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# Investigation of Graded $\text{La}_2\text{NiO}_{4+\delta}$ Cathodes to Improve SOFC Electrochemical Performance

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Mixed ionic and electronic conducting (MIEC) oxides are promising materials for use as cathodes in solid oxide fuel cells (SOFCs) due to their enhanced electrocatalytic activity compared with electronic conducting oxides. In this paper, the MIEC oxide  $\text{La}_2\text{NiO}_{4+\delta}$  was prepared by the sol-gel route. Graded cathodes were deposited onto yttria-stabilized zirconia (YSZ) pellets by dip-coating, and electrochemical impedance spectroscopy studies were performed to characterize the symmetrical cell performance. By adapting the slurries, cathode layers with different porosities and thicknesses were obtained. A ceria gadolinium oxide (CGO) barrier layer was introduced, avoiding insulating  $\text{La}_2\text{Zr}_2\text{O}_7$  phase formation and thus reducing resistance polarization of the cathode. A systematic correlation between microstructure, composition, and electrochemical performance of these cathodes has been performed. An improvement of the electrochemical performance has been demonstrated, and a reduction in the area specific resistance (ASR) by a factor of 4.5 has been achieved with a compact interlayer of  $\text{La}_2\text{NiO}_{4+\delta}$  between the dense electrolyte and the porous  $\text{La}_2\text{NiO}_{4+\delta}$  cathode layer. The lowest observed ASR of  $0.11 \Omega \text{ cm}^2$  at  $800^\circ\text{C}$  was obtained from a symmetrical cell composed of a YSZ electrolyte, a CGO interlayer, an intermediate compact  $\text{La}_2\text{NiO}_{4+\delta}$  layer, a porous  $\text{La}_2\text{NiO}_{4+\delta}$  electrode layer, and a current collection layer of platinum paste.

One of the most important goals in solid oxide fuel cell (SOFC) research is the reduction in the working temperature to about  $700\text{--}800^\circ\text{C}$  for future applications. However, at such intermediate temperatures, one of the main limiting factors is the high polarization resistance of standard cathode materials, such as the conventional perovskite oxides based on  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$  (LSM), which limits SOFC power densities.<sup>1,2</sup> Consequently, for some years, much attention has been focused on improving the cathodic performance by using both mixed ionic and electronic conducting materials, such as  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  (LSCF),<sup>3,4</sup> and by improving the microstructural design at the cathode/electrolyte interface. Recent studies<sup>5-7</sup> on mixed conductors indicated that the Ruddlesden-Popper phases with the  $\text{K}_2\text{NiF}_4$ -type structure have promising properties at intermediate operating temperatures due to their high ionic conductivity and high electrocatalytic activity,<sup>8-10</sup> which were correlated with additional oxygen on the interstitial site and the presence of cations with different oxidation states. Skinner and Kilner<sup>9</sup> showed that the oxygen tracer diffusion coefficient of lanthanum nickelate ( $\text{La}_2\text{NiO}_{4+\delta}$ ) is greater than that of LSM and LSCF, suggesting that the ionic conductivity of this oxygen excess material is superior.

Numerous authors have investigated the electrochemical performance of  $\text{La}_2\text{NiO}_{4+\delta}$  on yttria-stabilized zirconia (YSZ) electrolytes.<sup>8,11,12</sup> These initial studies have shown promising results, and Laberty et al.<sup>11</sup> observed that significant improvements in the area specific resistance (ASR) values can be achieved with the composites of  $\text{La}_2\text{NiO}_{4+\delta}$  and  $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$ , which may be due to better contacts. This study focuses on the preparation and electrochemical characterization of a design of lanthanum nickelate graded cathodes for SOFC systems. In this work, we investigated a cathode structure composed of a thin  $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-\delta}$  (CGO) interlayer deposited onto YSZ pellets, with an intermediate compact layer of  $\text{La}_2\text{NiO}_{4+\delta}$  and a thicker porous layer of  $\text{La}_2\text{NiO}_{4+\delta}$ .

The aim of using a layered microstructure design is to increase the number of contact points at the electrode/electrolyte boundary by introducing a thin intermediate layer of compact lanthanum nick-

elate between the electrode and electrolyte. A porous cathode layer deposited on top of this intermediate layer ensures adequate catalytically active sites for the oxygen reduction reaction to occur. This configuration allows an enlargement of the electrochemically active surface area at the cathode/electrolyte interface. In addition, enhancement of the electrode current collection is investigated by the addition of a continuous platinum layer on top of the  $\text{La}_2\text{NiO}_{4+\delta}$  electrode.

To achieve a layered electrode structure, sol-gel processing and dip-coating deposition have the advantage of being easy methods to control both the microstructure and the composition of the electrode materials. The composition of the graded cathodes of lanthanum nickelate and the electrochemical performance of these symmetrical cells are reported here. The ASR values and Nyquist diagrams are discussed, and the microstructure of the electrode layers is correlated with performance.

## Experimental

*Preparation of symmetrical cells.*— In this work, graded  $\text{La}_2\text{NiO}_{4+\delta}$  cells were prepared and deposited onto 0.5 mm thick YSZ electrolyte substrates of 12 mm diameter by dip-coating. Dense YSZ substrates were prepared by spark plasma sintering of sol-gel prepared YSZ powders. Various configurations of the symmetrical cells were constructed, composed of an 80 nm layer of CGO, an intermediate layer of 2  $\mu\text{m}$  thick compact  $\text{La}_2\text{NiO}_{4+\delta}$ , and an 8–15  $\mu\text{m}$  thick layer of porous  $\text{La}_2\text{NiO}_{4+\delta}$ . Each YSZ support was dipped either in a polymeric sol precursor of CGO or into slurries of  $\text{La}_2\text{NiO}_{4+\delta}$ . The withdrawal speed was  $5 \text{ cm min}^{-1}$  for all dip-coatings. The electrode layers for the symmetrical cell arrangements are given in Table I.

The CGO interlayer was prepared by a polymeric sol via a process similar to the Pechini<sup>13</sup> method. Solutions of the metal nitrates,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Gd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , were dissolved in deionized water in stoichiometric proportions to obtain  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$  as an oxide compound. In parallel, a polymeric solution was prepared with acetylacetone (acac) and hexamethylenetetraamine (HMTA) dissolved in acetic acid. Both solutions were mixed and heated at  $80^\circ\text{C}$  to induce the formation of a polymeric chain by a condensation reaction between acac and HMTA in acetic acid. The role of both HMTA and acac is to complex the metal ions. The HMTA/Acac

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**Table I. Calculated ASR values of cathode samples recorded at 800°C.**

	CGO interlayer (nm)	Intermediate La <sub>2</sub> NiO <sub>4+δ</sub> layer (μm)	Thick La <sub>2</sub> NiO <sub>4+δ</sub> layer (μm)	ASR (Ω cm <sup>2</sup> )
Sample 1			8	6.0
Sample 2			15	3.0
Sample 3	80		8	18
Sample 4	80		15	65
Sample 5		2	8	2.2
Sample 6	80	2	8	1.3
Sample 1 + Pt			8	1.4
Sample 6 + Pt	80	2	8	0.11
Pt				0.28

ratio is 1:1, and the ratio between these organic compounds (HMTA, acac) and metal ions is 27. The solution was heated in static air for 25 min until a sol viscosity of 40 mPa s at room temperature was achieved. The YSZ pellets were then dip-coated using the sol, and a thermal treatment in air was applied at 800°C during 2 h to obtain a single-phase oxide layer.

La<sub>2</sub>NiO<sub>4+δ</sub> powder was prepared by sol-gel via the modified Pechini method that has been described elsewhere.<sup>14</sup> Two slurries were prepared to obtain La<sub>2</sub>NiO<sub>4+δ</sub> layers with different microstructures and electrode layers of varying thicknesses and porosities.

To prepare the intermediate layer of La<sub>2</sub>NiO<sub>4+δ</sub>, the slurry was composed of 60 wt % powder calcinated at 900°C. A thermal pre-treatment at 500°C in air was applied to consolidate this thinner and more compact intermediate layer. The thicker porous cathode layers were prepared from a slurry composed of 80 wt % of La<sub>2</sub>NiO<sub>4+δ</sub> powder calcinated at 1000°C. Single or multiple dip-coatings into the slurry were made to obtain two different cathode thicknesses (8 or 15 μm thick).

In all cases, La<sub>2</sub>NiO<sub>4+δ</sub> powder was dispersed in an azeotropic mixture of methyl ethyl ketone-ethanol with 3% of BeycoStat C213 (CECA S.A.) as a dispersant. For all samples, after deposition, a thermal treatment at 1150°C for 2 h in air was performed to consolidate the layers. The phase purity of all materials was verified by X-ray powder diffraction on a D4 ENDEAVOR (Bruker) diffractometer with Cu Kα radiation over the angular range of 20–70° 2θ.

In a final symmetrical cell arrangement, a continuous layer of platinum paste was deposited onto the electrode by painting, and adherence to the electrode was achieved by heating to 800°C for 1 h in air.

**Layer characterization.**—Microstructural characterization of La<sub>2</sub>NiO<sub>4+δ</sub> graded cathodes was carried out using a scanning electron microscope operating with a field-emission gun (JEOL, model JSM 6700F).

A normalized adhesive (NF-A91-102 and NFT30-038) was used to permit a qualitative evaluation of coating adhesion onto the YSZ substrates. The test of adhesion consists of the application of the normalized adhesive before taking it out, and all the prepared cathode layers have been tested to have a qualitative evaluation of the layer adhesion.

**AC impedance measurements.**—The prepared samples were placed in an alumina support and held in position by spring loading. A Pt mesh was used as a current collector for all samples, with two samples having an additional painted platinum layer between the La<sub>2</sub>NiO<sub>4+δ</sub> electrode and the platinum mesh. Electrochemical impedance spectroscopy experiments were performed over the temperature range of 600–800°C under static air. The ac impedance data were recorded using a Solartron 1260 impedance analyzer in the frequency range of 13 MHz to 0.1 Hz using an electrical perturbation of 50 mV. The data obtained were analyzed, using equivalent circuit fitting with ZView software.<sup>15</sup> The fitting routines used two serial elements consisting of one resistance (*R*) in parallel with one

constant element phase. The capacitance and relaxation frequency of each contribution have been calculated according to Eq. 1 and 2, respectively<sup>16,17</sup>

$$C = (R^{1-n}Q)^{1/n} \quad [1]$$

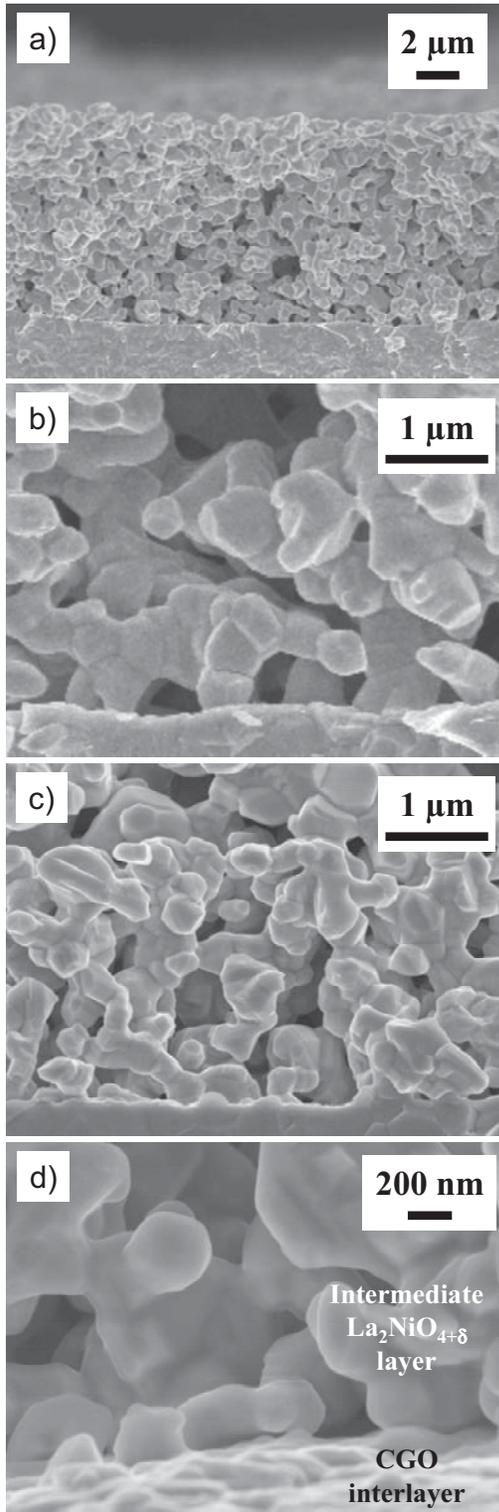
$$f_0 = (RQ)^{-1/n}/2\pi \quad [2]$$

The ASR was calculated from the polarization resistance (*R<sub>p</sub>*) and  $ASR = R_p S/2$ , where *S* is the surface area of the sample and is divided by 2 to take into account the symmetrical geometry of the half cells. The reported ASR values are based on an average of two readings under the same conditions to ensure the reproducibility of the results, and the standard deviation of each value is less than 3%.

## Results and Discussion

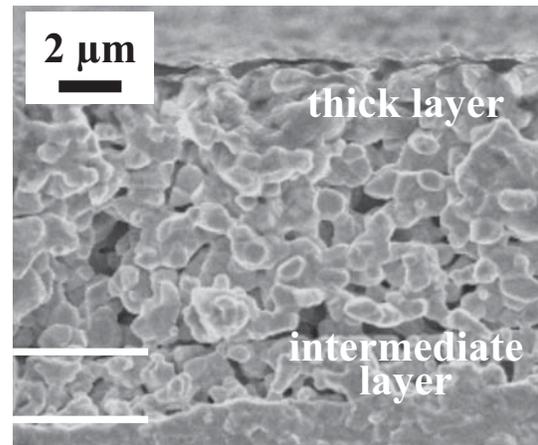
**Preparation of the graded cathodes.**—The microstructure of the electrode layers is shown in Fig. 1. The La<sub>2</sub>NiO<sub>4+δ</sub> cathode is porous, 8 or 15 μm thick with a grain size ranging from 0.5 to 1 μm (Fig. 1a) and pore size ranging from 0.5 to 1 μm. The intermediate layer of La<sub>2</sub>NiO<sub>4+δ</sub> is approximately 2 μm thick with a grain size of approximately 200 nm (Fig. 1c) and pore size ranging from 200 to 500 nm; this intermediate layer is more compact (i.e., less porous) than the thicker electrode layer. The microstructure of a graded cathode with the intermediate layer of La<sub>2</sub>NiO<sub>4+δ</sub> and the thick porous La<sub>2</sub>NiO<sub>4+δ</sub> layer is shown in Fig. 2. The microstructure at the interface between the electrolyte and cathode differed between the samples depending on the nature of the graded electrode structure. The intermediate compact layer of La<sub>2</sub>NiO<sub>4+δ</sub> increased the number of contact points between the electrolyte and the thicker cathode layer (Fig. 1c) compared with the interface between the thick electrode layer directly in contact with YSZ (Fig. 1b). The increase in the number of contact points was also observed between the intermediate compact La<sub>2</sub>NiO<sub>4+δ</sub> layer and the CGO interlayer (Fig. 1d). These comments are of use in explaining the electrochemical results that follow.

**ASR values at 800°C.**—The ASR values obtained are reported in Table I. It can be seen for samples 1 and 2 that increasing the electrode thickness by a factor of 2 reduces the ASR value by half. It was shown by Barbucci et al. that for an adequate oxygen reduction, electrode thicknesses ranging from 20 to 50 μm are desired.<sup>18</sup> Therefore, it is believed that further increasing the thickness of these cathodes would also decrease the ASR value. In samples 3 and 4, the addition of a CGO interlayer appears to detrimentally affect the performance, with a significant increase in the ASRs observed. The addition of CGO also mechanically affected the symmetrical cells, and delamination of the electrode layers was observed after electrochemical testing of sample 4. Additional adhesive tests were performed and confirmed poor adhesion between the thick La<sub>2</sub>NiO<sub>4+δ</sub> layer and the CGO interlayer. Therefore, the high ASR values obtained for samples 3 and 4 were attributed to poor adhesion between the CGO interlayer and the thick La<sub>2</sub>NiO<sub>4+δ</sub> electrode.



**Figure 1.** Micrographs of cross sections of typical cathode–electrolyte interfaces: [(a) and (b)] sample 1, (c) sample 5, and (d) sample 6.

