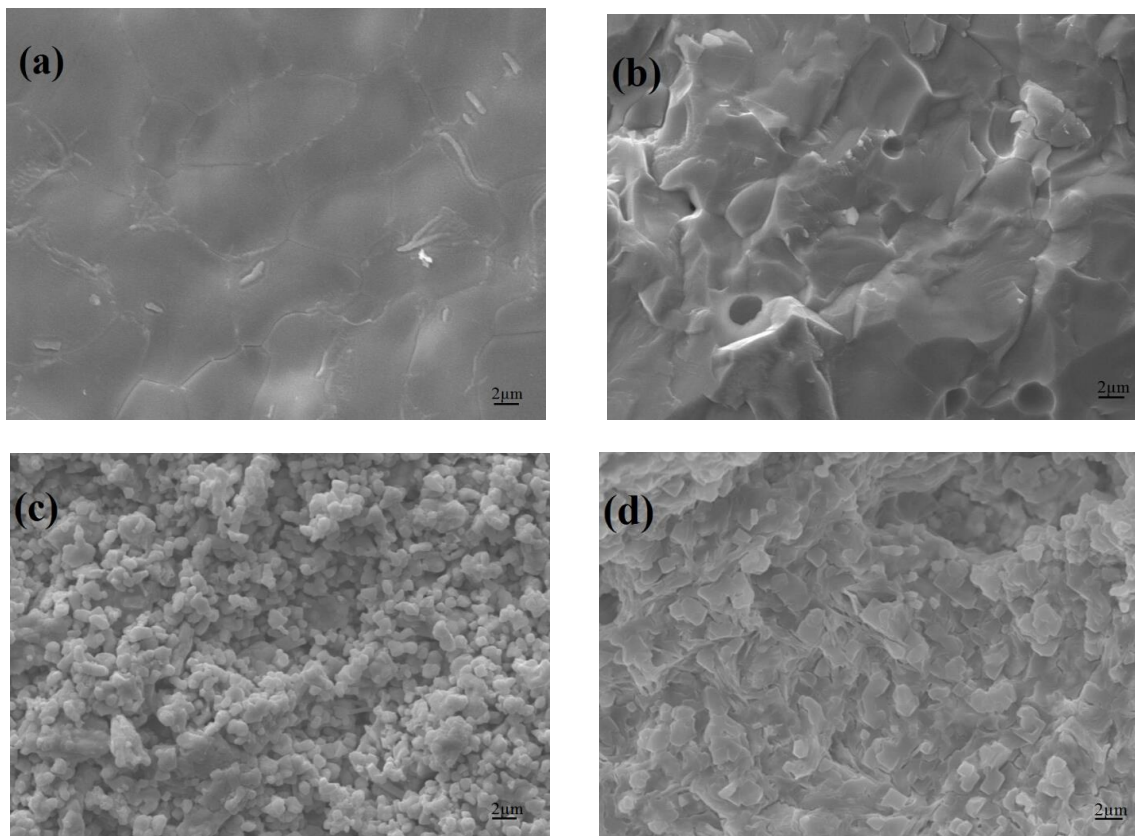


Figure 2. The SEM images of external and cross-sectional surface for SCGd-CNA (a,b) and SCGd-CNA-NK (c,d) samples.

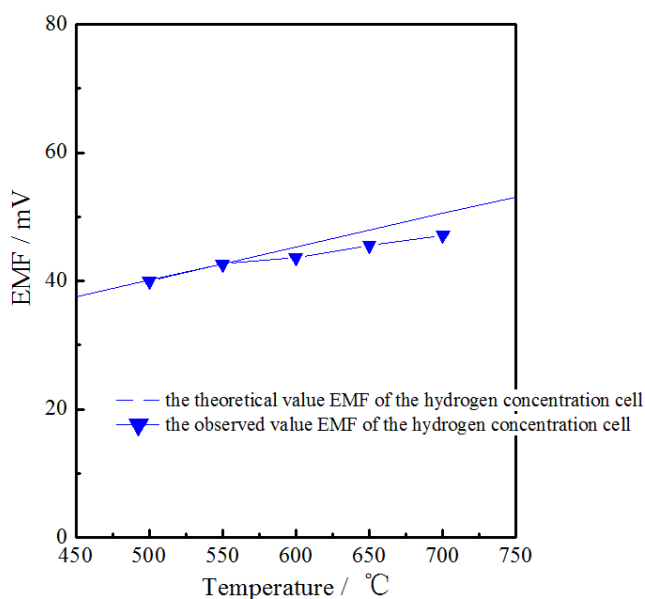


Figure 3. EMFs of hydrogen concentration cell (cell A) of SCGd-CNA. The operating temperatures are between 500 and 700 °C.

