

Electrode properties of porous $\text{La}_2\text{NiO}_{4+\delta}$ layers screen-printed on a $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ electrolyte

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A $\text{La}_2\text{NiO}_{4+\delta}/\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}/\text{La}_2\text{NiO}_{4+\delta}$ symmetrical cell was prepared using a screen-printing method by sintering at 1100 °C. The electrochemical properties of the cell were examined by the impedance spectroscopy technique under zero dc bias in air between 500-700 °C. The $\text{La}_2\text{NiO}_{4+\delta}$ electrodes displayed satisfactory chemical and thermodynamic compatibilities with the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ electrolyte. A comparatively low area specific resistance of 0.18 $\Omega \text{ cm}^2$ at 700 °C was determined for the $\text{La}_2\text{NiO}_{4+\delta}$ electrodes. Scanning electron microscope (SEM) observation revealed that the $\text{La}_2\text{NiO}_{4+\delta}$ electrodes showed a reasonable porosity, a well-necked connection among fine grains and a tight adhesion to the electrolyte support. The desired microstructure is regarded to be responsible for the superior electrode properties of the $\text{La}_2\text{NiO}_{4+\delta}$ layers.

Key words: $\text{La}_2\text{NiO}_{4+\delta}$, Mixed conductor, Electrode properties, Screen-printing, $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ electrolyte.

Introduction

Solid oxide fuel cells (SOFCs) are electricity generation devices with high efficiency and environmental advantages. There has been a considerable effort to reduce the operation temperature of SOFCs down to an intermediate temperature range (600-800 °C). As to the development of intermediate-temperature SOFCs, one of the major problems encountered is performance degradation at the reduced operation temperatures, to a great extent resulting from large cathodic polarization. Adopting electronic-ionic mixed conductors as the cathode has been widely recognized to be a viable solution to this problem due to the extension of the triple phase boundary (TPB) length and the promotion of cathode reaction kinetics at intermediate temperatures. Over the past decades, much work concerning the mixed conductors has been focused on oxygen-deficient perovskite-type (ABO_3) complex oxides with $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) as the representative system. The LSCF oxides have electronic conductivities exceeding $10^2 \Omega^{-1}\text{cm}^{-1}$, ionic conductivities of the order of 10^{-2} – $1.0 \Omega^{-1}\text{cm}^{-1}$ and high electrocatalytic activity towards oxygen reduction within the intermediate temperature range [1, 2]. Unfortunately, the LSCF oxides suffer from extraordinarily large thermal expansion coefficient (TEC) values, resulting in a difficulty in matching with other components of SOFCs, especially solid-state electrolytes. In overcoming the TEC incompatible problem, extensive research has been devoted to decreasing TEC by composition modification based on the LSCF

system, such as adjusting the content of acceptor dopant Sr at the A-sites and/or the Co/Fe ratio at the B-sites [3-5], replacing the La at the A-sites by smaller lanthanide elements [6, 7] and designing composite cathodes [8, 9]. On the other hand, attempts have also been made to search for novel cathode materials with both high mixed conducting properties and proper TEC values matching with electrolyte materials. Recently, oxygen hyperstoichiometric $\text{La}_2\text{NiO}_{4+\delta}$ -based compounds with a K_2NiF_4 -type (A_2BO_4) structure have attracted growing attention as a novel mixed conductor [10-15]. The $\text{La}_2\text{NiO}_{4+\delta}$ -based oxides exhibit high oxygen diffusion and surface exchange coefficients at intermediate temperatures, appreciable p-type electronic conductivity, moderate TEC values around $13.0 \times 10^{-6} \text{ K}^{-1}$ and sufficient structural stability with respect to changes in oxygen partial pressure. These desired properties make the $\text{La}_2\text{NiO}_{4+\delta}$ -based oxides promising candidate materials for the cathodes of intermediate-temperature SOFCs.

Previous research on SOFCs has indicated that the cathode polarization of a cell usually accounts for a dominant part of the whole cell polarization [16]. Therefore, the polarization characteristic is an important criterion of material selection for the cathode of SOFCs. Electrochemical impedance spectroscopy is an often-employed technique to qualitatively and quantitatively investigate electrode properties. The electrode properties of $\text{La}_2\text{NiO}_{4+\delta}$ have been examined by the technique with respect to various contributing factors, such as temperature, oxygen partial pressure and applied dc bias [17-22]. Much of these investigations were performed based on $\text{La}_2\text{NiO}_{4+\delta}$ working with a yttria-stabilized zirconia (YSZ) electrolyte [17, 18, 20, 21]. Only a few of them dealt

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with the electrode properties of $\text{La}_2\text{NiO}_{4+\delta}$ on samaria-doped ceria (SDC) [22] or strontium- and magnesium-doped lanthanum gallate (LSGM) [19]. As is well-known, these two materials have currently been viewed as the main candidates for the electrolyte of intermediate-temperature SOFCs because of their superior oxygen ionic conductivity at intermediate temperatures. It has been found that reaction kinetics of a cathode in contact with an electrolyte is significantly affected by the nature of the electrolyte [22, 23]. Therefore, further research is warranted on the electrode properties of $\text{La}_2\text{NiO}_{4+\delta}$ working with the intermediate-temperature electrolyte materials in view of its potential application in intermediate-temperature SOFCs.

In continuation of our earlier researches on $\text{La}_2\text{NiO}_{4+\delta}$ mixed conductor and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ electrolyte material [24-26], a $\text{La}_2\text{NiO}_{4+\delta}/\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}/\text{La}_2\text{NiO}_{4+\delta}$ symmetrical cell was prepared using a screen-printing method. The electrochemical properties of the $\text{La}_2\text{NiO}_{4+\delta}$ electrodes were investigated in terms of the polarization resistance by the impedance spectroscopy technique.

Experimental Procedures

$\text{La}_2\text{NiO}_{4+\delta}$ powder was synthesized by a polyamino-carboxylate complex method using reagent grade $\text{La}(\text{OH})_3$, $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and diethylenetriaminepentaacetic acid (H_5DTPA) as starting materials. The details of the synthesis process have been described elsewhere [24]. Field emission scanning electron microscopy (FESM, Hitachi S-4700) observations certified that the resulting power consisted of superfine and uniform particles of about 100 nm, as shown in Fig. 1.

$\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ powder was synthesized by an urea-combustion method using $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and urea ($\text{CO}(\text{NH}_2)_2$) as starting materials. The starting materials were dissolved into deionized water to form a solution. Heating the solution on a hot plate ignited

combustion and resulted in a swollen ash with a pure cubic fluorite phase. The ash was wet-milled with zirconia balls in a polyethylene jar for 48 h. The milled powder was compacted into pellets and sintered at 1250 °C for 4 h in air. The Archimedes measurement indicated that the ceramic pellets attained about 96% of the theoretical density. The urea-combustion synthesis, sinterability and electrical conducting properties of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ have been previously reported [25].

The ceramic $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ pellets were polished to a thickness of about 0.14 cm. The $\text{La}_2\text{NiO}_{4+\delta}$ powder was mixed with organic binders, additives and solvents to form a slurry-type ink. The weight fraction of the $\text{La}_2\text{NiO}_{4+\delta}$ powder in the ink was about 70%. The ink was screen-printed onto both surfaces of a $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ dense pellet to form a symmetrical cell. The cell was sintered at 1100 °C for 2 h in air. The electrode area was about 0.79 cm². Platinum meshes were placed on the $\text{La}_2\text{NiO}_{4+\delta}$ electrodes as current collectors. The impedance spectra of the cell were collected with a CHI 660C electrochemical workstation using a two-electrode configuration between 500-700 °C in air. The measurements were performed under zero dc bias in the frequency range of 0.01 Hz-100 kHz with an input sinuous signal amplitude of 5 mV. The measured data were analyzed by the Zview 3.0a software.

X-ray diffraction (XRD) analysis was performed for the $\text{La}_2\text{NiO}_{4+\delta}$ electrode layers sintered on the electrolyte pellet with a Philips X'Pert PRO X-ray diffractometry using Cu K α radiation. The morphology of the cell after sintering was observed with a Jeol JMS-5610LV scanning electron microscope (SEM). The thermal expansion of $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ was examined upon heating in air at a heating rate of 5 K·minute⁻¹ between 50-900 °C by a Netzsch DIL 402C dilatometer with alumina as calibration standard. $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ specimens sintered at 1300 °C and 1250 °C for 4 h in air, respectively, were used for the thermal expansion investigation. Our prior result indicated that the density of $\text{La}_2\text{NiO}_{4+\delta}$ ceramic sintered at 1300 °C for 4 h in air was about 93% of the theoretical density [26].

Results and Discussion

Chemical and thermodynamic compatibilities between $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ are important concerns when examining the polarization characteristics of the electrode based on the electrolyte. Fig. 2 shows an XRD pattern of the $\text{La}_2\text{NiO}_{4+\delta}$ layer sintered on the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ pellet at 1100 °C. For comparison purposes, the XRD patterns of the as-synthesized $\text{La}_2\text{NiO}_{4+\delta}$ powder and the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ pellet are also shown in Fig. 2. The peaks presented in the XRD pattern of the investigated specimen are assignable to $\text{La}_2\text{NiO}_{4+\delta}$ or $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ phases, respectively. There is a significant peak overlapping from the two phases. This is due to the nature of the $\text{La}_2\text{NiO}_{4+\delta}$ layer as a membrane on the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$

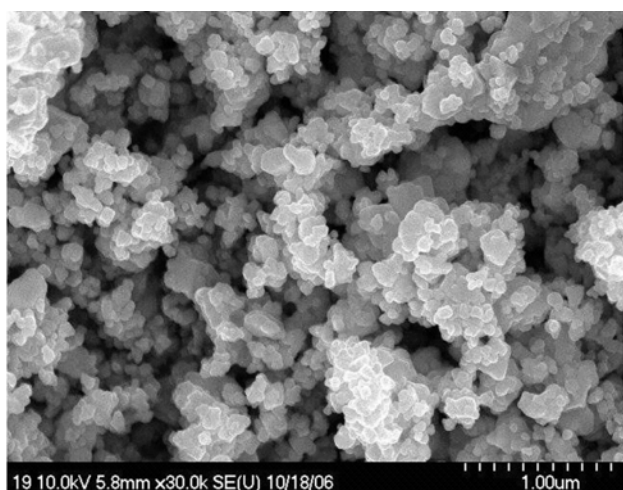


Fig. 1. FESM image of $\text{La}_2\text{NiO}_{4+\delta}$ powder synthesized by a polyaminocarboxylate complex method.

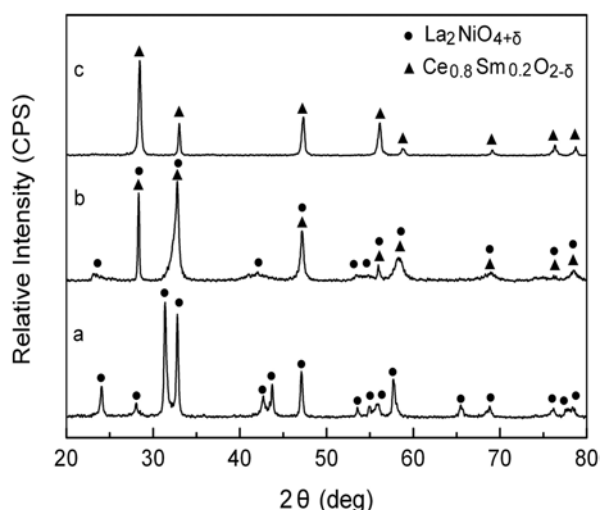


Fig. 2. XRD patterns of $\text{La}_2\text{NiO}_{4+\delta}$ electrode sintered on $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ pellet at 1100 °C, (a) as-synthesized $\text{La}_2\text{NiO}_{4+\delta}$ powder, (b) $\text{La}_2\text{NiO}_{4+\delta}$ electrode sintered on $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ pellet, (b) at 1100 °C and (c) $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ pellet.

