THE INFLUENCE OF NiO CONTENT ON CERAMIC-BASED SOLID OXIDE FUEL CELL ANODES

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ABSTRACT

Solid oxide fuel cell (SOFC) anodes based on electronically conducting ceramics have potential advantages over conventional Ni-YSZ anodes, including better fuel flexibility, stability under redox cycling, and sulfur tolerance. Here we report small additions of NiO to anodes based on La\(_{0.8}\)Sr\(_{0.2}\)Cr\(_{0.97}\)V\(_{0.03}\)O\(_3\) (LSCV) that also contained Ce\(_{0.9}\)Gd\(_{0.1}\)O\(_{1.95}\) (GDC), and describe results for these electrodes in SOFCs with GDC electrolyte supports. Microstructural evaluation showed a porous anode that varied significantly with anode firing temperature. Metallic Ni was observed in the anodes after reduction by x-ray diffraction for \(\geq 5\) weight percent NiO. Cell performance with hydrogen was evaluated using current-voltage measurements and electrochemical impedance spectroscopy (EIS) – total polarization resistance values at open circuit were \(~0.1\ \Omega\text{cm}^2\) at 800°C for \(\geq 2\) weight percent NiO. The maximum power density of the SOFCs decreased sharply with decreasing NiO content from 5 to 0 weight%, however, little effect was observed from 5 to 20 weight% NiO.

INTRODUCTION

The current state-of-the-art SOFC anode material is a cermet of Ni metal and yttria-stabilized zirconia (YSZ, Zr\(_{0.92}\)Y\(_{0.08}\)O\(_2\)) (1). However, there are still some issues with Ni-YSZ anodes. Cycling between oxidizing and reducing environments is known to cause anode degradation because of the large Ni-NiO volume change (2). Such reduction-oxidation (redox) cycling may occur accidentally and cause catastrophic failure in SOFC systems. It would also be desirable for use in small-scale SOFCs if the anodes could endure redox cycling routinely. Also, performance degradation in Ni-YSZ electrodes at 750°C has been observed for fuels containing sulfur, a common contaminant, in amounts as low as 1 ppm (3). Finally, for fuels other than pure hydrogen, Ni metal is a known catalyst for cracking of hydrocarbons, such that it is difficult to avoid coking and associated degradation of cell performance (4,5). Other, less critical, issues with Ni-YSZ anodes include the possibility of Ni sintering at SOFC operating temperatures resulting in decreasing anode performance over time (6), the relatively high cost of Ni, and the onset of creep in metals above \(\approx 40\%\) of the melting point \(\approx 420°C\) for Ni) (7).

As a consequence, new Ni-free or reduced-Ni SOFC anode materials are being investigated (8). Any new material must sufficiently replace the electronic conductivity and catalytic properties provided by nickel. The replacement of Ni with another non-
noble metal for conductivity purposes is possible, but in order to realize redox stability it will likely be necessary to minimize the volume fraction of metallic phases that will inevitably exhibit considerable expansion and contraction upon redox cycling. Thus, electronically conducting ceramics (such as lanthanum chromite) are interesting as anode materials. If the role of nickel is solely catalytic, it should be possible to significantly decrease the anode nickel content. In fact, one group previously reported the addition of < 1 wt% Ni to LSCV as a surface phase decreased the anode polarization resistance in humidified hydrogen (9).

Here we report results for a SOFC anode based on a 50:50 weight ratio (La,Sr)(Cr,V)O3-GDC composite, to which 0-20 wt% of NiO was added. Using GDC instead of YSZ as a second oxide phase has the advantages of 1) eliminating possible zirconate-forming reactions during electrode firing and use, 2) higher ionic conductivity than YSZ, and 3) electronic conductivity under reducing conditions that may help promote electrochemical reactions. Results on anode microstructure and phases present are also presented. In order to elucidate the role of Ni on electrochemistry, polarization resistances were measured using impedance spectroscopy for SOFCs with this anode in humidified hydrogen fuel.

