



Short communication

A symmetrical solid oxide fuel cell prepared by dry-pressing and impregnating methods

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ARTICLE INFO

Article history:

Received 8 June 2010

Received in revised form 16 July 2010

Accepted 20 July 2010

Available online 30 July 2010

Keywords:

Symmetrical solid oxide fuel cells

Perovskite oxide

Dry-pressing

Wet impregnation

Nickel/ceria catalyst

ABSTRACT

In this study, a simple and cost-effective dry-pressing method has been used to fabricate a symmetrical solid oxide fuel cell (SOFC) where the dense yttria-stabilized zirconia (YSZ) electrolyte film is sandwiched between two symmetrical porous YSZ layers in which $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) based anode and cathode are incorporated using wet impregnation techniques. The maximum power densities (P_{max}) of a single cell with 32 wt.% LSCM impregnated YSZ anode and cathode reach 333 and 265 mW cm^{-2} at 900 °C in dry H_2 and CH_4 , respectively. The cell performance is further improved with additional impregnation of a small amount of Sm-doped CeO_2 (SDC) or Ni. When 6 wt.% Ni as catalyst is added to both the anode and cathode, P_{max} values of 559 and 547 mW cm^{-2} can be achieved, which are better than with SDC. The effect of Ni on the cathode performance is also investigated by impedance spectra analysis.

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1. Introduction

Recently, there has been growing interest in solid oxide fuel cells (SOFCs) because of their many advantages such as high efficiency, low pollution and fuel flexibility [1–3]. A typical SOFC consists of at least three parts: an anode, a cathode and an electrolyte. These are typically sintered in sequence and have different thermal expansion coefficients (TECs). Therefore, candidate materials for them must have good thermo-mechanical compatibility in order to keep cells stable during preparation and operation. Otherwise, the electrodes may easily peel off and separate from the electrolyte for the electrolyte-supported SOFCs and cells with electrode-supported membrane SOFCs may become distorted or fracture. In addition, to perform as an ideal electrolyte, anode or cathode, the candidate materials should also meet further requirements regarding conductivity (ionic and/or electronic), mechanical strength, thermal and chemical stability, densification and catalytic activity [4]. It is therefore a difficult task to find materials fitting all these requirements. Recently a new concept of SOFC using the same material as both anode and cathode has been proposed. This will reduce the number of materials and interfaces, and considerably simplify the structure and fabrication process of the SOFCs [5–11].

Until now, the state-of-the-art electrolyte material has been yttria-stabilized zirconia (YSZ) because it exhibits good thermal

and chemical stability, high oxide-ion conductivity and adequate mechanical strength at elevated temperatures. The most commonly used anode for the zirconia-based SOFCs is Ni/YSZ cermets because of their good thermal compatibility, excellent catalytic activity towards the electrochemical oxidation of hydrogen and excellent current collection properties. Unfortunately, such cermets also exhibit some disadvantages related to low tolerance to sulfur and carbon deposition, and poor redox cycling with volume instability [1,2,12]. The first drawback, i.e. sulfur and carbon deposition, can be easily overcome for novel symmetrical SOFCs by reversing the gas flow [8,11]. Nonetheless, the Ni/YSZ cannot be used as both anode and cathode of the symmetrical SOFCs, because the Ni within the Ni/YSZ can be oxidized more easily and will lose its electronic conductivity and catalytic activity under cathode conditions. So far, only a few materials have been successfully demonstrated as possible electrodes for the novel symmetrical SOFCs. Most of these materials are oxides based upon the perovskite structure, such as $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) [5–8], $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Cr}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$ [9], $\text{La}_{0.8}\text{Sr}_{0.2}\text{Sc}_{0.2}\text{Mn}_{0.8}\text{O}_{3-\delta}$ [10] and $(\text{La}, \text{Sr})\text{TiO}_3$ [11], because these have good redox stability. Nevertheless, there is still some difference in TECs between the electrodes and electrolyte due to the use of different materials.

