Short communication

Electrochemical performance of a solid oxide fuel cell based on $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ electrolyte synthesized by a polymer assisted combustion method

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Abstract

A polyvinyl alcohol assisted combustion synthesis method was used to prepare $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) powders for an intermediate temperature solid oxide fuel cell (IT-SOFC). The XRD results showed that this combustion synthesis route could yield phase-pure SDC powders at a relatively low calcination temperature. A thin SDC electrolyte film with thickness control was produced by a dry pressing method at a lower sintering temperature of 1250 °C. With $Sm_{0.5}Sr_{0.5}Co_3$-SDC as the composite cathode, a single cell based on this thin SDC electrolyte was tested from 550 to 650 °C. The maximum power density of 936 mW cm^{-2} was achieved at 650 °C using humidified hydrogen as the fuel and stationary air as the oxidant.
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1. Introduction

It is generally desirable to operate solid oxide fuel cells (SOFCs) at a low temperature to reduce material costs, and also to avoid the interaction and interdiffusion between cell components [1]. However, a decrease in operating temperature below 700 °C poses a major challenge, since the electrolyte material must have a high ionic conductivity at lower temperatures [2,3]. Ceria based materials and thin films can meet the demand for the lower temperature SOFC application, and therefore, are generally used as the electrolyte materials in intermediate temperature solid oxide fuel cells (IT-SOFCs) [4,5]. In recent years, the development of a soft chemical synthesis routes to improve the properties of as-prepared powders has accelerates progress with the powder synthesis methods. Among these methods, the combustion synthesis method has many merits in the synthesis of the doped compound powders, which can produce nanopowders with a high surface area, a homogeneous structure and with fewer impurities in a short time and at a lower temperature [6,7].

Recently, a polyvinyl alcohol (PVA) assisted combustion synthesis method has been developed to prepare $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) powders in our laboratory [8]. This kind of synthesis route shows many advantages in the preparation of the doped compound powders, in which the dopants incorporate into the lattice by combustion and at a lower temperature for pure phase formation and produced a loose SDC powder. The aim of this work was to investigate the electrochemical performance of a solid oxide fuel cell based on $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) electrolyte obtained by PVA combustion synthesis method.

2. Experimental

2.1. Materials

Commercial NiO was used as one of the components of the anode. The SDC powders used in the anode, electrolyte and cathode were prepared by the PVA combustion method. Details of this synthesis process are shown in our previous paper [8]. $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) cathode powder was obtained by glycine combustion method [9].

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2.2. Cell preparation

The anode supported single cell consisted of NiO-SDC/SDC/SSC - SDC. The anode substrate was produced by uniaxial pressing. Thereafter, the SDC thin film was prepared by a dry pressing method and was co-fired at 1250 °C for 5 h. The electrolyte film thickness was controlled with the amount of SDC powder. The subsequent layer of the SSC-SDC composite cathode was screen printed onto the electrolyte, and then was sintered at 1000 °C. The effective area of the cell was 0.25 cm².

2.3. Characterization

X-ray powder diffraction (XRD) was used for phase analysis and crystal size calculations. The XRD pattern were recorded with a scanning rate of 0.05° 2θ min^{-1} in the ranges 10–80° on a Philips X'Pert Pro Super Diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The crystal size was calculated by the Scherrer equation using the XRD data from the (1 1 1), (3 1 1), (2 2 2) peaks. Fourier transform infrared (FTIR) spectra in the 4000–400 cm^{-1} range were measured using an EQUINOX55 FTIR spectrometer (Bruker). The tap density of the powders was measured by filling a known amount of powder samples into a graduated cylinder with a capacity of 10 mL and tapping it until a constant volume was obtained. The ratio between the weight and volume occupied by the powder gave the tap density [10].

The current and voltage data were collected using digital multi-meters (GDM-8145). AC impedance spectra measurements were carried out on single cell under open circuit conditions using an electrochemical impedance spectrum analyzer (CHI 600A, Chenhua Inc., Shanghai) in the frequency range of 0.1–100 kHz.

