A single layer solid oxide fuel cell composed of La_2NiO_4 and doped ceria-carbonate with H_2 and methanol as fuels

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Abstract

A single layer solid oxide fuel cell composed of La_2NiO_4 and samarium doped ceria (SDC)- $(\text{Li}_{0.67}\text{Na}_{0.33})_2\text{CO}_3$ is fabricated and characterized. La_2NiO_4 shows a K_2NiF_4 structure in an oxidizing atmosphere, and is decomposed to Ni and La_2O_3 in a reducing atmosphere at the operating temperature of the cell. The electrical conductivity of the composite material increases with the increase of the content of La_2NiO_4 . At 700 °C, the single cell composed of 30 wt.% La_2NiO_4 and 70 wt.% SDC- $(\text{Li}_{0.67}\text{Na}_{0.33})_2\text{CO}_3$ exhibits the highest power output of 340 and 331 mW cm^{-2} with H_2 and methanol as fuels, respectively. **The stability of the cell with H_2 and methanol as the fuels is investigated.**

Keywords: Single layer solid oxide fuel cell; La_2NiO_4 ; Composite material; Mixed ionic and electronic conduction; Methanol

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1. Introduction

A solid oxide fuel cell (SOFC) is an electrochemical device that directly converts chemical energy stored in fuels to electrical energy [1]. SOFC has drawn great attention in the past few decades because of its high system efficiency and low emissions as well as superior fuel flexibility [2, 3]. The conventional configuration of a SOFC consists of three major components, *i.e.*, anode, electrolyte and cathode. At the typical operating temperature of SOFCs (800-1000 °C), serious problems related to stability and compatibility between different components would arise, which hinders the practical application and commercialization of SOFCs [4-6]. Meanwhile, interfacial resistances between these components lead to large performance and efficiency losses.

In 2000, He *et al.* [7] fabricated a single layer SOFC based on $\text{La}_{0.9}\text{Sr}_{0.1}\text{InO}_{3-\delta}$, a perovskite-type material, with two sides functioning as the cathode and anode simultaneously working in oxidizing and reducing atmospheres, respectively. The middle part also acts as an electrolyte working at intermediate oxygen partial pressure. The single-layer structure avoids the incompatibility between different components. However, due to the thick cell layer (2.1 mm) and low electrical conductivity ($< 10^{-2} \text{ S cm}^{-1}$) of the material, the peak power density of the cell was only 3 mW cm^{-2} at 800 °C. In recent years, composite materials for single layer SOFCs have been explored intensively, most of which are composed of an ionic conductor and a semiconductor with efficient catalytic activity for both anodic and cathodic reactions [8-13]. Zhu *et al.* [14] fabricated a single layer SOFC with $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC)- Na_2CO_3 - LiCoNiO nanocomposite, and obtained a peak power density of 500 mW cm^{-2} at 550 °C.

La_2NiO_4 and its derivatives with a K_2NiF_4 -type structure have been applied recently as the electrode materials of SOFCs [15-17]. La_2NiO_4 is a p-type semiconductor with a high mixed

ionic-electronic conductivity in an oxidizing atmosphere [18, 19], and shows an efficient catalytic activity for oxygen reduction [20, 21]. In hydrogen atmosphere, it is reduced to a mixture of La_2O_3 and Ni [19], which not only possesses a promising electrical conductivity, but acts as a highly active catalyst for fuel oxidation as well [22, 23]. Meanwhile, the existence of La_2O_3 may prevent carbon deposition in a hydrocarbon atmosphere [24]. However, La_2NiO_4 is not suitable to be used alone as the material of a single layer SOFC because of its high electronic conductivity. Dong *et al.* [25] mixed $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ (SFM) with a pure ionic conductor, SDC- Na_2CO_3 , and obtained a balanced ionic-electronic conductivity, which is important for the performance of the single layer SOFC. In this work, a single layer SOFC is fabricated based on La_2NiO_4 -SDC- $(\text{Li}_{0.67}\text{Na}_{0.33})_2\text{CO}_3$ (La_2NiO_4 -SDC-LN) composite. SDC-LN shows high ionic conductivity with negligible electronic conduction, which has been widely used as the electrolyte of intermediate-temperature (500-700 °C) SOFCs [26]. The effect of the La_2NiO_4 content on the electrical conductivity of the composite is investigated. The performance of the cell with H_2 and methanol as fuels is measured in an intermediate temperature region (600-700 °C).

