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Article

Ni doped $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ symmetrical electrode for solid oxide fuel cells

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ABSTRACT

The conventional Ni cermet anode suffers from severe carbon deposition and sulfur poisoning when fossil fuels are used. Alternative anode materials are desired for high performance hydrocarbon fuel solid oxide fuel cells (SOFCs). We report the rational design of a very active Ni doped $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSFN) electrode for hydrocarbon fuel SOFCs. Homogeneously dispersed Ni-Fe alloy nanoparticles were in situ extruded onto the surface of the LSFN particles during the operation of the cell. Symmetric SOFC single cells were prepared by impregnating a LSFN precursor solution onto a YSZ (yttria stabilized zirconia) monolithic cell with a subsequent heat treatment. The open circuit voltage of the LSFN symmetric cell reached 1.18 and 1.0 V in humidified C_3H_8 and CH_4 at 750 °C, respectively. The peak power densities of the cells were 400 and 230 mW/cm^2 in humidified C_3H_8 and CH_4 , respectively. The electrode showed good stability in long term testing, which revealed LSFN has good catalytic activity for hydrocarbon fuel oxidation.

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1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical reactors that directly convert the chemical energy of a fuel gas into electrical energy in an environment-friendly way with high efficiency and fuel flexibility. Although the commonly used yttria stabilized zirconia (Ni/YSZ) cermet anodes in SOFCs show excellent electrocatalytic properties in H_2 fuel, they suffer from carbon deposition and sulfur poisoning problems when hydrocarbon fuels are used [1–4]. Moreover, Ni agglomeration in the cermet anodes make them insufficiently stable for long term

running. In recent years, significant efforts have been devoted to developing alternative anodes to alleviate carbon deposition, sulfur poisoning and volume instability problems encountered in Ni-based cermet anodes [5–9]. Recently, Ishihara et al. [10] reported a composite of $\text{Ce}_{0.6}\text{Mn}_{0.3}\text{Fe}_{0.1}\text{O}_2$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Mn}_{0.1}\text{O}_3$ as an anode for direct hydrocarbon SOFCs, which showed a high peak power density of 1 W/cm^2 at 800 °C when propane and butane were used as fuel. Unfortunately, this oxide anode has low catalytic activity for methane due to the stable structure and strong C–H bond in methane. Nickel-based catalysts have been widely used for hydrocarbon re-

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forming with high catalytic activity [11,12]. It is possible to produce high performance SOFCs with nanostructured electrodes by a wet infiltration method [13,14]. However, the agglomeration and enlargement of the nanoparticles inevitably cause performance degradation in long term operation. It is well known that nano-size phases can be grown controllably from perovskites by a judicious choice of composition [15]. Compared with the conventional tri-layer cell structure, symmetrical SOFCs have attracted increasing attention due to the improved thermo-mechanical compatibility of the electrolyte and electrodes, which reduces fabrication cost, and enhances resistance to coking and sulfur poisoning [16,17].

Herein, we report the rational design of a highly active Ni doped $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ electrode (LSFN) for symmetrical hydrocarbon fuel SOFCs. Homogeneously dispersed nano-sized Ni-Fe alloy particles were in situ segregated onto the LSFN surface during the fuel cell operation. The symmetrical cell with impregnated LSFN electrode showed good stability in long term testing.

2. Experimental

2.1. Sample preparation

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ (LSFN) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSF) were synthesized by a solid state reaction with commercial La_2O_3 (99.99%), SrCO_3 (99%), Fe_2O_3 (98.5%) and NiO (99.99%). La_2O_3 was pre-calcined at 1000 °C for 2 h before use. Stoichiometric proportions of La_2O_3 , SrCO_3 , Fe_2O_3 and NiO were mixed and ground thoroughly in ethanol until the ethanol was volatilized. The powder was calcined at 800 °C for 2 h in air. Then, it was ball milled again and calcined at 1300 °C for 4 h in air.

2.2. Characterization of materials

The size and morphology of the products were examined by scanning electron microscope (SEM, Hitachi-S4800) and transmission electron microscope (TEM). TEM images and X-ray energy-dispersive spectrometry (EDS) measurements were carried out on a JEOL ARM200F microscope operated at 200 kV. The composition of the samples was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Electron Corporation).