In this paper, a symmetrical SOFC has been fabricated in a single process by dry-pressing. The materials of the electrode matrices and electrolyte are all YSZ, which is expected to solve the problem of mismatching. Furthermore, the electrode surface areas and triple-phase boundary lengths can be substantially increased via

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impregnation. The test results also demonstrate good cell performance with both hydrogen and methane.

2. Experimental

2.1. YSZ powders preparation

YSZ powders used for electrolyte film fabrication were synthesized by a glycine nitrate process [13]. The highly loose and porous YSZ with an extremely low bulk density is the key to successfully prepare thin and dense YSZ electrolyte films by dry-pressing. $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (99.9%), Y_2O_3 (99.9%) and $\text{NH}_2\text{CH}_2\text{COOH}$ (>95%) were used as the starting materials. Stoichiometric amounts of Y_2O_3 were dissolved in dilute nitric acid to form a nitrate solution, then stoichiometric amounts of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_2\text{CH}_2\text{COOH}$ were added to form a mixed nitrate solution in which the Zr^{4+} and Y^{3+} concentrations match the formula $(\text{Y}_2\text{O}_3)_{0.08}(\text{ZrO}_2)_{0.92}$. The solutions were heated, dried and burned to form a grey ash that was then fired at 700°C for 2 h to produce loose and porous nano-crystalline YSZ powders with low bulk density. The YSZ single phase was confirmed by an X-ray diffraction (XRD, Rigaku D/max rB, Japan), using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$).

2.2. Symmetrical SOFCs fabrication

The raw NiO powder (Inco, Canada) and YSZ (TZ-8Y, Tosoh Corporation, Tokyo, Japan) were thoroughly mixed in the weight ratio 8:5 to form an electrode precursor. The precursor was evenly sprinkled on to the bottom of a stainless mold. On its surface the prepared loose YSZ powder was then added through a screen to promote even dispersion. Finally equal amounts of electrode precursor were added. The three layers were pressed together uniaxially and then sintered at 1400°C for 4 h to form a dense electrolyte layer and simultaneously produce two porous electrode layers. The symmetrical SOFCs obtained in this way were reduced in flowing hydrogen and then dipped in a dilute nitric acid for 12 h to soak out the Ni, in order to obtain two highly porous (~50% porous) electrode layers. Here, the Ni acts as an inorganic pore former. After preparing the three-layer YSZ matrix, 32 wt.% of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) was introduced into the two porous electrode layers using an aqueous nitrate solution. This impregnating solution was prepared by adding $\text{La}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3$, $\text{Mn}(\text{NO}_3)_2$ and urea to deionized water in the molar ratio 3:1:2:2:16, as described elsewhere [14]. After impregnation, the cell was heated at 300°C for 20 min to decompose the nitrate ions and the urea. This impregnating-heating cycle was repeated until the desired weight loading of LSCM was achieved. Finally, the cell was fired at 1100°C for 2 h to produce the perovskite phase that was confirmed previously [14]. In some of the cells, a small amount of Sm-doped CeO_2 (SDC) or Ni as catalyst was added by addition of aqueous solutions of the corresponding nitrate salts ($\text{Ce}_{0.8}\text{Sm}_{0.2}(\text{NO}_3)_x$ or $\text{Ni}(\text{NO}_3)_2$).

2.3. Cell characterization

The single cell was attached and sealed on one end of a ceramic tube. The cell performance were recorded on a Solartron SI 1287 electrochemical interface over the temperature range $700\text{--}900^\circ\text{C}$, measuring at 50°C intervals, with the cathode in ambient air and the anode in dry hydrogen or methane. The impedance spectra of the electrochemical half-cell were recorded at open circuit-voltage (OCV) with a 10 mV ac signal amplitude over the frequency range 0.1–91 kHz, using a SI 1260 impedance analyzer.