2. Experimental

2.1. Material preparation

La_2NiO_4 powder was synthesized through a nitrate-citrate sol-gel method [27]. Stoichiometric $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (> 98.0 %, Guangfu fine chemical, Ltd., China) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (> 98.0 %, Guangfu fine chemical, Ltd., China) were dissolved in distilled water to form an aqueous solution. Citric acid (>98.0 %, Guangfu fine chemical, Ltd., China) as the complexing agent was added to the solution. The molar ratio of citric acid to total metal cations was 2:1. The aqueous solution was evaporated at 80 °C in air with stirring until a gel was formed. The gel was decomposed at 350 °C

for 2 h and heated in air at 950 °C for 5 h to form Ruddlesden–Popper structure [28].

SDC powder with a composition of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ was prepared with an oxalate co-precipitation technique [29]. Stoichiometric $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and Sm_2O_3 were dissolved in diluted nitrate acid to form a mixed nitrate solution. The total concentration of the metal ions was 1 mol L^{-1} . The pH value of the solution was adjusted to around 6.8 with the addition of diluted $\text{NH}_3 \cdot \text{H}_2\text{O}$. A solution of oxalic acid with a concentration of 0.5 mol L^{-1} was added dropwise into the nitrate solution which was stirred constantly. The formed precipitate was filtrated and washed with deionized water for three times, followed by dispersed in ethanol by ultrasonic treatment. After being dried at 85 °C overnight, the oxalate precursor was calcined at 700 °C for 2 h in air to form the SDC powder. Li_2CO_3 and Na_2CO_3 were mixed with a mol ratio of 2:1 by ball milling for 4 h, and then heated at 700 °C in air for 1 h to form binary eutectic carbonate (LN). The SDC powder and the eutectic carbonate were mixed with a weight ratio of 7:3 and calcined at 700 °C in air for 1 h to form SDC-LN powder [30].

The La_2NiO_4 -SDC-LN composite powder was achieved with mixing the as-prepared La_2NiO_4 and SDC-LN powders with the prescribed ratio and sintered at 700 °C for 1 h. For the carbon deposition test, The 30 wt.% La_2NiO_4 - 70 wt.% SDN-LN composite powder was reduced in H_2 at 700 °C for 1 h, and subsequently treated with methanol at 700 °C for 2 h.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the composite powders were recorded at room temperature with a D8 Focus diffractometer (Bruker Corp., Germany) with Cu-K α radiation, 40 kV and 200 mA, at a scan rate of 8° min^{-1} . The surface morphology of the composite powders and the cross section of the single cell were observed with a Hitachi S-4800 scanning electron microscope

(SEM). H₂-temperature-programmed reduction (H₂-TPR) was carried out with a TP-5079 TPDRO instrument (Tianjin Xianquan Instrument Company) equipped with a thermal conductivity detector (TCD). The tests were performed in a quartz tube reactor with 8% H₂-92 % N₂ gas mixture as the reductant from room temperature to 900 °C at a heating rate of 5 °C min⁻¹.

2.3. Conductivity test

The powders were pressed under 500 MPa into pellets with a diameter of 13 mm and a thickness of 0.9 mm. The La₂NiO₄-SDC-LN and SDC-LN pellets were calcined at 700 °C in air for 1 h and the La₂NiO₄ pellet was calcined at 1250 °C in air for 5 h. Silver paste was coated on both sides of the pellets as the current collector. The electrical conductivity of the samples was measured with electrochemical impedance spectroscopy (EIS) technique between 600-700 °C in H₂ and air atmospheres, using an electrochemical workstation (VersaSTAT 3, Ametek) in a frequency range from 1 M Hz to 0.01 Hz with an amplitude of 10 mV.

