



## Short communication

Ni–LnO<sub>x</sub> (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) cermet anodes for intermediate-temperature solid oxide fuel cells

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## ABSTRACT

The cermet anodes for solid oxide fuel cells (SOFCs) usually consist of Ni and an oxygen ion conductor such as yttria-stabilized zirconia (YSZ) and doped ceria (DCO). In this work, Ni–LnO<sub>x</sub> cermets (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd), in which LnO<sub>x</sub> is not an oxygen ion conductor, are primarily investigated as the anodes for intermediate-temperature SOFCs. The electrochemical performances of the Ni–LnO<sub>x</sub> anodes are characterized using single SOFCs with Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> composite cathodes and Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.95</sub> electrolytes. When humidified H<sub>2</sub> is used as the fuel and ambient air as the oxidant, Ni–CeO<sub>2</sub> and Ni–Gd<sub>2</sub>O<sub>3</sub> anodes have exhibited very high performance, which is comparable to that of Ni–DCO anodes, the state-of-the-art electrodes for intermediate-temperature SOFCs with ceria electrolytes. The performance is further improved by increasing the anode porosity; peak power density up to 730 mW cm<sup>-2</sup> and total interfacial polarization resistance down to 0.12 Ω cm<sup>2</sup> are achieved for Ln = Sm, Eu, Ce, and Gd. The low interfacial polarization resistance and high power densities might be related to the high catalytic activity of LnO<sub>x</sub> and the optimized microstructures by increasing the porosity. These results suggest a promising alternative to the conventional anodes for SOFCs.

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## 1. Introduction

Solid oxide fuel cells (SOFCs) have received great attention due to their potential for providing a highly efficient and environmentally benign way of generating electricity [1–3]. At the present time, development of anode materials has focused on several classes of materials including Cu cermets [4–6], perovskites [7–9] and pyrochlores [10], etc. But the most advanced SOFCs are clearly those based on the so-called cermet anodes, which are composed of Ni and an oxygen ion conducting ceramic such as yttria-stabilized zirconia (YSZ) or doped ceria (DCO) [11,12]. In these anodes, Ni acts as both the catalyst for electrochemical oxidation of the fuel and electronic conducting phase, while the ceramic possess a substantial oxygen ionic conductivity, so that the reaction zone can be extended from the electrode–electrolyte interface to the bulk of the electrode.

In the case of Ni–YSZ cermets, zirconia additions have been reported to improve the oxidation kinetics without essential influence on the reaction mechanism by expanding the electrochemically active zone up to 10–20 μm from the electrolyte surface due to the ionic transport in the zirconia matrix. When YSZ is replaced by DCO, the kinetics is in principle further improved due to DCO having

higher oxygen ion conductivity in combination with higher electrocatalytic activity than YSZ. For example, using YSZ as the electrolyte layer, Ni–Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub> anodes exhibited overpotential of about 25 mV at 800 °C and 200 mA cm<sup>-2</sup> while Ni–(Y<sub>2</sub>O<sub>3</sub>)<sub>0.08</sub>(ZrO<sub>2</sub>)<sub>0.92</sub> anodes displayed 200 mV overpotential under the same conditions [13]. Generally, the higher the oxygen ionic conductivity of the added electrolyte, the lower is the anodic overpotential or the interfacial polarization resistance. This is demonstrated by comparison studies of anode materials with different levels of the oxygen ionic transport, namely, Ni–Y<sub>0.15</sub>Zr<sub>0.85</sub>O<sub>1.93</sub>, Ni–Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2-δ</sub>, Gd<sub>0.4</sub>Ce<sub>0.6</sub>O<sub>2-δ</sub>, La<sub>0.75</sub>Sr<sub>0.25</sub>Cr<sub>0.97</sub>V<sub>0.03</sub>O<sub>3-δ</sub>, and Zr<sub>0.71</sub>Y<sub>0.12</sub>Ti<sub>0.17</sub>O<sub>2-δ</sub>. It confirmed that increasing ionic conductivity leads to lower values of the total polarization resistance [14]. An analogous correlation was also found between the anodic overpotentials and ionic conduction in the cermet anodes made of Ni–SDC, Ni–Gd<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2-δ</sub>, Ni–Nd<sub>0.9</sub>Ca<sub>0.1</sub>Ga<sub>0.9</sub>Co<sub>0.1</sub>O<sub>3-δ</sub>, Ni–La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.115</sub>Co<sub>0.085</sub>O<sub>3-δ</sub>, Ni–Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, and pure Ni [15].

In addition to the reaction zone expansion, oxide components have also a number of important functions, including matching thermal expansion of the cell components, stabilizing the anode layer with respect to redox cycling, preventing sintering of metal particles, and acting as catalyst or catalyst support. Consequently, it is often impossible to separate the effects originating from ionic conduction in the oxide phase from changes in the catalytic behavior and anode microstructure. In some cases, catalytic activity is

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more important than the oxygen ion conductivity. Recently, the Ni–Sm<sub>2</sub>O<sub>3</sub> cermet anodes have been shown to have performance comparable to that of Ni–SDC anodes for intermediate-temperature SOFCs [16], even though ionic conductivity of Sm<sub>2</sub>O<sub>3</sub> is negligible comparing with SDC. The high cell performance is possibly due to the high catalytic activity of Sm<sub>2</sub>O<sub>3</sub>.

