Oxygen electrode characteristics of $\text{Pr}_2\text{NiO}_{4+\delta}$ -infiltrated porous $(\text{La}_{0.9}\text{Sr}_{0.1})(\text{Ga}_{0.8}\text{Mg}_{0.2})\text{O}_{3-\delta}$

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Abstract

$\text{Pr}_2\text{NiO}_{4+\delta}$ was wet infiltrated into porous LSGM scaffolds to form solid oxide cell oxygen electrodes on LSGM-electrolyte symmetrical cells. The minimum calcination temperature required to form this nickelate phase was between 950 °C and 1000 °C. X-ray diffraction measurements of electrodes tested at 650 °C showed little evidence of any phase change, in contrast to 650 °C annealed $\text{Pr}_2\text{NiO}_{4+\delta}$ powders that decomposed to $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ and Pr_6O_{11} . Polarization resistance followed an Arrhenius temperature dependence with an activation barrier of 1.40 eV, and a value as low as $0.11 \Omega\cdot\text{cm}^2$ was observed at 650 °C for a $\text{Pr}_2\text{NiO}_{4+\delta}$ loading of 14 vol%. The present resistance values appear to be the lowest reported to date for a Ruddlesden-Popper phase electrode, and are competitive with perovskite-structure electrodes. The low resistance, combined with the good stability of infiltrated $\text{Pr}_2\text{NiO}_{4+\delta}$ and the advantages of being Co- and Sr-free, make this an exciting new contender for intermediate-temperature solid oxide cell applications.

1. Introduction

Solid oxide cells (SOCs) are high efficiency, low emission, fuel flexible electrochemical conversion devices that hold promise for distributed electricity generation¹ and grid energy storage². Reduction of the operating temperature to 500-650 °C is desirable to reduce balance of plant requirements, to allow the use of low-cost metal interconnectors and alternative sealants, and to reduce the rates of important degradation mechanisms. However, at these intermediate temperatures, the resistance of conventional SOC becomes prohibitively large, with the oxygen electrode being particularly important^{3,4}. The development of improved oxygen electrodes, typically incorporating perovskite mixed ionic and electronic conducting (MIEC) materials, has produced polarization resistance R_p values $< 0.15 \Omega\cdot\text{cm}^2$ at 600–650 °C, as needed to produce high enough power density for commercial viability³. However, these materials (such as $(\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_{3-\delta}$ (LSCF) or $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC)) have issues including degradation by strontium surface segregation,^{5,6} thermal expansion coefficient mismatch⁷ with electrolyte materials, and difficult materials disposal associated with Co-containing oxides⁸.

Ruddlesden-Popper⁹ (R-P) series $(\text{AO})(\text{ABO}_3)_n$ materials are alternative MIECs with potential to provide low R_p while avoiding the above problems. In particular, the early rare earth (La, Nd, Pr) nickelates and cuprates demonstrate reasonable electronic conductivity (10-200 S/cm), and have high oxygen transport (self-diffusion and surface exchange) coefficients compared to the best perovskite MIECs¹⁰. Despite these promising properties, there has been only limited success in producing low-resistance R-P oxygen electrodes. Of the cuprates¹¹, only praseodymium cuprate seems to have formidable properties¹² with the best demonstrated polarization at $0.41 \Omega\cdot\text{cm}^2$ on a Gd-doped ceria (CGO) electrolyte at 700 °C¹³. Within the set of R-P nickelates, $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ has

attracted much attention since it is both stable in contact with common electrolytes and exhibits relatively fast oxygen transport coefficients^{10,14}. $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ has been prepared in the $n=1, 2$, and 3 phases^{15,16}, and even in combination as a functionally graded cathode that combines the high surface exchange of the $n=1$ phase with the superior electronic conductivity of the $n=3$ phase¹⁷, representing the current best-in-class cathode for $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ with a polarization resistance of $1.06 \Omega\cdot\text{cm}^2$ at 650°C . $\text{Nd}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ has proven to be reactive with some common electrolytes and has moderate oxygen transport coefficients compared with other rare earth nickelates¹⁸⁻²².