2.4. Fuel cell test

La₂NiO₄-SDC-LN composite powders were pressed under 500 MPa into pellets with a diameter of 13 mm and a thickness of 0.9 mm. The pellets were sintered at 700 °C for 1 h with a heating rate of 3 °C min⁻¹. Ag paste was used as a current collector at both sides of the pellet. The effective surface area of the cell was 0.64 cm².

A homemade device was used to measure the performance of the single cell. The fuel cells were tested in a temperature range of 600–700 °C under atmospheric pressure. The flow rate of the fuel gas (H₂ or gasified anhydrous methanol) was 80 ml min⁻¹ (STP) and that of O₂ was 20 ml min⁻¹ (STP). Before fueled with methanol, the fuel side was exposed in H₂ for 1 h at 700 °C. *I-V* and *I-P* curves of the cell were measured with the electrochemical workstation. EIS of the cells were also recorded in

the frequency range from 1 M Hz to 1 Hz under open-circuit voltage (OCV) with an amplitude of 10 mV. The stability of the cell was tested under a constant current of 200 mA cm^{-2} at 700°C with H_2 and methanol as fuels.

3. Results and discussion

3.1. Characterization

The XRD patterns of pure SDC (Fig. 1a) and La_2NiO_4 (Fig. 1c) show typical cubic fluorite and K_2NiF_4 -type structures, which are in good agreement with JCPDS files #75-0158 and #82-2176, respectively. The XRD result of SDC-LN (Fig. 1b) exhibits only the characteristic peaks of the SDC phase, and the carbonate exists as an amorphous phase as reported previously [30, 31]. The XRD pattern of La_2NiO_4 -SDC-LN (Fig. 1d) shows a combination of La_2NiO_4 and SDC-LN phases, and no other phase is observed, indicating that there is no obvious interaction between the two materials [32]. After reduced in H_2 at 700°C for 1 h, La_2NiO_4 in the composite is reduced to Ni (JCPDS #65-0380) and La_2O_3 (JCPDS #05-0602 and JCPDS #22-0369).

The H_2 -TPR results of La_2NiO_4 , SDC-LN and La_2NiO_4 -SDC-LN powders are shown in Fig. 2. The increase of H_2 consumption amount in SDC-LN curve corresponds to the gradual reduction of Ce^{4+} to Ce^{3+} [33], which starts at about 400°C and reaches its peak at about 800°C . For La_2NiO_4 , the peak between 300°C to 500°C is attributed to the reduction of $\text{Ni}^{3+} \rightarrow \text{Ni}^{2+}$, and the peak between 500°C to 800°C is due to the reduction of Ni^{2+} to metallic Ni^0 [34]. After mixing with SDC-LN, the reduction temperature of $\text{Ni}^{3+} \rightarrow \text{Ni}^{2+}$ in La_2NiO_4 is slightly increased from 388°C to 419°C , while that of $\text{Ni}^{2+} \rightarrow \text{Ni}^0$ is decreased from 660°C to 569°C . Therefore, in the operating temperature region ($600\text{--}700^\circ\text{C}$) in this work, La_2NiO_4 in the composite can be reduced to Ni and La_2O_3 in H_2 atmosphere.

Fig. 3a shows the SEM micrographs of 30 wt.% La_2NiO_4 -70 wt.% SDC-LN composite powder, in which La_2NiO_4 and SDC-LN distribute uniformly, and the particle size ranges from tens to a few hundred nanometers. After reduced in H_2 and treated in methanol at 700 °C for 2 h, carbon nanofibers are observed on the surface of the powder as reported previously (Fig. 3b) [17]. The SEM micrograph of the cross-section of the cell near the surface before the test is shown in Fig. 3c, which shows a porous structure, similar with that of O_2 -side of the cell after test (Fig. 3d). The H_2 -side of the cell after test looks more porous (Fig. 3e), which is probably due to the reduction of La_2NiO_4 [35]. The porous structure of both sides of the cell would facilitate the diffusion of the fuel and the oxidant to the functional electrode regions and reduce the concentration polarization.

