Study on SrNb-Oxide Cathode Material for Low-temperature Solid Oxide Fuel Cell

Dan Zheng¹, ², *, Qiong He¹, b, *, Ji Gao², c and Baoyuan Wang², d

¹Faculty of Electronic and Engineering, WuHan Vocational College of Software Engineering, Wuhan 430205, China.
²Faculty of Physics & Electronic Technology, Hubei University, Wuhan 430062, China.

a 25182718@qq.com, *, b Corresponding author email: 20040422@hubu.edu.cn,
c 1636588376@qq.com, d 7833679@qq.com

Abstract. In this paper, a novel semiconductor-ionic SrNb oxide (SNO)-Ce0.8Sm0.2O2-δ (SDC) composite has been prepared, characterized and developed as a membrane, which is sandwiched between two layers of Ni-foam coated with Ni0.8Co0.15Al0.05LiO2-δ (NCAL) to construct single layer fuel cell (SLFC, the branch of solid oxide fuel cell). Such a device presented an open circuit voltage (OCV) of 1.03V and maximum power density of 630 mW/cm² at 550 ℃ when the mass ratio of SNO to SDC is 1:9. The feasible study of solid oxide in fuel cells will provide experimental and theoretical support for the development of SLFC technology.

Key words: Solid Oxide Fuel Cells; Single Layer Fuel Cells; Samarium Coped Ceria; Mixed Ionic-electronic Conducting Membrane; Electrochemical performance.

1. Introduction

Fuel cell can directly convert the chemical energy of fuel into electrical power without fiercely burning. It is considered as the fourth generation of new energy technology behind hydraulic power, firepower and nuclear energy. The main by-products of fuel cell are water and CO₂, thus the fuel cell was a green and sustainable energy conversion equipment. In general, the cell configuration was consisted of anode, electrolyte and cathode three main components. Among them, the electrolyte was the vital component to determine the variety of fuel cell. Solid oxide fuel cell (SOFC) as a kind of fuel energy conversion device was composed of solid electrolyte, and exhibited unique advantages including high energy conversion efficiency (up to 50% - 80%), clean energy, flexible fuel selection and low noise. Thus SOFC is considered as the most promising energy conversion technology [1].

In SOFC, electrolyte is an doped metal oxide with ionic conduction and was used to transport ions to complete cell reaction. However, the traditional SOFC electrolyte materials need high operating temperature (800-1000°C) to achieve ideal conductivity. High temperature operation will aggravate the problem of chemical and thermodynamic mismatching among various components of the cell, which seriously limits the selection range of cell components, resulting in higher device manufacturing costs and limiting its commercial procedure. Therefore, it is urgent to develop economical SOFC to work at intermediate-low temperature range [2]. In order to break through the electrolyte limiting and reduce the
operating temperature, several research groups began to study a new type of single layer fuel cell (SLFC). Such kinds of cell has unique cell configuration, namely it has abandoned the conventional three-layer structure and just consisted of one core layer, which is composed of multi-functional nanocomposites and possesses the mixed electron-ion conduction [3]. The operating temperature of SLFC can be reduced to 300 °C, and its performance is comparable to or even higher than that of the traditional three component fuel cell. Moreover, the fabrication process is simple and the cost is low. Therefore, it can solve the critical issues of traditional fuel cell, such as serious interfacial polarization loss, complex fabrication process and high cost.