support. No noticeable impurity phase could be detected within the sensitivity of XRD, indicating a good chemical compatibility between the two components. A similar result has been reported for $\text{La}_2\text{NiO}_{4+\delta}$ sintered onto $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$ ($x = 0.1, 0.2, 0.3, 0.4$) at 1000 °C [22]. Fig. 3 shows the thermal expansion curves of the $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ specimens sintered at 1300 and 1250 °C, respectively. The thermal expansion curves of the two specimens are basically linear within the measured temperature ranges. The $\text{La}_2\text{NiO}_{4+\delta}$ specimen gives a TEC of $13.0 \times 10^{-6} \text{ K}^{-1}$ averaged between 50–900 °C. The

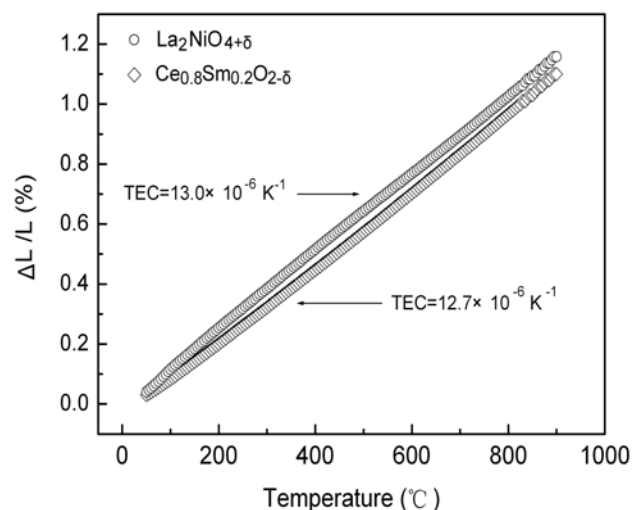


Fig. 3. Thermal expansion curves of $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ specimens sintered at 1300 °C and 1250 °C, respectively.

value is generally consistent with previous results on $\text{La}_2\text{NiO}_{4+\delta}$ -based ceramics [19, 22]. The $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ specimen offers an average TEC of $12.7 \times 10^{-6} \text{ K}^{-1}$, agreeing well with those of the Samarium-doped ceria (SDC) or gadolinia-doped ceria (GDC) [9, 22]. Thus, one can conclude a good thermodynamic compatibility between the electrode and electrolyte materials. This is advantageous to good adhesion between the electrode layers and the electrolyte pellet during the impedance spectrum measurement at various temperatures.

Fig. 4 shows the impedance spectra measured at different temperatures for the $\text{La}_2\text{NiO}_{4+\delta}/\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}/\text{La}_2\text{NiO}_{4+\delta}$ cell. It should be mentioned that inductive impedance