Here, lanthanide oxides (La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Pr<sub>6</sub>O<sub>11</sub>, Nd<sub>6</sub>O<sub>11</sub>, Sm<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, and Gd<sub>2</sub>O<sub>3</sub>) are primarily investigated as the ceramic components for Ni-based anodes. The oxides are cooperated with NiO to form NiO–LnO<sub>x</sub> composites, which are in situ reduced to Ni–LnO<sub>x</sub> and characterized using single cells based on Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.95</sub> electrolytes and Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> composite cathodes.

## 2. Experimental

### 2.1. Cell fabrication

Oxide powders involved in this work including lanthanide oxides (LnO<sub>x</sub>), NiO, Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.95</sub> (GDC, the electrolyte material) and Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> (SSC, the cathode material) were synthesized via a glycine–nitrate process (GNP) [17] with nitrates as the starting materials. The nitrates and glycine were dissolved in distilled water to form a solution with the mole ratio of glycine/metal of 2:1. The solution was then heated till self-combustion occurred. The resulted ash was heated at 800 °C for 2 h to form oxide powders. X-ray diffraction analysis showed that lanthanide oxides were in the form of La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Pr<sub>6</sub>O<sub>11</sub>, Nd<sub>6</sub>O<sub>11</sub>, Sm<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, and Gd<sub>2</sub>O<sub>3</sub>. A mixed powder of NiO and lanthanide oxides (in a weight ratio of NiO:LnO<sub>x</sub> = 60:40) was pressed at 20 MPa as anode substrates with a diameter of 13 mm. Samples with 20 wt.% spherical graphite as pore former were also prepared for comparison. GDC powder was then added, distributed uniformly, and co-pressed [18] onto the substrate at 280 MPa. The bilayer was subsequently sintered at 1150 °C for 5 h to burn out the graphite and result in a dense GDC film on the NiO–LnO<sub>x</sub> substrate. In order to evaluate the catalytic activity of Ni–LnO<sub>x</sub> as the anode, for comparison, single cells with Ni–GDC and Ni–Al<sub>2</sub>O<sub>3</sub> as the anodes were also fabricated with the same process. Al<sub>2</sub>O<sub>3</sub> is non-active for any catalytical oxidation reaction. SSC–SDC (in a weight ratio of SSC:SDC = 70:30) powders were mixed thoroughly with a 10 wt.% ethylcellulose–terpineol binder to prepare cathode slurry. The slurry was painted on the GDC electrolyte layers and fired at 950 °C for 2 h to form single cells. The fabricating process was kept as consistent as possible so that identical cathodic polarization resistance could be achieved. The thickness of the electrolyte and anode was about 30 μm and 0.4 mm, respectively. The single cell with Ni–LnO<sub>x</sub> as the anode is designated as FC–LnO<sub>x</sub>. For example, FC–La<sub>2</sub>O<sub>3</sub> represents a single cell with a Ni–La<sub>2</sub>O<sub>3</sub> anode, a GDC electrolyte, and an SSC–SDC cathode. The average grain size of the anode support was ~2.6 μm as estimated with scanning electron microscopy. And the measured average pore diameter of the anode support was ~1.3 μm as measured with mercury porosimetry.

### 2.2. Cell testing and microstructure characterization

The single cells were sealed onto alumina tubes with silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins). Humidified (3% H<sub>2</sub>O) hydrogen was used as the fuel with a flow rate of 50 mL min<sup>-1</sup> and ambient air as the oxidant. NiO was in situ reduced to Ni at 600 °C for 2 h. An Electrochemical Workstation (IM6e, Zahner) was used to characterize the single cells. The current–voltage curve was obtained by using a galvanostat mode and the electrochemical impedance spectra were measured under open-circuit conditions in the frequency range typically from 0.1 Hz to 1 MHz. The porosity and pore size distribution of the anode was measured

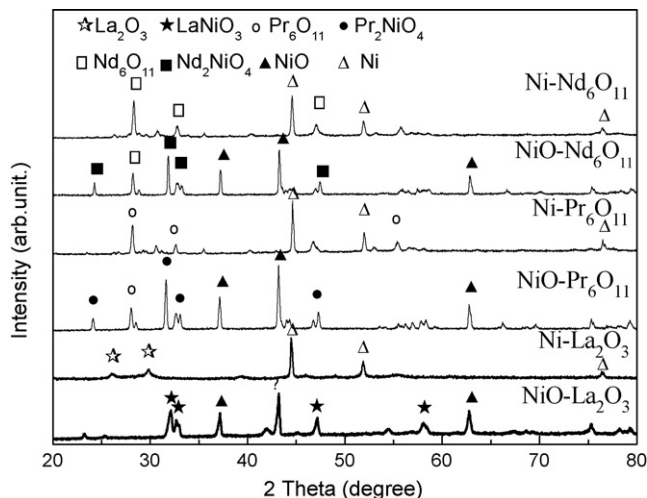


Fig. 1. XRD patterns of NiO–LnO<sub>x</sub> and Ni–LnO<sub>x</sub> composites (Ln=La, Pr and Nd). NiO–LnO<sub>x</sub> was sintered at 1150 °C for 5 h and Ni–LnO<sub>x</sub> was formed by reducing NiO–LnO<sub>x</sub> at 600 °C with humidified H<sub>2</sub>.