Doped ceria (SDC) is considered as one of the most commercial promising electrolyte materials for SOFC. However, the disadvantages of such materials are also obvious. For example, Shen et al. once found that the doped ceria is easy to be partial reduction by hydrogen in fuel cells [4]. As a result, the open circuit voltage (OCV) and maximum output power (P_{max}) of the assembled fuel cell decrease significantly as the working time extending. That is to say when tetravalent cerium cation in SDC is reduced to trivalence by hydrogen, SDC electrolyte will become a mixed ion-electron conductor, which will lead to the degradation of cell performance. However, Zhang et al. found that the SLFC based on SCDC (ionic conductor) – NCAL (semiconductor) composite exhibited superior cell performance and don’t cause the loss of OCV and P_{max}, even better than that of the pure SCDC cell, although the function layer simultaneously have the ion and electron conduction [5]. Li et al. fabricated the SLFC from SCNT(SrCo_{0.8}Nb_{0.1}Ta_{0.1}O_{3-δ})-SCDC(Ce_{0.8}Sm_{0.05}Ca_{0.15}O_{2-δ}) composite, the P_{max} value of the fuel cell is 1.2W/cm^2 and 0.7 W/cm^2 at 450 °C and 500 °C, respectively, and the impedance is very small [6]. This paper also tells us that the ratio of ionic conductor to semiconductor material is critical for the power output of SLFC. According to these researches, we are looking for a kind of mixed semiconductor material and ionic conductor SDC to study their application in SOFC. In this work, we have prepared semiconductor material SrNb oxide (SNO) through sol-gel method and then mixed with ionic conductor SDC to assemble SLFC. The electrochemical performance of SNO-SDC cell have been systematically investigated. We have optimized the cell performance through adjusting the mass ratio of SNO and SDC.

2. Experimental methods

2.1. Preparation of Experimental Materials
The synthesis method of semiconductor SrNb oxide (SNO) is sol-gel method. Nb_{2}O_{5} and Sr(NO_{3})_{2} powder were weighed according to the molar ratio of 0.5:0.5 and mixed all these materials with pure water through stirring. Then, the mixture was added with citric acid and stirred with a glass rod at 80 °C until the solution turned into a transparent gel. The colloidal substance was sintered in muffle furnace at 1200 °C for 10 h, then ground for 30 min. Finally, it was suffered from another calcination in muffle furnace at 1200 °C for 10 h, and the obtained milk white powder of SnO was bagged for standby.

The ionic conductor material SDC is synthesized by one-step co-precipitation method. The Ce(NO_{3})_{3}·6H_{2}O and Sm(NO_{3})_{3}·6H_{2}O was weighed on the molar ratio of 0.8:0.2 and completely dissolved in pure water to form 1M mixed solution through stirring. Then, 1 M ammonium bicarbonate solution was used as precipitant, and it was slowly poured into the above mixed solution drop by drop at the rate of 10 ml / min at a molar ratio of metal ion: CO_{3}^{2-} ion = 1:1.5. The mixed solution was continuously stirred until white precipitate was completely formed. After standing for a period of time, obvious stratification can be seen, in which the upper layer is colorless transparent solution and the lower layer is white suspension. Then the precipitate was filtered and cleaned for several times with suction filtration equipment and three pieces of filter paper. The precursor was dried in a drying oven at 120 °C for 24 hours. Then, the precursor was sintered in a muffle furnace at 800 °C for 4 h. Finally, the obtained material was fully ground into light yellow powder.

SNO-SDC composite is prepared by solid mixing method. In order to optimize the performance of SLFC, SNO and SDC powders were mixed with different mass ratios (1:9, 3:7, 5:5, 7:3) and ground for 15 min to obtain four different composites. In addition, the pure SDC powder was also used as intermediate layer material to fabricate SLFC for comparison.
Black powder Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$Li$_{2-\delta}$O$_2$ (NCAL) as industrial production was purchased from Tianjin Barmo Technology Co., Ltd, and was used as received without further purification in this work.

2.2. Materials Characterization
The X-ray diffraction (XRD) pattern of the experimental material samples was obtained by the advanced X-ray diffractometer of Bruke D8 in Germany. Cu Ka with incident wavelength of 1.54060 Å was used as the radiation source. The material morphology was measured by JSM7100 field emission scanning electron microscope (FE-SEM), which was operated at 15 kV accelerated voltage.

2.3. Fuel Cell Fabrication and Testing
The proper amount of black powder NCAL were mixed with terpineol and fully ground with mortar to obtain uniform NCAL slurry. The slurry is brushed evenly on one side of the nickel foam. The NCAL thickness is about $100 \, \mu m$ and it is dried at 85 °C to finish the Ni-NCAL layer preparation.