EXPERIMENTAL

La0.8Sr0.2Cr0.98V0.02O3-δ (LSCV) powder was synthesized by solid-state reacting La2O3 (99.99%), SrCO3 (99%), Cr2O3 (99%), and V2O5 (99.2%) for 6 h at 1200°C. The Sr was added to induce p-type conductivity and to match thermal expansion of other cell components, and V was added as a sintering aid (10). The LSCV was then attrition milled to an average particle size of ~ 0.2 μm. Nanoscale Ce0.9Gd0.1O1.95 (GDC) (NexTech) was calcined 4 h at 800°C, with a resultant particle size of 0.1-0.2 μm, whereas nanoscale NiO (Nanotek) was not calcined. These materials were mixed with a vehicle (Heraeus V-737) using a Netzsch three-roll mill to produce inks for screen printing. The anode inks were screen printed onto uniaxially pressed GDC electrolyte pellets that had been pre-fired 4 h at 1450°C. The printed anodes were subsequently fired for 3 h at temperatures ranging from 1100° to 1400°C. The electrolyte pellets were ~ 300 μm thick after sintering. Anode thickness was ~ 10 μm with an active area of ~ 0.5 cm².

A screen printing ink of La0.6Sr0.4Co0.2Fe0.8O3-δ (LSCF from Praxair) and GDC from Functional Coating Technology, LLC, was used for the cathode material. The cathodes were fired for 3 h at 1000°C resulting in 25-50 μm thick electrodes (area ~ 0.5 cm²). These cathodes are reported to provide low polarization resistances even at low temperatures (11).

The single cell testing setup was similar to that reported by other groups (12). The cell was sealed to an alumina tube with Ag paste. A current collection grid of Au paste (Heraeus) was screen printed on each electrode, and Ag wires were connected to the Au collector grids with Ag paint. Measurements were made using a constant current power supply in series with the cell, with a voltmeter in parallel. Impedance measurements were taken using a BAS-Zahner IM6 impedance analyzer with applied amplitude of 20-
50 mV. Fuels were bubbled through water at room temperature, adding \( \approx 3\% \) H\(_2\)O to the 50 sccm gas flow.

Scanning electron microscopy (Hitachi S-3500 VP SEM, 20 keV accelerating voltage) and the accompanying energy dispersive x-ray analysis (EDX) were employed to observe the electrode microstructure and composition. X-ray diffraction (XRD) (Rigaku diffractometer, 0.8 kW) was used to observe the phases present in the anodes.

**RESULTS AND DISCUSSION**

**SOFC Microstructure**

Figure 1a shows a fracture cross-sectional scanning electron microscope (SEM) image of a typical anode and a portion of the electrolyte. The anode (5 wt% NiO) was fired for 3 h at 1100°C and contains a high fraction of sub-micron particles.

![Figure 1](image1.jpg)

**Figure 1.** SEM cross-sections of 5 wt% NiO anodes fired at 1100°C (a), and 1400°C (b).

This is representative of the initial particle sizes of the green powders mentioned previously. The SEM cross-section of an anode with the same composition is shown in Figure 1b after firing for 3 h at 1400°C. Considerable coarsening has resulted from the high temperature firing, with resultant particle sizes of 1-2 \( \mu \)m. Figure 2 contains the EDX spectrum of the anode fired at 1100°C (from Figure 1a). The presence of Ni and other anode elements is readily detected. Consequently, x-ray mapping can be used to image the anode (Figure 3). The distribution of Ni changes noticeably between anodes fired at different temperatures ((a) 1100°C and (b) 1400°C), reflecting the increased particle sizes for the higher temperature sample. The lack of visible, large NiO particles in Figure 3a suggests that the NiO particles remain quite small after firing at 1100°C. Comparison of anodes with varying NiO contents also indicates this (Figure 4), as the amount of fine anode structure increases with NiO content from (a) 0 to (c) 20 wt%. EDX spectra clearly show the increasing Ni content of the anodes fired at 1100°C (Figure 5).
Figure 2. EDX spectra of a 5 wt% NiO anode fired at 1100°C.

Figure 3. EDX maps of 5 wt% NiO anodes fired at 1100°C (a) and 1400°C (b).

Figure 4. SEM cross-sections of anodes with (a) 0, (b) 5, and (c) 20 wt% NiO.
EDX results only identify the presence of Ni element, not the phase. X-ray diffraction scans of LSCV-GDC-NiO anode fired at 1100°C with 20 wt% NiO (followed by a 6+ hour reduction at 800°C in hydrogen) clearly reveal a separate metallic Ni phase (Figure 6). Metallic Ni was detected down to 5 wt% NiO. It is not yet known whether metallic Ni was present in our anodes fired at temperatures >1100°C.

