Improved Tolerance of Lanthanum Nickelate ($\text{La}_2\text{NiO}_{4+\delta}$) Cathodes to Chromium Poisoning Under Current Load in Solid Oxide Fuel Cells

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Lanthanum nickelate, $\text{La}_2\text{NiO}_{4+\delta}$ (LNO), is studied as a cathode material for use in solid oxide fuel cells with the objective of mitigating chromium poisoning. Under current load, both electrochemical and chemical reactions cause chromium poisoning, and high current density and humidity accelerate the poisoning. However, compared with a standard strontium-doped lanthanum manganite cathode, the LNO cathode has a much higher tolerance for chromium poisoning. This can be ascribed to a greatly reduced chromium deposition in LNO.

INTRODUCTION

Intermediate temperature (600–800°C) solid oxide fuel cells (IT-SOFCs) are considered as potential energy conversion systems because of their high efficiency and low emissions.^{1–3} Among the many metal alloys, ferritic stainless steels are the most promising interconnects at intermediate temperatures due to their high oxidation resistance and great thermal compatibility with other SOFC components. Vapor phase chromium species formed from the ferritic stainless steel interconnects and depositing in the triple-phase boundaries of the cathode^{4–8} lead to cell performance deterioration. Mitigation strategies that combine protective

coatings on metallic interconnects^{9–12} and chromium-tolerant cathodes of the type investigated in this study will offer the best long-term solution to address chromium poisoning.

It has been reported that Sr- and Mn-containing cathode materials, such as $(\text{La},\text{Sr})(\text{Co},\text{Fe})\text{O}_3$ (LSCF) and $(\text{La},\text{Sr})\text{MnO}_3$ (LSM), are sensitive to Cr poisoning. The main compounds formed through reaction with Cr-vapor phase species and the aforementioned cathodes, leading to degradation, are SrCrO_4 , Cr_2O_3 and $(\text{Cr},\text{Mn})_3\text{O}_4$.^{13–15} Thus, new Sr and Mn-free cathodes are desirable. Komatsu et al.¹⁶ investigated the effect of chromium poisoning on perovskite-structured $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (LNF) as a cathode material and found that the cathodic overpotential of LNF was not a function of the presence of chromium.

Rare earth nickelates, with the $\text{Ln}_2\text{NiO}_{4+\delta}$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Pr}, \text{etc.}$) formula, with alternating blocks of perovskite LnNiO_3 and rock-salt, Ln_2O_2 layers are known to be good SOFC cathodes.¹⁷ This layered structure can accommodate excess lattice oxygen in interstitial sites, resulting in high oxygen ion diffusivities and oxygen surface exchange coefficients.^{18,19} Laberty et al.²⁰ showed that power density of 2.2 W/cm² can be achieved using LNO

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cathodes. Other rare-earth nickelates have also been studied as SOFC cathodes.^{21–23} Our group previously studied the stability of the $\text{Ln}_2\text{NiO}_{4+\delta}$ - $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ (LNO-LDC) composite cathode and found that decomposition of the LNO phase can be stabilized by tuning the composition of LNO as well as the dopant level in doped ceria.^{24,25} Because rare-earth nickelates are free of Sr and Mn, they are also considered to possess better Cr-poisoning tolerance than conventional LSM or LSCF cathodes.^{26–30} Lee et al.²⁶ studied the Cr-poisoning effect of $\text{La}_2\text{NiO}_{4+\delta}$ by infiltrating Cr into the symmetric cell electrode, and they reported that performance of LNO is less sensitive to Cr than LSCF although the reaction product LaCrO_3 was observed. Hou et al.²⁹ and Lee et al.³⁰ investigated chromium poisoning of La_2NiO_4 and $\text{Nd}_2\text{NiO}_{4+\delta}$ using symmetric cells, respectively, and they showed insignificant poisoning effects on the electrode performance and microstructure.

In this study, to better understand the effects of chromium poisoning on rare-earth nickelates, $\text{La}_2\text{NiO}_{4+\delta}$ electrodes were applied onto both electrolyte-supported half-cells (as working electrode) and anode-supported full-cells (as cathode). Half-cells were cathodically polarized or held under open-circuit condition, and the ohmic and polarization resistances of the electrode were periodically characterized using galvanostatic current interruption. Different from previous studies reported by other researchers,^{26–30} in this work, anode-supported cells (ASC) with an $\text{La}_2\text{NiO}_{4+\delta}$ electrode were also tested with or without current load, during which voltage–current (V – I) measurements were conducted periodically. The V – I curves were analyzed using a polarization model, and the effects of chromium poisoning on different polarization resistances of LNO electrode were studied for the first time and compared with baseline LSM electrodes. To better simulate the realistic SOFC stack operation, a chromia-forming alloy in a mesh form was placed directly in contact with the investigated electrodes. The effects of current density and humidity on chromium poisoning were carefully studied. After the cell testing, scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS) were used to measure the extent of Cr deposition.