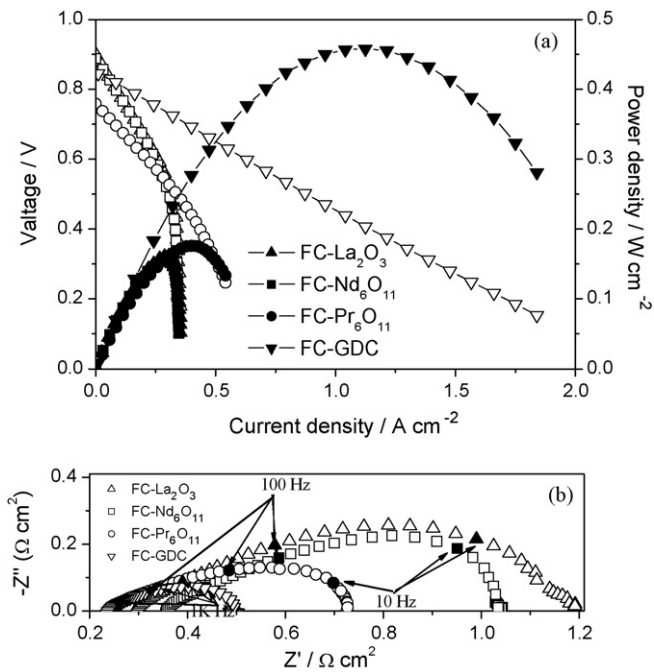
with mercury porosimetry (Poremaster GT-60). The phase identification of porous NiO–LnO<sub>x</sub> substrates was conducted with X-ray diffraction (XRD) analysis using Cu Kα radiation (D/Max-gA) at room temperature. The microstructure was observed via a scanning electron microscope (SEM, JSM-6700F, JEOL).

## 3. Results and discussion

### 3.1. Ni–LnO<sub>x</sub> (LnO<sub>x</sub> = La<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub> and Nd<sub>6</sub>O<sub>11</sub>)

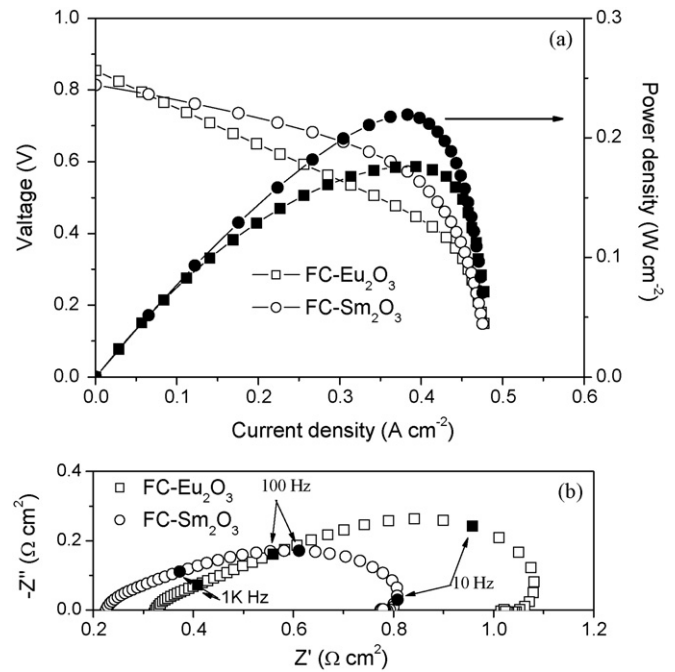
Fig. 1 shows the XRD patterns of NiO–LnO<sub>x</sub> and Ni–LnO<sub>x</sub> composites, in which LnO<sub>x</sub> = La<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub>, and Nd<sub>6</sub>O<sub>11</sub>. Significant reactions took place between NiO and LnO<sub>x</sub> when the composites were co-fired at 1150 °C for 5 h in air. The reactions resulted in new compounds; perovskite structured LaNiO<sub>3</sub>, K<sub>2</sub>NiF<sub>4</sub> type structure of Pr<sub>2</sub>NiO<sub>4</sub> and Nd<sub>2</sub>NiO<sub>4</sub>, respectively. These are consistent with previous studies by Zaghrioui et al. [19], who synthesized the compounds with NiO and LnO<sub>x</sub> at 1350 °C using a solid-state reaction method. Diffraction peaks corresponding to NiO also present on the patterns, indicating the reactions have not consumed all the NiO since the NiO to LnO<sub>x</sub> weight ratio was 60:40 in the starting materials. It looks very likely that La<sub>2</sub>O<sub>3</sub> reacts completely with NiO while the reaction between Pr<sub>6</sub>O<sub>11</sub> or Nd<sub>6</sub>O<sub>11</sub> and NiO is not complete in the cell fabricating conditions. When the NiO–LnO<sub>x</sub> composites were treated at 600 °C for 10 h with humidified H<sub>2</sub>, NiO was reduced to Ni as expected. The treatment also had effect on the newly formed compounds; LaNiO<sub>3</sub> decomposed to La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>NiO<sub>4</sub> to Nd<sub>6</sub>O<sub>11</sub>, and Pr<sub>2</sub>NiO<sub>4</sub> to Pr<sub>6</sub>O<sub>11</sub> (Fig. 1).