It has been reported that Ni (at low percentages) can substitute on the B-site of the LaCrO₃ phase, but it is unclear whether the Ni exsolves from the perovskite structure under reducing atmospheres (13). Sauvet and Irvine suggested temperatures approaching 1400°C are required to fully dissolve nickel into lanthanum chromite. They reported the presence of Ni-rich regions (by x-ray mapping) in the anode (10 mol% Ni) upon reduction, which were described as a Ni/Cr spinel. In the same study, thermogravimetric reduction in 5% hydrogen indicated a reduction of Ni³⁺ to Ni²⁺, but not Ni⁰ (13). Behavior indicative of Ni metal upon reduction was reported for 10 mol% Ni substitution of La₀.₈Ca₀.₂Cr₁₋ₓO₃ in a separate methane catalysis experiment (14). Another group of
researchers, using temperature programmed reduction, also reported the reduction of Ni was limited to the Ni$^{2+}$ state in La$_{0.85}$Ca$_{0.15}$Cr$_{0.9}$Ni$_{0.1}$O$_{3}$. They suggested the full reduction to Ni metal was kinetically inhibited, since the metal phase was predicted by thermodynamic calculations (15). None of these groups reported x-ray diffraction evidence of a separate Ni phase. These low percentages of Ni may be near the x-ray detection limit. Based on these results, it is unclear whether Ni metal will be present in the LSCV-GDC-NiO anodes fired above 1100°C in this study after reduction.

**Hydrogen Performance**

Figure 7 shows the performance of a GDC electrolyte-supported cell utilizing H$_2$ fuel at the LSCV-GDC-NiO (47.5 : 47.5 : 5 wt%, 1100°C firing temperature) anode and air at the LSCF-GDC cathode. A maximum power density of > 250 mW/cm$^2$ was measured at 800°C (150 mW/cm$^2$ at 750°C). The open circuit voltage (OCV) for the cell decreases with increasing temperature, a characteristic of GDC electrolyte cells, due to the mixed conductivity exhibited by GDC under reducing conditions. Despite the decreasing OCV, the maximum power density improves with increasing temperature, because of the decrease in electrolyte resistance and better electrode kinetics.

**Figure 7. Cell performance for a 5 wt% NiO-LSCV-GDC anode fired at 1100°C in H$_2$.**

Figure 8 exhibits the lower performance of 5 wt% NiO-LSCV-GDC anodes after sintering at 1400 versus 1100°C. The corresponding microstructures for these anodes were discussed previously and are pictured in Figure 1. The increase in particle size is the suggested source of the performance decrease, although it may also be due to Ni dissolving in the chromite rather than being a separate metallic phase.

Figure 9 plots the maximum power density achieved at 800°C for LSCV-GDC-NiO anodes with varying NiO content (constant LSCV:GDC weight ratio of 1:1) fired at 1100°C on GDC electrolyte-supported cells. The power density increases rapidly with increasing NiO content from 0 to 5%, after which it appears to level off for 10 and 20 wt%. As even 20 wt% NiO (~ 21 vol%) is below the percolation limit, Ni is not expected
to be the primary electronic conductor. Improvement in the electronic conductivity of lanthanum chromite, due to the incorporation of 5 mol% Ni onto the B-site of La$_{0.8}$Sr$_{0.2}$CrO$_3$, is relatively minor in fuel atmosphere, about 33% \(^{(16)}\). Consequently, it is suggested that large changes in anode performance with changing Ni content are due to a catalytic role of metallic Ni particles in the anode reaction.

![Figure 8. Cell performance in H$_2$ for 5 wt% NiO-LSCV-GDC anodes fired at 1100°C and 1400°C.](image)

**Figure 8.** Cell performance in H$_2$ for 5 wt% NiO-LSCV-GDC anodes fired at 1100°C and 1400°C.

![Figure 9. Maximum power densities in H$_2$ at 800°C for various wt% NiO-LSCV-GDC anodes fired at 1100°C.](image)