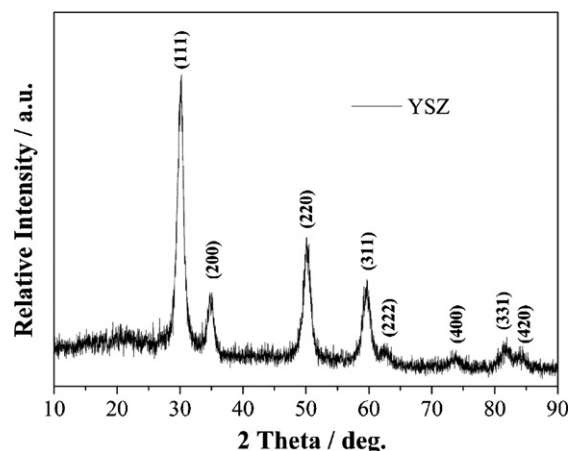


Fig. 1. Powder X-ray diffraction data for YSZ synthesized by a glycine nitrate process and fired at 700°C for 2 h.

3. Results and discussion

3.1. Structure of YSZ powder

The grey ash obtained during the YSZ preparation was fired at 700°C for 2 h and then characterized by XRD. The results are presented in Fig. 1. The diffraction pattern shows the peaks relative to the crystalline structure of YSZ (cubic, JCPDS Card No. 30-1468) with no additional phases, providing evidence that heating the ash at 700°C results in a pure YSZ phase. According to the study of Wang et al., the pure YSZ phase can be obtained if the ash is calcined above 600°C [15]. The average crystallite sizes of YSZ were about 10 nm, as determined by the Scherrer equation [15].

3.2. Cell microstructure

Fig. 2a shows the cross-sectional microstructures of a typical SOFC prepared by the single dry-pressing process after sintering at 1400°C for 4 h. The boundaries between the electrodes and electrolyte are blurred because all have become dense after the high-temperature sintering at 1400°C . After reducing and acid cleaning the Ni was removed from the two electrode layers, as shown in Fig. 2b. As a result, a highly porous structure was formed, which makes it possible to add LSCM to the electrodes via the wet impregnation process. The boundaries, in Fig. 2b, between the porous electrode and the dense electrolyte membrane are well distinguished. The layers are bonded together well and their thicknesses are ~200, ~20 and ~200 μm , respectively. Fig. 2c presents a view of the inner surface of a pore prior to impregnation, in which only the flat YSZ surface can be seen. After impregnation with LSCM (Fig. 2d), the YSZ surface was covered with a well-connected array of particles.

3.3. Single cell performance

Fig. 3 presents the current–voltage characteristics and the corresponding power densities for a typical symmetrical SOFC based on 32 wt.% LSCM impregnated YSZ electrodes at different temperatures, with dry H_2 or CH_4 as the fuel and ambient air as the oxidant. Using H_2 , it produced maximum power densities (P_{max}) of 87, 131, 192, 286 and 333 mW cm^{-2} at 700, 750, 800, 850 and 900°C , respectively. When the fuel was changed to dry CH_4 , the corresponding values changed to 36, 71, 116, 192 and 265 mW cm^{-2} . It can be seen that the cell performance is better than that of the conventional electrolyte-supported symmetrical SOFCs, especially with CH_4 , which shows ~130% increase at 900°C [6]. This increase must