$\text{Pr}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ electrodes have shown the lowest R_p amongst the R-P materials^{23,24}, but there are significant stability issues. The $n=1$ compound powder has been observed to decompose to the $n=3$ phase and Pr_6O_{11} below $\sim 1000^\circ\text{C}$ ²⁵. The material is also reactive with yttria stabilized zirconia (YSZ) and unstable on ceria electrolytes²¹. Pr_2NiO_4 (PNO) in contact with (CGO) has been reported to decompose to PrNiO_3 and Pr_6O_{11} , and perhaps NiO ,¹⁴ different than for PNO powder alone. The decomposition of PNO on $(\text{La}_{0.9}\text{Sr}_{0.1})(\text{Ga}_{0.8}\text{Mg}_{0.2})\text{O}_{3-\delta}$ (LSGM) does not follow the same sequence as on CGO or in powder form¹⁴. PNO based cathodes on LSGM²³ have yielded $R_p = 0.87 \Omega\cdot\text{cm}^2$ at 600°C . PNO based cathodes on CGO²⁴ have been reported to yield R_p as low as $0.08 \Omega\cdot\text{cm}^2$ at 600°C (although more recent reports by the same group give a value of $0.28 \Omega\cdot\text{cm}^2$)¹⁴; these relatively low resistances are somewhat surprising given that the nickelate is unstable and may react with the electrolyte as suggested by the appearance of NiO peaks in X-ray¹⁴. Substitution of Sr ²⁶, La , Cu or Ga ^{27,28} in Pr_2NiO_4 has been shown to improve stability, polarization resistance, and oxygen diffusivity.

There is relatively little information on the long-term resistance stability of R-P electrodes, an especially important question given the above-mentioned phase stability issues. One report of a PNO electrode prepared on LSGM showed good stability,²³ but there are no reports of polarization resistance versus time for praseodymium nickelate on CGO.

Finally, even though infiltration has been widely used to produce high-performance perovskite electrodes²⁹⁻³¹, there are only two prior reports of infiltrated R-P electrodes – La_2NiO_4 and $\text{La}_4\text{Ni}_3\text{O}_{10}$ on YSZ¹⁵ and $\text{Nd}_2\text{NiO}_{4+\delta}$ on scandia stabilized zirconia³². These yielded relatively low R_p values at 750°C of $0.120 \Omega\cdot\text{cm}^2$, $0.068 \Omega\cdot\text{cm}^2$ and $0.059 \Omega\cdot\text{cm}^2$, respectively, despite reactivity with YSZ²¹.

In the present work we describe the fabrication, performance, and stability of infiltrated Pr_2NiO_4 cathodes on LSGM. Besides providing R_p values comparable to the best prior reports of R-P electrodes, the infiltrated Pr_2NiO_4 shows improved stability compared to prior reports on this material.

2. Experimental

The cathodes were prepared on LSGM electrolyte supported symmetrical cells. LSGM powder was synthesized from stoichiometric amounts of SrCO_3 (Sigma), La_2O_3 (Sigma), Ga_2O_3 (Sigma), and MgO (Alfa Aesar), which were ball milled for 24 hours in ethanol, dried, and then reacted at 1250°C for 12 hours. This LSGM powder was then ball milled in ethanol and 2 wt. % polyvinyl butyral (Aldrich) binder, dried, and pressed into 500 mg 19 mm diameter pellets. The green bodies were then sintered at 1450°C for 4 hours. LSGM scaffolds were screen printed onto the electrolyte pellets using an ink composed of commercially available LSGM (Praxair), Heraeus 737 vehicle, and 30 wt% of KS4 graphite flakes (Timrex) as pore former. Four screen printed layers were applied to each side, then heated to 600°C for one hour to burn away the pore former, and then fired at 1200°C for 4 hours to form a porous scaffold layer with interconnected LSGM