**Figure 9.** Maximum power densities in H$_2$ at 800°C for various wt% NiO-LSCV-GDC anodes fired at 1100°C.

Typical electrochemical impedance spectroscopy (EIS) data for a cell with 5 wt% NiO anode at OCV at 800°C is plotted in Figure 10. Data for other anodes with varying NiO contents under identical conditions were similar in shape. The results illustrate a key point regarding the present SOFC tests: the thick GDC electrolyte contributed >75% of the total cell resistance at zero current. Thus, in order to assess the potential of these anodes in high-performance SOFCs with thin electrolytes, the EIS data must be used to isolate the electrode impedance contribution. However, interpretation of the data is complicated in the present case by the electronic current in the GDC electrolyte. This can
be seen in the pronounced positive curvature of the current-voltage curves in Figure 7, due to the decrease in electronic electrolyte current as the cell voltage decreases. Liu and co-workers (18) have described a correction for this effect, which was used to correct the present data. The corrected polarization resistance, $R_p$, is given by

$$R_p = \frac{R_T - R_b}{V_{OC} \left[ 1 - \frac{R_b}{R_T} \left( 1 - \frac{V_{OC}}{E_N} \right) \right]} \quad [1]$$

where $V_{OC}$ is the measured open circuit voltage and $R_T$ and $R_b$ are the total and bulk resistances, respectively.

$$\lim_{\omega \to \infty} \{Z\} = R_b \quad \lim_{\omega \to 0} \{Z\} = R_T$$

Figure 10. Electrochemical impedance spectroscopy data at OCV in H$_2$ at 800°C for a 5 wt% NiO-LSCV-GDC anode fired at 1100°C.

Table 1 shows the ohmic resistance, the total polarization resistance, and the corrected total polarization resistance obtained from the data for anodes with varying NiO content. The most obvious effect in these data is the decrease in polarization resistance, by a factor of ≈10 times, on going from 0 to 2% NiO. While the polarization resistance appears to decrease further with increasing NiO content, even a small amount of NiO clearly has a major impact. Corrected polarization resistance values are ≈0.1 Ωcm$^2$ for NiO contents ≥5%. EIS data on symmetric cells with this cathode and electrolyte material yielded polarization resistances of ≈0.03 Ωcm$^2$ at 800°C, suggesting that ≈30% of the polarization loss was due to the cathode. Thus, these anodes could be expected to provide reasonable power densities in cells with thin electrolytes.

The data in Table 1 also includes the EIS results from a cell fired at 1400°C with 5 wt% NiO in the anode. The polarization resistance was substantially larger in this case, consistent with the cell test results shown in Figure 8.
Table 1. Resistances from IS data at OCV in H₂ at 800°C for 0-20 wt% NiO-LSCV-GDC anodes fired at 1100°C**. Total polarization resistance is corrected in the final column for the electrolyte being a mixed conductor.

| Ni Content | Offset Resistance (Ωcm²) | Measured Polarization Resistance (Ωcm²) | Corrected Polarization Resistance (Ωcm²) |
|------------|--------------------------|----------------------------------------|----------------------------------------|
| 0          | 0.611                    | 1.247                                  | 2.393                                  |
| 2          | 0.446                    | 0.141                                  | 0.277                                  |
| 2          | 0.416                    | 0.056                                  | 0.127                                  |
| 5          | 0.352                    | 0.088                                  | 0.169                                  |
| 5          | 0.310                    | 0.052                                  | 0.107                                  |
| 5*         | 0.346                    | 0.070                                  | 0.146                                  |
| 10         | 0.311                    | 0.041                                  | 0.078                                  |
| 20         | 0.308                    | 0.052                                  | 0.098                                  |
| 20         | 0.380                    | 0.070                                  | 0.163                                  |
| (1400) 5** | 0.562                    | 0.220                                  | 0.447                                  |

* Resistances for sample shown in Figure 10.
** Data for 5 wt% NiO anode fired at 1400°C.

CONCLUSIONS

The main conclusions are as follows:

1. The addition of NiO was crucial to the electrochemical performance of the anodes, as evidenced by the order of magnitude drop in polarization resistance at 800°C with 2% NiO addition. This correlated with the presence of a metallic Ni phase observed in anodes with ≥5 wt% NiO, fired at 1100°C, and subsequently reduced.

2. Coarsening of the anode during high temperature firing was deleterious to electrochemical performance.

3. For anodes containing NiO, the cell performance at low currents was limited mainly by the thick GDC electrolytes, which yielded relatively low OCV values and high ohmic resistances.

4. