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Development of lanthanum nickelate as a cathode for use in intermediate temperature solid oxide fuel cells

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ABSTRACT

The performance of lanthanum nickelate, $\text{La}_2\text{NiO}_{4+\delta}$ (LNO), as a cathode in IT-SOFCs with the electrolyte cerium gadolinium oxide, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ (CGO), has been investigated by AC impedance spectroscopy of symmetrical cells. A significant reduction in the area specific resistance (ASR) has been achieved with a layered cathode structure consisting of a thin compact LNO layer between the dense electrolyte and porous electrode. This decrease in ASR is believed to be a result of contact at the electrolyte/cathode boundary enhancing the oxygen ion transfer to the electrolyte. An ASR of $1.0 \Omega \text{ cm}^2$ at 700°C was measured in a symmetrical cell with this layered structure, compared to an ASR of $7.4 \Omega \text{ cm}^2$ in a cell without the compact layer. In addition, further improvements were observed by enhancing the cell current collection and it is anticipated that a symmetrical cell consisting of a layered structure with adequate current collection would lower these ASR values further.

Keywords:

Lanthanum nickelate
AC impedance
Mixed conducting oxides
SOFCs

1. Introduction

The mixed ionic-electronic conductor, lanthanum nickelate, ($\text{La}_2\text{NiO}_{4+\delta}$, LNO) is being considered as a potential cathode for intermediate temperature solid oxide fuel cells (IT-SOFCs) due to its high oxygen tracer diffusion coefficients and good electronic conductivity [1–4]. The K_2NiF_4 -type structure consists of perovskite layers of LaNiO_3 separated by rocksalt layers of LaO , with a network of unoccupied interstitial sites. Upon oxidation of the material, excess oxygen is accommodated in the interstitial sites and compensated for by the formation of Ni holes in the form of Ni^{3+} ions [5,6]. $\text{La}_2\text{NiO}_{4+\delta}$ has shown relatively high solubility for oxygen excess, with values of δ as high as 0.3 being reported [7].

In SOFCs, the cathode is subject to large activation polarisation due to the slow reaction of the oxygen on its surface, producing a high overpotential. With the aim of reducing the cathode overpotential, mixed ionic-electronic conductors have been studied and are considered favourable IT-SOFC cathodes due to the increased triple phase boundary length that is inherent in materials that have both ionic and electronic conduction. Electronic conductivity measurements of $\text{La}_2\text{NiO}_{4+\delta}$ indicate that there is a transition from semiconducting to p-type metallic-like behaviour at about 600 K [1,4,8], whilst the ionic conductivity is a result of the hyperstoichiometric oxygen interstitial network.

Rare-earth nickelates, with the general formula $\text{Ln}_2\text{NiO}_{4+\delta}$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$) have shown promising cathode performance with various electrolyte materials, such as yttria stabilised zirconia (YSZ), $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$, and $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ (LSGM) [9–12]. In addition, composites of LNO with $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$ have shown an improved performance compared with the pure LNO material on $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$ and YSZ electrolytes [12,13]. However, to date, there has been little reported work on the electrochemical performance of LNO with the common IT-SOFC electrolyte ceria gadolinium oxide, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ (CGO). It is therefore the aim of this work to investigate the electrochemical behaviour of $\text{La}_2\text{NiO}_{4+\delta}$ on CGO in the intermediate temperature regime.

The thermal expansion coefficient for LNO is reported to be $13.0 \times 10^{-6} \text{ K}^{-1}$ [2] compared with $11.9 \times 10^{-6} \text{ K}^{-1}$ for CGO [14], suggesting that there should be a good match between electrode and electrolyte layers and therefore good adherence at the interface. The reactivity between electrodes and electrolyte in SOFCs is of considerable importance as the formation of any barrier layers can adversely affect cell performance. Previous work has investigated the reactivity of LNO with CGO and LSGM [15]. The authors report a reaction between LNO and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ after 24 h at 900°C , with no reaction observed between LNO and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ after 72 h at 1000°C . Here we present a study of the electrical performance with LNO electrodes on a CGO electrolyte.

2. Experimental

Lanthanum nickelate, synthesised by spray pyrolysis, was supplied by CerPoTech. Single phase powder was obtained by calcination at

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1200 °C for 2 h and ballmilling for 24 h to achieve a particle size of approximately 2 µm. LNO ink was formulated for screen printing using a proprietary ink vehicle supplied by Fuel Cell Materials; the ink was composed of 67 wt.% powder. Initial mixing of the powder and vehicle was with a mortar and pestle, followed by triple roll milling of the ink to achieve good particle dispersion in the ink vehicle. Dense (>98% theoretical density), single phase pellets of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ (CGO10) electrolyte were obtained by uniaxial and isopressing commercial (Rhodia) powder into green pellets, followed by sintering at 1400 °C for 5 h. The CGO surface was polished with 800 grit SiC paper to obtain a flat surface prior to screen printing with LNO ink to create symmetrical cells. Adherence of the ink to the CGO surface was achieved after calcining at 1100 °C for 2 h in air. Three cells were investigated; LNO ink deposited on CGO (Cell A), LNO ink deposited on CGO with platinum paste deposited on the cathode as a current collector (Cell B), and a layered LNO structure consisting of a thin compact layer of LNO deposited on CGO by dip-coating and a porous screen printed LNO layer deposited on to the compact layer (Cell C).

Impedance spectra were recorded over a frequency range of 13 MHz–0.01 Hz using a Solartron 1260 FRA, over the temperature range of 673–1073 K in static air. All micrograph images were obtained using a JEOL 5610 SEM and FEI Phenom SEM.

3. Results and discussion

The microstructure of the deposited cathode layers is shown in the SEM fracture surface images in Fig. 1. The screen printed LNO layer has a uniform distribution of particles in the range of 1–2 µm and consists of a porous network of interconnected particles, allowing for gas diffusion through the electrode. Typical thicknesses of the layers are 12 µm for the porous cathode layer, 5 µm for the Pt current collector layer and 1–2 µm for the compact LNO layer.

Impedance spectra recorded at 450 °C for the symmetrical cells are shown in Fig. 2. Each of the impedance spectra recorded at temperatures above 450 °C were modelled using resistance elements (R) in parallel with constant phase elements (CPE) in the equivalent circuit shown below;



where R_{ohmic} is the resistance attributed to the electrolyte and contacts, R_{int} is the resistance assigned to oxygen ion transfer across the electrode-electrolyte interface and the resistance associated with the cathode is composed of two components (R_{p1} and R_{p2}). The total polarisation resistance, R_{p} (the total resistance associated with the electrode) is therefore a summation of these terms, where,

$$R_{\text{p}} = R_{\text{int}} + R_{\text{p1}} + R_{\text{p2}}.$$

The impedance arcs were assigned to various responses based on the modelled capacitance values. In Fig. 2, R_{int} is the impedance arc between 10 kHz and 100 Hz and is assigned to oxygen ion transfer across the electrode/electrolyte boundary in to the electrolyte, with capacitance values of 10^{-6} to 10^{-5} F [12,16]. R_{p1} and R_{p2} are the arcs at frequencies below 100 Hz and are assigned to oxygen diffusion through the electrode layer and the charge transfer reaction at the cathode surface, with capacitance values in the range 10^{-3} to 10^{-2} F [12].

Fig. 3 shows the calculated area specific resistances (ASR) for each of the symmetrical cell configurations. The ASR has been calculated by considering the total R_{p} at each electrode and multiplying by the surface area, SA ; $\text{ASR} = (R_{\text{p}}/2) \times \text{SA}$. The calculated ASRs at 700 °C are given in Table 1, with symmetrical cell configurations from literature given for comparison. At 700 °C the lowest ASRs are observed on Cell B (LNO with Pt paste) and Cell C (LNO compact layer and LNO porous layer), both with an ASR of $1.0 \Omega \text{ cm}^2$, approximately 7 times less than the ASR of LNO on CGO (Cell A). These values are an improvement on the ASR of $1.3 \Omega \text{ cm}^2$ at 800 °C reported by Laberty et al. [13] for LNO on yttria stabilised zirconia (YSZ) and in the region of the ASR reported by Pérez-Coll et al. [12] on samarium doped ceria. The ASR of the common IT-SOFC cathode material $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ (LSCF) has been obtained by Ralph et al. [17] and is shown in Table 1. It can be seen that the minimum ASR for symmetrical cells of LNO is 5 times