EXPERIMENTAL DETAILS

Powder Preparation

The $\text{La}_2\text{NiO}_{4+\delta}$ powder was synthesized by solid-state reaction. A stoichiometric mixture of precursors La_2O_3 and NiO were ball milled in ethanol for 24 h using 1-cm-diameter zirconia milling media. After drying in an oven at 70°C, the powders were calcined at 1200°C for 4 h. Formation of the single phase LNO was confirmed via x-ray diffraction.

Cell Fabrication

The details of the half- and full-cell fabrication are given in the supplementary material. The schematic of the cells featuring LSM and LNO cathodes are shown in Fig. 1.

Half-Cell Testing

For half-cell testing, a Crofer 22H mesh (Fe–Cr–Mn alloy, Fiachell Sarl, Switzerland) was applied in direct contact with the working electrode for use as a current collector and chromium source. On the counter electrode side, the current collector was a silver mesh that was attached to the electrode using silver paste. The cell was sandwiched between two alumina tubes. A gold O-ring and a mica gasket were used to seal the cell. On the working electrode (WE), two silver wires were attached to a silver mesh, which was pressed on the Crofer 22H mesh by spring loading. These wires were used as current lead and voltage probe. On the counter electrode side, a silver wire was connected to the silver mesh of the counter electrode (CE), and another silver wire was connected to the reference electrode (RE). The cells were tested at 800°C. Dry air or 10% humidified air was circulated on the WE side, and dry air was circulated on the CE side. The air flow rate was 200 cc min^{−1}. Galvanostatic current interruption (GCI) measurements³¹ (using PARSTAT 4000) at a current density of 50 mA cm^{−2} were performed every 24 h after the cell was initially stabilized at 800°C for 24 h. In between the electrochemical measurements, a constant cathodic current was applied, which varied depending on the experiment conducted. A description of the conditions during the four experiments is shown in Table I. Note that half-cell 4 was neither subject to GCI measurements every 24 h nor did it see any current but was simply heat treated under the conditions noted in Table I. The purpose of this experiment was to measure the baseline effects of the chemical reaction of chromium poisoning without the superimposed effects of the electrochemical reaction.

The electrode performance parameters measured by GCI are summarized in Table II. The relationship between E_{cathode} and R_p , R_Ω is given by

$$E_{\text{cathode}} = j(R_\Omega + R_p) \quad (1)$$

where j is the current density applied to the cell.

The results for half-cell 1 and half-cell 2 are compared with the results of the LSM half-cell tests.

Full-Cell Testing

Crofer 22H and Ni meshes applied on the cathode and anode, respectively, were used as the current collectors. The cell activation procedure is described in prior work.¹⁵ After the cell had equilibrated at

Fig. 1. Configuration of (a) LNO-based half-cell, (b) LSM-based half-cell, (c) LNO-based full-cell and (d) LSM-based full-cell.

Table I. Experimental conditions		
Cell no.	Atmosphere in WE side	Current
Half-cell 1	Dry air (21% oxygen)	50 mA cm ⁻²
Half-cell 2	10% Humidified air	50 mA cm ⁻²
Half-cell 3	Dry air (21% oxygen)	200 mA cm ⁻²
Half-cell 4	Dry air (21% oxygen)	–

Table II. Electrode performance parameters measured by GCI with WE and RE		
Parameter	Unit	Description
E_{cathode}	V	WE potential with respect to RE
R_p	$\Omega \text{ cm}^2$	Polarization resistance
R_Ω	$\Omega \text{ cm}^2$	Ohmic resistance

open circuit voltage (OCV) for 48 h, the initial voltage versus the current density (V – I) curve was measured. After the initial measurement, the cell was operated at a constant current density of 0.5 A cm⁻² for 120 h, and the galvanostatic operation of the cell was interrupted only to obtain voltage versus current density measurements every 24 h. During each measurement session, the V – I curves were obtained using two different oxidizing atmospheres, which were dry air (21% oxygen) and 100% oxygen. Measuring the V – I curves under these different oxidant conditions is important from the standpoint of polarization modeling as explained in “Full-Cell Testing” section. Details of the full-cell testing setup and procedures are described elsewhere.^{10,15}

Microstructure Analysis

After cell testing, the cross sections of the cells were analyzed using SEM (Zeiss Ultra 55) and EDS to investigate the morphology and composition of the deposited chromium-containing phase. XRD (Bruker D8 Discover) was used to characterize the

phases on the surface of the electrode before and after the cell testing.

RESULTS

The Effect of Cathode Composition on Chromium Poisoning

Half-Cell Testing

As mentioned in “Half-Cell Testing” section, half-cell 1 and half-cell 2 were operated under different working electrode atmospheres (dry air and 10% humidified air, respectively) with 50 mA cm⁻² cathodic current density. The electrochemical results for these cells are compared with the results for the (La_{0.8}Sr_{0.2})_{0.95}MnO_{3-δ} (LSM) cells (Fig. 2).