3.2. Electrical conductivity

Fig. 4 shows the conductivities of the La_2NiO_4 -SDC-LN composites with different components. The conductivities increase with the increase of the temperatures in both air and H_2 atmospheres. The electrical conductivity of pure La_2NiO_4 measured in air is about 17 S cm^{-1} at 700 °C, much higher than that of SDC-LN, which is generally considered as a pure ionic conductor [36]. Therefore, the increase of the La_2NiO_4 content results in the enhancement of the electrical conductivity of the composites. In H_2 atmosphere, La_2NiO_4 is reduced to La_2O_3 and Ni. The formation of the La_2O_3 insulating phase leads to a lower conductivity of the reduced La_2NiO_4 , which is only about 0.3 S cm^{-1} at 700 °C. Therefore, the conductivity of the composite material in H_2 is lower than that in air.

3.3. Single cell performance

The OCV of the single layer SOFC made of pure La_2NiO_4 is only 0.04 V at 700 °C with H_2 as the fuel, which is due to the serious internal short circuit since the electronic conductivity of

La₂NiO₄ is much higher than its ionic conductivity ($\sim 0.02 \text{ S cm}^{-1}$) [37]. After adding a certain amount of SDC-LN, the electronic conduction is significantly suppressed, while the ionic conduction is improved since the ionic conductivity of SDC-LN ($0.05\text{-}0.07 \text{ S cm}^{-1}$ at 700°C , Fig. 4) is much higher than that of La₂NiO₄, resulting in an improvement of the OCV, as shown in Fig. 5a. The single layer SOFC with 40 wt.% La₂NiO₄ exhibits an OCV of 0.89 V at 700°C . When the content of La₂NiO₄ is reduced to 30 wt. %, the OCV reaches 0.97 V, close to the theoretical potential of the cell with H₂ as the fuel at 700°C ($\sim 0.99 \text{ V}$), and the maximum power density (P_{max}) is 340 mW cm^{-2} , much higher than the P_{max} of the single layer SOFC with a similar structure based on a SFM-SDC-Na₂CO₃ composite at the same temperature (about 250 mW cm^{-2}) reported previously. [25]. However, SDC-LN has a lower catalytic activity and electronic conductivity compared to La₂NiO₄, leading to an increased electrode polarization with the decrease of the La₂NiO₄ content. Therefore, the OCV and the P_{max} of the single cell decreases with the reducing of the La₂NiO₄ content when the La₂NiO₄ content is less than 30 wt. %. The EIS results of the single cells at 700°C are shown in Fig. 5b. The high-frequency intercepts on the real axis are mainly result from the ohmic resistances, which increases with the decrease of the La₂NiO₄ content. Meanwhile, the electrode polarization of the cell, which is shown as the arc in the EIS result, also becomes larger with the decrease of the La₂NiO₄ content since the catalytic activity of La₂NiO₄ is higher than that of SDC-LN.

Fig. 6a shows the I - V and I - P characteristics of the single layer SOFC composed of 30 wt. % La₂NiO₄ with H₂ as the fuel at various temperatures. The cell exhibits P_{max} of 80, 200 and 340 mW cm^{-2} at 600 , 650 and 700°C , respectively. The enhancement of the cell performance with the increase of the operating temperature is attributed to the improved catalytic activity as well as the

enhanced electrical conductivity of the composite material. The performance of the cell fed with methanol is comparable with that of the cell fed with H_2 , as shown in Fig. 6b. $P_{\max}$ of 96, 155 and 331 mW cm^{-2} are obtained at 600, 650 and 700°C , respectively. The theoretical potential of the cell with methanol as the fuel is about 1.25 V at 700°C , higher than that of the cell fed with H_2 at the same temperature. However, since the thermal cracking of methanol happens above 600°C [38], the anodic gas is the mixture of methanol, H_2 and CO, and the OCV depends on the electrode reaction that near the equilibrium state, which should be the electrochemical oxidation of H_2 since H_2 is the most active. Therefore, the cell fed with methanol shows similar OCV and performance with that fed with H_2 .

