



Cr-poisoning under open-circuit condition in $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ -based nano composite cathodes for solid oxide fuel cells prepared by infiltration process

Yeong-Ju CHOE, Jeong-Uk SEO, Kyoung-Jin LEE, Min-Jin LEE, Hae-Jin HWANG

Department of Materials Science and Engineering, Inha University, 22212, 100, Inha-ro, Nam-gu, Incheon, Korea

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Abstract: $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ (LNF) powders were synthesized by the glycine–nitrate process and LNF–gadolinium-doped ceria (GDC) nanocomposite cathodes for solid oxide fuel cells (SOFCs) were fabricated by infiltration from LNF porous backbones. Electrochemical properties and Cr-poisoning behavior of LNF–GDC cathodes were studied. Single phase perovskite LNF could be obtained at the glycine to nitrate molar ratio of 1:1. The polarization resistance of the LNF–GDC nanocomposite cathode was significantly decreased in comparison with the LNF. This phenomenon was associated with enhanced catalytic activity and enlarged triple-phase boundary (TPB) length by GDC nano particles. In addition, the nanocomposite cathode showed good Cr tolerance under open circuit condition. The LNF–GDC nanocomposite cathodes were expected for use as a potential cathode in intermediate-temperature solid oxide fuel cells (IT-SOFC).

Key words: Cr-poisoning; perovskite; infiltration; solid oxide fuel cell; $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$

1 Introduction

A solid oxide fuel cell (SOFC) is an all-solid-state electrochemical device that converts the chemical energy of fuels (hydrogen) and an oxidant (oxygen or air) directly into electricity. Since SOFCs operate in the high temperature range of 800–1000 °C, they have various advantages such as high efficiency, multi-fuel capability, and no requirement of noble metal catalysts compared with other fuel cells [1,2]. On the other hand, the high temperature requires the use of expensive alloys and temperature cycling can introduce mechanical stress. In addition, high temperatures promote the diffusion of constituents of the electrode into the electrolyte. In this regard, the operating temperature of SOFCs should be lowered to an intermediate temperature range (650–850 °C) and this has been one of the most important research issues in the past few decades [2,3].

Cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFC) are required to have not only a high electrochemical activity but also high tolerance to chromium poisoning because of the exposure to gaseous chromium species resulting from stainless steel interconnects [4–6]. Many researchers have reported that the reaction between Mn or Sr in

lanthanum strontium manganite (LSM) and lanthanum strontium cobalt ferrite (LSCF) cathodes and the gaseous chromium species is responsible for chromium poisoning and results from increased cathode polarization [6,7].

$\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (LNF) with a perovskite structure is considered to be a promising cathode material for IT-SOFCs [8]. LNF exhibits a high electrical conductivity, compatible thermal expansion coefficient with yttrium-stabilized zirconia (YSZ) electrolyte, and good tolerance against gaseous chromium species. However, the electrochemical performance of LNF is not adequate compared with commonly used cathode materials such as LSCF and LSM [8]. In this study, a LNF–GDC nanocomposite cathode was fabricated by infiltrating GDC nanoparticles into the LNF cathode backbone. The infiltration technique is a great strategy to disperse nano-sized particles into a porous oxide backbone to improve the electrochemical activity of cathode materials [9,10]. The $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (LNF) powder used for the cathode backbone was synthesized by the glycine nitrate process (GNP). The electrochemical performance of symmetrical cells consisting of a GDC electrolyte and LNF–GDC nanocomposite cathodes was investigated. In addition, the Cr-poisoning behaviors of LNF and the LNF/GDC

nanocomposite cathode were also examined.

2 Experimental

The $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ powders were synthesized by the glycine–nitrate process shown in Fig. 1 [11]. The starting materials were $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich, USA), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich, USA), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.5%, Sigma-Aldrich, USA), and glycine (99.0%, Junsei, Japan). The metal nitrates were dissolved in distilled water and then, glycine was added into the mixed nitrate solution at fuel to nitrate molar ratios of 1:1, 1.5:1 and 0.5:1. The solution was heated to 200 °C and the combustion reaction subsequently occurred. The precursor powders were then calcined at 700 °C for 5 h.

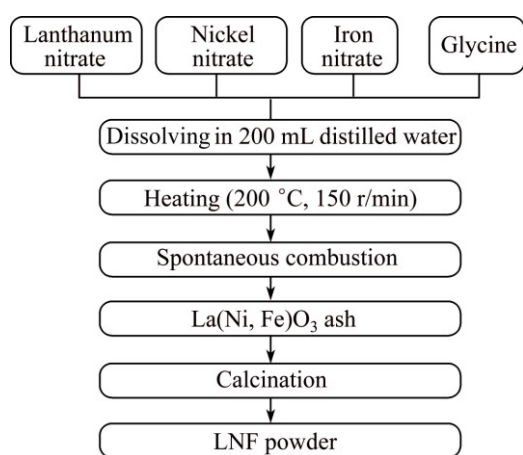


Fig. 1 Schematic diagram of synthesis of $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ powders

The solution for infiltration was prepared from $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich, USA), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.0%, Sigma-Aldrich, USA), and ethanol. The gadolinium to cerium molar ratio was 2:8 and the concentration of the nitrate solution was 1 mol/L. The porous LNF backbone was coated on both sides of the GDC electrolyte disk (20 mm in diameter) by screen printing and was subsequently heat-treated at 1000 °C for 2 h. Infiltration was performed by dropping 30 μL of the infiltration solution into the porous LNF backbone using a micro pipet, as shown in Fig. 2. After infiltration,

the sample was placed in a vacuum oven for uniform coating and homogeneous precipitation. The infiltrated samples were calcined at 350 °C for 2 h. The infiltration and calcination processes were repeated 7 times.

The Cr-poisoning behaviors of the LNF and LNF–GDC nanocomposite cathode were evaluated using the symmetrical cell exposed to the gaseous chromium species produced from the chromium oxide (Cr_2O_3) powder (99.0%, Junsei, Japan) compact, as shown in Fig. 3. The sample was heat-treated at 800 °C for 100 h in an atmosphere containing gaseous chromium species. The Cr_2O_3 powder was uniaxially pressed into a disk type and sintered at 1000 °C for 1 h. For comparison, the same sample was heat-treated at 800 °C for 100 h in a dry air atmosphere.

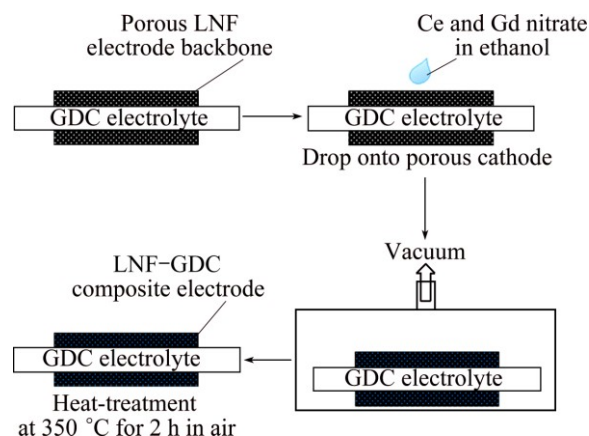


Fig. 2 Schematic illustration showing fabrication of electrode by infiltration of GDC components into porous LNF backbone and schematic of structure of LNF–GDC composite cathode

Phase identification of the synthesized powder was performed using a powder diffractometer (DMAX–2500, Rigaku, Japan) with Ni-filtered $\text{Cu K}\alpha$ radiation. The microstructure of the cathode was observed by a field emission scanning electron microscope (FE-SEM, S–3200, Philips). The electrochemical performance of the symmetrical cells was measured by electrochemical impedance spectroscopy (EIS). AC impedance spectroscopy was performed with an excitation potential of 20 mV over a frequency range of 1 MHz to 0.1 Hz generated by a frequency analyzer (IM6e, Zhaner).

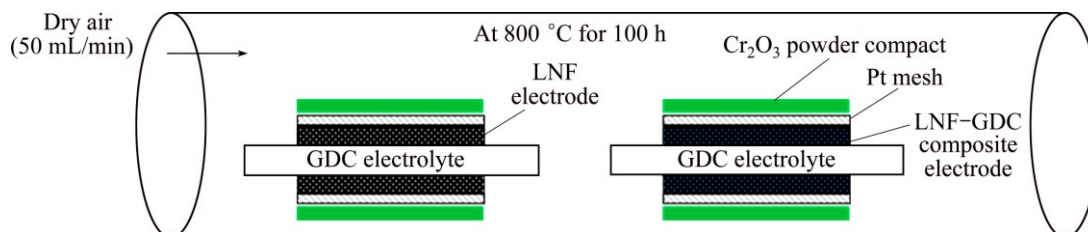


Fig. 3 Schematic diagram of Cr-poisoning experimental setup

3 Results and discussion

Figure 4 shows the XRD patterns of the $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ powders calcined at 700 °C for 5 h in air. In the case of a glycine to nitrate molar ratio of 1:1, the reflections corresponding to the identified phases are labeled and closely match the JCPDS data (File No. 01–088–0637). It can be seen that the synthesized powder can be identified as a single-phase perovskite with a general formula of $\text{ABO}_{3-\delta}$ [8,12]. On the other hand, secondary phases such as La_2O_3 , NiO and $\text{La}_4\text{Ni}_3\text{O}_{10}$ were detected in powder samples at the glycine to nitrate molar ratios of 0.5:1 and 1.5:1. The molar ratio of glycine to nitrate is a very important parameter in the glycine nitrate process. When the molar ratio is too small (in the case of the glycine to nitrate molar ratio of 0.5:1), the perfect chelation of nitrates does not occur and this can result in inhomogeneity of the powder composition or in the appearance of unreacted starting materials. In the case of the glycine to nitrate molar ratio of 1.5:1, it seems that the excess glycine made the flame temperature too much higher, which can allow non-uniform reaction [11,13].

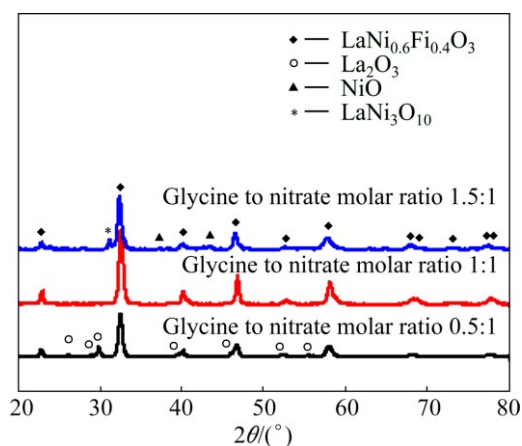


Fig. 4 XRD patterns of synthesized $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ powders calcined at 700 °C as function of glycine to nitrate molar ratio

Figures 5 (a) and (b) show the impedance spectra of the LNF cathodes and GDC-infiltrated LNF (LNF–GDC) composite cathodes, respectively, as a function of temperature. The polarization resistances of the LNF and LNF–GDC nanocomposite cathodes decreased with increasing temperature. The LNF–GDC nanocomposite cathodes showed low polarization resistances at all temperatures. For example, the polarization resistance decreased from 84.8 to 0.35 $\Omega\cdot\text{cm}^2$ at 650 °C. This result indicates that the GDC nanoparticles are effective in enhancing the catalytic activity for the oxygen reduction reaction at the cathode. The infiltrated GDC nanoparticles cause the triple-phase boundary (TPB)