Comparing the initial polarization resistance of the LSM half-cell and the LNO half-cell, it can be seen that the polarization resistance for the LNO half-cell is a factor of 8 smaller than the polarization resistance for the LSM half-cell. This is because LNO is a mixed ionic and electronic conductor, and LSM is a predominantly electronic conductor. The porosity of both electrodes is between 35% and 40% as measured by using ImageJ analysis of SEM images with grain sizes in the range of 2–3 μm (Fig. 3a, b). The LNO working electrode has a slightly coarser grain size than the baseline LSM working electrode.

Under dry air and 50 mA cm⁻², for the LSM half-cell (Fig. 2a), the polarization resistance increased dramatically from 3.5 Ω cm² to 11.5 Ω cm² once the cathodic constant current was applied. From day 1 to 8, the polarization resistance continued increasing. However, for the LNO half-cell (Fig. 2b), the polarization resistance was relatively constant. Similar results were observed under 10% humidified air and 50 mA cm⁻². The polarization resistance of the LSM half-cell (Fig. 2c) increased from 4.0 Ω cm⁻² to 11.3 Ω cm⁻² on the first day after the cathodic current was applied, and then the polarization resistance leveled off. The polarization resistance for the LNO half-cell (Fig. 2d) decreased from 0.62 Ω cm² to 0.4 Ω cm² over the course of the whole experiment.

Fig. 2. Electrochemical results for the LNO half-cell and LSM half-cell under dry air (a, b) and 10% humidified air (c, d).

In contrast to the relatively constant ohmic resistance of LSM half-cells (Fig. 2a, c), the ohmic resistance of the LNO half-cell was also observed to decrease during the cell testing (Fig. 2b, d). The decreased ohmic resistance was likely due to improved adhesion of the interface between YSZ and GDC or between GDC and LNO during cell testing, which was not included in LSM half-cells. Such improvement in ohmic resistance was also observed when we tested the LSCF or LSF-based cell where there was also a GDC barrier layer. This phenomenon needs further investigation. The electrochemical results indicated that chromium poisoning is not as deleterious for LNO as LSM in dry air as well as 10% humidified air.

After the electrochemical measurements, post-test microstructural analysis was performed to supplement the observations from the electrochemical results. EDS was used to quantify the amount of chromium. The EDS spectrum obtained is complicated because of the interference among the cerium, lanthanum and chromium peaks. The $\text{Ce}_{L\beta}$ (5.26) peak overlaps with the $\text{La}_{L\beta}$ (5.38) and $\text{Cr}_{K\alpha}$ (5.41) peaks. Therefore, the deconvolution function of the

EDAX software was used to subtract out the cerium peak (Fig. 3c). In the cerium-subtracted spectrum, the $\text{La}_{L\beta}$ and $\text{Cr}_{K\alpha}$ peaks overlap, and they are difficult to separate. Thus, a Cr-enrichment ratio as defined in Eq. 2 was used as an effective metric to judge the extent of the chromium deposition. The higher this ratio was, the higher the chromium content in the sample.³²

$$\text{Cr-enrichment ratio} = \frac{\text{La}_{L\beta} + \text{Cr}_{K\alpha}}{\text{La}_{L\alpha}} \quad (2)$$

A baseline ratio of approximately 0.17 was measured with a pristine Cr-free LSM cell.

Figure 3d and e shows the chromium concentration gradient across the working electrode. Each point shows the Cr-enrichment ratio obtained from the EDS spectrum by scanning a rectangular area which is 1 μm thick (perpendicular to electrolyte) by 10 μm long (parallel to electrolyte). Figure 3d compares the LNO and LSM half-cells that operated under dry air and 50 mA cm^{-2} , and Fig. 3e compares the LNO and LSM half-cells that operated under 10% humidified air and 50 mA cm^{-2} . It is found that the Cr-enrichment ratio at the triple-

Fig. 3. The microstructure of the (a) LNO working electrode and (b) LSM working electrode; (c) an example of the EDS spectrum including La, Ce, Gd and Cr before and after deconvolution. The chromium concentration gradient for the LSM working electrode and LNO working electrode for the cell after electrochemical measurements under (d) dry air and (e) 10% humidified air.

phase boundaries (TPBs) for LNO is much smaller than the ratio for LSM in both cases. This is in agreement with the results of electrochemical measurements. The chromium poisoning at the TPB is significantly reduced in an LNO working electrode compared with an LSM working electrode. For the LSM working electrode, the Cr-enrichment ratio is very high at the TPBs and decreases with distance away from the TPBs. However, for the LNO working electrode, the Cr-enrichment ratio increases with distance from the TPBs. In other words, the Cr-enrichment ratio is the highest at the interface between the Crofer mesh and electrode. This will be discussed in detail in “Discussion” section.