particles 1-3 microns in size. A current collector was then applied on each scaffold by screen printing one layer of an $(\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_{3-\delta}$ ink consisting of the same vehicle, pore former, and LSCF powder (Praxair). Note that the current collector was omitted for samples to be studied with X-ray diffraction, in order to avoid additional reflections from LSCF. The entire assembly was then fired at 1100 °C for one hour to produce a suitably porous current collector that was also well bonded to the scaffold. The resulting scaffold thickness was ~ 40 µm and the LSCF layer was ~ 10 µm thick.

The cathode infiltrate was a 2 M nitrate solution prepared by dissolving stoichiometric amounts of $\text{Pr}(\text{NO}_2)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) and $\text{Ni}(\text{NO}_2)_3 \cdot 3\text{H}_2\text{O}$ (Fischer) in water and subsequently adding 0.06 mol of Triton X-100 (VWR). This solution was stirred for 24 hours to ensure good mixing. Each scaffold was infiltrated with this solution using excess fluid (~6 µL) and removing the excess after allowing solution to infiltrate the porous scaffold for 5 minutes. The infiltrate was decomposed by heating to 450 °C for 0.5 hours, leaving oxides of the respective metal ions. After the desired number of infiltrations, ranging from 4 to 16, was complete, the symmetric cells were typically fired at 1000 °C for 4 hours. All specimens were cooled no faster than 5 °C/min. Infiltrate volume fractions were determined from the mass difference between the final cell and the structure prior to infiltration. The infiltrate volume fraction was obtained from this mass difference and the theoretical density of Pr_2NiO_4 , and then dividing by the total electrode volume. Finally, powders were produced by drop casting the infiltrate solution onto an alumina plate and subjecting it to a similar firing program as above with the maximum temperature ranging from 900 to 1100 °C. The resulting material was gently scraped from the plate and ground by mortar and pestle for powder X-ray.

A silver current-collector grid was screen printed onto each cathode using Heraeus unfritted silver paste, and a silver wire attached for electrochemical impedance testing. Impedance testing was performed using a Zahner IM6 between 10^5 and 10^{-1} Hz. All EIS data sets were modeled using an equivalent circuit consisting of three RQ elements and a resistor in series. The fits were used to obtain polarization resistances and the ohmic resistance. X-ray diffraction data was collected using a Scintag XDS2000 using Cu K α 1.54 Å and a solid state detector.

3. Results and Discussion

3.1 Processing and Phase Formation

Figure 1 shows that nitrate solutions fired at 900 and 950 °C for 4 hours result in a mixture of NiO and Pr_6O_{11} . Nitrate solutions fired at 1000 °C and 1100 °C for four hours result in the n=1 R-P phase (Pr_2NiO_4) with small amounts of Pr_6O_{11} . These x-ray results suggest that the nickelate-forming reaction between the NiO and Pr_6O_{11} phases is not spontaneous below 950-1000 °C, but that Pr_2NiO_4 is formed at higher temperature. This is consistent with previous studies,^{25,33} which indicated that Pr_2NiO_4 is stable at temperature >850-950 °C.

Similar to the powder results in Figure 1, Pr_2NiO_4 is also obtained after infiltrating and firing at 1000 °C in the scaffold, as shown by XRD (Figure 2b). Based on these results, all further PNO infiltrated electrodes in this study were treated at 1000 °C for 4 hours.

Fig. 1. X-ray diffractograms of the PNO powders after 4 hour heat treatments in air at 900, 950, 1000, and 1100 °C. Reacting the oxides at 1000 °C for 4 hours produces Pr_2NiO_4 .

Figure 2a shows a fracture cross-section SEM image of the infiltrated scaffold, current collector, and a portion of the electrolyte of a typical as-prepared cell after infiltrate firing at 1000 °C. The current collector and infiltrated LSGM scaffold show similar porous contrast, whereas the LSGM appears reasonably dense. The EDS line scan superimposed on the image shows that both porous electrode layers contain Pr and Ni, including the region near the electrode/electrolyte interface. The apparent Pr signal in the LSGM was due to an overlap of the Pr peak with the La peak. Figures 2c and d show higher magnification fracture cross-sectional SEM images of an un-infiltrated LSGM scaffold, for comparison with similar images taken from an infiltrated but otherwise identical scaffold (Figures 2e and f). Although there was low contrast between the LSGM and the infiltrated phase, the presence of the infiltrate is suggested by the slight roughness seen at high magnification.

Fig. 2. a) EDS line scan of an infiltrated cell showing the entire thickness of the cathode contains Pr and Ni. b) X-ray scan of an infiltrated cathode fired at 1000 °C and without current collector.

The microstructure of an uninfiltrated scaffold is shown in c) and d), and compared with that of an 8-times infiltrated scaffold shown in e) and f).

3.2. Phase Stability

Figure 3 compares the X-ray diffractograms from the as-prepared bulk Pr_2NiO_4 powder (prepared at 1000 °C as described above and also shown in Figure 1) (a) and the same powder subsequently annealed in air for 100 hours at 650 °C (b). The X-ray results shows that the lower-temperature treatment fully decomposed the Pr_2NiO_4 powder into $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ (the $n=3$ R-P phase) and Pr_6O_{11} . That is, Pr_2NiO_4 is unstable at 650 °C. This is consistent with prior reports showing that Pr_2NiO_4 decomposes to $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ and Pr_6O_{11} in air at temperatures below 900 °C.^{25,33} Thus, while Pr_2NiO_4 can be produced by firing at ≥ 1000 °C, it is expected to decompose if used in a solid oxide cell at lower temperature.

Fig. 3. x-ray diffraction scans from (a) as-prepared Pr_2NiO_4 powder; (b) the powder shown in (a) after aging for 100 hours at 650 °C; (c) the 12-times infiltrated Pr_2NiO_4 cathode and (d) the cathode shown in (c) after aging for 100 hours at 650 °C. The inset (e) highlights the reflection at 24.4°, the only Pr_2NiO_4 peak not overlapped with a peak from another phase. All unlabeled peaks correspond to LSGM. The infiltrated cathodes were prepared the same as those used in EIS measurements, except that the LSCF current collector was omitted to eliminate its extra x-ray reflections.

Figure 3 also compares the x-ray scans from the as-prepared PNO infiltrated cathode, shown in Figure 2 to be predominantly Pr_2NiO_4 (c) compared with the same electrode annealed in air for 100 hours at 650 °C (d). Unlike the powder results, there is little apparent effect of annealing; both scans show peaks as expected for $\text{Pr}_2\text{NiO}_{4+\delta}$, along with peaks from the LSGM scaffold. This suggests that the $n=1$ phase is retained when annealed in the LSGM scaffold. This can be seen more clearly in Figure 3 (e), which shows a magnified view of the $n=1$ peak at 24.4°, the only RP-phase peak not overlapped with another peak, for all four samples. This peak is present in the as-prepared powder (a), but is not present in the aged powder (b) because of the transformation from $n=1$ to $n=3$. For the infiltrated LSGM scaffolds, this peak does not change

after annealing at 650 °C, indicating that, at most, only a small fraction of the material transformed to n=3. That is, the n=1 phase in the LSGM scaffold was more stable than the powder. This may be explained by the physical constraint on any transformation with an associated volume change or distortion, caused by the intimate contact between the infiltrate and LSGM. In particular, the a and b lattice constants remain relatively unchanged for the transformation from n=1 to n=3, but the c direction in the n=3 phase (27.50 Å) is smaller than would be expected relative to the n=1 (12.45 Å) phase given the number of atoms in the unit cell^{25,33}. Alternatively, there may be significant interdiffusion during infiltrate firing at 1000 °C: diffusion of lanthanum, strontium or gallium from the LSGM into the PNO could help stabilize the n=1 phase. Both lanthanum and gallium have been shown to increase the low temperature stability of the n=1 phase, material^{18,27,34}. Phillippeau *et al* reported a reaction between PNO and LSGM at 1150 °C forming a praseodymium gallate, which is not observed for our processing temperature, but does show the possibility of gallium diffusion¹⁴.