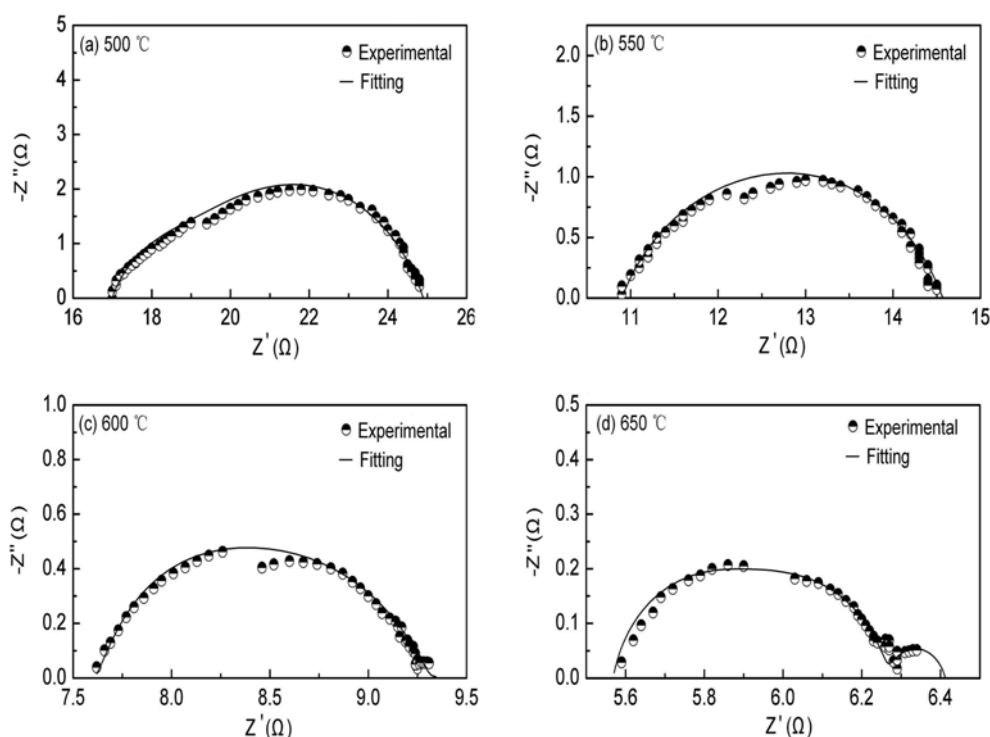


Fig. 4. Impedance spectra measured at different temperatures under zero dc bias in air for a $\text{La}_2\text{NiO}_{4+\delta}/\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}/\text{La}_2\text{NiO}_{4+\delta}$ cell.

response was detected at each of the measurement temperatures, displaying a high-frequency tail below the real axis. The contributions from induction are not included in Fig. 4, because, as is well-known, they were caused by the measuring device and electrical connections [20]. The spectrum measured at 500 °C appears as an apparently depressed semicircle (Fig. 4(a)). The high-frequency intercept of the spectrum with the real axis indicates the ohmic resistance of the cell, predominantly coming from the bulk resistance of the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ pellet. The low-frequency intercept reflects the whole resistance of the cell. The difference between the two intercepts represents the total polarization resistance of the cell, which is essentially related to the electrode reaction kinetics. One can note that the spectrum is obviously asymmetrical in shape, implying contributions from more than one electrode process to the spectrum. These processes mainly include charge transfer of oxygen ions through the electrode/electrolyte interface and an oxygen exchange reaction occurring at the electrode/gas interface, with the former and later accounting for the high and low frequency regions of the semicircle, respectively [8, 20, 27]. A similar depressed semicircle was observed in the spectrum measured at 550 °C, which became smaller in size as expected (Fig. 4(b)). An additional impedance response appeared in the lowest frequency domain in the spectrum measured at 600 °C (Fig. 4(c)) and turned out to be an incomplete semicircle at higher measurement temperatures (Fig. 4(d)). These obscure impedance responses might be associated with the gas-phase diffusion of oxygen [27, 28].

The measured spectrum data were fitted to the equivalent circuit described in the literature [20–22]. The spectra measured at 500–600 °C and higher temperatures were fitted based on the models of $R_{\text{el}}(R_1Q_1)(R_2Q_2)$ and $R_{\text{el}}(R_1Q_1)(R_2Q_2)(R_3Q_3)$, respectively. The R_{el} is the ohmic resistance of the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ pellet and the (RQ) components reflect involved electrode processes. The R is a resistance, the Q represents a constant phase element (CPE) and the subscript numbers correspond to the processes of the electrode/electrolyte charge transfer reaction, electrode/gas oxygen exchange reaction and oxygen gas-phase diffusion, respectively. From Fig. 4, one can find that the fitted results generally agree with the experimental data. The values of the ohmic resistance of the electrolyte pellet and the polarization resistances of individual electrode processes were extracted from the spectrum fitting.

