

The effect of Pr co-dopant on the performance of solid oxide fuel cells with Sm-doped ceria electrolyte

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Abstract

Samaria-doped ceria $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{1.95}$ (SDC) and samaria and praseodymium co-doped ceria $\text{Ce}_{0.9}\text{Sm}_{0.08}\text{Pr}_{0.02}\text{O}_{1.95}$ (SPDC) powders were synthesized by glycine nitrate process. SDC and SPDC electrolytes were made using the corresponding powders to press pellets and sinter them in air at 1400 °C. SEM and open porosity measurement showed the electrolytes were not dense and SPDC was more porous than SDC. Raman spectra indicated the oxygen vacancy concentration of SPDC was higher than SDC. Solid oxide fuel cells (SOFCs) with SPDC and SDC electrolytes were made and tested. The SOFC with SPDC electrolyte had higher power density but lower open circuit voltage. Impedance measurement was undertaken for the SOFCs at open circuit and the results showed that both the Ohmic and polarization resistances for SPDC electrolyte are smaller than for SDC. It is explained that co-doping Pr in Sm-doped ceria may increase the oxygen ionic conductivity by changing the grain boundary conditions so that more oxygen vacancies may exist and move faster. The electrochemical catalytic activity of Pr may play an important role in decreasing the polarization of electrolyte–electrode interface of the SOFCs.

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1. Introduction

Solid oxide fuel cell (SOFC) has attracted increasing attention due to its high efficiency and low emission as an electrochemical energy conversion device [1]. Yttrium stabilized zirconia (YSZ) has been commonly used as the electrolyte material of SOFCs. YSZ is an oxygen ionic conductor with high oxygen ionic transference number. It is stable in an oxidizing and reducing atmosphere in which SOFCs are operated [2]. However, its conductivity is not high enough at lower temperature and it must work at very high temperature (~1000 °C) to obtain practical conductivity. Some difficulties on material selection and component manufacturing arise in making SOFCs with YSZ electrolyte because of the extremely high operating temperature. Meanwhile, many interface reactions between different components also appear to decrease the performance and stability of SOFCs. These facts

promote people to search for alternative electrolyte materials with higher ionic conductivity at lower temperature. Alkaline earth- and rare earth elements-doped ceria possess much higher ionic conductivity than YSZ and show good promise in replacing YSZ as the electrolyte materials for SOFCs [3]. However, at low oxygen partial pressures, Ce^{4+} in these doped ceria tends to be reduced to Ce^{3+} and this results in some electronic conductivity. Electronic conduction in electrolyte will decrease the performance of SOFCs because it creates internal Ohmic loss. To make doped ceria applicable as electrolyte material for SOFCs, the electrolytic domain of the electrolyte must be expanded to the oxygen partial pressure range suitable for SOFC operation. The electrolytic domain, also called “the application region of the electrolyte”, is defined as the oxygen partial pressure (P_{O_2}) when semiconduction starts to be the dominating conduction mechanism over the pure ionic conductivity [4]. Maricle et al. [5] reported that by co-doping small quantities of praseodymium in gadolinium-doped ceria $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}$ (GDC) solid solutions, the application region of the electrolyte is shifted by

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two orders of magnitude to lower oxygen partial pressure, and this effect was attributed to the trapping of electrons by the $\text{Pr}^{3+}/\text{Pr}^{4+}$ redox behavior. Huang et al. [6] reported similar results. Meanwhile, others showed the bulk conductivity of GDC could be rarely affected by Pr dopant and they argued that at the prevailing Po_2 the Pr ion would only exist as Pr^{3+} , and the observed effect on the electrolytic domain had been likely to be due to changes in the grain boundary behaviors [7,8]. Lübke and Wiemhöfer [9] investigated Pr-doped GDC in detail and found that the p-type conductivity of the material can be increased by co-doping Pr and the ionic conductivity may increase because of the decrease of grain boundary electrical resistance. Kharton and coworkers [10,11] reported that even though the doping of Pr in GDC may not affect the ionic conductivity obviously, the electrode–electrolyte polarization is likely to be reduced because of Pr's electrochemical catalytic property. Nevertheless, it seems one thing is certain: the performance of SOFCs with doped ceria electrolyte can be improved by Pr co-doping.