3. Results and discussion

3.1. XRD pattern

In our previous studies, the influence of the PVA content on the properties of the SDC powder had been investigated. In this paper, P:C (the ratio of PVA to cations) was set at 1.0, which is an optimal proportion for achieving powder with excellent properties. Fig. 1 shows the XRD patterns for the powders synthesized at different temperatures when the stoichiometric proportion of the PVA content was added to the nitrate solution. All the peaks were well indexed as a fcc structure of fluorite. The XRD measurements results showed that the phase formation temperature of SDC powder was very low, and a calcination temperature of 350 °C was sufficient. Low synthesis temperature could be attributed to the assistance of PVA, which was an efficient fuel for the combustion synthesis reaction. It is well known that a high calcination temperature leads to an increase of crystal size. SDC powder with a crystal size of 49.8 nm was obtained when the calcination temperature was 750 °C, while a low calcination temperature obviously produced powder with a small crystal size, which was only 23.4 nm.
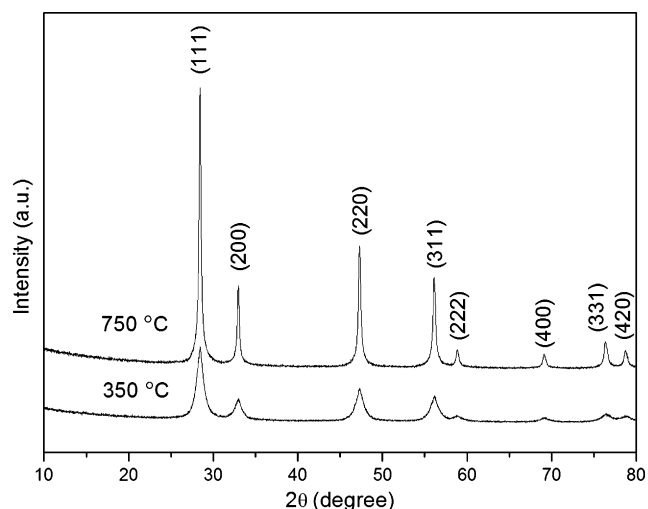

Fig. 1. XRD patterns of the powders synthesized at different temperatures when stoichiometric PVA was used.

3.2. FTIR measurements

FTIR measurements were used to obtain the information on the presence of residual organics and hydroxyl ions in the as-prepared SDC samples. The FTIR spectra (Fig. 2) of the samples synthesized at different temperatures shows a broad band at 3450 cm^{-1}, which results from the surface adsorbed water. In addition, the band at 1630 cm^{-1} relates to the scissor bending of H–O–H. The band for Ce–O can be observed below 770 cm^{-1}. A strong band at 1384 cm^{-1} in the samples sintered at 350 °C might belong to the physical adsorption of CO_2 or be caused by residual NO_3^- [11]. The intensity of this band decreased with increasing temperature. The investigation done by Mokkelbost et al. [12] showed that small amounts of carbonate species in the region 1200–1700 cm^{-1} were left even after calcinations at 1000 °C for 12 h. Therefore, although a low synthesis temperature of 350 °C was sufficient for the phase formation of SDC samples in our experiments, SDC powder with higher purity was obtained by calcining the samples above 750 °C.
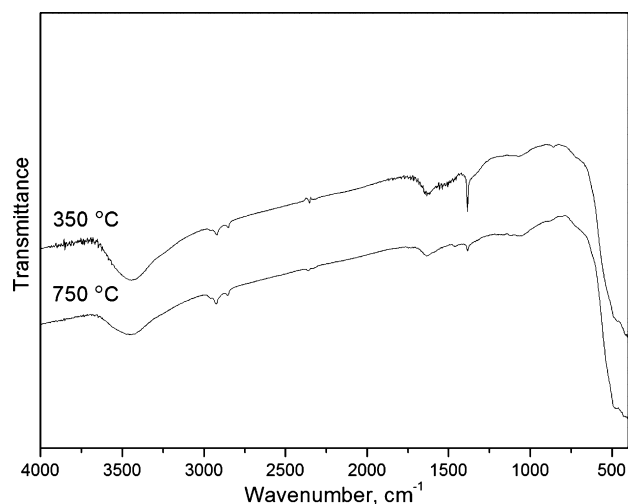