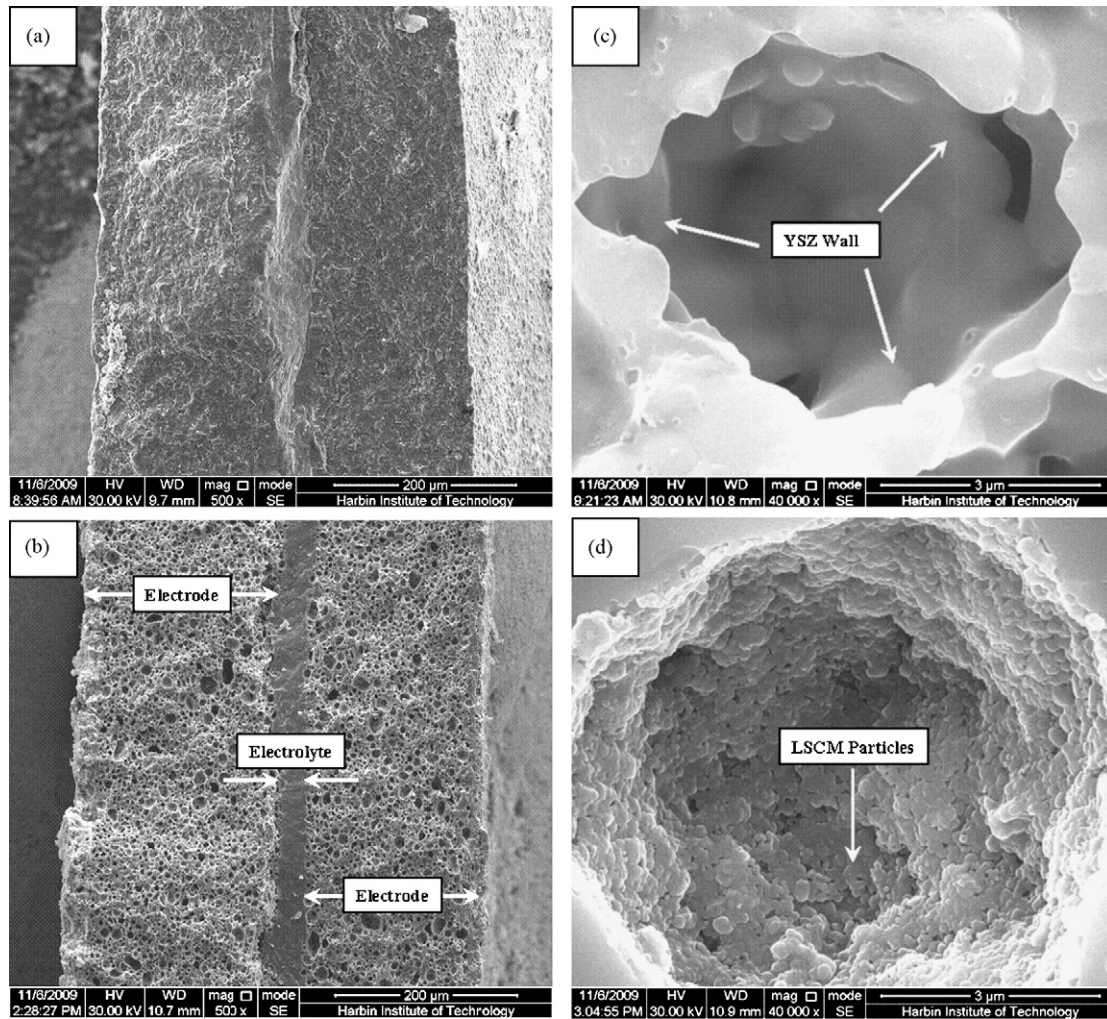


Fig. 2. Cross-sectional SEM micrographs of the sintered SOFCs with two symmetrical NiO/YSZ electrodes (a) before and (b) after reduction and acid cleaning; cross-sectional SEM micrographs of the porous electrodes (c) before and (d) after impregnation with LSCM.

be attributed to the increase of the anode surface areas and triple-phase boundary lengths, and the decrease of the YSZ electrolyte thickness.

In SOFC research, it is a common practice to use CeO_2 -based materials as catalysts because they have excellent oxygen storage and release properties and thus show high catalytic activity towards both fuel oxidation and oxidant reduction, indicating they can be used as both anode and cathode. Recently, a composite of CeO_2 , YSZ and Pt has been used as both anode and cathode for a symmetrical SOFC, and produced a P_{max} of 140 mW cm^{-2} at 950°C with H_2 as fuel, using a thick YSZ electrolyte [16]. In addition, the author predicted that 500 mW cm^{-2} might be expected using a thin YSZ electrolyte layer under identical experimental conditions. Accordingly, some symmetrical SOFCs in this study, after impregnation of LSCM, were soaked in $\text{Ce}_{0.8}\text{Sm}_{0.2}(\text{NO}_3)_x$ solution. This process was conducted in vacuum conditions to improve the distribution of the SDC [17]. After the introduction of 5 wt.% of SDC catalyst, the cell performance improved to 93, 145, 237, 305 and 395 mW cm^{-2} in H_2 and 61, 102, 135, 242 and 298 mW cm^{-2} in CH_4 , respectively, as shown in Fig. 4.