Full-Cell Testing

Figure 4a and c shows the $V-I$ curves and power density versus current density ($P-I$) curves for a complete single SOFC (henceforth referred to as a “full-cell” to distinguish it from the previously discussed half-cells), comprising an LNO cathode, measured every 24 h for a total duration of 120 h. These results are compared with the $V-I$ and $P-I$ curves (Fig. 4b, d) for an LSM-YSZ full-cell, which is run under identical conditions by Wang et al.¹⁵ For the LNO full-cell, the power density improved every day.

The initial maximum power density for the LNO full-cell is 0.38 W cm^{-2} , and after 120 h of 0.5 A cm^{-2} galvanostatic current, the maximum power density increased by 37% to 0.52 W cm^{-2} . However, for the LSM full-cell, the performance decreased every day. The initial maximum power density for the LSM full-cell was 0.44 W cm^{-2} , and it decreased by 44% to 0.24 W cm^{-2} after 120 h of constant current operation.

It is worth mentioning that the initial performance of the LSM-based full-cell appears to be higher than that of the LNO-based one. This is attributed to two reasons: (1) an LNO single electrode was used in this work, but an LSM-YSZ functional layer was added in between the YSZ electrolyte and LSM current collector. When mixed with doped ceria, the LNO electrode is expected to have a much higher performance due to improved ionic conductivity in the functional layer. (2) A $6\text{-}\mu\text{m}$ -thick GDC barrier layer was inserted in between the YSZ electrolyte and LNO electrode but was not included in the LSM-based cell. The GDC barrier layer is expected to increase the ohmic resistance of the full-cell.

To examine the effect of chromium poisoning on the individual polarization losses, we use a modified

form of the current–voltage model in Eq. 3 originally developed by Kim et al.^{33,34}:

$$E_c = E_0 - iR_\Omega - \underbrace{\frac{2RT}{F} \ln \left\{ \frac{1}{2} \left[\left(\frac{i}{i_{o,c}} \right) + \sqrt{\left(\frac{i}{i_{o,c}} \right)^2 + 4} \right] \right\}}_{\text{Activation polarization (Cathode)}} + \underbrace{\frac{RT}{4F} \ln \left(1 - \frac{i}{i_{cs}} \right)}_{\text{Concentration polarization (Cathode)}} + \underbrace{\frac{RT}{2F} \ln \left(1 - \frac{i}{i_{as}} \right) - \frac{RT}{2F} \ln \left(1 + \frac{p_{\text{H}_2}^0 i}{p_{\text{H}_2\text{O}}^0 i_{as}} \right)}_{\text{Concentration polarization (Anode)}} \quad (3)$$

Open circuit potential
Ohmic polarization
Activation polarization (Cathode)
Concentration polarization (Cathode)
Concentration polarization (Anode)

Fig. 4. V – i curves from (a) LNO full-cell and (b) LSM full-cell. Experimental data and fits for (c) the LNO full-cell and (d) LSM full-cell. (e) Cross-sectional microstructures of LNO full-cell. (f) Chromium concentration profile across LNO cathode in the full-cell after electrochemical measurements in dry air.

Table III. Fitting parameters for the LSM full-cell and LNO full-cell

Fitting parameters	LNO		LSM	
	0 h	120 h	0 h	120 h
i_o (A cm ⁻²)	0.12	0.34	0.146	–
i_{as} (A cm ⁻²)	3.27	3.27	2.21	–
i_{cs} (A cm ⁻²)	1.50	1.50	1.76	–
R_Ω (Ω cm ²)	0.2	0.2	0.169	–
$R_{conc,cathode}$ (Ω cm ²) at $i = 0.45$ A cm ⁻²	0.022	0.022	0.018	–
$R_{conc,anode}$ (Ω cm ²) at $i = 0.45$ A cm ⁻²	0.106	0.106	0.120	–
R_{act} (Ω cm ²) at $i = 0.45$ A cm ⁻²	0.363	0.226	0.345	–
R_{tot} (Ω cm ²) at $i = 0.45$ A cm ⁻²	0.69	0.55	0.65	1.07

Equation 3 has four fitting parameters, the area-specific ohmic resistance, R_Ω (Ω cm²), cathodic exchange current density, $i_{o,c}$ (A cm⁻²), cathodic limiting current density, i_{cs} (A cm⁻²), and anodic limiting current density, i_{as} (A cm⁻²). In accord with prior work,^{15,35} we assume that activation polarization in the anode is negligible compared with that in the cathode.

We refer the reader to our prior work^{15,34,35} for the individual steps in the analysis and fitting of the polarization data.