The cell is prepared by dry pressing method. The specific process is described as follows: Firstly the pressing mold is wiped clearly with anhydrous ethanol paper, Ni-NCAL layer, SNO-SDC composite material (or pure SDC powder) and Ni-NCAL layer are successively put into the mold to form sandwich structure. Then the assembled mold was placed in the powder pressing machine and pressed with 5-10 MPa pressure to obtain a thickness of 1 mm cylindrical single cell with an effective area of 0.64 cm$^2$. The cell have a symmetrical configuration of Ni-NCAL/SNO-SDC/NCAL-Ni. Wherein, the two Ni-NCAL layers were used as collector electrodes, nickel foam provide a support and also was served as a catalyst for the oxidation of fuel cells, the SNO-SDC membrane was worked as multifunctional layer to conduct ion and separate fuel and air.

During the performance testing, the hydrogen and air are continually supplied as fuel and oxidant with a gas flow rate of 80 ml / min and 120 ml/ min, respectively. The current density-power density (I-P) and current density-voltage (I-V) performance of the cells were recorded by the IT8511 program-controlled electronic load of ADEX Electronics Co., Ltd. By adjusting the weight percentage of SNO and SDC, the cell performance was optimized to obtain the optimal ratio. In addition, the low-temperature performance of the assembled cell was evaluated at 550 °C, 525 °C, 500 °C and 475 °C.

The electrochemical impedance spectroscopy (EIS) was recorded by CHI660E electrochemical workstation of Shanghai Chenhua Instrument Co., Ltd. under open circuit voltage condition, and the frequency range of AC signal was 1 MHz to 0.1 Hz.

3. Result and analysis
3.1. X-ray Diffraction Pattern
Fig. 1 shows the XRD patterns of SDC, SNO and SNO-SDC composite (mass ratio of 1:9). Compared with the standard diffraction pattern of SDC (PDF card number: 75-0160), the location and intensity of the diffraction peak are basically consistent with the standard card, indicating the prepared SDC presented cubic fluorite structure and there are no other impurities in the prepared SDC. At the same time, no single phase of Sm2O3 was observed, which indicates that Sm ions have been completely doped into the CeO$_2$ lattice. The XRD pattern of SNO well agreed with the standard PDF number: 77-2431, verifying that the prepared SNO material was perovskite structure. In addition, no diffraction peaks concerning with impurity were detected. The XRD patterns of SNO-SDC composites with mass ratio of 1:9 were indexed to SDC phase, the diffraction peaks of SNO almost can not be detected, which may be due to the low content of SNO in the 10SNO-90SDC composites. However, it can be seen from the figure that the XRD pattern of SNO-SDC composite corresponding to the highest SNO peak has a slight bulge, which further confirms the existence of SNO component. No other impurity peaks was emerged in the SNO-SDC composite, indicating there is no chemical reaction between SDC and SNO.
3.2. Scanning Electron Microscope (SEM) Images
Fig. 2 (a) and (b) are SEM images of SDC samples prepared with ammonium bicarbonate as precipitant. It can be seen from the pictures that the grains of SDC samples are roughly evenly distributed, and the morphology is irregular lamellar structure superimposed to form a layered structure, and its length is in the range of 2-6 μm and width is in the range of 1-2 μm. The structure of SDC samples is loose and porous without obvious agglomeration, which may be caused by the lattice expansion and the increase of pores between grain boundaries after Sm ion doping into the CeO$_2$ lattice [7, 8]. Fig. 2 (c) and (d) are SEM images of SNO samples prepared by sol-gel method. From the diagram, we can see that the samples have regular spherical morphology, and the size of the samples varies from 1 to 5 μm. Fig. 2 (e) and (f) are SEM images of SNO-SDC composite (mass ratio of 1:9), which shows a uniform distribution of two phases, and it can be clearly seen from Fig. 2 (f) that the small SDC particles are attached on SNO spheres in the composite. From the above characteristics, it can be seen that the SNO-SDC composite material satisfies the basic conditions of forming the middle layer of a single component fuel cell, which is conducive to establish continuous charge transport paths for the semiconductor phase (SNO) and the ionic phase (SDC).
3.3. Cell Performance

Fig. 3 shows the current density-voltage (left Y-axis) and current density-power density (right Y-axis) characteristic curves of SNO-SDC cells with different proportions. In order to study the effect of SNO toward cell performance, we have assembled a SLFC from pure SDC as functional layer for comparison.