Fig. 2. FTIR spectra of the samples obtained at different calcination temperatures when stoichiometric PVA was used.
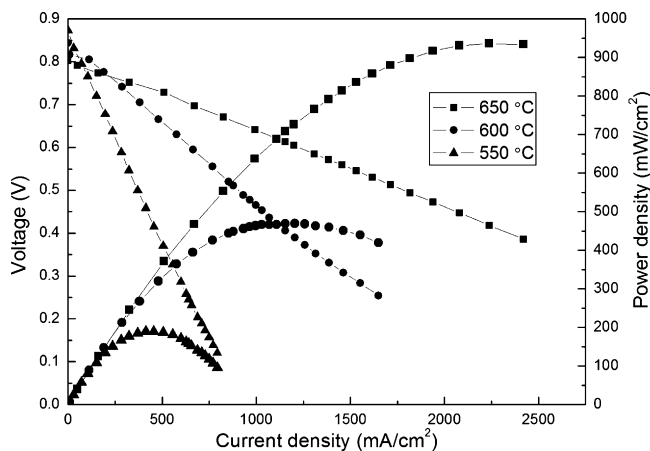
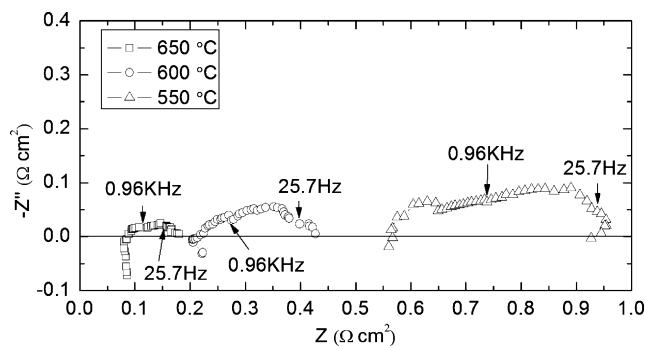Fig. 3. The *I–V* and *I–P* characteristics for the single cell consisting of NiO-SDC/SDC/SSC-SDC.

Fig. 4. Impedance spectra of a single cell tested at 650, 600 and 550 °C.

Fig. 5. Arrhenius plots of $\ln(\sigma T)$ vs. $1/T$ for SDC film and bulk materials.

3.3. Single cell performance

To test the electrochemical performance of a cell made from the SDC powders prepared by the PVA-induced combustion synthesis method, a single cell consisting of a NiO-SDC anode, a SDC thin electrolyte and a $Sm_{0.5}Sr_{0.5}CoO_3$-SDC composite cathode was prepared. All the SDC powders used in the two electrodes and the electrolyte were prepared by this combustion method. In the experiments, humidified hydrogen (3% H_2O) was used as the fuel and stationary air as the oxidant. Shown in Fig. 3 are the cell voltages and power densities as a function of current density at different operating temperatures. A power density of 936 mW cm^{-2} was obtained at 650 °C, showing good cell performance and achieved using the thin electrolyte film prepared from the as-prepared SDC powders. In addition, the *I–V* plots were close to linear at various operating temperatures, illustrating that the Ni-SDC anode support has enough porosity and the SSC - SDC composite cathode possesses good catalytic activity. The maximum power density of 936 mW cm^{-2} was higher than the value of 869 mW cm^{-2} reported by Ai et al. [13] using a single cell consisting of Ni-SDC/SDC/$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF). Although the result was encouraging, unfortunately, the cell showed an obvious degradation in electrochemical performance at low operating temperatures. It is well known that the interfacial resistance, mainly coming from the cathode resistance, plays an important role in the cell performance, especially at lower temperatures. Therefore, the cell performance can be further improved by using other kinds of cathode with a high catalytic activity (such as BSCF).

Fig. 4 demonstrates the impedance spectra of a single cell under open circuit conditions at between 550 and 650 °C. The ohmic resistance of the electrolyte and interfacial resistance can be achieved from the intercept with the real axis at high frequency and the difference between the low frequency and high frequency intercepts with the real axis, respectively. From Fig. 5, it is seen that the electrolyte resistance of 0.089 Ω cm^2 at 650 °C is close to that of the interfacial resistance, which is only 0.095 Ω cm^2. The interfacial resistance of 0.095, 0.20, 0.38 Ω cm^2 is close to the minimum value reported by the Xia et
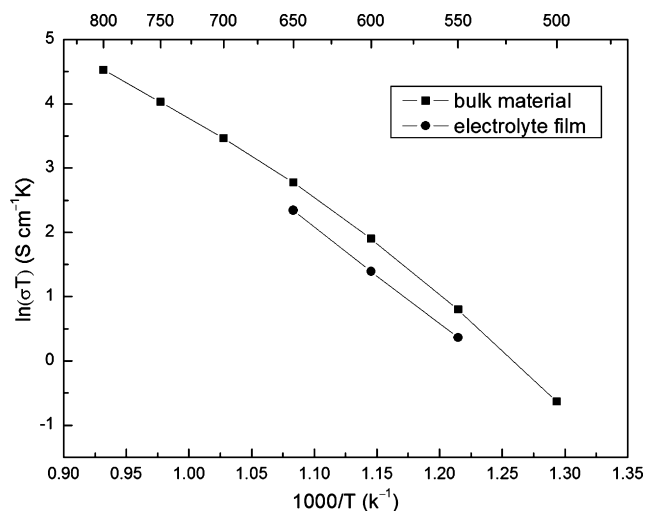
al. [9]. Low interfacial resistance composed of anode and cathode resistance was one of the factors in achieving excellent cell power densities in our experiments.