This can be attributed to the CNA method which can obtain a nano powder with high specific surface area. As seen in Fig. 2(c,d), NaCl/KCl inorganic salt is linked to SrCe_{0.9}Gd_{0.1}O_{3-α} (1100 °C) particles which uniformly act as the SrCe_{0.9}Gd_{0.1}O_{3-α} particle binder after sintering at 750 °C for 1 h [1–8].

In hydrogen-containing atmospheres, the hydrogen concentration cell was established as follows.

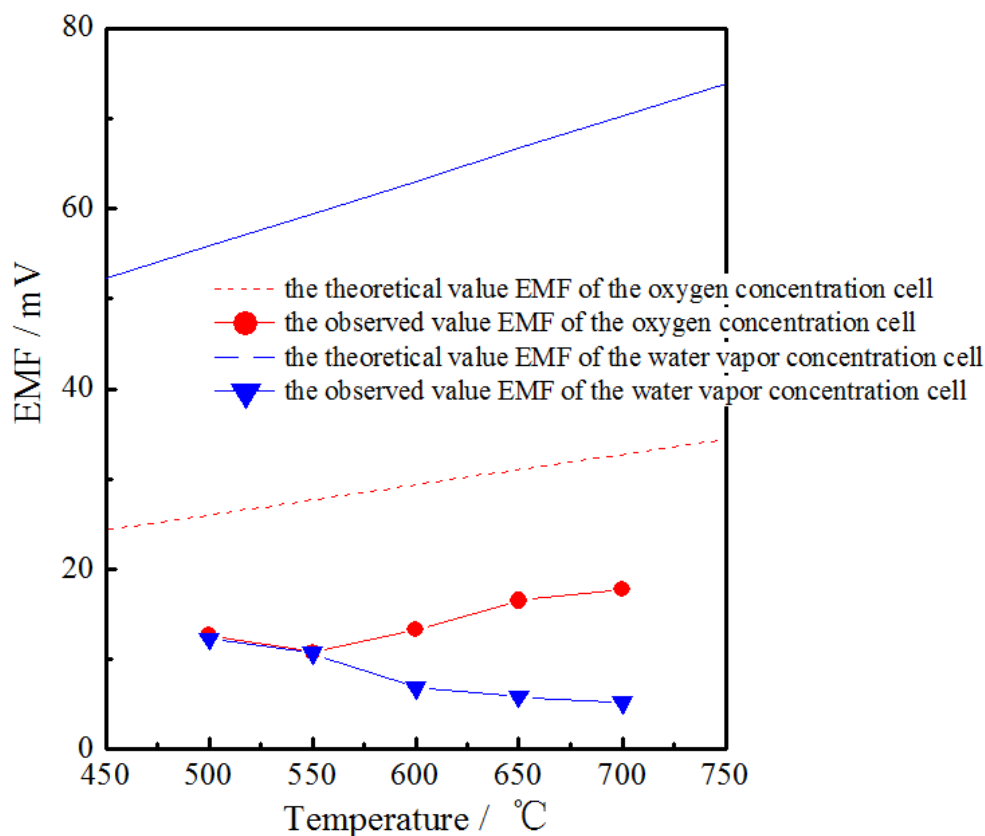
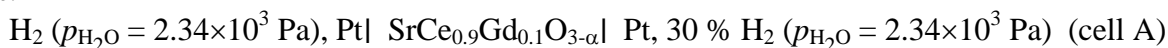
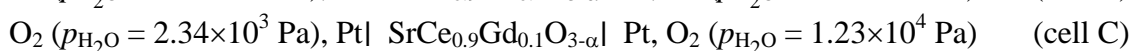
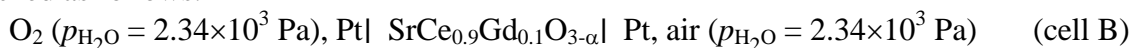


Figure 4. EMFs of oxygen concentration cell (cell B) and EMFs of water vapor concentration cell (cell C) of SCGd-CNA. The operating temperatures are between 500 and 700 °C.