In an attempt to further improve the cell performance, another commonly used anode catalyst Ni was considered, since this has been regarded as the ideal catalyst for electrochemical oxidation of hydrogen. However, it is well known that Ni-based anodes are not good candidates for operating with dry carbon-containing

fuels due to the tendency of Ni to catalyze C–C bond formation [18]. However, a low concentration of small, highly dispersed Ni particles is unlikely to cause coking [14,17,19]. Therefore, in the present study, we attempted to introduce a small amount of Ni into the anode and cathode simultaneously, by impregnation of an aqueous nitrate solution containing La^{3+} , Sr^{2+} , Cr^{3+} , Mn^{2+} , Ni^{2+} and urea with a molar ratio of 3:1:2:2:4:16. This impregnation process has been described in detail elsewhere [20]. In previous reports, there have been three or fourfold increases in the anode performance following the introduction of small amounts of Ni, and no coking was found after operating in dry CH_4 [14,17,20]. It demonstrated that using a small amount of Ni as a catalyst for the LSCM-based anodes is feasible. However, the effect of Ni on the cathode performance is still unknown. In this study, this was investigated by impedance spectra analysis of two symmetrical SOFCs, one with 32 wt.% LSCM impregnated YSZ electrodes and the other with 32 wt.% LSCM + 6 wt.% Ni co-impregnated YSZ electrodes. The two cells were tested at 900°C , with the two electrodes exposed to ambient air simultaneously, and the test results are shown in Fig. 5. It can be seen from the impedance spectra that the ohmic resistance, calculated from the high-frequency intercept on the real-axis, increases from 0.07 to $0.08 \Omega \text{ cm}^2$ with the introduction of Ni. This is because the Ni should be oxidized to NiO under the cathode conditions, losing its conductivity, and the non-conductive NiO mixed with LSCM causes a further reduction of the LSCM con-

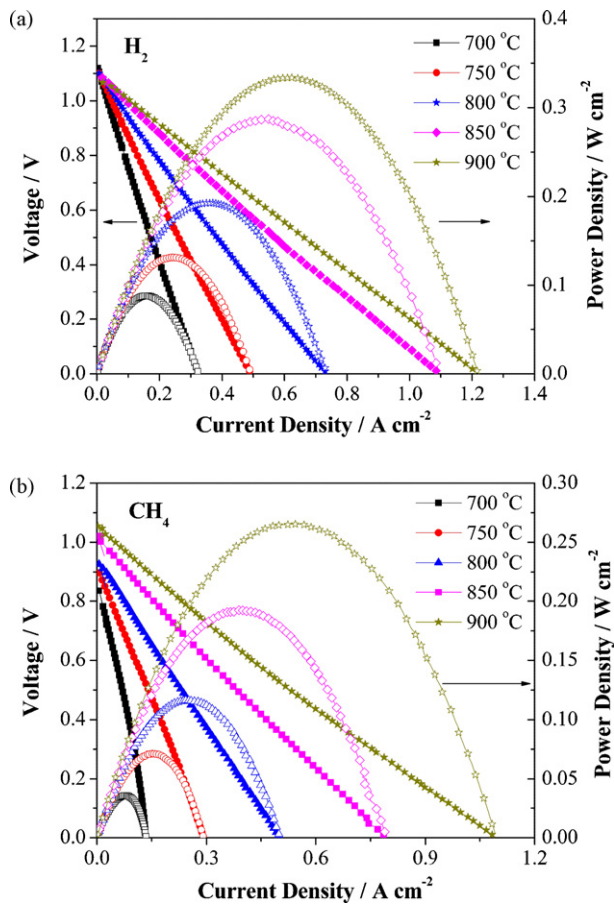


Fig. 3. Voltage–current density and performance curves of a typical symmetrical SOFC with 32 wt.% LSCM impregnated YSZ electrodes operating at 700–900 °C with dry (a) H₂ or (b) CH₄ as the fuel.