3.4. SDC film with thickness control

It was reported that extremely loose SDC powders with a low bulk density made it possible to prepare a very thin SDC film by the dry pressing process [14]. In our experiments, using this low temperature synthesis method, very loose SDC powders were produced. Therefore, relatively thin films could be obtained in this study. Table 1 summarizes the tap densities of the SDC powder when different PVA contents were used. When P:C was set to 0.5, the solution was not ignited due to the deficiency in PVA fuel. While, when a stoichiometric proportion of the PVA content was applied in the combustion synthesis, low tap densities were produced. However, with further increase in the PVA content, no significantly low tap densities were obtained. In addition, high PVA content could also lead to more residual carbon. Therefore,

Table 1
Tap densities of SDC powder with different P:C ratios

P:C	0.5	0.8	1.0	1.2	1.5
Tap densities (g cm^{-3})	0.454	0.144	0.062	0.059	0.053

the powder used for the electrolyte thin film was prepared using a stoichiometric proportion of the PVA content.

The thickness of the electrolyte film was controlled by the quantities of the SDC powders. The value of the film thickness was calculated by Eq. (1):

$$d = \frac{M}{\rho S} \tag{1}$$

where M is the quantities of the electrolyte powder, S is the area of anode substrate ($S = 1/4\pi D^2$, D is the diameter of anode, which is 15 mm) and ρ is the theoretical density of SDC powder (7.22 g cm^{-2}). According to Eq. (1), the achievement of a film with a thickness of 10 μm requires 0.0127 g cm^{-2} SDC powders. Since the powders obtained using this PVA combustion method were loose, therefore, a very thin film could be prepared by the dry pressing method.

3.5. Electrical properties

Electrical conductivity of the SDC electrolyte film sintered at 1250 °C for 5 h was obtained from the data in the impedance spectra (Fig. 4). For comparison, the conductivity of a bulk SDC made from dry-pressing powder and sintered at 1300 °C was also measured. Fig. 5 illustrates the Arrhenius plots of ln(σT) versus $1/T$ for the SDC bulk and thin samples. Our prior experimental results showed that sintering temperature of 1300 °C was favorable for the formation of excellent conductivity and density of bulk materials [8]. Higher sintering temperature (such as 1400 °C) had a bad effect on the achievement of high density and conductivity. This result also showed that the as-prepared SDC powder had a high sintering activity by the PVA combustion method. As shown in Fig. 3, the activation energy of the conductivity for the SDC film and bulk material had almost the same values of 1.28 eV. However, the conductivity of the SDC film was lower than that of the bulk material. The conductivities of the film were 0.011, 0.0046 and 0.0017 S cm^{-1}, while the conductivities of bulk materials were 0.017, 0.0077 and 0.0027 S cm^{-1} at 650, 600 and 550 °C. This was caused by the difference in porosity and electrode processing in the film and bulk materials. The difference in electrode processing was the main reason. Under the measurement condition of the SDC bulk material, Ag was used as an electrode on both sides of the SDC pellets. However, the two electrodes were different, one was a SSC-SDC, and the other was a Ni-SDC. Secondly, when considering the porosity, the porosity of film may have played an important role in the lower conductivities, which could be improved by optimizing and/or modifying the microstructure of the SDC electrolyte film.

4. Conclusions

Samarium doped Ceria (Ce$_{0.8}$Sm$_{0.2}$O$_{2-\delta}$) powders and thin film materials have been successfully prepared. Ce$_{0.8}$Sm$_{0.2}$O$_{2-\delta}$ (SDC) powders were synthesized at a lower temperature by the polyvinyl alcohol (PVA) assisted combustion method. This low temperature synthesis route for the SDC powder allowed thin films to be made for solid oxide fuel cell applications. In our experiments, a thin SDC electrolyte film with a thickness of 10 μm was prepared on a porous NiO-SDC anode substrate by the dry pressing method. A single cell consisting of NiO-SDC/SDC/SSC-SDC was tested with humidified hydrogen as the fuel and stationary air as the oxidant. A power density of 936 mW cm^{-2} was obtained at 650 °C, showing that good cell performance can be achieved using the thin electrolyte film prepared by our SDC powders. The excellent electrochemical performance could be attributed to the thin electrolyte film with a reduced ohmic resistance and low interfacial resistance.

Acknowledgment

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