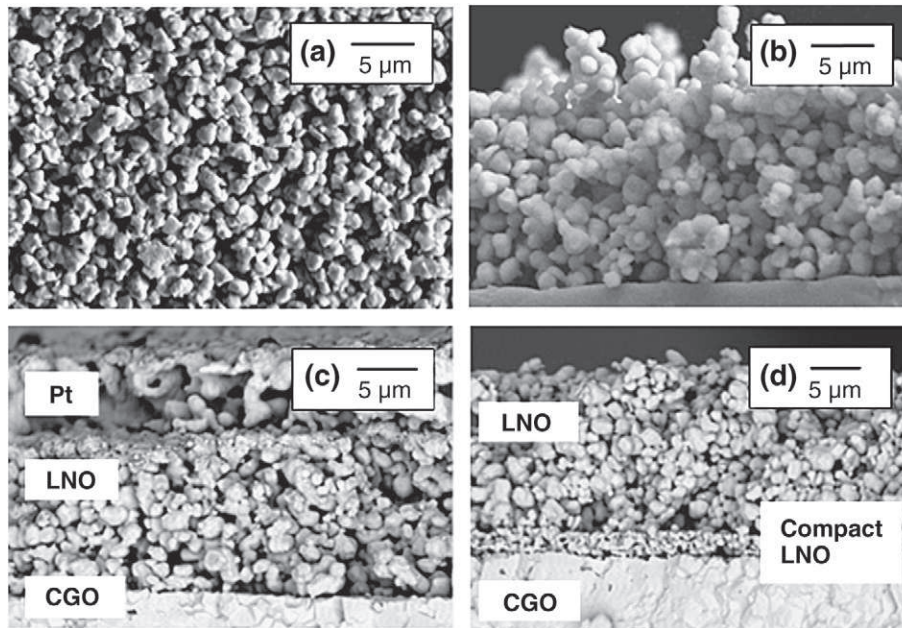


Fig. 1. SEM micrograph showing (a) the LNO powder used to make the ink after ballmilling and fracture surfaces of (b) LNO cathode screen printed onto dense electrolyte after sintering at 1100 °C for 2 h (c) LNO cathode screen printed onto dense electrolyte with platinum current collector (d) LNO layered structure with LNO screen printed layer deposited on to thin compact LNO layer dipcoated on to CGO10.

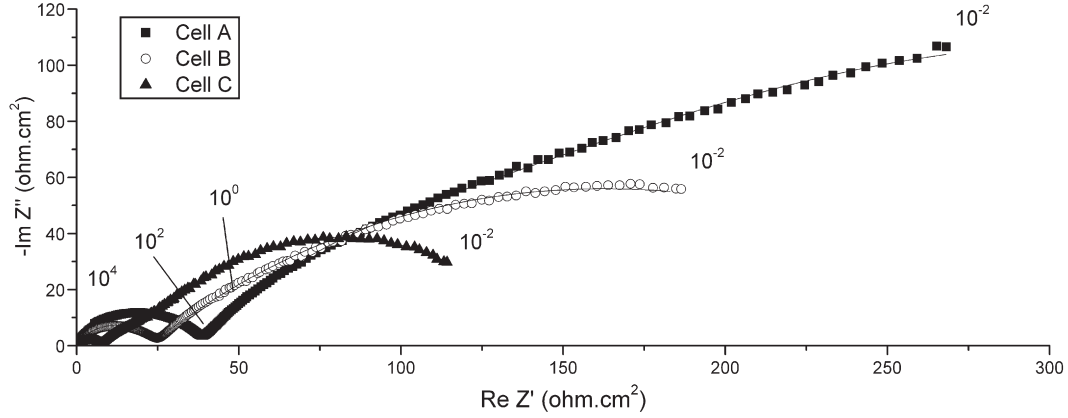


Fig. 2. Impedance arcs for symmetrical cells with LNO cathode on CGO10 electrolyte for three different cell arrangements obtained at 450 °C; (Cell A) LNO screen printed on CGO10, (Cell B) same as (Cell A) but with Pt paint as a current collector, (Cell C) same as (A) but with a thin compact LNO layer between the porous LNO cathode and dense electrolyte. The symbols represent the measured data and the lines represent the fitted data based on the equivalent circuit models. Exponents are the frequency in Hz.