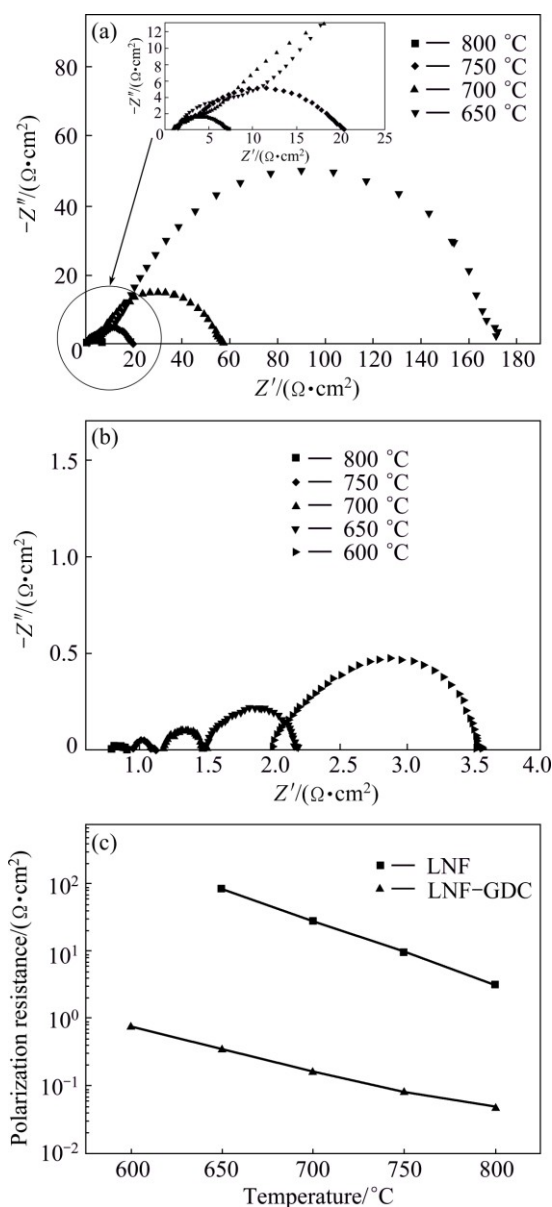


Fig. 5 Impedance spectra of LNF (a) and GDC-infiltrated LNF composite cathodes (b) as function of temperature, Arrhenius plots of polarization resistances of LNF and LNF–GDC composite cathodes (c)

length to enlarge and the conducting pathway to connect, which facilitates high electrochemical performance and effective charge transport [9]. There are two basic types of infiltration methods, structures of ionic conductor particles with an electronic conductor backbone and electronic conductor particles with an ionic conductor backbone [10,14,15]. In this study, the LNF–GDC cathodes correspond to the former case. The advantage of infiltrating the electrolyte nanoparticles into the electrode backbone is that there is no requirement to heat them at high temperatures over 850 °C in order to form the perovskite phases [16]. It also reduces coarsening of the infiltrated nanoparticles compared with the

electrolyte backbone.

Cross-sectional and high magnification SEM images of the LNF and LNF–GDC nanocomposite cathodes are shown in Fig. 6. As evident in Figs. 6(a) and (c), the thickness of the cathodes was $\sim 23\ \mu\text{m}$ and the cathodes exhibited porous microstructures in good interfacial contact with the GDC electrolyte, with no signs of delamination. The infiltrated GDC nanoparticles were homogeneously distributed in the LNF backbone and the size of the GDC was estimated to be approximately a few tens of nanometer, as can be seen in Fig. 6(d). It appears that both LNF and GDC make a 3-dimension network structure which resulted in the enhanced catalytic activity of the LNF–GDC nanocomposite cathode.

To analyze the chromium poisoning behavior under open circuit condition, the polarization resistances of the

LNF/GDC/LNF and LNF–GDC/GDC/LNF–GDC cells were measured before and after exposure to gaseous chromium species. The results are shown in Fig. 7 and Table 1. Almost the same polarization resistance was obtained in the two cases in spite of the exposure to chromium vapors, which demonstrates that the LNF and LNF–GDC composite cathodes have high tolerance to Cr-poisoning, as reported by other researchers [8,17,18]. In our previous study, there is a degradation of LSCF electrode under same condition [19]. Although there is literature about degradation of electronic conductivity of LNF under current load because of the nickel chromate formation by nickel segregation, it was reported to have no significant change on the cathode performance in comparison to the LSM [18]. Chromium deposition is generally observed at the electrode/electrolyte interface in the case of materials vulnerable to chromium such as