Figure 4c and d shows the fitting results for the LSM full-cell and the LNO full-cell, and Table III shows the fitting parameters: area specific ohmic resistance, R_Ω (Ω cm²), cathodic exchange current density, $i_{o,c}$ (A cm⁻²), cathodic limiting current density, i_{cs} (A cm⁻²), and anodic limiting current density, i_{as} (A cm⁻²). To obtain reasonable fits for the LNO cell, it was only necessary to change the $i_{o,c}$. All other parameters for the LNO cell were left unchanged from their values at 0 h. Note that after 120 h of 0.5 A cm⁻² galvanostatic operation, the performance of the LSM full-cell deteriorates so substantially that the maximum current density only reaches 0.9 A cm⁻². With this limited data set we were not able to deconvolute the various polarization losses. Therefore, we used a simple linear fit to the LSM full-cell V - I data after 120 h of galvanostatic operation. The total resistance, which is inclusive of the ohmic, activation and concentration polarization phenomena, is 1.07 Ω cm². For comparison, we calculated the total resistance for each of the cells at a specified current density. The definition of the total area-specific resistance is given in Eq. 4 below (the absolute value of the derivative of the cell voltage in Eq. 3 with respect to the current density at a fixed current density). The total resistances of the cells as well as the deconvoluted resistances associated with ohmic polarization, activation polarization, and anode and cathode concentration polarizations were all evaluated at $i = 0.45$ A cm⁻² and are listed in Table III. These resistances are simply the derivatives associated with each polarization term in Eq. 3. The current

density of $i = 0.45$ A cm⁻² was chosen as it is the current density at which the LSM cell performance after 120 h of operation reached maximum power density.

$$R_{tot} = \left| \frac{dE_C}{di} \right|_{i=0.45} \quad (4)$$

Comparing each cell over 120 h of operation, the total resistances at $i = 0.45$ A cm⁻² for both the LSM and the LNO cell were roughly equal at the start of the cell tests, 0.65 Ω cm² and 0.69 Ω cm². However, the total resistance at 0.45 A cm⁻² decreased for the LNO full-cell by 20%, whereas it increased for the LSM full-cell by 65% over the 120-h period. Based on impedance spectroscopy results not discussed here, we assumed that the ohmic resistance of the LNO cell is constant throughout the duration of the cell test. The decrease in activation polarization resistance during cell testing with current load is commonly referred to as the “cell break-in” effect. Such “cell break-in” is commonly observed in the LSM-based cathode, which is suggested to be due to elimination³⁶ or formation³⁷ of impurity phases such as SrO. For the LNO-based cell, similar microstructural changes at the electrode/electrolyte interface may occur. Specific aspects of interdiffusion between LNO and GDC are discussed later in “Discussion” section of the article. For the LSM-based cell, although “cell break-in” is expected to occur, the Cr-poisoning effect is dominant and electrode activation is thus less prominent, resulting in an increase in activation polarization. Overall, the observed decrease in the total resistance of the LNO cell and the increase of the total resistance of the LSM cell provide conclusive evidence for higher tolerance to chromium poisoning of LNO over LSM.

SEM and EDS analysis were used to determine the chromium concentration in the LNO full-cell. The chromium concentration gradient is shown in Fig. 4f. The results are similar to the results for the half-cells in Fig. 3d. The Cr-enrichment ratio is high at the triple-phase boundary and on the surface of the cathode.

Fig. 5. The electrochemical results for LNO half-cell under dry air (a) with 50 mA cm^{-2} ; (b) with 200 mA cm^{-2} . The chromium concentration gradient for LNO half-cell under dry air with (c) half-cell 1 (50 mA cm^{-2}), half-cell 3 (200 mA cm^{-2}) and (d) half-cell 4 (without current).

The Effect of Current Density on Chromium Poisoning

LNO half-cell 3 is operated under dry air and 200 mA cm^{-2} , and the electrochemical results are compared with the results for LNO half-cell 1 under dry air and with 50 mA cm^{-2} (Fig. 5a, b). The overall trends for the results under 50 mA cm^{-2} and 200 mA cm^{-2} are similar. However, the polarization resistance for half-cell 1 decreases from $0.51 \Omega \text{ cm}^2$ on day 0 to $0.34 \Omega \text{ cm}^2$ on day 1 and then increases to $0.56 \Omega \text{ cm}^2$ in the following 3 days. For half-cell 3, the polarization resistance is $0.49 \Omega \text{ cm}^2$ initially and then decreases to $0.21 \Omega \text{ cm}^2$ on day 8.

Again, the observed results can be explained by assuming that there are two competing and concurrent phenomena, cell break-in and chromium poisoning. When operated at 50 mA cm^{-2} , with the working electrode polarized cathodically, the effect of the cell break-in process dominates the chromium poisoning process, and on day 1 to day 3, the chromium poisoning process suppresses the effect of the cell break-in process. However, at 200 mA cm^{-2} , the cell break-in process dominates throughout.

The microstructure and composition of half-cell 3 were determined by SEM and EDS. The chromium concentration gradient is shown in Fig. 5c. The Cr-enrichment ratio for half-cell 3 was much higher at the TPB than the Cr-enrichment ratio for half-cell 1.