Fig. 2a shows the cell performance when the NiO–LnO<sub>x</sub> composites were in situ reduced and used as the anodes. A cell based on a Ni–GDC composite anode, which was prepared with the same fabrication procedure, is also tested for comparison. The performance of FC–GDC is similar to those reported in the literature with Ni–SDC or Ni–GDC anodes, which usually generate peak power density of about 400 mW cm<sup>-2</sup> at 600 °C [17,18,20–22]. Peak power densities at 600 °C are only 160, 176 and 154 mW cm<sup>-2</sup> for FC–La<sub>2</sub>O<sub>3</sub>, FC–Pr<sub>6</sub>O<sub>11</sub>, and FC–Nd<sub>6</sub>O<sub>11</sub>, respectively. The power densities are much lower than that of FC–GDC, which generates peak power density of about 457 mW cm<sup>-2</sup> at 600 °C. The relatively low power densities suggest poor activity of Ni–La<sub>2</sub>O<sub>3</sub>, Ni–Pr<sub>6</sub>O<sub>11</sub> and Ni–Nd<sub>6</sub>O<sub>11</sub> anodes. Fig. 2b is impedance spectra measured under open-circuit conditions. The total interfacial polarization resistance, which is derived from the difference between



**Fig. 2.** (a) I–V curves measured at 600 °C for the single cells with Ni–LnO<sub>x</sub> (Ln=La, Pr, and Nd) and Ni–GDC anodes and (b) impedance spectra at the same temperature measured under open-circuit conditions.

low and high frequency intercepts at the real axis, is 0.90, 0.48 and 0.68 Ω cm<sup>2</sup>, respectively. The resistances are much higher than the typical value of 0.2 Ω cm<sup>2</sup> reported for Ni–SDC and Ni–GDC based fuel cells [17,18,20–22]. They are also higher than that for FC–GDC, 0.25 Ω cm<sup>2</sup> (Fig. 2b). Since the cathodes have the same composition and are fabricated with the same process, the resistance associated with the cathodic polarization process should be very close for FC–LnO<sub>x</sub> and FC–GDC. Therefore, the high resistance should be attributed to the low electrochemical activity of Ni–La<sub>2</sub>O<sub>3</sub>, Ni–Pr<sub>6</sub>O<sub>11</sub> and Ni–Nd<sub>6</sub>O<sub>11</sub> anodes. In addition to the high interfacial polarization resistances under open-circuit conditions, FC–La<sub>2</sub>O<sub>3</sub> and FC–Nd<sub>6</sub>O<sub>11</sub> exhibited high concentration polarization when current density was higher than 0.3 A cm<sup>-2</sup>. The poor anodic performance might due to solid-state reactions occurred between NiO and LnO<sub>x</sub> in the cell fabrication process although NiO was subsequently released and reduced to Ni under fuel-cell oper-

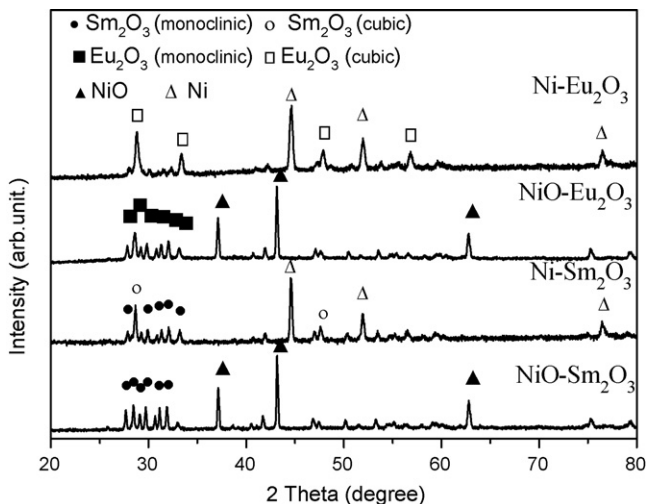


**Fig. 4.** (a) I–V curves measured at 600 °C for single cells with Ni–LnO<sub>x</sub> (Ln=Sm, Eu) anodes and (b) impedance spectra measured at the same temperature under open-circuit conditions.

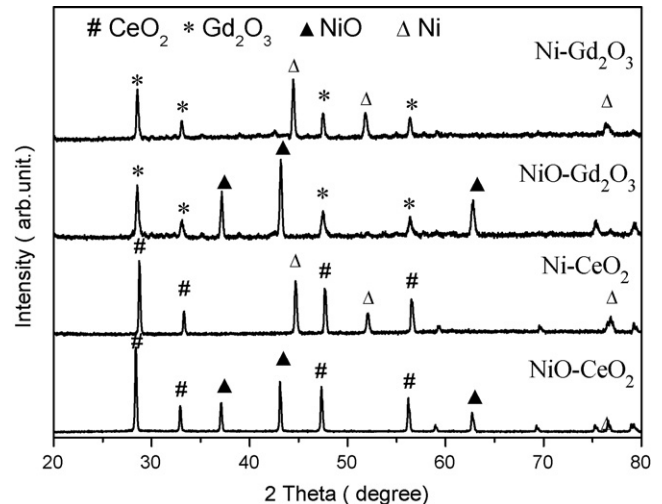
ation conditions. Because of the poor performance and solid-state reaction, the three lanthanide oxides could not be good candidates as SOFC anode materials.