Fig. 7 shows the output voltage of the cells at 700°C as a function of time under a current density of 200 mA cm^{-2} with H_2 and methanol as fuels, respectively. The voltage of the single layer SOFC with 30 wt. % La_2NiO_4 with H_2 as the fuel keeps almost constant during the 120-minute discharge, indicating that the single layer SOFC is stable in H_2 . For the cell fed with methanol, its performance decreases slowly with a total drop of 5.38 % within 120 minutes. The degradation of the cell is mainly caused by the carbon deposition at the anodic region, as illustrated in Fig. 3b. Further study is still needed to improve the stability of the single layer SOFC with carbon containing fuels.

4. Conclusions

A single layer SOFC based on a composite material of La_2NiO_4 and $\text{SDC}-(\text{Li}_{0.67}\text{Na}_{0.33})_2\text{CO}_3$ is fabricated and tested with H_2 and methanol as the fuels. La_2NiO_4 at the anode side is reduced to La_2O_3 and Ni particles at the operating temperature. The electrical conductivities of the composite material in oxidizing and reducing atmospheres both increase with the increase of the content of

La₂NiO₄. The composition of the material remarkably influences the electrochemical performance of the cell. The single cell with 30 wt.% La₂NiO₄ exhibits $P_{\max}$ of 340 and 331 mW cm⁻² at 700 °C with H₂ and methanol as the fuels, respectively. The cell also shows a promising stability with methanol as the fuel at 700 °C. The performance of the cell fed with methanol decreases 5.38 % within 120-minute discharge.

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References

- [1] Steele BCH, Heinzel A. -Materials for fuel-cell technologies. *Nature*. 2001;414:245-52.
- [2] Steele BCH. Appraisal of Ce_{1-y}Gd_yO_{2-y/2} electrolytes for IT-SOFC operation at 500 degrees C. *Solid State Ionics*. 2000;129:95-110.
- [3] Ishihara T, Matsuda H, Takita Y. Doped LaGaO₃ Perovskite Type Oxide as a New Oxide Ionic conductor. *J Am Chem Soc*. 1994;116:3801-3
- [4] Huang P, Horky A, Petric A. Interfacial reaction between nickel oxide and lanthanum gallate during sintering and its effect on conductivity. *J Am Ceram Soc*. 1999;82:2402-6.
- [5] Tietz F. Thermal Expansion of SOFC Materials. *Ionics*. 1999;5:129-39.
- [6] Kim K, Kim B, Son J, Kim J, Lee H-W, Lee J-H, et al. Characterization of the electrode and electrolyte interfaces of LSGM-based SOFCs. *Solid State Ionics*. 2006;177:2155-8.
- [7] He HP, Huang XJ, Chen LQ. Sr-doped LaInO₃ and its possible application in a single layer SOFC. *Solid State Ionics*. 2000;130:183-93.
- [8] Zhu B, Raza R, Qin H, Fan L. Single-component and three-component fuel cells. *Journal of Power Sources*. 2011;196:6362-5.
- [9] Zhu B, Ma Y, Wang XD, Raza R, Qin HY, Fan LD. A fuel cell with a single component functioning simultaneously as the electrodes and electrolyte. *Electrochemistry Communications*. 2011;13:225-7.