This result confirms that high current density increases the reaction rate of the electrochemical chromium deposition reaction.

The Baseline Chemical Reaction for Chromium Poisoning

To explore the existence of a purely chemical reaction, as mentioned in “Half-Cell Testing” section, LNO half-cell 4 was also tested at 800°C in dry air, in direct contact with a Crofer 22H interconnect for 8 days. No electrochemical tests were performed on this cell. The Cr-enrichment ratio profile measured using SEM-EDS is shown in Fig. 5d.

The Cr-enrichment ratio at the TPBs is close to the baseline value; however, as the distance from the TPBs increases, the Cr-enrichment ratio increases. This trend indicates that a chemical reaction between chromium gas species and the LNO cathode material does exist.

DISCUSSION

By comparing the results of the LSM cells and the LNO cells, it is evident that LNO has a higher tolerance to Cr poisoning than LSM in both half-cell and full-cell tests. When the compositional results for all four half-cells are combined (Fig. 6), a few salient comments can be made:

Electrochemical Chromium Poisoning Reaction

At the TPBs for each LNO half-cell, the Cr-enrichment ratios exhibit the following trend:

$$R_{\text{cell}2} > R_{\text{cell}3} > R_{\text{cell}1} \approx R_{\text{cell}4} \approx R_{\text{baseline}} = 0.17$$

This trend indicates that the electrochemical chromium poisoning reaction is occurring at the TPBs, where during current passage, the chromium vapor phase species obtain electrons and react with oxygen to form chromium-containing solid products. Furthermore, the results show that humidity and high current density accelerate and enhance chromium poisoning. This is consistent with the higher total vapor pressure of chromium-containing species in 10% humidified air than in dry air.³⁸ The Cr-enrichment ratio at the TPBs for the full-cell is also higher than the baseline ratio, which confirms the existence of an electrochemical chromium poisoning reaction.

In transition metal perovskite oxides in which oxygen vacancies are the predominant oxygen point defects, chromium deposition is thought to occur through the following oxygen vacancy-mediated reaction:

Under normal SOFC operation, under current load, there is a distribution of oxygen partial pressure, decreasing from the air/cathode interface to some lower value that depends on the average cell current density and the microstructure of the cathode. Thus, the oxygen vacancy concentration is higher closer to the electrolyte/cathode interface. This drives the enhanced formation of chromium oxide near the TPBs and gives rise to an enhanced enrichment ratio (defined previously) close to the TPBs. Under open circuit potential where the oxygen vacancy concentrations are lower (i.e., equilibrated with air across the cathode), the enrichment ratio is quite low across the cathode thickness and is elevated only near the electrolyte/electrode interface. In

Fig. 6. The compositional results for the LNO half-cells under different experimental conditions.

fact, this is observed in conventional cathodes such as strontium-doped lanthanum manganite.^{10,14,15}

By contrast, in La_2NiO_4 the predominant oxygen point defects are oxygen interstitials. The concentration of oxygen interstitials in materials that have predominant anion Frenkel defects increases with increasing oxygen partial pressure. Since oxygen interstitials and not vacancies are the predominant oxygen point defects at higher oxygen partial pressures, the oxygen vacancy concentrations are not expected to rise as rapidly in LNO and related materials as in conventional perovskite cathode materials. Thus, there is no rise in the enrichment ratios across the cathode thickness except at the electrolyte/cathode interface where the oxygen partial pressure is expected to be the lowest (Fig. 3).

Chemical Chromium Poisoning Reaction

The Cr-enrichment ratios increase with distance from the TPBs for the LNO cells, and the Cr-enrichment ratios on the surface of the cathode are always approximately 0.28, which appears to suggest a relationship with the solubility limit of chromium in LNO.

Egger et al.²⁸ investigated the long-term behavior of $\text{La}_2\text{NiO}_{4+\delta}$ as an electrode material under a Cr-containing atmosphere with convergent beam electron diffraction (CBED). They conclude that the product phase that forms upon exposure to chromium is a $\text{LaNi}_{1-x}\text{Cr}_x\text{O}_3$ perovskite. Furthermore, they conclude from TEM-EDS measurements that the Cr/Ni-ratio in the product perovskite phase is 0.3:0.7. We performed x-ray diffraction on the surface of the LNO full-cell before and after testing as well as on the bulk of the LNO full-cell after testing (Fig. 7). As can be seen, a solid single phase of $\text{LaNi}_{1-x}\text{Cr}_x\text{O}_3$ perovskite was detected on the surface of the LNO-cell after test.

Fig. 7. X-ray diffractions of LNO full-cell before and after test.

Fig. 8. The line scans for LNO cells after the experiments: (a) half-cell 1 with dry air and 50 mA cm^{-2} current; (b) half-cell 2 with 10% humidified air and 50 mA cm^{-2} current; (c) full-cell with dry air and 0.5 A cm^{-2} current; (d) the detailed TPB for full-cell with dry air and 0.5 A cm^{-2} current.