### 3.2. Ni–LnO<sub>x</sub> (LnO<sub>x</sub> = Sm<sub>2</sub>O<sub>3</sub> and Eu<sub>2</sub>O<sub>3</sub>)

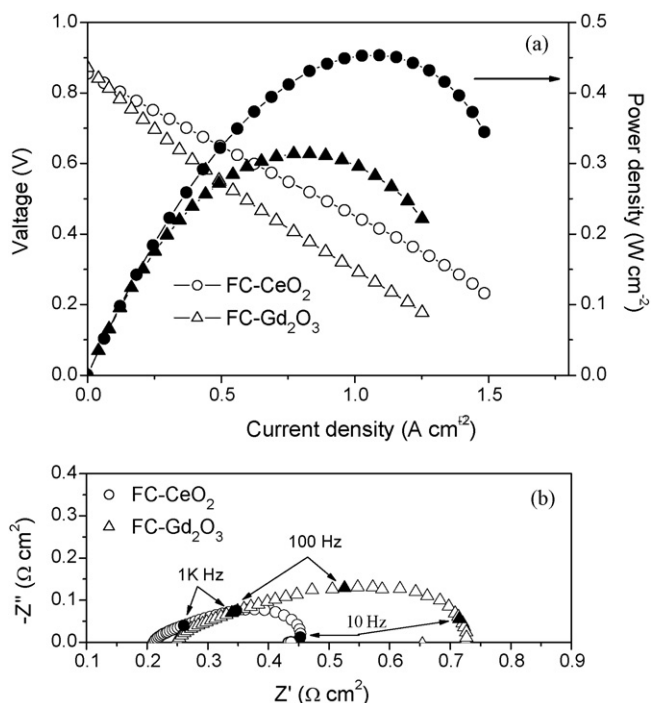
Fig. 3 is the XRD patterns of NiO–LnO<sub>x</sub> (LnO<sub>x</sub> = Sm<sub>2</sub>O<sub>3</sub> and Eu<sub>2</sub>O<sub>3</sub>) and their reduced products. Unlike La<sub>2</sub>O<sub>3</sub>, Nd<sub>6</sub>O<sub>11</sub> and Pr<sub>6</sub>O<sub>11</sub>, Sm<sub>2</sub>O<sub>3</sub> and Eu<sub>2</sub>O<sub>3</sub> do not react with NiO to form any new compounds when they are sintered at 1150 °C for 5 h. Although Eu<sub>2</sub>O<sub>3</sub> is compatible with NiO, it changes its crystal structure from monoclinic with a space group C2/m(1 2) to cubic fluorite with a space group Ia $\bar{3}$ (206) when it is treated at 600 °C with humidified H<sub>2</sub>. So does Sm<sub>2</sub>O<sub>3</sub>, which partly changes to cubic phase from monoclinic structure. Single cells with Ni–Sm<sub>2</sub>O<sub>3</sub> and Ni–Eu<sub>2</sub>O<sub>3</sub> composite anodes generate peak power densities of 219 and 176 mW cm<sup>-2</sup>



**Fig. 3.** XRD patterns of NiO–LnO<sub>x</sub> and Ni–LnO<sub>x</sub> composites (Ln=Sm, Eu).

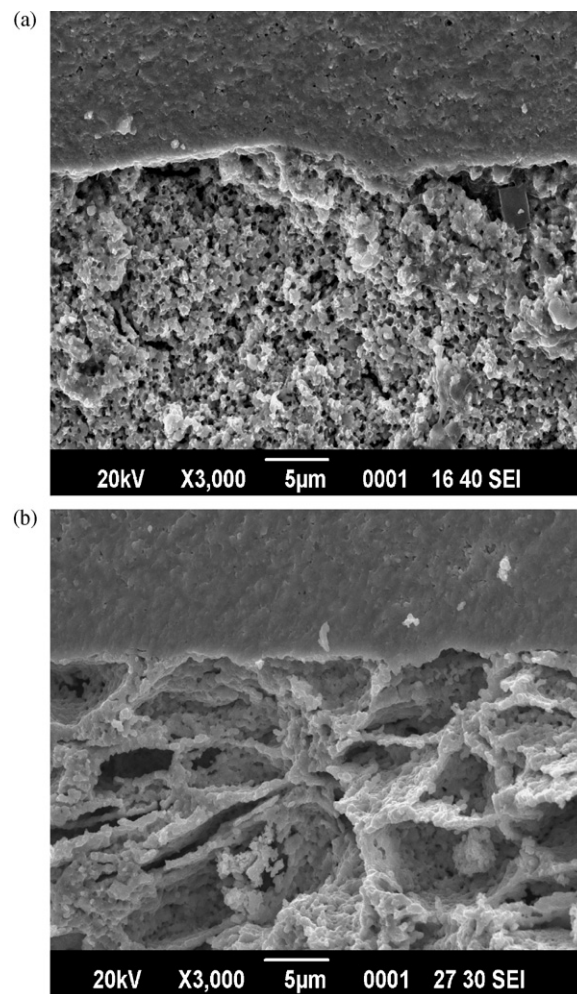


**Fig. 5.** XRD patterns of NiO–LnO<sub>x</sub> and Ni–LnO<sub>x</sub> composites (Ln=Ce, Gd).



**Fig. 6.** (a) I–V curves measured at 600 °C for the single cells with Ni–LnO<sub>x</sub> (Ln = Ce, Gd) anodes and (b) impedance spectra measured at the same temperature under open-circuit conditions.

at 600 °C (Fig. 4a), respectively. The interfacial polarization resistances under open-circuit conditions are 0.55 and 0.70  $\Omega\ cm^2$  (Fig. 4b), respectively. Concentration polarization is observed when the current density is over 0.4  $A\ cm^{-2}$ . The cell performance as well as the anodic activity is also lower than those derived from Ni–GDC