The transport numbers of total ions ($t_{\text{ion}} = t_{\text{H}} + t_{\text{O}} = \text{EMF}_{\text{obs}} / \text{EMF}_{\text{cal}}$) at 500–700 °C were obtained by using a hydrogen concentration cell (cell A). As shown in Fig. 3, the transport numbers of total ions ($t_{\text{ion}} = 0.93\text{--}1.00$) at 500–700 °C are very close to the theoretical value electromotive forces, EMF_{cal} ($\text{EMF}_{\text{cal}} = \frac{RT}{2F} \ln [p_{\text{H}_2 (A)} / p_{\text{H}_2 (B)}]$), of the hydrogen concentration cell. This result indicates that the ionic conduction of SrCe_{0.9}Gd_{0.1}O_{3-α} is good in hydrogen containing atmospheres [21].

In oxygen-containing atmospheres, water vapor and oxygen concentration cells were established as follows.



The transport numbers of total ions ($t_{\text{ion}} = t_{\text{H}} + t_{\text{O}} = \text{EMF}_{\text{obs}} / \text{EMF}_{\text{cal}}$) and proton ions at 500–700 °C were obtained by using an oxygen concentration cell (cell B) and a water vapor concentration cell (cell C), respectively. As shown in Fig. 4, the transport numbers of total ions (t_{ion}) and proton ions (t_{H}) are calculated to be 0.39–0.54 and 0.07–0.21 at 500–700 °C, respectively. The results indicate that there is a certain degree of oxide ionic and protonic conduction in oxygen-containing atmospheres [21].

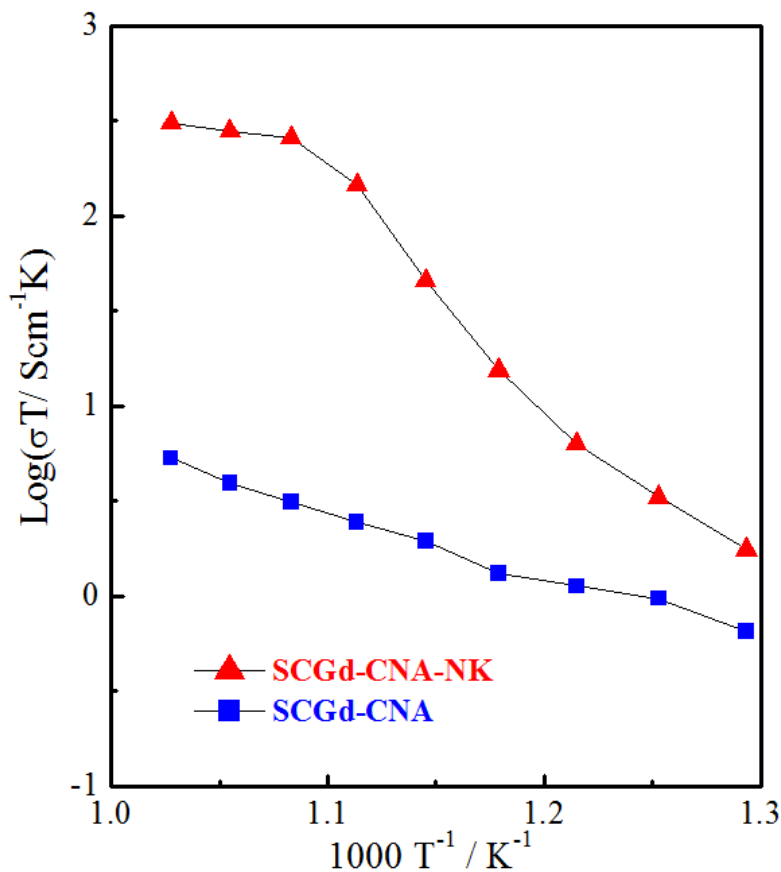


Figure 5. The plots of $\log(\sigma T) \sim 1000 T^{-1}$ in dehumidified air of SCGd-CNA and SCGd-CNA-NK between 500 and 700 °C.

The conductivity–temperature plots of SCGd-CNA and SCGd-CNA-NK in dehumidified air at 500–700 °C are shown in Fig. 5. The conductivities of SCGd-CNA-NK are much higher than SCGd-CNA below the melting point of the NaCl/KCl chlorides. For example, $5.2 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ for SCGd-CNA-NK and $2.2 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ for SCGd-CNA at 600 °C, respectively. It is revealed that adding 20 wt% amount of NaCl/KCl chlorides could promote the ionic conduction velocity, as confirmed in our earlier study [20]. Meanwhile, the $\log(\sigma T) \sim 1000 T^{-1}$ slope of SCGd-CNA-NK becomes smaller above the melting point (650 °C) of the NaCl/KCl chlorides. This shows that SCGd-CNA-NK has low activation energy above 650 °C. The SCGd-CNA-NK contains a $\text{SrCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\alpha}$ perovskite phase and a NaCl/KCl inorganic salt phase. The molten NaCl/KCl phase caused a high conduction region between the perovskite phase and the inorganic salt phase [9].