- [10] Zhu B, Qin HY, Raza R, Liu QH, Fan LD, Patakangas J, et al. A single-component fuel cell reactor. *International Journal of Hydrogen Energy*. 2011;36:8536-41.
- [11] Zhu B, Raza R, Abbas G, Singh M. An Electrolyte-Free Fuel Cell Constructed from One Homogenous Layer with Mixed Conductivity. *Advanced Functional Materials*. 2011;21:2465-9.
- [12] Zhu B, Raza R, Liu Q, Qin H, Zhu Z, Fan L, et al. A new energy conversion technology joining electrochemical and physical principles. *RSC Advances*. 2012;2:5066.
- [13] Zhu B, Fan LD, Lund P. Breakthrough fuel cell technology using ceria-based multi-functional nanocomposites. *Applied Energy*. 2013;106:163-75.
- [14] Zhu B, Lund PD, Raza R, Ma Y, Fan L, Afzal M, et al. Schottky Junction Effect on High Performance Fuel Cells Based on Nanocomposite Materials. *Advanced Energy Materials*. 2015;5.
- [15] Escudero MJ, Fuerte A, Daza L. $\text{La}_2\text{NiO}_{4+\delta}$ potential cathode material on $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ electrolyte for intermediate temperature solid oxide fuel cell. *Journal of Power Sources*. 2011;196:7245-50.
- [16] Laguna-Bercero MA, Kinadjian N, Sayers R, El Shinawi H, Greaves C, Skinner SJ. Performance of $\text{La}_{2-x}\text{Sr}_x\text{Co}_{0.5}\text{Ni}_{0.5}\text{O}_{4\pm\delta}$ as an Oxygen Electrode for Solid Oxide Reversible Cells. *Fuel Cells*. 2011;11:102-7.
- [17] Li P, Zhao Y, Yu B, Li J, Li Y. Improve electrical conductivity of reduced $\text{La}_2\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_{4+\delta}$ as the anode of a solid oxide fuel cell by carbon deposition. *International Journal of Hydrogen Energy*. 2015;40:9783-9.
- [18] Boehm E, Bassat JM, Dordor P, Mauvy F, Grenier JC, Stevens P. Oxygen diffusion and transport properties in non-stoichiometric $\text{Ln}_{2-x}\text{NiO}_{4+\delta}$ oxides. *Solid State Ionics*. 2005;176:2717-25.
- [19] Yang G, Su C, Ran R, Tade MO, Shao Z. Advanced Symmetric Solid Oxide Fuel Cell with an Infiltrated K_2NiF_4 -Type La_2NiO_4 Electrode. *Energy & Fuels*. 2014;28:356-62.
- [20] Solak N, Zinkevich M, Aldinger F. Compatibility of La_2NiO_4 cathodes with LaGaO_3 electrolytes: A computational approach. *Solid State Ionics*. 2006;177:2139-42.
- [21] Zhao K, Xu Q, Huang DP, Chen M, Kim BH. Electrochemical evaluation of $\text{La}_2\text{NiO}_{4+\delta}$ -based composite electrodes screen-printed on $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ electrolyte. *J Solid State Electr*. 2012;16:2797-804.
- [22] Sun J, Qiu X, Wu F, Zhu W. H_2 from steam reforming of ethanol at low temperature over $\text{Ni}/\text{Y}_2\text{O}_3$, $\text{Ni}/\text{La}_2\text{O}_3$ and $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts for fuel-cell application. *International Journal of Hydrogen Energy*. 2005;30:437-45.
- [23] Tu B, Dong Y, Liu B, Cheng M. Highly active lanthanum doped nickel anode for solid oxide fuel cells directly fuelled with methane. *Journal of Power Sources*. 2007;165:120-4.
- [24] Yan A, Phongaksorn M, Nativel D, Croiset E. Lanthanum promoted NiO -SDC anode for low temperature solid oxide fuel cells fueled with methane. *Journal of Power Sources*. 2012;210:374-80.
- [25] Dong X, Tian L, Li J, Zhao YC, Tian Y, Li YD. Single layer fuel cell based on a composite of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ - Na_2CO_3 and a mixed ionic and electronic conductor $\text{Sr}_{2-x}\text{Fe}_{1.5-x}\text{Mo}_{0.5}\text{O}_{6-\delta}$. *Journal of Power Sources*. 2014;249:270-6.
- [26] Zhao Y, Xu Z, Xia C, Li Y. Oxide ion and proton conduction in doped ceria-carbonate composite materials. *International Journal of Hydrogen Energy*. 2013;38:1553-9.
- [27] Perez-Coll D, Aguadero A. Electrochemical Performance of La_2NiO_4 -based Cathode for Solid Oxide Fuel Cells. *Single Cell Test. Fuel Cells*. 2011;11:91-101.
- [28] Klande T, Efimov K, Cusenza S, Becker K-D, Feldhoff A. Effect of doping, microstructure, and CO_2 on $\text{La}_2\text{NiO}_{4+\delta}$ -based oxygen-transporting materials. *Journal of Solid State Chemistry*. 2011;184:3310-8.
- [29] Jain SL, Nabae Y, Lakeman BJ, Pointon KD, Irvine JTS. Solid state electrochemistry of direct carbon/air fuel cells. *Solid State Ionics*. 2008;179:1417-21.
- [30] Yu J, Yu B, Li Y. Electrochemical oxidation of catalytic grown carbon fiber in a direct carbon fuel cell using $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ -carbonate electrolyte. *International Journal of Hydrogen Energy*. 2013;38:16615-22.