The phases and purity of the samples were examined by X-ray powder diffraction (XRD) performed on a Bruker D8-Advance diffractometer with $\text{Cu } K_\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Gas chromatography-mass spectrometer (GC-MS) analysis was carried out on a Shimadzu QP2010 Plus instrument.

2.3. Fabrication and testing of cells

Tri-layer porous|dense|porous YSZ-electrolyte monolithic cells were fabricated by laminating one dense YSZ tape and two porous YSZ tapes on both sides with subsequent co-firing at 1350 °C. The porous layers were filled with 45 wt% starch as the fugitive material, yielding porosities of 45% as measured using the Archimedes' method. Symmetrical cells were fabri-

cated by impregnating the LSFN or LSF precursor solutions onto both porous layers and calcined at 500 °C, and then at 800 °C. The YSZ skeleton infiltrated with the catalyst were weighed before and after each impregnation-calcination cycle to estimate the loading of the impregnated LSFN or LSF catalyst, which were expressed as the mass ratio of the impregnated oxides to the porous YSZ backbones.

Electrochemical characterization was measured with a Zahner IM6 electrochemical workstation. Silver inks were applied on the electrode surface and silver wires were used as the voltage and current leads. All fuels were wetted with 3% H_2O .

3. Results and discussion

The compositions of the samples were determined by ICP and EDS since perovskite oxides can form A-site and B-site non-stoichiometric phases. Table 1 shows the ICP and EDS results of the synthesized LSFN and LSF powder. In a H_2 -3% H_2O atmosphere at 750 °C similar to the anode operating environment in SOFCs, it was observed that the LSFN sample showed a quite different morphology compared to that of the LSF sample. As shown in Fig. 1(a)–(c), many smaller nanoparticles with a size range of 10–20 nm had evenly segregated onto the surface of the LSFN particles after reducing for 2 h. However, this phenomenon was not observed in the case of the LSF sample (Fig. 1(d)–(f)). The phase purity and crystal structure of the products were examined by XRD. Fig. 1(g) shows the XRD patterns of the LSFN and LSF powder calcined at 1300 °C, which were indexed as a pure perovskite phase. From Fig. 1(g), it can be seen that LSNF and LSF still maintained the perovskite structure after they were calcined in the reducing atmosphere at 750 °C.

The morphology and structure of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ powder after calcination in a wet H_2 atmosphere at 750 °C for 2 h were characterized by high resolution TEM. Fig. 2(a)–(c) are typical TEM images of the reduced $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ powder. It can be clearly seen that the surface of the big bulk particle was covered with uniformly dispersed smaller nanoparticles with an average diameter of ~20 nm. Clear lattice fringes were observed throughout the particle, as shown in the HRTEM image (Fig. 2(b)), which suggested the nanoparticles were single crystals. Fig. 2(d) shows an annular dark-field (ADF) scanning transmission electron microscope (STEM) image and the EDS elemental mapping of Ni, Fe, La, Sr and O of the reduced $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ powder. To further clarify the chemical composition of the segregated nanoparticles, the EDS

Table 1
ICP and EDS analysis of the synthesized LSFN and LSF samples.

Sample	Element	ICP (at%)	EDS (at%)
LSFN	La	30.2	29.63
	Sr	19.9	22.57
	Fe	45.5	44.00
	Ni	4.4	3.80
	Total	100.0	100.00
LSF	La	30.4	30.87
	Sr	20.6	21.68
	Fe	49.0	47.45
	Total	100.0	100.00

Fig. 1. SEM images of LSFN (a) and LSF (d); SEM images of LSFN (b, e) and LSF (c, f) after reduction in H_2 -3% H_2O at 750 °C for 2 h; (g) XRD patterns of LSFN, LSF, and the samples calcined in H_2 -3% H_2O at 750 °C.

line-scanning profile is shown in Fig. 2(e). This clearly demonstrated that the segregated nanoparticles were Ni-Fe alloys. Therefore, these nanoparticles should have a cubic structure, which was confirmed by the fast Fourier transform (FFT) pattern (inset in Fig. 2(c)) in which the lattice spacings of 0.208 and 0.129 nm observed in the HRTEM image corresponded to the (111) and (220) planes of the cubic structure, respectively. Ni-Fe alloy has a high catalytic activity for a carbon based fuel [18,19]. As a SOFC anode, the catalytic activity of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ would be significantly improved by the in situ formed Ni-Fe nanoparticles. The XRD results indicated that the LSFN cathode decomposed into LaSrFeO_4 , La_2O_3 , Fe and Ni at over 800 °C, as shown in Fig. 3. As far as structural stability is concerned, these results suggested that LSFN-based materials are not suitable for use as a SOFC anode above 800 °C.