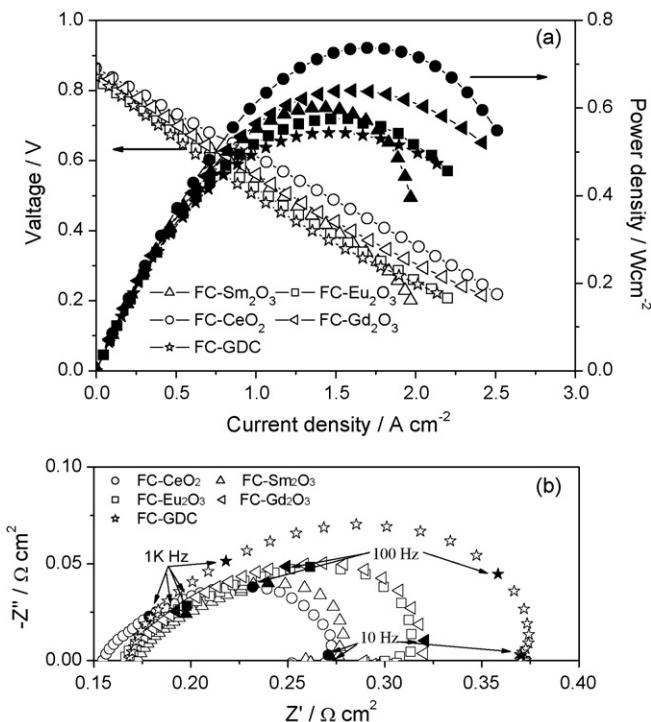


**Fig. 8.** Cross-sectional views (SEM micrographs) of GDC–electrolyte and Ni–Sm<sub>2</sub>O<sub>3</sub> anode components after fuel-cell performance testing. (a) Ni–Sm<sub>2</sub>O<sub>3</sub> anodes prepared without pore formers. (b) Ni–Sm<sub>2</sub>O<sub>3</sub> anodes prepared with pore formers.

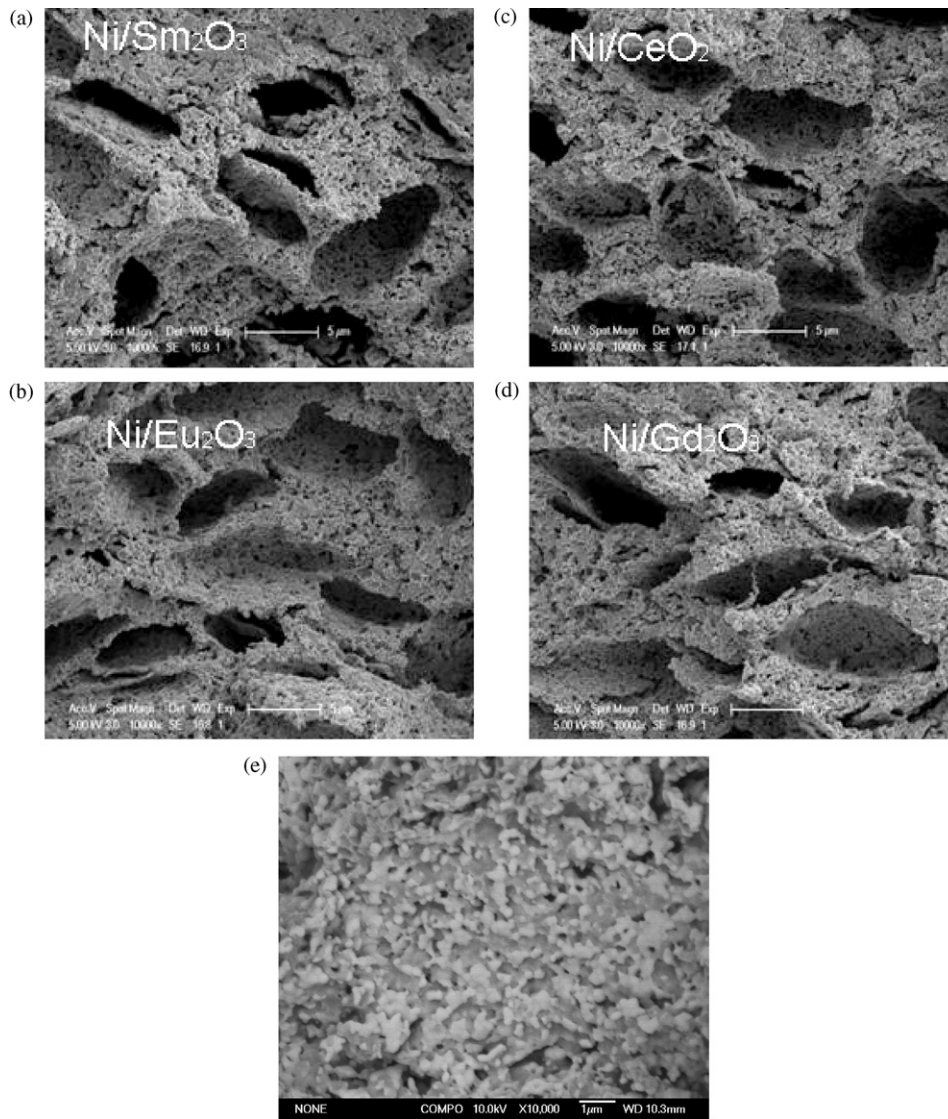
anodes. Phase change might be the reason for the relatively low power export associated with concentration polarization.