It can be found that the open circuit voltage (OCV) of pure SDC cell was 1.07 V, and the maximum power density \( P_{\text{max}} \) was 450 mW/cm\(^2\). In addition, it can be seen from the figure that the OCV of the SNO-SDC fuel cell can be maintained at a high level (1.03-1.1 V) with the increase of SNO content until the mass fraction of SNO is 10%. Although there is no obvious change in OCV as the SNO content changed, the \( P_{\text{max}} \) of these fuel cell are significantly improved. The results show that the cell based on 10SNO-90SDC function layer can achieve \( P_{\text{max}} \) of 630 mW/cm\(^2\) and OCV of 1.04 V. However, with the continuous increase of SNO content, the \( P_{\text{max}} \) of the cell began to decrease. When the mass fraction of SNO is 50% or 70%, the OCV is only 0.8-0.9 V and \( P_{\text{max}} \) is only 50-60 mW/cm\(^2\). The reason for this phenomenon is that when the content of SNO is higher than a certain amount, the excessive SNO will bring about overwhelming electronic conductivity to causes serious short circuit problem. Based on the previous reports of Li et al. [6], we can say that a certain balance between the electronic conductivity and the ionic conductivity plays an important role in achieving high performance of the cell.

![Figure 3. The I-V and I-P characteristic of SNO-SDC fuel cell with different compositions at 550 °C](image)

Fig. 4 further shows the curves of open circuit voltage and maximum power density as a function of SNO content. It can be seen from the figure that when 10SNO-90SDC was used as the electrolyte membrane in SLFC, its OCV reaches 1.03 V at 550 °C, which is close to the theoretical voltage value of traditional hydrogen oxygen fuel cell at such temperature [9,10]. Therefore, the short-circuit loss caused by the electronic conductivity of SNO in 10SNO-90SDC composites can be ignored. On the other hand, compared with the cell based on pure SDC electrolyte membrane, the maximum power density increases significantly after the incorporation of SNO semiconductor into electrolyte.
AC impedance spectroscopy (EIS) can be used to further understand the effect of electron conduction on cell performance. This EIS test is carried out simultaneously with I-V and I-P performance tests, and air and hydrogen was continually introduced during the testing. Fig. 5 shows the EIS data of SNO-SDC fuel cell with different SNO content at 550 °C. The curves are all composed of a semicircle and an upward curve above the real axis. In general, the first intersection of the curve and the real axis is the ohmic resistance of the device, including the ion conduction and electron migration [9]. The ohmic resistances of pure SDC, 10% SNO, 30% SNO, 50% SNO and 70% SNO are 0.26 Ω cm², 0.18 Ω cm², 0.54 Ω cm², 0.67 Ω cm² and 0.79 Ω cm², respectively. If only considering the high electronic conductivity of SNO, the ohmic resistance of the cell should be decreased with the increase of SNO content. On the contrary, the ohmic resistance of the cell does not decrease but increases instead as the SNO content increased from 10% to 70%. This maybe due to the enhancement effect of ion conduction in SNO-SDC semiconductor-ion conductor composite, which have been widely detected in previous reports [11].

The potential of these SNO-SDC SLFC have been evaluated in intermediate-low temperature range. Fig. 6 shows the typical I-V and I-P curves of SNO-SDC SLFC based on the best composition (10% SNO) in the temperature range of 475-550 °C. It can be seen from the figure that with the working temperature rising from 475 °C to 550 °C, the maximum output power of the cell is significantly
enhanced (from 180 MW / cm² to 630 MW / cm²). The ionic conductivity of SNO-SDC functional layer should be significantly improved as the temperature increase, which bring about the enhancement of power output. However, the cell at 475 ℃ demonstrated the highest OCV value, such result can be easily deduced from Nernst equation. It is surprising that the P_max of the cell remains at 250 mW / cm² at 500 ℃, which indicates that the SLFC based on SNO-SDC membrane has good low-temperature performance, and the SNO-SDC membrane exhibited enormous potential in application of low-temperature SOFC.