YSZ has a lower ionic conductivity at a lower operating

Fig. 2. TEM images of the reduced $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ powder. (a) Low magnification; (b, c) High magnification (Inset: FFT pattern taken from the marked area); (d) ADF STEM image and the EDS elemental mappings; (e) EDS line-scanning profiles along the arrow shown in (d).

temperature [20]. Tri-layer porous dense porous monolithic cells with a porous micro/nanostructure have demonstrated excellent performance in reduced-temperature SOFCs [21,22]. Furthermore, symmetrical SOFCs with a redox stable material as both the anode and cathode have many advantages, including the elimination of sulfur poisoning and coke formation by reversing the electrode as well as having enhanced cathode stability [9,23,24]. Therefore, to enable the LSFN electrode to work well at a lower temperature, we used a symmetrical LSFN-YSZ|YSZ|LSFN-YSZ monolithic cell configuration to evaluate the electrochemical performance. Fig. 4(a) presents a SEM

Fig. 3. XRD patterns of the LSFN sample reduced at different temperatures.

Fig. 4. (a) Cross-sectional SEM image showing the dense electrolyte layer and porous YSZ backbones and (b) high magnification SEM image of the impregnated LSFN catalyst; (c) Electrochemical performance of symmetrical single cells with different LSFN loadings in H_2 at 750 °C; (d) XRD pattern of one side of LSFN 30 wt% loading single cell after impregnating the electrode.

image of a typical YSZ-electrolyte monolithic cell consisting of a dense electrolyte layer 15 μm thick and two porous layers. The porosity of the porous layers was 45% and they were 300 μm thick. The effective electrode area was 0.385 cm^2 (0.7 cm diameter). Symmetrical single cells were fabricated by impregnating a LSFN or LSF precursor solution onto the porous layers of YSZ backbones with a subsequent heat treatment. Fig. 4(b) shows a higher magnification view of the impregnated electrode. After impregnating and calcining, the LSFN particles uniformly filled the pores and adhered to the YSZ backbone support. The average particle size of the electrode material was 200 nm. We also optimized the amount of LSFN electrode loading. The electrochemical performances of cells with different electrode loadings are shown in Fig. 4(c). For the cells with a low LSFN loading, the electrode material would not form a continuous conducting network. For the cell with 40 wt% LSFN loading, the effective triple-phase boundary (TPB) of anode was decreased due to the over coverage by the LSFN particles. The cell with 30 wt% loading showed the best performance. The infiltrated LSFN layer was porous but well internally connected at this loading. As shown in Fig. 4(d), there are only diffraction peaks from fluorite YSZ and perovskite LSFN in the XRD pattern of the single cell pellet with 30 wt% LSFN loading.

Fig. 5(a) and (b) show the cell voltage and power density as a function of the current density for the monolith cell with different electrodes and various fuels. From the comparison, it can be found that LSFN as a symmetrical electrode exhibited better catalytic activity for the oxidation of hydrocarbon fuels at 750 °C. The peak power densities of cells with impregnated LSFN electrodes reached 280, 230, and 400 mW/cm^2 in H_2 , CH_4 and