Some previous research [12,13] indicated that CeO_2 doped with 10 mol.% Sm_2O_3 ($\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$) gives the highest conductivity among the doped ceria. Our further research showed that CeO_2 doped with 5 mol.% Sm_2O_3 ($\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{1.95}$) is even better [14]. In this paper, we report the performance of SOFCs with Sm and Pr co-doped ceria electrolyte $\text{Ce}_{0.9}\text{Sm}_{0.08}\text{Pr}_{0.02}\text{O}_{1.95}$ (SPDC). The results are compared with SOFCs with Sm-doped ceria electrolyte $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{1.95}$ (SDC). The data and mechanisms are analyzed and discussed.

2. Experiment

Samaria-doped ceria with and without Pr co-dopant was prepared by glycine-nitrate process [15]. Reagent-grade metal nitrates $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and glycine (bought from Beijing Chemical Plant) were used in the experiments. Oxides Sm_2O_3 and Pr_6O_{11} (Purity > 99.9%, bought from Shanghai Chemical Plant) were completely dissolved in HNO_3 to obtain corresponding nitrates. Then, Ce, Pr, Sm nitrates and glycine were dissolved and mixed in deionized water according to the proposed metal mole ratio in $\text{Ce}_{0.9}\text{Sm}_{0.08}\text{Pr}_{0.02}\text{O}_{1.95}$ and $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{1.95}$, respectively. The solutions were heated on a hot plate until they auto-ignite, producing metal-oxide “ash”. The $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{1.95}$ and $\text{Ce}_{0.9}\text{Sm}_{0.08}\text{Pr}_{0.02}\text{O}_{1.95}$ “ashes” were ground and pressed at a pressure of about 200 MPa to obtain green compact pellets with thickness of ~ 0.5 mm and diameter of ~ 13.6 mm. Then the pellets were sintered in air at 1400°C for 10 h.

The open porosity of the electrolyte was simply measured based on Archimedes principle. The pellet to be measured was weighed first to get a weight datum of W_0 . Then, the pellet was emerged and boiled in water for ~ 10 min and then was cooled down to room temperature. The pellet was taken out of the water and the surface was wiped carefully to remove the water on the surface. Then the pellet was weighed to

get a weight datum of W_1 . The volume V_0 of the pellet can be calculated by measuring the diameter and thickness. The open porosity is $(W_1 - W_0)/\rho V_0$ where ρ is the density of water.

The mixture of NiO and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ by the weight ratio of 1:1 was used as anode. NiO and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ were made by similar glycine-nitrate process as mentioned above. The obtained NiO and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ powders were weighed by a weight ratio of 1:1 and mixed completely by grinding the mixture with glycerine to get a slurry with fine particle distribution. The anode slurry was applied to one side of each electrolyte pellet, dried in open air and then sintered in air at 1200°C for 4 h.

The cathode $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ (LSCF) with 50 wt.% of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ was made in a similar way by which the anode was made. In making LSCF, glycine-nitrate process was used again and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used as the original materials. LSCF and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ were mixed with glycerine to obtain a well-distributed slurry. The cathode slurry was applied on the other side of each electrolyte pellet with anode and sintered in air at 950°C for 4 h.

Silver grid was painted on each electrode surface to be as current collectors. Two silver leading wires were contacted to the current collectors of cathode and anode, respectively. The pellet was attached to one end of an alumina tube with the anode inside by using the mentioned silver paste for sealing.

The system of measuring the properties of SOFC was the same as described before [16]. Hydrogen produced by CH2500 hydrogen generator (HP) was fed into the alumina tube as fuel with a flow rate of 200 mL min^{-1} , while oxygen in the air was used as oxidant.

Raman spectra were obtained by using a JY-HR800 spectrometer with a He–Ne ion laser. The excitation wave-number is 632.8 nm . The resolution is 1 cm^{-1} . Microstructures of the samples were examined in a JEOL JSM-5500VL scanning electron microscope (SEM) on the broken sections of the specimens. The impedance measurements were taken with a Solatron 1260 impedance analyzer. The frequency range was $0.2\text{--}3.13 \times 10^6 \text{ Hz}$. The fuel cell test data were collected using SI 1287 Electrochemical Interface.

3. Results and discussions

3.1. Microstructure of the electrolyte

Fig. 1 shows the SEM picture on the section of the Pr-doped electrolyte $\text{Ce}_{0.9}\text{Sm}_{0.08}\text{Pr}_{0.02}\text{O}_{1.95}$ (SPDC) (a), and the picture of the electrolyte without Pr doping $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{1.95}$ (GDC) (b) is also shown for comparison. It can be seen that SPDC is more porous with more grain boundaries and particle surfaces caused by the pores. This is confirmed by the open porosity measurement giving the rough results of 2.3% for SPDC and 1.7% for SDC. Some previous studies

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