ductivity. There is also an increase from 0.14 to 0.21 $\Omega \text{ cm}^2$ in the electrode polarization resistance corresponding to the depressed arcs between high- and low-frequency intercepts. This shows that Ni has a negative effect on the cathode properties. Compared with the anode, however, the effect of Ni on the cathode performance is smaller, indicating that it is worth trying to use Ni as a catalyst. A typical symmetrical SOFC with the 32 wt.% LSCM + 6 wt.% Ni co-impregnated YSZ electrodes was tested under H₂/air and CH₄/air

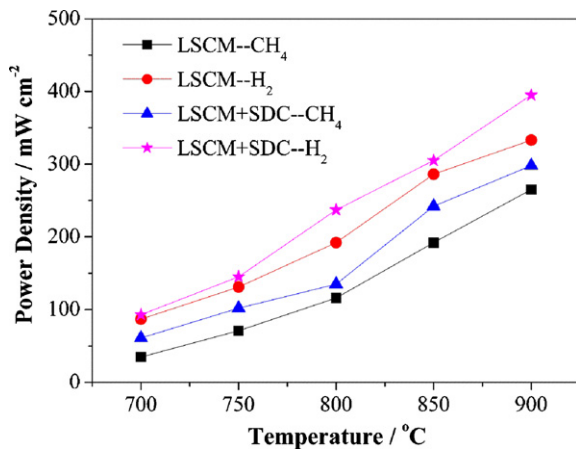


Fig. 4. A comparison of P_{max} s between two symmetrical SOFCs based on 32 wt.% LSCM impregnated YSZ electrodes and 5 wt.% SDC + 32 wt.% LSCM impregnated YSZ electrodes, with dry H₂ and CH₄ as fuels at different temperatures.

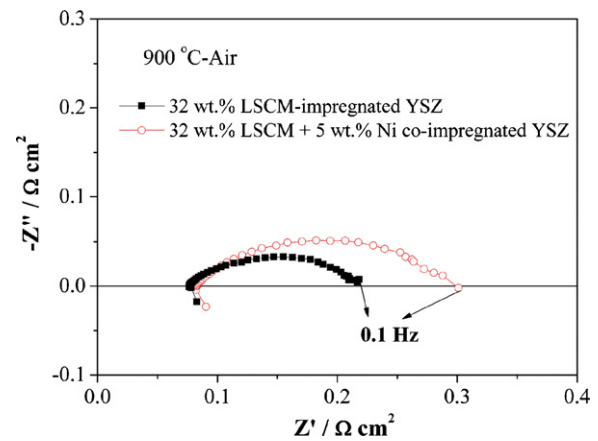


Fig. 5. Impedance spectra of the 32 wt.% LSCM impregnated YSZ and 6 wt.% Ni + 32 wt.% LSCM co-impregnated YSZ electrodes exposed to ambient air at 900 °C.

conditions, and the test results are presented in Fig. 6. The cell performance is increased by a factor of two after the introduction of Ni. It can be seen that the cell performance in CH₄ is comparable with that in H₂, but in previous reports the performances of the symmetrical SOFCs in CH₄ were significantly lower than that in H₂ [5–11]. This may be attributed to the novel structure of the cell and the electrodes. Moreover, as shown in Fig. 7, the open circuit voltage (OCV) of the cell with only LSCM impregnated YSZ electrodes was clearly reduced (from 1.05 to 0.84 V) with decreasing temperature when CH₄ was used as the fuel. Under identical conditions,