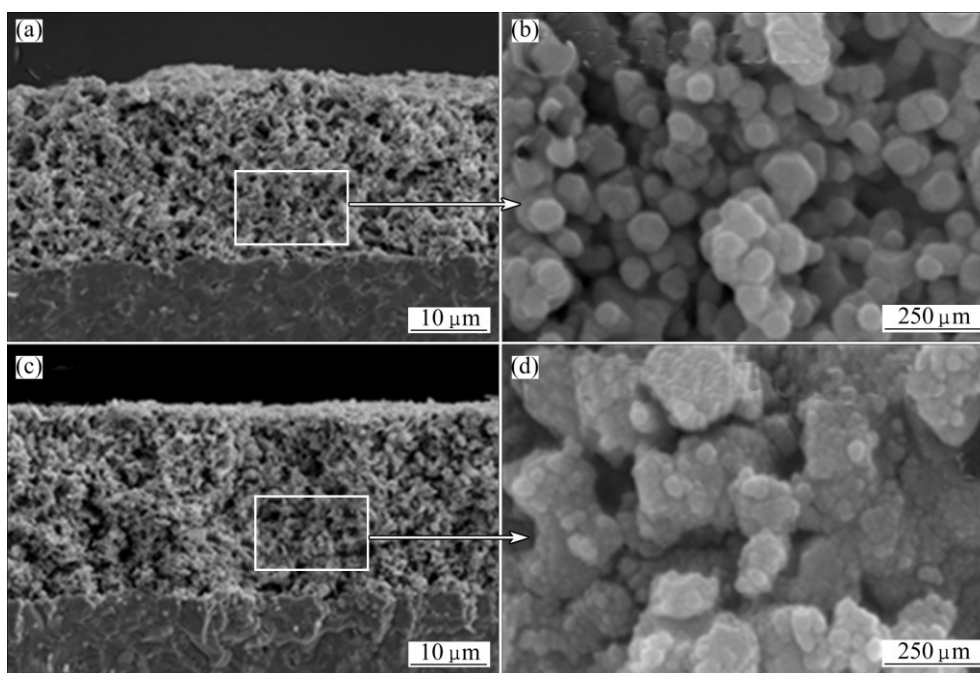


Fig. 6 SEM images of LNF (a, b) and GDC-infiltrated LNF electrode (c, d)

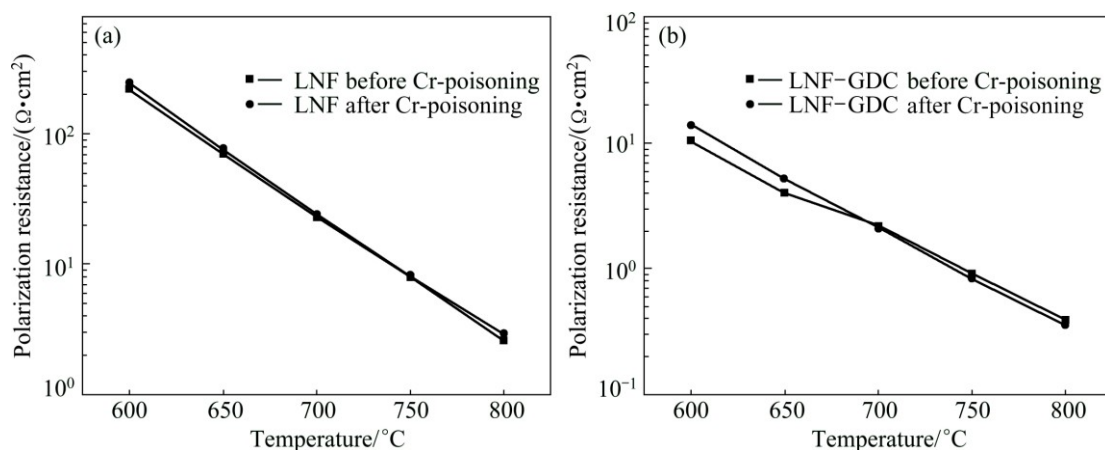


Fig. 7 Arrhenius plots of polarization resistances (R_p) of LNF (a) and LNF–GDC composite cathodes (b) before and after Cr-poisoning

Table 1 Polarization resistances of LNF and LNF–GDC composite cathodes before and after Cr-poisoning

Temperature/ °C	$R_p/(\Omega \cdot \text{cm}^2)$			
	LNF before Cr- poisoning	LNF after Cr- poisoning	LNF–GDC before Cr- poisoning	LNF–GDC after Cr- poisoning
600	221.649	246.616	10.431	13.979
650	70.567	76.474	4.017	5.202
700	23.047	24.008	2.201	2.121
750	7.969	8.185	0.919	0.845
800	2.614	2.917	0.391	0.36

LSM and LSCF [6,7,17]. ZHEN et al [8] reported that there was no visible Cr deposition at 900 °C at the LNF/YSZ interface in the presence of a Fe–Cr alloy.