Considering the thickness and electrode area of the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ pellet, the electrical conductivity (σ_{el}) of the electrolyte was determined from the R_{el} values yielded. Fig. 5 shows the Arrhenius plot of the electrical conductivity σ_{el} of the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ pellet. The electrolyte provides an electrical conductivity of $4.2 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$ at 700 °C and an activation energy of 0.52 eV for the electrical conduction between 500–700 °C. These results are in good agreement with our prior data obtained with the same measurement temperature conditions from $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ ceramics derived from the urea-combustion procedure [25].

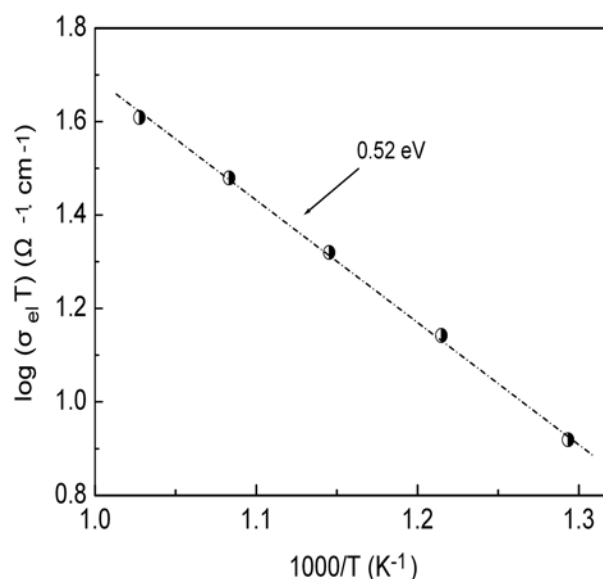


Fig. 5. Arrhenius plot of electrical conductivity (σ_{el}) for the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ pellet.

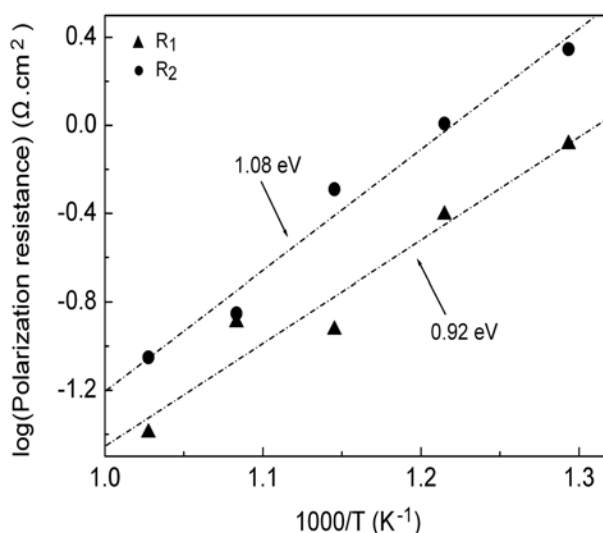


Fig. 6. Arrhenius plots of polarization resistances for various electrode processes.

In the case of the symmetrical cell configuration, the polarization resistances of various electrode processes result from the co-contribution of the two electrodes. Thus, the polarization resistances were divided by 2 and multiplied by the electrode area for normalization purposes. Fig. 6 shows the Arrhenius plots of the polarization resistances of various electrode processes. In general, the R_1 and R_2 values decrease with an increase in the measurement, which is consistent with previous results [21]. The two electrode processes present activation energies of 0.92 and 1.08 eV, respectively. By comparison, the R_3 values remained nearly unchanged at 650 and 700 °C (5.6×10^{-2} and $5.3 \times 10^{-2} \Omega \text{cm}^2$), showing a basically temperature-independent behavior. This occurrence coincides well with the thermal behavior of oxygen gas-phase diffusion resistance [28].