C_3H_8 , respectively. In C_3H_8 , the open circuit voltage (OCV) of the cell with the LSFN electrodes was 1.18 V, which was much higher than that in H_2 (~ 1.05 V), indicating that LSFN has excellent catalytic activity in C_3H_8 . In CH_4 , the OCV of the cell was 1.00 V, which was higher than with a $Ce(Mn,Fe)O_{2-x}$: $La(Sr)Fe(Mn)O_3$ composite anode (~ 0.6 V at 800 °C) [10], while the OCV of the cell with impregnated LSF electrodes was much lower in CH_4 , indicating a lower catalytic activity for hydrocarbon oxidation. The peak power densities of the cell with impregnated LSF electrodes were only 220, 80, and 240 mW/cm^2 in H_2 , CH_4 and C_3H_8 , respectively. As a symmetrical electrode, the LSFN has superior catalytic activity for CH_4 and C_3H_8 oxidation relative to the perovskite $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ [23] and K_2NiF_4 -type structured $Pr_{0.8}Sr_{1.2}(Co,Fe)_{0.8}Nb_{0.2}O_{4+\delta}$ catalyst [24]. To further examine the stability of the cell impregnated with LSFN and LSF electrodes, the current densities of the cell were recorded as a function of time under a constant voltage of 0.7 V in humidified C_3H_8 . As shown in Fig. 5(c), it can be seen that the symmetrical cell with LSFN electrodes showed excellent stability in humidified propane fuel at 750 °C and only a slight power output degradation was observed after more than 36 operation. However, the current density of the cell with LSF electrodes fluctuated strongly in humidified C_3H_8 . Moreover, a lot of tar-like substance was collected from the exhaust gas. However, the tar-like substance was not observed for the cell with the LSFN electrodes. The tar-like substance was analyzed by GC-MS (Table 2). There were more than 35 peaks in the GC-MS pattern. For simplicity, we only selected the peaks with an area more than 4%, which accounted for 61% of the total peak area. The MS results of the selected peaks are shown in

Fig. 5. Cell voltage (left) and power density (right) as a function of the current density for the monolith cell with different electrodes: LSFN (a), LSF (b), and (c) Current densities measured at 750 °C in C_3H_8 as a function of time for the cell with different electrodes operated at a constant voltage of 0.7 V in humidified C_3H_8 .

Table 2

Compounds assigned to the selected peaks of the GC-MS results.

Peak No.	Peak area (%)	Possible compounds, name and CAS No.	Peak No.	Peak area (%)	Possible compounds, name and CAS No.
6	5.09	Indene 95-13-6	20	4.70	Biphenyl 92-52-4
8, 9	4.90, 4.91	2-Methylindene 2177-47-1			Acenaphthene 83-32-9
		1-Methylindene 767-59-9			2-Vinylnaphthalene 827-54-3
12	5.97	Azulene 275-51-4	21	5.35	Biphenylene 259-79-0
		1,2-Benzofulvene 2471-84-3			Acenaphthylene 208-96-8
		Naphthalene 91-20-3	29	6.02	Anthracene 120-12-7
15, 16	8.23, 7.09	1-Methylnaphthalene 90-12-0			Phenanthrene 85-01-8
		2-Methylnaphthalene 91-57-6	34	4.20	Pyrene 129-00-0
		Benzonorbornadiene 4453-90-1			1,2-Benzacenaphthene 206-44-0
					Diphenylbutadiyne 886-66-8

Table 2, from which it can be seen that most of the products contained a benzene ring. This result indicated that C_3H_8 was not completely oxidized with the LSF electrode. All these results showed that the Ni doped $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ has better cata-

lytic activity for hydrocarbon oxidation than $La_{0.6}Sr_{0.4}FeO_{3-\delta}$. The enhancement of the catalytic activity of the LSFN was attributed to the high dispersion of the in situ segregated Ni-Fe nanoparticles.

Graphical Abstract

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Ni doped $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ symmetrical electrode for solid oxide fuel cells

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We report the rational design of a highly active Ni doped $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSFN) electrode for hydrocarbon fuel solid oxide fuel cells. Homogeneously dispersed Ni-Fe alloy nanoparticles were in situ extruded onto the surface of the LSFN particles during the operation of the cells. The electrode showed good stability in long term testing.

4. Conclusions

Pure phase perovskite compounds $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ (LSFN) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSF) were synthesized and studied as anodes for hydrocarbon fuel SOFCs. After reduction at 750 °C in H_2 -3% H_2O , highly active Ni-Fe alloy nanoparticles were in situ segregated onto the surface of LSFN particles. Symmetrical electrodes for SOFC single cells were prepared by impregnating the precursor solution onto the porous layers of YSZ monolithic cells and a subsequent calcination. The peak power density of a symmetrical LSFN-YSZ|YSZ|LSFN-YSZ monolithic cell reached 400 and 230 mW/cm^2 at 750 °C in humidified CH_4 and C_3H_8 fuels, respectively. The cell showed excellent long term stability at 750 °C for more than 36 h without coking and tar formation. The results demonstrated that the Ni doped $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ is a promising alternative anode for low temperature SOFCs and as both electrode materials for symmetrical SOFCs. The extraordinarily high performance of the new electrode would provide a very promising strategy for designing a highly active electrode material for SOFCs and as catalysts for other applications.