![Graph showing electrochemical performance of 10SNO-90SDC SLFC at different temperature (475-550 ℃)](image)

**Figure 6.** The electrochemical performance of 10SNO-90SDC SLFC at different temperature (475-550 ℃)

Fig.7 shows the EIS of 10SNO-90SDC SLFC in the temperature range of 475-550 ℃. It can be found that the ohmic resistance of the cell decreases from 0.56 Ω cm² to 0.18 Ω cm² with the increase of working temperature, demonstrating thermal active process. In general, the EIS contained two arc, the first arc in high frequency range was assigned to charge transfer process, and the second arc in low frequency came from mass transfer process. Obviously, the diameter of the first arc was increase as the temperature improve, indicating that the charge transfer resistance gradually increase. The second arc of the Nyquist curve decreases or even disappears, which indicates that the catalytic activity of the electrode is also enhanced. Combined with Fig.6, it is shown that both the electronic conductivity of SNO and the ionic conductivity of SDC follow the rule of thermal activation.

![Impedance spectra of fuel cell based on 10%t SNO membrane in the 475-550 ℃ diaphragm](image)

**Figure 7.** Impedance spectra of fuel cell based on 10%t SNO membrane in the 475- 550 ℃ diaphragm
4. Conclusion

In this paper, SrNb oxide (SNO) was synthesized by Sol-gel method, and we focused on the characterization of SNO-SDC composites and systematically investigated the properties of such novel composite. The SNO-SDC composite was applied as multifunctional layer to fabricate SLFC, such device exhibited a Pmax of 630 MW/cm² at 550 ℃, which was 40% higher than that of single component fuel cell with pure SDC electrolyte as interlayer material, demonstrating that the incorporation of semiconductor SNO into multifunctional layer can significantly enhance the cell performance. In addition, we found that when the mass fraction of SNO and SDC is 10% and 90% respectively, the cell can achieve the best electrochemical performance. This paper further confirmed the practicability and feasibility of semiconductor-ion conductor SNO-SDC composite as functional layer in the field of SLFC, which provided more possibilities for the commercial development of solid oxide fuel cells in the future.

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References

[1] O'hayre R, Che Shuoyuan, Colella W, et al., Fuel Cell Fundamentals (Electronic Industry Press, Beijing, 2007), pp.6–8.
[2] Zhang Junliang, Jiang Fengjing, Fuel cell: Principle, Key Materials and Technologies(Shanghai Jiaotong University Press, Shanghai, 2014), pp.187-188.
[3] Hu Huiqing, Lin Qizhao, Zhu bin, Modern Chemical Industry 2, 31-35(2017).
[4] Shen S, Yang Y, Guo L, et al., J. Power Sources 256, 43-51(2014).
[5] Zhang W, Cai Y, Wang B, et al., Int. J. Hydrog. Energy 41, 18761-18768(2016).
[6] Li M, Zhao M, Li F, et al, Nat. Commun. 8, 13990-13995(2017).
[7] Yin Yanhong, Yang Shuting, Xia Changrong, et al., Journal of Henan Normal University (Natural Science Edition) 33(2), 56-59(2005).
[8] Li Jianjun, Yang Hao, Han yunyun, et al., Chemical Engineering and Equipment 2, 20-23(2014).
[9] Hou Ming, Yi Baolian, Fuel Cell - principle, Technology and Application ( Chemical Industry Press, Beijing, 2003), pp.1-35.
[10] Hou Ming, Yi Baolian, Electrochemistry 18(1), 1-13(2012).
[11] Wang Baoyuan, Wang Yi, Fan Liangdong, et al., J. Mater. Chem. A 4(40), 15426–15436(2016).