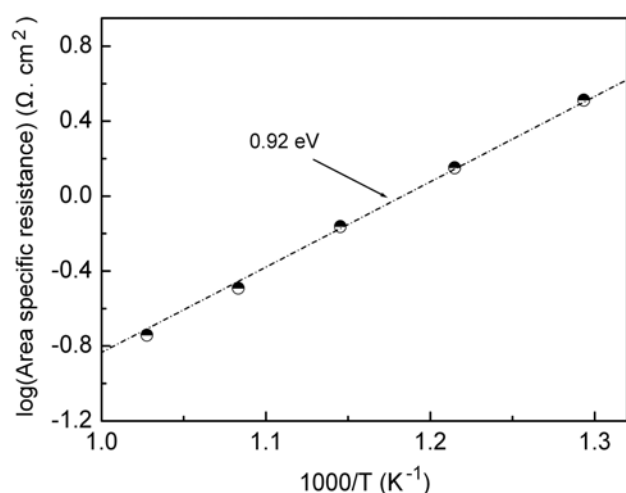


Fig. 7. Arrhenius plot of area specific resistance (ASR) for $\text{La}_2\text{NiO}_{4+\delta}$ electrodes.

The area specific resistance (ASR) of the $\text{La}_2\text{NiO}_{4+\delta}$ electrodes was determined from the sum of the polarization resistances of individual electrode processes. The Arrhenius plot of the ASR offers a linear relation, as shown in Fig. 7. The activation energy of the overall electrode reaction was calculated from the slope of the line. The activation energy (0.92 eV) is lower compared to the literature data of 1.2 eV and 1.24 eV for $\text{La}_2\text{NiO}_{4+\delta}$ electrodes supported on YSZ and LSGM, respectively [19, 21].

The discrepancy in the activation energy of the electrode reaction for $\text{La}_2\text{NiO}_{4+\delta}$ between the present study and previous research may be attributed to different electrode microstructures and/or varied electrolytes working with $\text{La}_2\text{NiO}_{4+\delta}$, which can substantially affect the electrode reaction kinetics. The $\text{La}_2\text{NiO}_{4+\delta}$ electrodes shows the ASR values of 3.04, 0.69 and $0.18 \Omega \text{ cm}^2$ at 500, 600 and 700 °C, respectively. The ASR value at 700 °C is considerably lower than the literature data of 1.00 and $0.41 \Omega \text{ cm}^2$ at 800 °C for $\text{La}_2\text{NiO}_{4+\delta}$ electrodes painted on $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ and 2 mol % Co-doped $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$, respectively [22].

Fig. 8 shows SEM images of the $\text{La}_2\text{NiO}_{4+\delta}/\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}/\text{La}_2\text{NiO}_{4+\delta}$ cell. From the low magnification cross-sectional view (Fig. 8(a)), one can see a porous electrode layer deposited on a dense electrolyte support. The electrode layer gave a generally uniform thickness of about 15 μm and a good adherence to the electrolyte pellet. The cross-sectional view at a higher magnification gives further evidence of a tight bonding and a continuous contact between the two components (Fig. 8(b)). The surface views at different magnifications evidently demonstrate the porous microstructure of the electrode layer, composed of fine (about 0.5 μm) and well-necked grains together with homogeneously-distributed micro-pores (Fig. 8(c)). In general, these microstructural features can be regarded to be desirable for electrode reaction kinetics. The uniformly-dispersed pores at a micrometre enable the diffusion of