References

- [1] E. D. Wachsman, K. T. Lee, *Science*, **2011**, 334, 935–939.
- [2] C. W. Sun, U. Stimming, *J. Power Sources*, **2007**, 171, 247–260.
- [3] A. Atkinson, S. Barnett, R. J. Gorte, J. T. S. Irvine, A. J. Mcevoy, M. Mogensen, S. C. Singhal, J. Vohs, *Nat. Mater.*, **2004**, 3, 17–27.
- [4] S. McIntosh, R. J. Gorte, *Chem. Rev.*, **2004**, 104, 4845–4865.
- [5] L. Yang, S. Z. Wang, K. Blinn, M. F. Liu, Z. Liu, Z. Cheng, M. L. Liu, *Science*, **2009**, 326, 126–129.
- [6] S. W. Tao, J. T. S. Irvine, *Nat. Mater.*, **2003**, 2, 320–323.
- [7] Z. L. Zhan, S. A. Barnett, *Science*, **2005**, 308, 844–847.
- [8] C. W. Sun, Z. Xie, C. R. Xia, H. Li, L. Q. Chen, *Electrochem. Commun.*, **2006**, 8, 833–838.
- [9] C. H. Yang, Z. B. Yang, C. Jin, G. L. Xiao, F. L. Chen, M. F. Han, *Adv. Mater.*, **2012**, 24, 1439–1443.
- [10] T. H. Shin, S. Ida, T. Ishihara, *J. Am. Chem. Soc.*, **2011**, 133, 19399–19407.
- [11] Y. H. Hu, E. Ruckenstein, *Catal. Rev.*, **2002**, 44, 423–453.
- [12] W. Wang, C. Su, Y. Z. Wu, R. Ran, Z. P. Shao, *Chem. Rev.*, **2013**, 113, 8104–8151.
- [13] J. M. Vohs, R. J. Gorte, *Adv. Mater.*, **2009**, 21, 943–956.
- [14] S. P. Jiang, *Int. J. Hydrogen Energy*, **2012**, 37, 449–470.
- [15] D. Neagu, G. Tsekouras, D. N. Miller, H. Menard, J. T. S. Irvine, *Nat. Chem.*, **2013**, 5, 916–923.
- [16] G. M. Yang, C. Su, Y. B. Chen, M. O. Tadé, Z. P. Shao, *J. Mater. Chem. A*, **2014**, 2, 19526–19535.
- [17] C. Su, W. Wang, M. L. Liu, M. O. Tadé, Z. P. Shao, *Adv. Energy Mater.*, **2015**, 5, 1500188.
- [18] Z. X. Zhao, H. X. Dai, J. G. Deng, Y. C. Du, Y. X. Liu, L. Zhang, *Microporous Mesoporous Mater.*, **2012**, 163, 131–139.
- [19] B. Huang, S. R. Wang, R. Z. Liu, T. L. Wen, *J. Power Sources*, **2007**, 167, 288–294.
- [20] C. W. Sun, R. Hui, J. Roller, *J. Solid State Electrochem.*, **2010**, 14, 1125–1144.
- [21] Z. L. Zhan, D. M. Bierschenk, J. S. Cronin, S. A. Barnett, *Energy Environ. Sci.*, **2011**, 4, 3951–3954.
- [22] D. Han, X. J. Liu, F. R. Zeng, J. Q. Qian, T. Z. Wu, Z. L. Zhan, *Sci. Reports*, **2012**, 2, 462.
- [23] D. M. Bastidas, S. W. Tao, J. T. S. Irvine, *J. Mater. Chem.*, **2006**, 16, 1603–1605.
- [24] Q. Liu, X. H. Dong, G. L. Xiao, F. Zhao, F. L. Chen, *Adv. Mater.*, **2010**, 22, 5478–5482.