3.3 Electrochemical Characteristics

Cells were infiltrated 4, 8, 12, or 16 times, resulting in measured volume fractions of ~ 10, 12, 14, and 16%, respectively. Five cells were fabricated for each level of loading, and considerable variation in polarization resistance, by as much as a factor of 2, were observed, but the shapes and peak frequencies of the impedance responses did not vary significantly. Figure 4 shows Nyquist and Bode plots of the EIS data measured in air at 650 °C from the best devices at each infiltrate loading. There was one main depressed arc in all cases, peaked at a frequency of ~ 30 Hz, that decreased with increasing loading. A smaller response is also observed at ~1000 Hz. The polarization resistance R_p , measured by fitting the responses using an equivalent circuit, decreased with increasing loading to a minimum of 0.11 $\Omega \cdot \text{cm}^2$ at 12 infiltrations, and appeared to increase slightly at 16 infiltrations. This is similar to the loading dependence observed previously for infiltrated LSCF and SSC perovskite cathodes^{30,31}. This dependence has been explained by an increase in the infiltrate surface area and an increase in the fraction of infiltrated particles that are electrically percolating and, therefore, active for the oxygen reduction reaction^{30,35}.

Figure 5 shows Nyquist and Bode plots of the EIS data taken from the 12-infiltration cathode at various temperatures. The main polarization response increases rapidly in magnitude with decreasing temperature, and also shifts to lower frequency, as expected given the resistance increase. The model used for fitting is shown in figure 5. Two R-Q elements are used to model the main polarization response as they resulted in better fits for all EIS data, especially at longer times where two responses are apparent (Figure 7). Both responses are thought to correspond to a co-limited ORR process involving oxygen surface exchange and bulk diffusion, similar to previous work on infiltrated cathodes^{30,31}. A third response at high frequency, $> 10^5$ Hz, also appears at low temperature. This high frequency response is likely an interfacial process, either from grain boundaries or from the transport of oxygen across the PNO/LSGM interface.

Figure 6 shows the R_p values measured for all samples at each loading, plotted versus inverse temperature. The activation energies versus infiltration number, obtained by fitting the temperature dependences for each cell, are displayed as an inset in figure 6. The value obtained is 1.4 eV $\pm$ 0.2 eV. Loading beyond 12 infiltrations offers minimal further decrease in R_p , and may actually slightly increase

R_p . The average polarization resistance for 8 devices at 650 °C and 12 infiltrations is $0.16 \Omega \cdot \text{cm}^2$, with values ranging from 0.11 to $0.22 \Omega \cdot \text{cm}^2$.

Fig. 4. Nyquist and Bode plots of the electrochemical impedance response measured in air at 650 °C for cells infiltrated 4, 8, 12, and 16 times. The high-frequency intercept of the fitted equivalent circuit was set to zero in the Nyquist plots to allow easy comparison of the polarization arcs.

Fig. 5. Nyquist and Bode plots of the electrochemical impedance response measured from a 12-times infiltrated cell in air at various temperatures. The high-frequency intercept of the fitted equivalent circuit was set to zero in the Nyquist plots to allow easy comparison of the polarization arcs. An example of an equivalent circuit is shown on the plot.

Fig. 6. Polarization resistance plotted versus inverse temperature for all cells tested at each loading level. The lines show the best overall fits to an Arrhenius dependence for the data at each loading. The inset shows a plot of the activation energies obtained from Arrhenius fits to all cells, versus number of infiltrations.