By adding an intermediate compact layer of  $\text{La}_2\text{NiO}_{4+\delta}$  (samples 5 and 6), polarization resistances were significantly reduced. It is



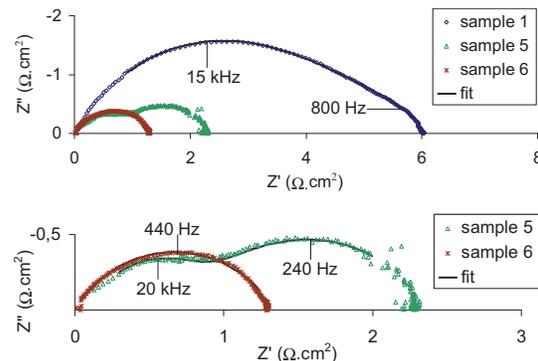
**Figure 2.** Micrographs of the cross section of a graded cathode with the intermediate layer of  $\text{La}_2\text{NiO}_{4+\delta}$  and the thick porous  $\text{La}_2\text{NiO}_{4+\delta}$  layer.

believed that this is a result of the number of contact points being increased between the YSZ substrate and the porous cathode layer. This would lead to an increase in oxygen surface exchange and would therefore improve oxygen diffusion toward the electrolyte. Furthermore, in sample 6, a CGO diffusion barrier layer has been added, and there was a good adherence between the CGO interlayer and the intermediate compact  $\text{La}_2\text{NiO}_{4+\delta}$  layer. This arrangement (sample 6) resulted in improved ASRs and no delamination between layers because there are more contact points between the CGO and the intermediate layer than between the CGO and only the thick cathode layer.

ASR values obtained for a symmetrical cell arrangement that incorporates an intermediate compact  $\text{La}_2\text{NiO}_{4+\delta}$  layer (samples 5 and 6) were 2.2 and 1.3  $\Omega \text{ cm}^2$ , respectively, at 800°C. These values are lower than those previously reported for the symmetrical cells of porous  $\text{La}_2\text{NiO}_{4+\delta}$  deposited on YSZ; Escudero et al.<sup>19</sup> and Mauvy et al.<sup>12</sup> obtained ASR values from  $\text{La}_2\text{NiO}_{4+\delta}$  on YSZ of 2.5 and 4  $\Omega \text{ cm}^2$ , respectively.

*Study of Nyquist diagrams recorded at 800°C.*—Nyquist diagrams obtained for samples 1, 5, and 6 are reported in Fig. 3. Polarization resistances, capacitances, and relaxation frequencies obtained by fitting with an equivalent circuit model using ZView software<sup>15</sup> are collated in Table II.

Two arcs, one at medium frequency and one at low frequency, were observed for samples 1 and 5, suggesting that there were two main contributions to the polarization resistance. Based on consid-



**Figure 3.** (Color online) Nyquist diagrams obtained from samples 1, 5, and 6 at 800°C and the corresponding fits.

**Table II. Resistances, capacitances, and relaxation frequencies obtained by modeling impedance diagrams of samples 1, 5, and 6 at 800°C.**

	Contribution no. 1			Contribution no. 2			ASR total ( $\Omega \text{ cm}^2$ )
	$R_1$ ( $\Omega \text{ cm}^2$ )	$C_1$ ( $\text{F cm}^{-2}$ )	$f_{0,1}$ (kHz)	$R_2$ ( $\Omega \text{ cm}^2$ )	$C_2$ ( $\text{F cm}^{-2}$ )	$f_{0,2}$ (kHz)	
Sample 1	$4.06 \pm 0.06$	$2.6 \times 10^{-6}$	15	$1.93 \pm 0.03$	$1.0 \times 10^{-4}$	0.81	$5.99 \pm 0.09$
Sample 5	$0.72 \pm 0.02$	$1.1 \times 10^{-5}$	20	$1.51 \pm 0.02$	$4.5 \times 10^{-4}$	0.23	$2.23 \pm 0.04$
Sample 6				$1.33 \pm 0.03$	$2.8 \times 10^{-4}$	0.43	$1.33 \pm 0.03$

eration of the capacitance values and the literature,<sup>19,20</sup> the contribution at medium frequency may be due to  $\text{O}^{2-}$  transfer at the electrolyte–cathode interface. At low frequency, the impedance response is due to electrode reaction phenomena (adsorption, dissociation, oxygen reduction and  $\text{O}^{2-}$  transfer into the cathode thickness, etc.).<sup>19,20</sup> The benefit of introducing an intermediate compact layer of  $\text{La}_2\text{NiO}_{4+\delta}$  was clearly demonstrated by the ASR reduction observed for sample 5. It is believed that increasing the number of contact points at the electrode–electrolyte interface leads to the observed decrease in the contribution from the interface polarization resistance.