Two single cells of SCGd-CNA and SCGd-CNA-NK were tested at 700 °C, as shown in Fig. 6. The open circuit voltage of SCGd-CNA-NK is 1.05 V, as shown in Fig. 6(b).

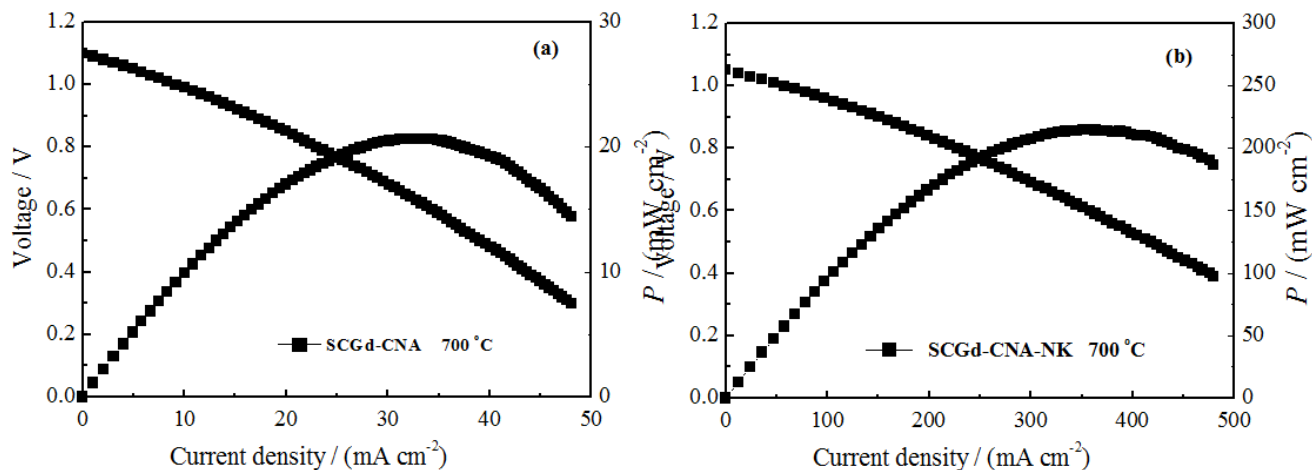


Figure 6. *I-V* and *I-P* curves of the H₂/O₂ fuel cells using SCGd-CNA (a) and SCGd-CNA-NK (b) as electrolytes at 700 °C.

This indicates that the introduction of NaCl/KCl melts to fill in the pores above 650 °C [7-9]. The best performance of SCGd-CNA-NK is 215 mW·cm⁻², which is much higher than maximum power density of SCGd-CNA with 20.7 mW·cm⁻² at 700 °C in Fig. 6(a). The enhanced power density of the SCGd-CNA-NK composite electrolyte is due to the molten NaCl/KCl phase and the interfaces between the SrCe_{0.9}Gd_{0.1}O_{3-α} particles and the inorganic salt phase.

4. CONCLUSIONS

In this work, a novel SrCe_{0.9}Gd_{0.1}O_{3-α} electrolyte was successfully prepared by a citric-nitrate auto-combustion method at 1100 °C for the first time. The XRD results have shown that no reactions between SrCe_{0.9}Gd_{0.1}O_{3-α} and NaCl/KCl took place. The hydrogen concentration cell result indicates that the ionic conduction of the SrCe_{0.9}Gd_{0.1}O_{3-α} is good in hydrogen-containing atmospheres. The water vapor and oxygen concentration cells results exhibit that there is a certain degree of oxide ionic and protonic conduction in oxygen-containing atmospheres. The highest conductivity of SCGd-CNA-NK is 0.32 S·cm⁻¹ in dehumidified air at 700 °C, which is higher than that of single SrCe_{0.9}Gd_{0.1}O_{3-α} material. The optimum performance of SCGd-CNA-NK composite electrolyte is generated with a maximum power density of 215 mW·cm⁻² at 700 °C, which is also higher than that of single SrCe_{0.9}Gd_{0.1}O_{3-α} material.

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