3.4 Electrochemical Stability

In order to provide a preliminary measure of electrode stability, three identical symmetric cells, each infiltrated 12 times, were maintained at 650 °C in air for 500 hours. Figure 7 shows representative Nyquist and Bode plots of the EIS data taken periodically during the test. Figure 8 shows the R_p values versus time derived from fits to the EIS data. The response changes significantly in the first 100 hours – the main response at ~ 30 Hz decreases slightly and shifts to slightly higher frequency, while a new smaller response at ~ 1 Hz appears – resulting in a slight overall decrease in R_p . After ~ 100 h, the shape of the response does not change, but the size of the responses increases gradually, with R_p increasing by ~0.05 $\Omega \cdot \text{cm}^2/\text{kh}$ following the initial drop in the first 100 h. Longer term tests will be required to determine if R_p eventually stabilizes or continues to increase.

The initial changes in electrode response shown in Figures 7 and 8 are presumably caused by equilibration of the electrode to the testing conditions. The steady increase in R_p of both responses at longer times may be related to a decrease in the PNO surface area due to coarsening²⁹. It may also arise from a partial phase transformation of the n=1 nickelate phase, although the X-ray results shown in Figure 3 suggest that this was mostly suppressed in these electrodes. Recent reports utilizing low energy ion

scattering suggest that A-site surface enrichment may occur in R-P materials, which may also account for the resistance increase.³⁶

Fig. 7. Bode and Nyquist plots of EIS data taken from a cell with 12-times infiltrated PNO/LSGM electrodes taken during a 500 h life test in air at 650 °C.

Fig. 8. Polarization resistance versus time for 3 identically processed 12-times infiltrated cells at 650 °C.

3.5 Comparison with Other MEIC Electrodes

Figure 9 shows R_p as a function of temperature for the present best cathode compared to prior reported values for R-P electrodes. The present electrodes are as good or better than prior electrodes except for one report which gives a value of $0.08 \Omega \cdot \text{cm}^2$ at 600 °C²⁴. Also shown for comparison are the values reported for the perovskite cathodes LSCF³¹ and SSC.³⁰ These were prepared using a similar infiltration method as the present nickelate cathodes, including infiltration with aqueous metal nitrates and optimized levels of active material loading. The infiltrated PNO electrodes provide similar R_p values as these state-of-the-art perovskite MIEC electrodes, although the comparison is not perfect as the LSCF and SSC cathodes were infiltrated into CGO scaffolds, not LSGM, and they were calcined at a lower temperature.

Fig. 9. Comparison between single phase RP cathodes^{14,17,20}, and infiltrated LSCF³¹, SSC³⁰, and PNO (this work) in the temperature range from 450-650 °C on the indicated electrolyte.

4. Conclusions

The Ruddlesden-Popper oxide Pr_2NiO_4 was synthesized by infiltration onto an LSGM scaffold and firing at a temperature > 950 - 1000 °C. The lowest polarization resistance was obtained for electrodes with 14 vol% PNO (12 infiltrations), ranging from 0.11 to $0.21 \text{ } \Omega \cdot \text{cm}^2$ measured at 650 °C in air. Preliminary life tests showed a polarization resistance increase of $\sim 10\%$ after 500 hours operation at 650 °C. However, the infiltrated Pr_2NiO_4 electrodes showed no evidence of the decomposition to $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ and Pr_6O_{11} normally observed for Pr_2NiO_4 powders and powder-based electrodes maintained below 900 °C. Given resistance values that are competitive with infiltrated perovskite cathodes, and the absence of the Sr segregation and cobalt disposal issues associated with the perovskites, infiltrated PNO on LSGM is a promising IT-SOFC oxygen electrode material. Further study is warranted, especially to understand long-term stability.

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6. References

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