To identify the composition of the chromium phase in this work, detailed EDS line scans were performed (Fig. 8). Based on the line scan results, average ratios of Cr to Ni in the purple rectangles near the surface of the cathode were calculated. The ratios were also determined to be approximately 0.3:0.7, which indicates that on the surface of the La_2NiO_4 cathode, the chromium dissolves into the LaNiO_3 blocks of the $\text{La}_2\text{NiO}_{4+\delta}$ structure to form $\text{LaNi}_{0.7}\text{Cr}_{0.3}\text{O}_3$, consistent with the observations of Egger et al.²⁸

According to Yang³⁹, $\text{LaNi}_{1-x}\text{Cr}_x\text{O}_3$ crystallizes in the rhombohedral structure for $0 \leq x < 0.2$ and in the orthorhombic structure for $x > 0.3$. Both phases co-exist for $0.2 \leq x \leq 0.3$.

The results in this work show that $x = 0.3$, which indicates that the $\text{LaNi}_{1-x}\text{Cr}_x\text{O}_3$ in the $\text{La}_2\text{NiO}_{4+\delta}$ is close to the two-phase regime. Since the cells were electrochemically tested $< 200 \text{ h}$, it is possible that this apparent saturation point is transient. After longer term cell operation, with additional chromium pickup in the cathode, the $\text{LaNi}_{1-x}\text{Cr}_x\text{O}_3$ phase may switch to an orthorhombic structure. These are open questions, and the long-term

electrochemical performance of LNO in the presence of chromium impurities needs to be evaluated.

Lanthanum Diffusion Layer

Another interesting detail of the line scans shown in Fig. 8d is at the interface between the GDC barrier layer and the LNO cathode where lanthanum diffusion into the GDC barrier layer occurs.

In recent work Cetin et al.²⁴ report that in contact with ceria, La_2NiO_4 decomposes at elevated processing temperatures, and the decomposition product La_2O_3 dissolves into the ceria phase. The results of the lanthanum line scans show lanthanum diffusion into the GDC layer, consistent with the findings of Cetin et al.²⁴

The lanthanum diffusion layer is only formed during the electrode sintering process at 1225°C . Furthermore, the decomposition of La_2NiO_4 and the subsequent diffusion into the GDC layer are self-limiting once the solubility limit of La_2O_3 in GDC has been attained. The combined solubility of rare earths La and Gd in CeO_2 is close to a cation site fraction of

0.46 according to Cetin et al.²⁴ Montenegro-Hernandez et al.⁴⁰ conclude that La_2NiO_4 prepared by solid-state reaction in contact with GDC does not show any reactivity after annealing at 900°C for 72 h. Thus, La_2NiO_4 should be stable against further decomposition in contact with GDC during extended electrochemical testing at 800°C.

CONCLUSION

La_2NiO_4 has a higher tolerance for chromium poisoning than LSM. SOFCs featuring the LNO cathode perform well under different experimental conditions in a chromium atmosphere. Electrochemical test results show that chromium poisoning is not as deleterious for LNO as LSM in dry air as well as 10% humidified air. Post-test compositional analyses using SEM-EDS show that the Cr-enrichment ratio on the TPBs for the LNO-cathode cells is much smaller than that for the LSM-cathode cells under identical test conditions. The Cr-enrichment ratio increases as the distance from the TPBs increases. Two kinds of reactions with chromium impurity, electrochemical and chemical, are occurring in the LNO cathode. In the electrochemical chromium poisoning reaction, both high current density and humidity accelerate the chromium poisoning. During the chemical reaction, the chromium dopes into the B-site of the LaNiO_3 perovskite blocks in the La_2NiO_4 structure. However, open questions remain about the long-term electrochemical performance of the La_2NiO_4 cathode. The GDC barrier layer, which is a necessary component at the cathode/electrolyte interfaces that employ LNO cathodes, appears to be stable during cell operation, consistent with prior determination of phase equilibria in this system.

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ELECTRONIC SUPPLEMENTARY MATERIAL