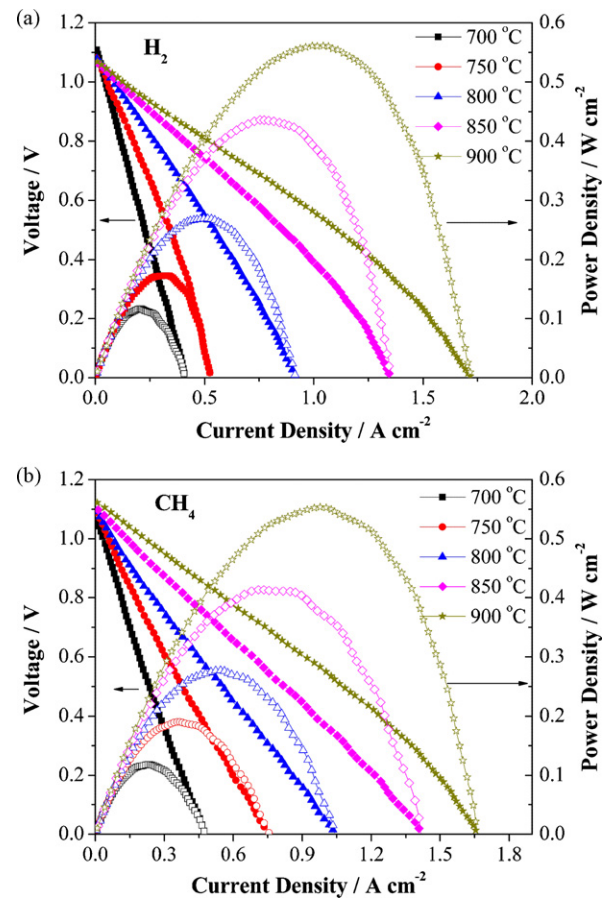


Fig. 6. Voltage–current density and performance curves of a typical symmetrical SOFC with 6 wt.% Ni + 32 wt.% LSCM co-impregnated YSZ electrodes operating at 700–900 °C with dry (a) H₂ or (b) CH₄ as the fuel.

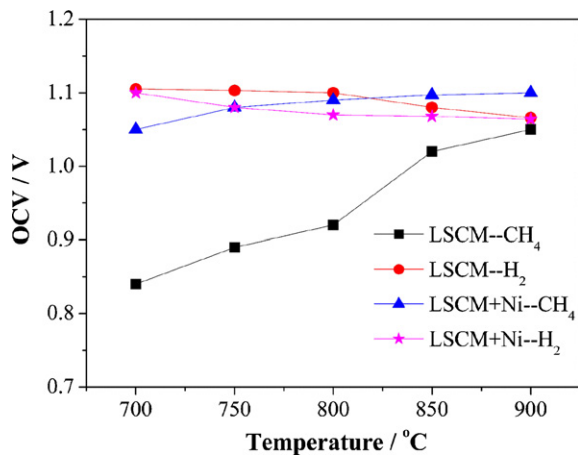


Fig. 7. Cell OCV vs. temperature for two symmetrical SOFCs with 32 wt.% LSCM impregnated YSZ and 6 wt.% Ni+32 wt.% LSCM co-impregnated YSZ electrodes, respectively, operating in dry H₂ and CH₄.

however, the obvious decrease of OCV in CH₄ was not observed for the LSCM + Ni co-impregnated YSZ electrode. In addition, the OCV values are not lower than 1.05 V at the testing temperatures, which may be caused by the increase of active sites that may increase the rate of gas adsorption and desorption. In addition, the presence of Ni should accelerate the partial oxidation of CH₄ to produce CO and H₂ [20].

4. Conclusions

In the present study, a symmetrical SOFC was successfully fabricated by dry-pressing and impregnation methods. This design basically solves the problem of thermal mismatching and is expected to relax the requirements for electrode materials. The cell displayed excellent performance, especially with CH₄. Compared with SDC, the catalytic activity of Ni is higher. A higher performance is expected for Ni-free cathodes under identical experimental con-

ditions. Furthermore, the proposed preparation method can also be used in asymmetrical SOFC configurations.

Acknowledgements

This work was supported by Ministry of Science and Technology of China (2007AA05Z139) and the Natural Science Foundation of China (20901020 and 50902032).

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