greater than for LSCF at 700 °C. It has been determined [18] that the oxygen tracer diffusion coefficient of LNO is 1 to 2 orders of magnitude greater than that of LSCF in the intermediate temperature range (550 °C to 700 °C); however the surface exchange coefficient is approximately half an order of magnitude lower in LNO. This suggests that the electrode performance of LNO is not limited by mass transport properties but may be affected by other factors such as electronic conductivity.

The reduction in ASR observed for the cell with a compact layer of LNO between the dense electrolyte and porous electrode is of interest as it would be expected that a denser electrode layer would inhibit cell performance, acting as a barrier to gas diffusion through the electrode. At lower temperatures this appears to be the case, with high ASRs observed below 450 °C. As the temperature increases, the compact layer improves the cell performance; we believe this is due to an increase in the number of contact points at the electrode/electrolyte interface, leading to enhanced oxygen ion transfer across this boundary.

The resistance associated with oxygen ion transfer across the electrode/electrolyte boundary, R_{int} , decreases with increasing tem-

perature in all cell arrangements and is beyond measureable range at approximately 650 °C. Comparison of R_{int} in Fig. 2 (visible as the high frequency impedance arc) and in Table 2 shows that at low temperatures the addition of the compact layer between the electrolyte and porous electrode significantly reduces the value of R_{int} . The value of R_{int} will also be affected by the formation of any barrier layers which result from secondary phases formed by contact between the electrode and electrolyte. Additional phases have been observed when LNO is in contact with CGO at temperatures above 900 °C [15], and although the maximum testing temperature is 800 °C, the symmetrical cells are annealed at 1100 °C for 2 h during fabrication. It would therefore be expected that with an increase in contact between the electrolyte and compact layer, the extent of the secondary phase formation would increase. In the temperature range studied here it is clear that this does not appear to increase the overall ASR, suggesting that anneal time was not long enough for significant phase formation, or that the reaction product does not detract from the cell performance.

The addition of the compact layer between the electrolyte and porous electrode also reduces the resistances assigned to the electrode processes (R_{p1} and R_{p2}), which can be seen as the high frequency arcs in Fig. 2. Therefore the interlayer also improves the electrode processes of mass transport and charge transfer and this suggests that the LNO cathode is behaving as a traditional electrode where the oxygen reduction reaction occurs at triple-phase boundaries, as opposed to behaving as a mixed ionic-electronic conductor.

In [12] and [13], an additional current collection layer is used and supports the observation made here that improvements in current