The addition of an 80 nm CGO layer between the YSZ electrolyte and the intermediate compact layer of  $\text{La}_2\text{NiO}_{4+\delta}$  (sample 6) produced an impedance response composed of a single low frequency contribution. The addition of a CGO interlayer avoided the formation of a  $\text{La}_2\text{Zr}_2\text{O}_7$  insulating phase and led to a significant enhancement (lowering) of the ASR values when deposited with a thin compact intermediate layer of  $\text{La}_2\text{NiO}_{4+\delta}$ .

*Effect of current collection.*—Platinum paste has been used as an additional current collector on samples 1 and 6. As a reference, a symmetrical cell composed of YSZ with platinum painted electrodes was tested. The resulting ASR data are collated in Table I.

The electrochemical performance of samples 1 and 6 was significantly improved by the addition of a continuous current collection layer of platinum, with the ASR of sample 6 reduced by a factor of 10 to  $0.11 \Omega \text{ cm}^2$  at 800°C. Lalanne et al.<sup>6</sup> and Laberty et al.<sup>11</sup> previously reported an improvement in the ASR of  $\text{K}_2\text{NiF}_4$ -type electrodes by the addition of an electronic conductor such as  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  at the surface of the cathode. Therefore, it is likely that the improvement observed here is due to the insufficient electronic conductivity in the electrode layer, which is enhanced by the presence of a continuous platinum current collection layer.

The ASR of a symmetrical cell with platinum electrodes is greater than that of a symmetrical cell with thick  $\text{La}_2\text{NiO}_{4+\delta}$  electrodes (sample 1 + Pt) but is worse than that of a symmetrical cell with a CGO interlayer + an intermediate  $\text{La}_2\text{NiO}_{4+\delta}$  layer + a thick  $\text{La}_2\text{NiO}_{4+\delta}$  electrode (sample 6 + Pt). This indicates that platinum acts not only as an electrode in this case (sample 6) but mainly acts as a current collector, and we notice the benefit of graded cathodes.

### Conclusions

The symmetrical cells of YSZ with graded cathodes based on lanthanum nickelate ( $\text{La}_2\text{NiO}_{4+\delta}$ ) with a CGO interlayer between the electrode and electrolyte have been prepared by the polymeric precursor route, and layers have been deposited by dip-coating. The graded cathodes were deposited on  $\text{ZrO}_2$ -8%  $\text{Y}_2\text{O}_3$  substrates before heat-treatment. To evaluate the various designs, electrochemical impedance spectroscopy was performed, and a significant decrease in the ASR was achieved by incorporating an intermediate layer of compact  $\text{La}_2\text{NiO}_{4+\delta}$  between the electrolyte and the porous electrodes.

The lowest ASR of  $0.11 \Omega \text{ cm}^2$  at 800°C corresponds to a symmetrical cell consisting of an 80 nm CGO interlayer, deposited beneath an intermediate 2  $\mu\text{m}$  thick  $\text{La}_2\text{NiO}_{4+\delta}$  compact layer with a fine microstructure, coated by a porous 8  $\mu\text{m}$  thick  $\text{La}_2\text{NiO}_{4+\delta}$  layer with a coarser microstructure and a continuous platinum current collector layer. The benefit of the CGO interlayer is to avoid the formation of the insulating phase at the YSZ– $\text{La}_2\text{NiO}_{4+\delta}$  interface, and the addition of the intermediate compact  $\text{La}_2\text{NiO}_{4+\delta}$  layer leads to an increase in the number of contact points at the electrode/electrolyte boundary resulting in a ready  $\text{O}^{2-}$  transfer toward the electrolyte.

This study underscores the importance of the derived sol–gel method for synthesizing controlled cathodic interlayers (composition and porosity) and optimizing the electrochemical performance of layered cathode structures.

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