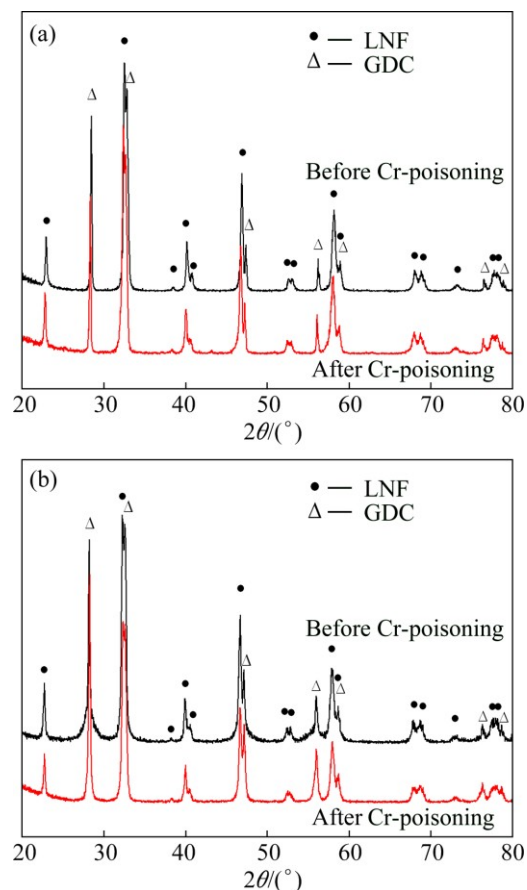
After the cells were heat-treated at 800 °C for 100 h in the atmosphere consisting of gaseous chromium species, the LNF backbone and GDC particles were well adhered. Also, degradation of the electrochemical performance was not observed in the LNF cathodes or the LNF–GDC composite cathodes shown in Fig. 7. Although the polarization resistance of the LNF–GDC nanocomposite cathode increased after heat treatment at 800 °C in air, this phenomenon resulted from coarsening of infiltrated GDC particles at high temperature. The LNF–GDC nanocomposite has potential for use in IT-SOFC cathodes with a high tolerance to Cr-poisoning. Although Ni chromate can form by nickel segregation, it was reported to have a negligible effect on the cathode performance [20].

To examine the reaction between LNF and gaseous chromium species, we confirmed the phase change before and after Cr-poisoning, and the resulting XRD patterns are shown in Fig. 8. There were no additional peaks due to the reaction between the LNF or GDC and the gaseous chromium species. Compared with reports in Refs. [21,22] in which the LSCF reacts with the gaseous chromium species to produce strontium chromite, it seems that LNF is a relatively stable material against Cr vapors, which is related to the almost same polarization resistance obtained before and after Cr-poisoning.

4 Conclusions

$\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ (LNF) powders were synthesized by glycine nitrate process (GNP) and LNF–GDC nanocomposite cathodes were fabricated by infiltration from the LNF porous backbone. The catalytic activity of the LNF–GDC nanocomposite cathode was significantly improved compared with that of the LNF cathode. The addition of GDC into the LNF cathode resulted in an enhanced ionic conductivity and triple-phase boundaries. Although the polarization resistances of the LNF–GDC nanocomposite cathodes were slightly increased after heat treatment at 800 °C for 100 h, they were much

lower than that of the LNF cathode. It was found that the nanocomposite cathode showed good durability against Cr-poisoning under open-circuit condition and can be considered for use as a potential cathode in intermediate-temperature solid oxide fuel cells (IT-SOFC).

**Fig. 8** XRD patterns of LNF (a) and LNF–GDC composite cathodes (b) before and after Cr-poisoning

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熔渗法制备固体氧化燃料电池

LaNi_{0.6}Fe_{0.4}O_{3-δ}基纳米复合阴极在开路条件下的铬中毒

Yeong-Ju CHOE, Jeong-Uk SEO, Kyoung-Jin LEE, Min-Jin LEE, Hae-Jin HWANG

Department of Materials Science and Engineering, Inha University, 22212, 100, Inha-ro, Nam-gu, Incheon, Korea

摘要: 利用甘氨酸–硝酸盐方法合成 LaNi_{0.6}Fe_{0.4}O_{3-δ}(LNF)粉末, 采用 LNF 多孔主干熔渗法制备掺杂二氧化锆 LNF–钆(GDC)固体氧化燃料电池纳米复合阴极。研究了 LNF–GDC 纳米复合阴极的电化学性能和铬中毒行为。当甘氨酸和硝酸盐的摩尔比为 1 : 1 时可得到单相钙钛矿 LNF。与 LNF 相比, LNF–GDC 纳米复合阴极的极化阻抗显著降低, 这与增强的催化活性和增大的三相边界长度有关。另外, 在开路条件下, 纳米复合阴极有较好的铬容忍。在中温固体氧化燃料电池中, LNF–GDC 纳米复合阴极有望成为一种颇具潜力的阴极材料。

关键词: 铬中毒; 钙钛矿; 熔渗; 固体氧化燃料电池; LaNi_{0.6}Fe_{0.4}O_{3-δ}

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