一种高活性 Ni 掺杂 $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ 作为碳基燃料固体氧化物燃料电池对称电极

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摘要: 固体氧化物燃料电池 (SOFCs) 是一种在中高温下可以直接将储存在燃料中的化学能转换成电能的全固态电化学反应装置. 因其具有能量转换效率高、环境友好、全固态结构以及可以使用碳氢化合物燃料等优点, 近年来受到了广泛的关注. 在诸多电极材料当中, Ni 基金属陶瓷是 SOFCs 中最常使用的阳极材料, 这是由于金属 Ni 具有优良的电子电导和催化性能. 然而当使用碳基化合物燃料时, 传统的 Ni 金属陶瓷阳极材料面临严重的积碳、Ni 颗粒长大以及硫中毒等问题. 这些问题不仅会影响 SOFCs 的寿命, 而且还会严重地降低 SOFC 的商业化进程. 因此, 开发具有高催化活性、抗积碳的阳极材料对碳氢化合物为燃料的固体氧化物燃料电池的发展至关重要. 与金属基阳极相比, 氧化物阳极的热膨胀系数与电解质材料更匹配, 性能的可调控性更强.

铁酸锶镧 (LSF) 是一种分子式为 ABO_3 的钙钛矿结构的氧化物, 在高温下具有较高的电子电导率. 据报道 LSF 作为阴极材料时, 表现出了良好的性能. 但是 LSF 作为阳极材料时, 却存在着催化性能不足的问题. 我们研究了 Ni 掺杂的 $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSFN), 以提高其作为 SOFCs 阳极材料的催化性能. 同时采用将 LSFN 在 SOFC 工作气氛下原位还原的方法, 在 LSFN 颗粒表面原位生长出分布均匀的纳米颗粒. 透射电镜分析结果表明该偏析的颗粒为 Ni-Fe 合金. 有报道显示, Ni-Fe 合金对碳氢化合物氧化具有良好的催化活性, 所以在 LSFN 颗粒表面生成这种合金颗粒有利于提高阳极材料的催化活性. 对于 Ni-Fe 合金以均匀的纳米颗粒析出的原因, 还有待进一步研究.

为了研究 LSFN 作为 SOFC 电极材料的性能, 我们采用浸渍法将 LSFN 前驱体溶液浸渍到氧化钇稳定氧化锆 (YSZ) 一体化电池的对称多孔骨架中, 经过焙烧, 得到了具有对称结构的 SOFC 单电池. 所使用的 YSZ 一体化骨架为中间层薄而致密, 两边厚而多孔的三层结构, 这种结构可以显著地降低电解质的厚度, 从而达到降低单电池的阻抗的目的. 这一新型对称电池结构具有如下优点: 阳极表面上可能发生的硫毒化和积碳问题有可能通过将阳极和阴极反用而消除; 氧化剂 (空气) 将冲走吸附在电极上的硫和碳粒子, 从而使电极得以再生. 此外, 氧化还原稳定的阴极预期将提高阴极的寿命. 对单电池的电化学测试结果表明, LSFN 电极材料的最佳浸渍量为 30 wt%, 这是因为较低的 LSFN 浸渍量 (< 30 wt%), 不能形成连续的电子传导网络, 电极的电子传导能力不足; 而 LSFN 电极材料的浸渍量高于 30 wt% 时则会降低电极反应的三相界面, 从而影响电池的性能.

在 750 °C 下, LSFN 为电极的单电池在以湿润 C_3H_8 为燃料时其开路电压 (OCV) 达到了约 1.18 V, 高于以 H_2 为燃料电池的电压. 以 CH_4 为燃料时, LSFN 为电极的单电池的开路电压远高于 LSF 为电极的单电池. 在 750 °C 下, 以 C_3H_8 为燃料时, LSFN 和 LSF 为电极的电池的峰值输出功率密度分别达到 400 和 230 mW/cm^2 . 这些结果表明, 通过 Ni 掺杂和原位焙烧, 在 LSFN 电极颗粒表面制备了均匀分布的 Ni-Fe 合金纳米颗粒, 极大地提高了铁酸锶镧材料对碳基燃料的催化活性. 长期放电测试结果表明, LSF 为电极的单电池在测试过程中, 尾气可以收集到类似焦油状的黑色物质; 而 LSFN 为电极的单电池在测试过程中并没有观察到明显的焦油状物质生成. 通过气相色谱-质谱联用分析, 发现所产生的焦油状物质主要成分是含苯环、碳碳双键或碳碳三键的烃类. 这说明 LSF 电极只能使 C_3H_8 部分氧化, LSFN 对 C_3H_8 等碳氢化合物燃料的氧化具有高的催化活性和良好的耐久性. Ni 掺杂的 $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ 阳极材料是一种有希望的碳基燃料 SOFCs 对称电极.

关键词: 固体氧化物燃料电池; Ni 掺杂 $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$; 对称电极; 碳基燃料

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