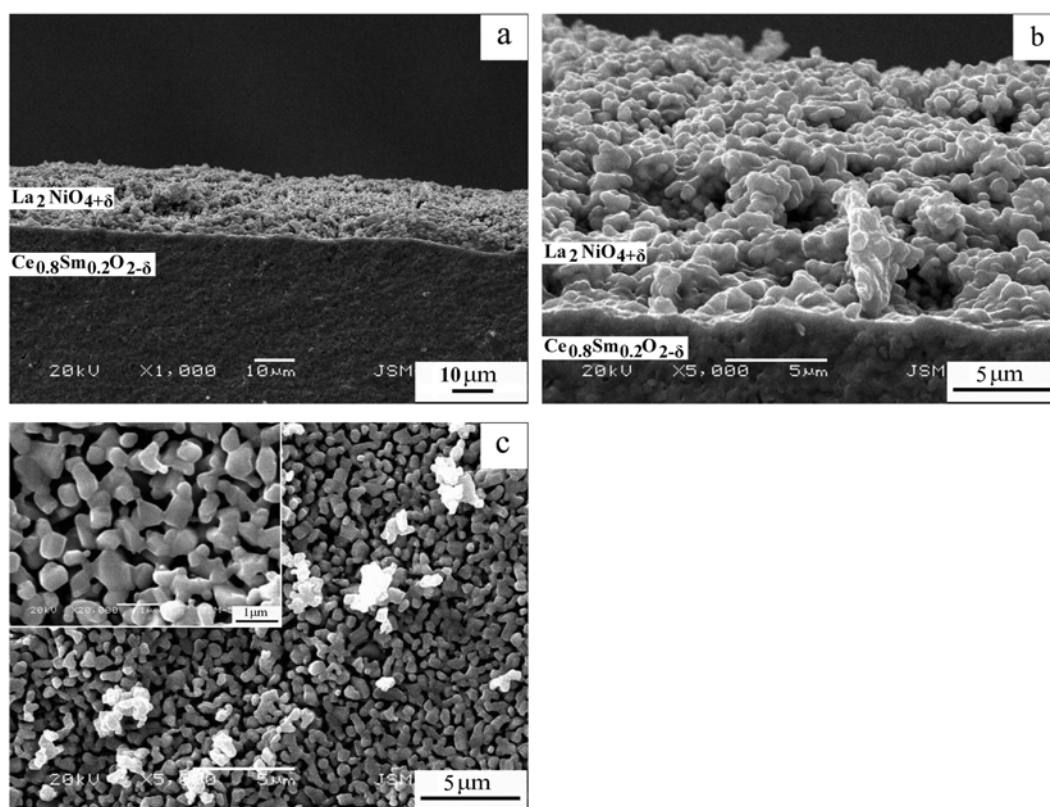


Fig. 8. SEM images of (a) cross-sectional view, (b) higher magnification cross-sectional view and (c) surface views for $\text{La}_2\text{NiO}_{4+\delta}/\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}/\text{La}_2\text{NiO}_{4+\delta}$ cell.

molecular oxygen within the electrodes. This increases the internal surface area of the electrodes and enlarges catalytically the active zone (i.e. the electrode/gas interface), which as a result benefits the surface exchange reaction between oxygen and the electrodes [21]. The fine morphology of the grains also serves to increase the catalytically active surface area [20]. The well-necked grains can act as continuous pathways for the transport of oxygen ions through the electrodes. The close adhesion between the electrode layers and the electrolyte is favorable to the transport of oxygen ions across the electrode/electrolyte interface. Thus, the improved electrode properties in the present study compared to the literature data are assumed to be attributed to microstructural modification.

Conclusions

Fine and uniform $\text{La}_2\text{NiO}_{4+\delta}$ powder (about 100 nm) has been synthesized by a polyaminocarboxylate complex method. A $\text{La}_2\text{NiO}_{4+\delta}/\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}/\text{La}_2\text{NiO}_{4+\delta}$ symmetrical cell has been prepared using a screen-printing method by sintering at 1100 °C for 2 h. The electrochemical properties of the cell have been inspected by the impedance spectroscopy technique under zero dc bias in air. Satisfactory chemical and thermodynamic compatibilities have been confirmed between the electrodes and the electrolyte. The $\text{La}_2\text{NiO}_{4+\delta}$ electrodes showed a relatively low area specific resistance of 0.18 $\Omega \text{ cm}^2$ at 700 °C. A desired porous microstructure was confirmed for the $\text{La}_2\text{NiO}_{4+\delta}$ electrodes via SEM observations. The improvement in electrode properties of the $\text{La}_2\text{NiO}_{4+\delta}$ electrodes compared to literature data is suggested to be attributed to microstructural modification.

Acknowledgments

This work was financially supported by Natural Science Foundation of China (50572079), Wuhan Science and Technology Bureau (200851430485) and Korea Research Foundation Grant funded by Korean Government (KRF-2008-521-D00187 and MOEHRD KRF-2007-211-D00053).

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