### 3.3. Ni–LnO<sub>x</sub> (LnO<sub>x</sub> = CeO<sub>2</sub> and Gd<sub>2</sub>O<sub>3</sub>)

Fig. 5 shows the XRD patterns of NiO–LnO<sub>x</sub> and Ni–LnO<sub>x</sub> composites, in which LnO<sub>x</sub> = CeO<sub>2</sub> and Gd<sub>2</sub>O<sub>3</sub>. No solid solutions are formed between NiO and either of the two oxides when they are sintered at 1150 °C for 5 h. When NiO–LnO<sub>x</sub> composites are treated at 600 °C with hydrogen, NiO is reduced to Ni. Meanwhile, no obviously phase changes occur. FC–CeO<sub>2</sub> and FC–Gd<sub>2</sub>O<sub>3</sub> produce peak power densities of 545 and 314  $mW\ cm^{-2}$  (Fig. 6a), while the interfacial polarization resistances are 0.23 and 0.48  $\Omega\ cm^2$  (Fig. 6b), respectively. The exhibited performances are much higher than those of FC–La<sub>2</sub>O<sub>3</sub>, FC–Pr<sub>6</sub>O<sub>11</sub>, FC–Nd<sub>6</sub>O<sub>11</sub>, FC–Sm<sub>2</sub>O<sub>3</sub>, and FC–Eu<sub>2</sub>O<sub>3</sub>. In addition, the performance is consistent with our previous results [16]. It seems that the performance is critically related to the stability of LnO<sub>x</sub> when it is used as the anode component. Both solid-state reaction in cell fabrication processes and phase change in the process when NiO is reduced to Ni might cause deteriorating electrochemical performance. Unlike Gd<sub>2</sub>O<sub>3</sub>, which is chemically stable under anodic conditions, CeO<sub>2</sub> can be partially reduced,  $Ce^{4+} = Ce^{3+} + e$ , resulting in some ionic mobility as well as a degree of electronic conductivity. The reduction and its associated ionic and electronic conduction might be other reasons for the high performance of FC–CeO<sub>2</sub>.



**Fig. 7.** (a) Cell voltages and power densities as a function of current density measured at 600 °C for fuel cells based on Ni–LnO<sub>x</sub> (Ln = Sm, Eu, Ce, Gd) and Ni–GDC anodes when pore former was used. (b) Impedance spectra measured at the same temperature under open-circuit conditions.



**Fig. 9.** (a)–(d) SEM micrographs for cross-section views of NiO–LnO<sub>x</sub> (LnO<sub>x</sub> = Sm<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Gd<sub>2</sub>O<sub>3</sub>) anodes prepared with pore formers. (e) EBSD micrographs of cross-section for Ni–Gd<sub>2</sub>O<sub>3</sub> anode.

### 3.4. Effect of anode porosity

Concentration polarization is observed although no solid-state reaction occurs between NiO and Sm<sub>2</sub>O<sub>3</sub> or Eu<sub>2</sub>O<sub>3</sub>. So, it is very likely that phase changes might be the reason for the concentration polarization, which is usually due to the low porosity of electrodes. The polarization might be minimized by increasing the anode porosity. In order to investigate the effect of anode porosity on fuel-cell performance, spherical graphite of 20 wt.% to NiO–LnO<sub>x</sub> was added as the pore former. Fig. 7a shows typical current–voltage curves at 600 °C for FC–Sm<sub>2</sub>O<sub>3</sub>, FC–Eu<sub>2</sub>O<sub>3</sub>, FC–CeO<sub>2</sub> and FC–Gd<sub>2</sub>O<sub>3</sub> that are prepared with the pore former. FC–GDC prepared with pore former is also shown for comparison. The open-circuit voltages (OCVs) are in the range of 0.84–0.87 V, close to those with Ni–GDC anodes and GDC electrolytes. The peak power densities are 600, 575, 738, and 640 mW cm<sup>−2</sup>, respectively, higher than that of 544 mW cm<sup>−2</sup> obtained with FC–GDC when pore former is used. Cell performances of FC–Sm<sub>2</sub>O<sub>3</sub> and FC–Eu<sub>2</sub>O<sub>3</sub> are relatively lower than those of FC–CeO<sub>2</sub> and FC–Gd<sub>2</sub>O<sub>3</sub>, which could be caused by the phase change of Sm<sub>2</sub>O<sub>3</sub> and Eu<sub>2</sub>O<sub>3</sub>. However, the power densities are higher than that prepared without pore former (Fig. 4a). Shown in Fig. 8 is the microstructure comparison of Ni–Sm<sub>2</sub>O<sub>3</sub>

anodes prepared with and without graphite addition. In both cases, the GDC electrolyte is strongly attached to the anodes and shows a well defined interface. It can be seen that the use of pore former has increased not only the porosity but also pore size. The anode without using pore former has small pores about 1–2 μm in size, whereas the anodes prepared with pore former has not only the small pores but also big pores, about 10 μm in size. The difference between the power densities shown in Fig. 4a and Fig. 7a is most possibly due to the microstructure difference of the anodes (Fig. 8). Therefore, the performance of FC–Sm<sub>2</sub>O<sub>3</sub> and FC–Eu<sub>2</sub>O<sub>3</sub> can be substantially improved by increasing the anode porosity.

Fig. 7b shows the impedance spectra under open-circuit conditions. The ohmic resistances of FC–LnO<sub>x</sub> (LnO<sub>x</sub> = Sm<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and Gd<sub>2</sub>O<sub>3</sub>) corresponding to the real axis intercepts at high frequency, are 0.171, 0.171, 0.161, and 0.171 Ω cm<sup>2</sup>, which are very close to each other. The total interfacial polarization resistances are 0.081, 0.131, 0.121, and 0.121 Ω cm<sup>2</sup>, respectively, lower than the value of 0.20 Ω cm<sup>2</sup> for FC–GDC prepared with pore former, and much lower than those obtained without graphite addition.