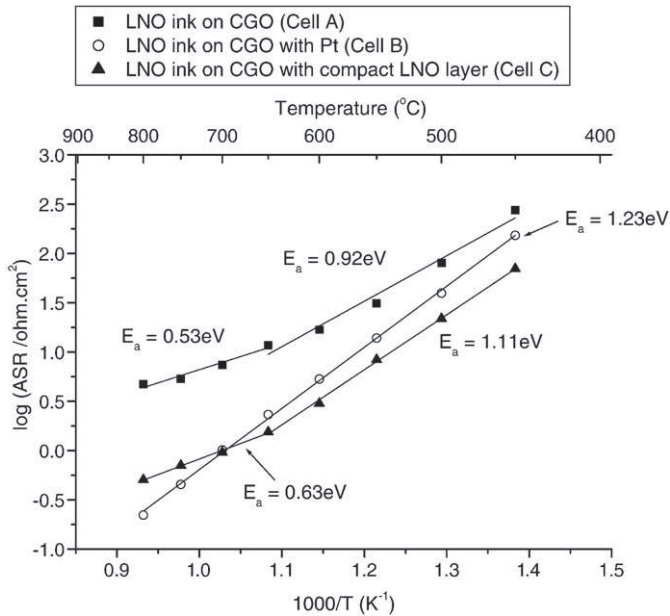


Fig. 3. Area Specific Resistances obtained by AC Impedance for three symmetrical cell arrangements; (Cell A) LNO screen printed on CGO10, (Cell B) same as (Cell A) but with Pt paint as a current collector, (Cell C) same as (Cell A) but with a thin compact LNO layer between the porous LNO cathode and dense electrolyte.

Table 1

ASR values at 700 °C for the three cell arrangements and a symmetrical cell of Pt paste on CGO electrolyte. Cell arrangements from literature are given for comparison.

Reference	Cell configuration	Current collection	Cathode ASR at 700 °C ($\Omega \cdot \text{cm}^2$)
Cell A [This work]	LNO on CGO	Pt mesh	7.4
Cell B [This work]	LNO on CGO	Pt paint and Pt mesh	1.0
Cell C [This work]	Porous LNO on compact	Pt mesh	1.0
Pt electrodes [This work]	LNO on CGO	Pt paint on CGO	6.7
Ralph et al. [17]	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-x}$ on CGO	Pt mesh	0.2 at 700 °C
Laberty et al. [13]	LNO on YSZ (asymmetrical cell)	$\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ and silver mesh	0.9 at 800 °C
Pérez-Coll et al. [12]	LNO on Co doped, samarium doped ceria	Pt paint and Pt mesh	0.4 at 800 °C

Table 2

The resistance associated with oxygen ion transport across the electrode/electrolyte boundary, R_{int} , as a function of temperature, for the symmetrical cell arrangements; (Cell A) LNO screen printed on CGO10, and (Cell C) same as (A) but with a thin compact LNO layer between the porous LNO cathode and dense electrolyte.

Temperature	R_{int} Cell A ($\Omega \text{ cm}^2$)	R_{int} Cell C ($\Omega \text{ cm}^2$)
300 °C	1490.4	144.81
450 °C	52.0	12.6
600 °C	6.9	3.5

collection are enhancing the electronic performance of the LNO cathode and hence resulting in a reduced ASR. The ASR for Pt paste electrodes on CGO is given in Table 1 and is approximately 7 times greater than the ASR measured for Cell B, indicating that in Cell B the cathode response is from LNO and platinum is acting as a current collector. The activation energy (E_a) for the total polarisation resistances (normalised for surface area) are shown in Fig. 3. For Cells A and C there appears to be a change in E_a at 650 °C, which does not occur in the cell with Pt paste applied as a current collector. This suggests that the change may be associated with the electronic conductivity and it is worth noting that Daroukh et al. [19] determine the maximum electronic conductivity in LNO to occur at ~600 °C. The values obtained for the activation energy of Cells A and C are 0.92 eV and 1.11 eV, respectively, above 650 °C and compare well with previously reported values for mixed ionic-electronic conductors [16].

Further study of the symmetrical cell performance of LNO on IT-SOFC electrolytes has been performed with varying oxygen partial pressures and detailed discussion of the electrode processes is underway [20]. Additional discussion on the effects of interlayers to improve LNO electrode performance can be found in [21].

4. Conclusions

It is clear that a complex set of processes occurs in mixed ionic-electronic conducting LNO cathodes and that there exists a series of variables to enhance the performance of these electrodes. Significant improvements can be made by enhancing the electronic conductivity through adequate current collection. In addition, a thin compact layer of electrode material at the boundary between the electrolyte and porous electrode significantly reduces ASR values; it is thought that

this is the result of improved contact at the boundary layer enhancing the oxygen ion transfer to the electrolyte. A symmetrical cell arrangement that combines a layered electrode structure and adequate current collection has the potential to reduce ASRs further. In addition the previously observed reactivity between LNO and CGO may not be a barrier to cell performance below 900 °C; however, long term testing is required to verify this.

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