Functionally graded composite $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$ solid oxide fuel cell cathodes

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Abstract

Functionally graded electrodes have been fabricated from members of the $(\text{LaNiO}_3)_n\text{LaO}$ Ruddlesden-Popper family. These consist of a thin compact layer of $\text{La}_2\text{NiO}_{4+\delta}$ deposited on the electrolyte, topped by a thicker porous $\text{La}_2\text{NiO}_{4+\delta}+\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$ composite layer, completed by a thin porous $\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$ layer acting as a current collector. The microstructure and electrochemical role of these layers is discussed in detail. It was found that using a 50:50 wt.% mix in the composite layer gave the best performance; ASRs at 500, 550, 600, 650, and 700 °C were 15.6, 5.53, 2.29, 1.06 and 0.53 Ωcm^2 respectively. This represents high performance for this class of material, particularly notable at the lower-end of the temperature range. As such this grading process is an attractive proposition for further research towards lowering the operating temperature of SOFCs.

Keywords: Ruddlesden-Popper, composite, functionally graded, solid oxide fuel cell, cathode

Abbreviations: R-P – Ruddlesden-Popper; L2N1 – $\text{La}_2\text{NiO}_{4+\delta}$; L3N2 – $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$; L4N3 – $\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$;

σ_i – ionic conductivity; σ_{tot} – total conductivity

1. Introduction

Recently, layered Ruddlesden-Popper (R-P) phases have been studied as potential solid oxide fuel cell (SOFC) cathode materials. These materials have the generic formula $(\text{ABO}_3)_n\text{AO}$ and consist of perovskite-like ABO_3 slabs n layers thick separated by a single rock salt-like AO layer. Interest in these phases, particularly those containing lanthanum and nickel, was stimulated by the discovery of mixed ionic-electronic conductivity (MIEC) in $\text{La}_2\text{NiO}_{4+\delta}$ (L2N1) at temperatures relevant to SOFCs[1, 2]. This phase has attractive ionic conductivity however its performance as a cathode is limited by its electronic conductivity. Various efforts have been made to improve this by doping on the A-site, occupied by lanthanum, and/or the B-site, occupied by nickel[3-5]. Alternatively, it is known that electronic conductivity in these phases increases with n hence higher-order R-P phases have been considered; $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ (L3N2) and $\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$ (L4N3)[6-8]. Recently we explored composite cathodes made from L2N1 and L4N3 [9]. We found that this leads to improved performance over the single phases, particularly from 600 to 700 °C. This was ascribed to the complimentary nature of the two phases, L2N1 with high ionic and L4N3 with high electronic conductivity. A 50:50 wt.% mix was found to be optimal and showed area-specific resistance (ASR) values that are amongst best-in-class for these materials. The microstructure of these cathodes however was not ideal, leading us to believe that these values could be improved upon.

A strategy for this is the fabrication of functionally graded electrodes. These utilise layers with different compositions, each geared towards a certain role in the electrode. A typical advantage of this is the accommodation of large thermal expansion coefficient (TEC) strains between electrolyte and cathode materials. This is overcome by a gradual change in composition over the graded layers [10-12]. This however is not a problem for the materials used in this study – L2N1 and L4N3 are well-matched with the electrolyte used, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM). TEC's are 13.8, 13.2[7], and 12.4[13] $\times 10^{-6} \text{ K}^{-1}$ for L2N1, L4N3 and LSGM respectively. Hence the application of functional grading in this work is geared towards improving the electrode electrochemically and microstructurally. For the former it is known that polarisation resistances can be improved by having a composition with high ionic conductivity adjacent to the electrolyte, and grading to a composition

with greater electronic conductivity as the thickness of the electrode is increased [10-12, 14]. For the R-P phases used in this study this would correspond to a greater L2N1 content grading to a greater L4N3 content. Microstructurally, different approaches have been explored. One can fabricate the layer adjacent to the electrolyte to have a smaller particle size with a view to maximising the electrocatalytically active area in this region [11, 15]. Alternatively, this layer can be made denser than the bulk electrode with a view to improving the electrolyte/electrode contact. This has been successfully used to improve the performance of single-phase L2N1 electrodes [16-18] and is the approach chosen here; functionally graded electrodes will start with a thin compact L2N1 layer. The bulk of the electrode will be made up of the porous L2N1+L4N3 composite used in our previous work as this gave better performance than either of the respective single phases [9]. The outer region will be a porous L4N3 layer. This is designed to increase the electronic conductivity, acting as a current-collector, whilst not blocking gas transport to the rest of the electrode. A schematic of this design is presented in Figure 1. Symmetrical cells with graded electrodes composed of a range of L2N1+L4N3 composites are fabricated and their properties explored at the various grading stages.

2. Experimental

2.1. Electrode fabrication

The R-P phases and inks were made as per our previous study [9]. Briefly, L2N1 was obtained from a commercial source (CerPoTech) synthesised by spray pyrolysis, and L4N3 synthesised via a sol-gel route. Phase identity was confirmed by powder XRD (Figure 2) matching to standard ICDD data; PDF 01-080-1910 for L2N1 and PDF 00-050-0243 for L4N3. Electrode inks were made by ball-milling powders for 24h then three-roll milling with a commercial ink vehicle (Fuel Cell Materials 311006). To make a graded symmetrical cell the stages in Table 1 were carried out sequentially, an L2N1 layer was screen-printed onto each side of a >95% dense LSGM pellet and sintered at 1300 °C × 4 hours; a thicker L2N1+L4N3 composite layer brush coated and sintered at 1000 °C × 4 h; finally a L4N3 layer screen-printed and sintered at 1200 °C × 4h. Some characterisation was carried out between these steps and is detailed in the relevant sections below.

2.2. Characterisation techniques

AC Impedance spectroscopy (ACIS) was carried out using a Solartron 1260a impedance/gain-phase analyser with a thermocouple positioned close to the tested cell to accurately record the temperature. Data were obtained over a frequency range of $10^6 - 10^{-2}$ Hz with an AC amplitude of 25 mV. Symmetrical cells were first equilibrated in the testing rig at 500 °C for 2.5 hours, and allowed to stabilise for 30 minutes at each subsequent testing temperature before data collection. Scanning electron microscopy (SEM) images were obtained using a JEOL 6010 LA in SEI mode. XRD patterns were collected using a PANalytical X'Pert Pro MPD using Ni filtered Cu K_α radiation with tube voltage/current at 40 kV/40 mA.

3. Results and discussion

3.1. XRD

Figure 2 shows the XRD patterns for as-received L2N1 and as-synthesised L4N3 powders; Figure 3 presents patterns collected as-sintered after each stage of the electrode grading process. For the initial L2N1 layer in the electrode this was consistent with the starting powder apart from a small peak at $2\theta = 30.7^\circ$. This peak does not correspond to any binary or ternary La-Ni-O phase, and neither could it result from the LSGM pellet underneath. As such, it remains unidentified. The addition of the composite layer was as expected; the pattern is a linear combination of L2N1 and L4N3. Upon sintering the final L4N3 layer, completing the grading process, some phase changes are evident towards L3N2 (PDF 00-050-0244, ICDD) and nickel oxide. This is due to the high sintering temperature of 1200 °C (*cf.* Table 1), required for the L4N3 layer to adhere to the rest of the electrode. From the phase diagram proposed by Zinkevich and Aldinger[19] it is known that at these temperatures L4N3 is unstable with respect to lower-order phases and NiO. We observed similar behaviour when sintering L4N3 electrodes directly onto LSGM at these temperatures; despite the slight decomposition good electronic conductivity is maintained in this layer [9].

3.2. Electrochemical testing

ACIS measurements were carried out on symmetrical cells from 500 – 700 °C to determine the suitability of these graded electrodes with regard to IT-SOFC cathode use. Typical Nyquist plots are shown in Figure 4, along with the equivalent-circuit model (ECM) used to fit the data. There is an inductive response at high frequency from the measuring apparatus; this was not included in the analysis. In an effort to deconvolute the contributions of each individual layer to the overall impedance of the graded electrode it could be tempting to use an ECM with three resistor/constant-phase element (R/CPE) components. However, it was found that a single R/CPE component best represented the electrode, so this model was used in the analysis. ASR values are obtained from R_1 corrected for sample geometry. Figure 5 shows an Arrhenius plot of $\log(\text{ASR})$ vs $1000/T$ for the graded electrodes. This is compared to the best performing from our previous study, an ungraded 50:50 wt.% L2N1+L4N3 composite [9]. The slopes for the graded cells in this figure are constant with activation energies of the order of 0.52 eV. This indicates unchanging electrode kinetics over the temperature range. Using a 50:50 composite in the graded electrodes gave the best performance, better than 60:40 or 40:60. ASRs at 500, 550, 600, 650, and 700 °C for L2N1|50:50|L4N3 were 15.46, 5.53, 2.28, 1.06 and 0.53 Ωcm^2 respectively. This is consistent with our previous work where we found a 50:50 composite to be the optimal composite for an ungraded electrode. Figure 5 demonstrates that the graded electrodes gave better performance than ungraded, and that this was particularly apparent at the lower-end of the temperature scale. Figure 6 compares the data at 500 °C for ungraded 50:50 with graded L2N1|50:50|L4N3 electrodes. As well as having a lower polarisation resistance, the graded electrode arc is closer to a true semicircle than the ungraded. This indicates that the microstructure of the graded electrode is superior; this will be discussed in detail later. The shapes of the arcs in Figure 6 are manifested in the exponents, n , of the CPEs used in the ECM fitting (*cf.* Figure 4). $n = 1$ corresponds to a perfect capacitor, and $n < 1$ indicates deviations from ideality[20]. For the graded cells n was of the order of 0.85. Equivalent capacitance values can be calculated for a CPE provided n is close enough to 1. For the graded electrodes this is valid and values of the order of 10^{-2} F were obtained. From the suggested interpretations of capacitance given by Irvine *et al.* this reflects electrochemical reactions occurring at the electrode[21].

Hildenbrand *et al.* [18] have recently presented work on graded electrodes with a dense ≈ 400 nm thick L2N1 layer deposited by pulsed laser deposition (PLD) topped by a thicker porous L2N1 layer. These gave excellent performance, *e.g.* $0.85 \Omega\text{cm}^2$ at 600°C . It is noted that the CPE exponents fitted to these electrodes by Hildenbrand are also close to capacitive behaviour, indicating the similarity between that work and the data presented here.

Turning attention to the role of the different layers in the graded electrodes, Figure 7 shows the performance at each stage of fabrication. Data were obtained for a thin L2N1 layer, after the addition of the thick composite layer, and after the thin L4N3 layer completing the grading process. The L2N1 layer on its own provides a poor electrode. From the SEM images in Figure 8 (further discussed later) it is seen that this is too thin and coarse-grained to give good performance in isolation - it is known that an optimal electrode requires a sufficient thickness [22, 23]. There are two regions in the Arrhenius plot for this layer; a change of gradient is apparent from 0.44 eV between 500 and 600°C , to 0.15 eV between 600 and 700°C . Similar behaviour has been observed in studies on porous L2N1 electrodes and indicates a change in the electrode-limiting step, believed to be due the limited electronic conductivity of L2N1 [8, 9, 17, 18]. The next step in the grading regime is adding the thick porous composite layer. This improves the electrode performance and suppresses the change in gradient, meaning that the performance enhancement is largest at the higher-end of the temperature range. The enhancement is assigned to the increased electrode thickness and porosity giving a much larger region for oxygen reduction and incorporation, as well as the inherently better properties of an L2N1+L4N3 composite over pure L2N1 as shown in our earlier work. Adding a thin L4N3 layer completes the grading and gives a further performance enhancement, acting as a current collector. Total conductivity in these R-P phases is known to increase with n [7, 24], and it has been shown that this is maintained in porous electrode layers [9], so it is consistent that an outer L4N3 layer lowers the polarisation resistance. Current collectors are known to improve electrode performance and have been utilised with these La-Ni R-P materials before [16, 17, 25]. However, in those cases the collector was a layer of platinum; due to the expense of this element it is unreasonable to expect that a commercial

SOFC could utilise such a modification. Hence the L4N3 layers used as current collectors in this case are considered to be much more realistic with regard to viable devices.

Considering the graded electrode as a whole, it is believed that ionic conductivity (σ_i) increases with each layer closer to the electrolyte ($\sigma_i \text{ L2N1} > \sigma_i \text{ composite} > \sigma_i \text{ L4N3}$), and total conductivity (σ_{tot}) increases with each layer away from the electrolyte ($\sigma_{\text{tot}} \text{ L4N3} > \sigma_{\text{tot}} \text{ composite} > \sigma_{\text{tot}} \text{ L2N1}$). As discussed, this is the ideal arrangement for a graded electrode [10-12, 14], helping to explain the high performance seen.

3.3. *Post-test microstructural analysis*

Figure 8 presents SEM images of a graded electrode cross-section obtained after electrochemical testing. In this case a L2N1|50:50|L4N3 was chosen; these images are representative for the other composites used. The thin L2N1 layer – ‘b’ in Figures 1 & 8 – is clearly distinguishable from the rest of the electrode and is approximately 5 μm thick. It is well-adhered to the LSGM electrolyte and shows excellent interconnectivity. The L2N1+L4N3 composite making up the bulk of the electrode – ‘c’ in Figures 1 & 8 – is well-adhered to the thin L2N1 layer and again is highly interconnected. One cannot distinguish between L2N1 and L4N3 in the composite layer which is as expected given the nature of the physical processes occurring during image acquisition. The outer L4N3 layer can be identified by a slight change in microstructure. In our previous work[9] we observed a difference between L4N3 and composite electrodes, the former presenting a broader particle-size distribution and a series of voids throughout its thickness. These features are apparent in the outer 10 μm of the graded electrode – ‘d’ in Figures 1 & 8 – allowing us to tentatively assign this as the L4N3 current collector.

The L2N1 layer has larger particles than the composite layer – approx. 3 μm vs. approx. 1 μm – and is less porous. This is a feature of the sintering conditions and materials chemistry. Over the course of the grading process the L2N1 layer will have been sintered at 1300, 1000, then 1200 $^{\circ}\text{C}$ for 4 hours each; the composite layer at 1000 then 1200 $^{\circ}\text{C}$ for 4 hours each (*cf.* Table 1). It is the high temperature of the initial 1300 $^{\circ}\text{C}$ sintering that promotes grain growth and densification in the L2N1

layer. In the finished graded electrode the role of this is to increase the number of electrolyte/electrode contact points and as such it is ideal that L2N1 densifies as seen. This allows for very good adherence to the LSGM electrolyte, and it is seen in Figure 8 that the subsequent composite layer adheres very well to L2N1. Compared to our previous work on ungraded composite electrodes the overall contact between the composite layer and the LSGM is better when mediated by the thin compact L2N1 layer. As such this could be described as an ‘interlayer’. These are thin layers between two phases in an SOFC that provide an overall performance enhancement. Often the function of these is to prevent deleterious reactivity between phases, for example a CGO interlayer avoids contact between YSZ and LSC[26] or LSCF [27-29]. In the case of the graded La-Ni R-P cathodes developed in this work reactivity with LSGM is not believed to be an issue [7, 30], so the interlayer is focussed on improving the electrolyte/electrode connectivity. L2N1 is a novel material to use as an interlayer and has some advantages over other materials such as CGO. The presence of catalytically-active nickel and appreciable mixed ionic-electronic conductivity in L2N1 means that this interlayer will also provide active sites for oxygen reduction and incorporation, as well as improving the conductive pathway between porous electrode and electrolyte. Active sites will not be present in a CGO interlayer so it would therefore be of value to test dense L2N1 interlayers with more traditional SOFC cathode materials. Hildenbrand has shown that L2N1 interlayers can be deposited by PLD [18]. These will maximise the electrolyte/electrode contact as they are more uniform and of higher density than those made by screen printing used in this present study. The low ASRs found by Hildenbrand indicate that PLD is the optimal interlayer deposition method for electrodes fabricated in-house, however this process may be difficult to apply to any eventual larger scale.

The final sintering step used to make these L2N1/L4N3 graded electrodes was at 1200 °C. This does not lead to noticeable densification of the composite or the L4N3 layer. This is a feature of the materials chemistry of L4N3; it is known to resist densification even with isostatic pressing and sintering[7]. Having this phase in the composite layer allows it to maintain the desired porosity during the fabrication process. The current-collecting layer should not be continuous such that it blocks gas

transport to the bulk of the electrode; this is the case for the L4N3 layer. The microstructure of this could however still be improved upon in terms of pore and particle size distribution.

4. Conclusion

We have fabricated functionally-graded L2N1/L4N3 electrodes consisting of three layers;

- A thin compact L2N1 layer adjacent to the electrolyte. This improves the electrolyte/electrode contact as well as providing more active sites for oxygen reduction and incorporation.
- A thicker more porous L2N1+L4N3 composite, for which a 50:50 wt.% mix gave the best performance. It is here that the bulk of the oxygen reduction and incorporation is assumed to occur.
- A thin outer layer of porous L4N3 acting as a low cost current collector.

The lowest ASRs were for a L2N1|50:50|L4N3 electrode; 15.6, 5.53, 2.29, 1.06 and 0.53 Ωcm^2 at 500, 550, 600, 650, and 700 °C respectively. This represents high performance for these La-Ni R-P phases. Particularly notable was the large improvement at lower temperatures (500 – 600 °C) of the graded electrodes compared to ungraded La-Ni R-P electrodes. This makes this particular grading process an attractive proposition for further research with respect to lowering the operating temperature of SOFCs.

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Figure Captions

Figure 1: Schematic of graded electrode layers deposited on LSGM electrolyte. *N.B.* Tested cells were symmetrical

Figure 2: XRD patterns for as-received $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$ powders used to make inks for fabrication of functionally graded electrodes

Figure 3: XRD pattern for each stage of the electrode grading process. Marked peaks are: a - unknown; b - L3N2 ; c - NiO .

Figure 4: Typical Nyquist plots at 500, 600, and 700 °C for a $\text{L2N1}|50:50|\text{L4N3}$ symmetrical cell. Circles: collected data; dotted lines: fitted data. Inset shows the equivalent circuit model used for fitting

Figure 5: Arrhenius plot of $\log(\text{ASR})$ vs. $1000/T$ for graded symmetrical cells from this study, with comparison to best performing ungraded cell from our previous work[9]

Figure 6: Nyquist plots comparing electrode performance of ungraded 50:50 electrode at 504 °C with graded $\text{L2N1}|50:50|\text{L4N3}$ electrode at 500 °C. Data normalised to zero series resistance to aid comparison. Circles: collected data; dotted lines: fitted data

Figure 7: Arrhenius plot of $\log(\text{ASR})$ vs. $1000/T$ demonstrating the electrode performance for each stage of the grading process

Figure 8: SEM images of $\text{L2N1}|50:50|\text{L4N3}$ electrode deposited on LSGM electrolyte. a: LSGM; b: L2N1 ; c: 50:50; d: L4N3 . Upper image shows whole cross-section; lower shows the $\text{LSGM}|\text{L2N1}|50:50$ region at higher magnification. Images obtained after electrochemical testing up to 700 °C

Table 1

Fabrication method and sintering conditions for functionally graded symmetrical cells

	Layer	Fabrication method	Sintering conditions
a	LSGM electrolyte	Powder isostatically pressed	1450 °C × 8h
b	compact L2N1	screen printed	1300 °C × 4h
c	porous L2N1+L4N3 composite	brush coated	1000 °C × 4h
d	porous L4N3	screen printed	1200 °C × 4h

a

b

c

d

a: LSGM electrolyte

b: compact L2N1

c: porous L2N1+L4N3
composite

d: porous L4N3