The electrochemical performance of an anode depends on the catalytic activity of the materials and its microstructure characteristics including porosity. It has been revealed that Ni–LnO<sub>x</sub>

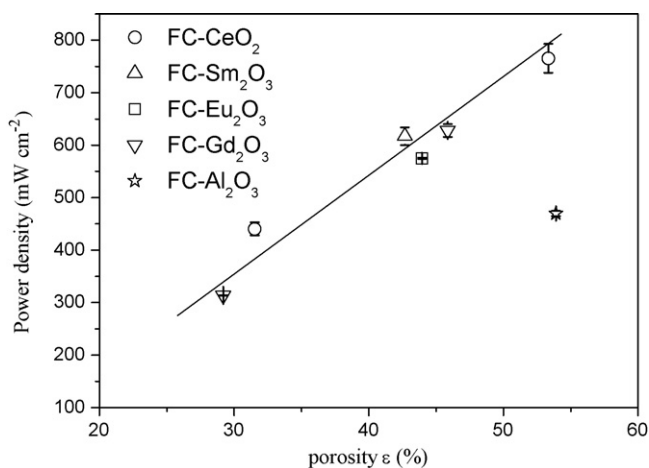


Fig. 10. The peak power densities measured at 600 °C at different anode porosity for cells FC-Sm<sub>2</sub>O<sub>3</sub>, FC-Eu<sub>2</sub>O<sub>3</sub>, FC-CeO<sub>2</sub>, FC-Gd<sub>2</sub>O<sub>3</sub> and FC-Al<sub>2</sub>O<sub>3</sub>.

composites (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) have shown high activity in the oxidative conversion of methane to syngas [23]. These catalysts differ in activity from each other but only to a small extent. Therefore, the catalytic of the Ni-LnO<sub>x</sub> anodes is reasonably assumed to be close to each other. The microstructure of the Ni-LnO<sub>x</sub> (Ln = Sm, Eu, Ce, and Gd) anodes prepared with graphite are also similar. Fig. 9 shows their cross-sectional micrographs for the samples that have been used for performance test. These anodes display very similar microstructures; pores with size up to 10 μm present in the anodes, the particles of Ni and LnO<sub>x</sub> are very fine and have similar size, which is far smaller than the pore size. As can be seen from Fig. 9e, the two phases (Ni and LnO<sub>x</sub>) are uniformly distributed and well connected. This characteristic is desirable for both catalytic reaction and electronic conduction. For the Ni-Gd<sub>2</sub>O<sub>3</sub> anode, it is clearly seen that the Gd<sub>2</sub>O<sub>3</sub> forming isolated fine grains, and the dark one (Ni particles) are uniformly distributed and well connected. It is noted that although the microstructures are similar to each other, Ni-CeO<sub>2</sub> has the highest porosity, which might due to different sintering behavior of NiO-LnO<sub>x</sub>. Simultaneously, FC-CeO<sub>2</sub> has the highest power density and lowest interfacial polarization resistance as shown in Fig. 7.

Fig. 10 shows the peak power density versus Ni-LnO<sub>x</sub> porosity. The porosity is high enough so that concentration polarization is negligible. The power density increases almost linearly with the porosity, indicating the porosity has a determine effect on the performance of Ni-LnO<sub>x</sub> anodes. It also infers that the electrochemical activity of LnO<sub>x</sub> is very similar for Ln = Sm, Eu, Ce, and Gd when the Ni-LnO<sub>x</sub> anode is free of concentration polarization. This agrees well with the previous report by Choudhary et al, who have demonstrated that LnO<sub>x</sub> have similar activity for oxidation [23,24]. The electrochemical activity of LnO<sub>x</sub> is further illustrated with single cells using Ni-Al<sub>2</sub>O<sub>3</sub> as the anode (Fig. 10). The power density of FC-Al<sub>2</sub>O<sub>3</sub> is much lower than that of FC-CeO<sub>2</sub> although the two cells have similar porosities. Al<sub>2</sub>O<sub>3</sub> is believed to be not active for oxidation reactions. Choudhary et al. have also demonstrated that Ni-LnO<sub>x</sub> catalysts are much superior to Ni-Al<sub>2</sub>O<sub>3</sub> in the oxidative conversion of methane to syngas [23]. It should be noted that the different porosity is obtained although NiO-LnO<sub>x</sub> is fabricated with the same procedure, which infers the different sintering behavior of LnO<sub>x</sub>.

The performance of a Ni-cermet anode depends usually on the conductivity of its ceramic component. However, this work demonstrates that when the catalytic activity is high enough, the oxygen ionic conductivity might not so important. In addition to the catalytic activity, the porosity might be more critical than that has been ever considered. Therefore, the difference in electrochemical performance might be directly related to the porosity of the anode.

#### 4. Conclusions

Ni-LnO<sub>x</sub> (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) composite are preliminary investigated as the anodes for solid oxide fuel cells. When Ln = La, Pr, and Nd, the cells have shown very low performance, which might be caused by the solid-state reactions between NiO and La<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub> or Nd<sub>6</sub>O<sub>11</sub> during the cell fabrication processes. When Ln = Sm and Eu, the anodes performance is limited by concentration polarization, which is possibly caused by phase change of Sm<sub>2</sub>O<sub>3</sub> and Eu<sub>2</sub>O<sub>3</sub> as well as the low anodes porosity. When Ln = Ce and Gd, high performance is achieved. The performance is comparable to that reported for Ni-DCO anodes, and can be further improved by increasing the anode porosity. When the porosity is high enough to eliminate concentration polarization, the Ni-LnO<sub>x</sub> (Ln = Ce, Sm, Eu, and Gd) anodes exhibit very high performance; power density over 600 mW cm<sup>-2</sup> is achieved at 600 °C with these anodes. These results suggest new anode materials for SOFCs.

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