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REFERENCES

1. S.P.S. Badwal and K. Foger, *Ceram. Int.* 22, 257 (1996).
2. B.C.H. Steele, *Solid State Ionics* 134, 3 (2000).
3. K. Choy, W. Bai, S. Charojrochkul, and B.C.H. Steele, *J. Power Sources* 71, 361 (1998).
4. Y. Matsuzaki and I. Yasuda, *Solid State Ionics* 132, 271 (2000).
5. S.C. Paulson and V.I. Birss, *J. Electrochem. Soc.* 151, A1961 (2004).
6. J.W. Fergus, *Int. J. Hydrog. Energy* 32, 3664 (2007).
7. E. Konyshcheva, H. Penkalla, E. Wessel, J. Mertens, U. Seeling, L. Singheiser, and K. Hilpert, *J. Electrochem. Soc.* 153, A765 (2006).
8. E. Park, S. Taniguchi, T. Daio, J. Chou, and K. Sasaki, *Solid State Ionics* 262, 421 (2014).
9. Z. Sun, R. Wang, A.Y. Nikiforov, S. Gopalan, U.B. Pal, and S.N. Basu, *J. Power Sources* 378, 125 (2018).
10. R. Wang, Z. Sun, U.B. Pal, S. Gopalan, and S.N. Basu, *J. Power Sources* 376, 100 (2018).
11. Z. Sun, U.B. Pal, S. Gopalan, and S.N. Basu, *Surf. Coat. Technol.* 323, 49 (2017).
12. W. Huang, S. Gopalan, U.B. Pal, and S.N. Basu, *J. Electrochem. Soc.* 155, B1161 (2008).
13. J.A. Schuler, Z. Wuillemin, and A. Hessler-Wyser, *J. Power Sources* 211, 177 (2012).
14. R. Wang, M. Würth, U.B. Pal, S. Gopalan, and S.N. Basu, *J. Power Sources* 360, 87 (2017).
15. R. Wang, U.B. Pal, S. Gopalan, and S.N. Basu, *J. Electrochem. Soc.* 164, F740 (2017).
16. T. Komatsu, R. Chiba, H. Arai, and K. Sato, *J. Power Sources* 176, 132 (2008).
17. T. Nakamura, R. Oike, Y. Ling, Y. Tamenori, and K. Ameszawa, *Phys. Chem. Chem. Phys.* 18, 1564 (2016).
18. S.J. Skinner and J.A. Kilner, *Solid State Ionics* 135, 709 (2000).
19. E.V. Tsipis and V.V. Kharton, *J. Solid State Electrochem.* 12, 1367 (2008).
20. C. Laberty, F. Zhao, K.E. Swider-Lyons, and A.V. Virkar, *Electrochem. Solid State Lett.* 10, B170 (2007).
21. C. Ferchaud, J.C. Grenier, Y. Zhang-Steenwinkel, M.M. Van Tuel, F.P. Van Berkel, and J.M. Bassat, *J. Power Sources* 196, 1872 (2011).
22. F. Hauveau, J. Mougin, J.M. Bassat, F. Mauvy, and J.C. Grenier, *J. Power Sources* 195, 744 (2010).
23. E. Dogdibegovic, W. Guan, J. Yan, M. Cheng, and X.D. Zhou, *J. Electrochem. Soc.* 163, F1344 (2016).
24. D. Cetin, S. Poizeau, J. Pietras, and S. Gopalan, *Solid State Ionics* 300, 91 (2017).
25. D. Cetin, S. Poizeau, J. Pietras, and S. Gopalan, *Solid State Ionics* 307, 14 (2017).
26. S.N. Lee, A. Atkinson, and J.A. Kilner, *ECS Trans.* 57, 605 (2013).
27. N. Schrödl, E. Bucher, A. Egger, P. Kreiml, C. Teichert, T. Höschen, and W. Sitte, *Solid State Ionics* 276, 62 (2015).
28. A. Egger, N. Schrödl, C. Gspan, and W. Sitte, *Solid State Ionics* 299, 18 (2017).
29. B. Hou, C.C. Wang, X. Cui, and Y. Chen, *R. Soc. Open Sci.* 5, 180634 (2018).
30. K.J. Lee, J.H. Chung, M.J. Lee, and H.J. Hwang, *J. Korean Ceram. Soc.* 56, 160 (2019).
31. S.P.S. Badwal and N. Nardella, *Solid State Ionics* 40, 878 (1990).
32. B. Wei, K. Chen, L. Zhao, Z. Lü, and S.P. Jiang, *Phys. Chem. Chem. Phys.* 17, 1601 (2015).
33. J.W. Kim, A.V. Virkar, K.Z. Fung, K. Mehta, and S.C. Singhal, *J. Electrochem. Soc.* 146, 69 (1999).
34. K.J. Yoon, P. Zink, S. Gopalan, and U.B. Pal, *J. Power Sources* 172, 39 (2007).
35. K.J. Yoon, S. Gopalan, and U.B. Pal, *J. Electrochem. Soc.* 156, B311 (2009).
36. S.P. Jiang, *J. Solid State Electrochem.* 11, 93 (2007).
37. Y. Yu, J. Liu, H.O. Finklea, H. Abernathy, P.R. Ohodnicki, T. Kalapos, and G.A. Hackett, *ECS Trans.* 78, 701 (2017).
38. R. Wang, Chromium poisoning of cathode in solid oxide fuel cells: mechanisms and mitigation strategies, PhD Thesis, Boston University (2017).
39. J. Yang, *Acta Crystallogr. B Struct. Sci.* 64, 3281 (2008).
40. A. Montenegro-Hernandez, J. Vega-Castillo, L. Moggi, and A. Caneiro, *Int. J. Hydrog. Energy* 36, 15704 (2011).

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