- [31] Xia C, Li Y, Tian Y, Liu Q, Wang Z, Jia L, et al. Intermediate temperature fuel cell with a doped ceria-carbonate composite electrolyte. *Journal of Power Sources*. 2010;195:3149-54.
- [32] Raza R, Wang XD, Ma Y, Liu XR, Zhu B. Improved ceria-carbonate composite electrolytes. *International Journal of Hydrogen Energy*. 2010;35:2684-8.
- [33] Desauvay T, Bonura G, Chiodo V, Freni S, Couzinie JP, Bourgon J, et al. Surface-dependent oxidation of H₂ on CeO₂ surfaces. *J Catal*. 2013;297:193-201.
- [34] Zhao B, Wang R, Yao W, Yang X, Zhou B. The Effect of Copper Substitution on La₂Ni_{1-x}Cu_xO₄ Catalysts Activity for Simultaneous Removal of NO_x and Diesel Soot. *Catal Lett*. 2009;132:41-9.
- [35] Fan L, Wang C, Osamudiamen O, Raza R, Singh M, Zhu B. Mixed ion and electron conductive composites for single component fuel cells: I. Effects of composition and pellet thickness. *Journal of Power Sources*. 2012;217:164-9.
- [36] Zhao YC, Xu ZR, Xia C, Li YD. Oxide ion and proton conduction in doped ceria-carbonate composite materials. *International Journal of Hydrogen Energy*. 2013;38:1553-9.
- [37] Bassat J. Anisotropic ionic transport properties in La₂NiO_{4+δ} single crystals. *Solid State Ionics*. 2004;167:341-7.
- [38] Cimenti M, Buccheri MA, Hill JM. Direct Utilization of Methanol and Ethanol on La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} Anodes for Solid Oxide Fuel Cells. *Electrocatalysis-Us*. 2012;3:59-67.

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Fig. 2. H₂-TPR profiles of (a) SDC-LN, (b) La₂NiO₄ and (c) La₂NiO₄-SDC-LN.

Fig. 3. SEM micrographs of (a) 30 wt.% La_2NiO_4 -70 wt.% SDC-LN composite powder, (b) reduced composite powder after treated in methanol at 700 °C for 2 h, (c) the cross-section of the corresponding single cell near the surface before the test, (d) O₂-side and (e) H₂-side cross-section of the cell after test.

Fig. 4. Electrical conductivities of composite materials with different contents of La₂NiO₄ measured in (a) air and (b) H₂ atmospheres.

Fig. 5. (a) *I-V* and *I-P* characteristics and (b) EIS curves of single layer SOFCs with various compositions at 700 °C with H₂ as a fuel.

Fig. 6. *I-V* and *I-P* characteristics of the single layer SOFC with 30 wt.% La_2NiO_4 at various temperatures with (a) H_2 and (b) methanol as the fuels.

Fig. 7. Chronopotentiometry results of the single layer SOFC with 30 wt.% La_2NiO_4 under 200 mA cm^{-2} at 700 °C with H_2 and methanol as the fuels.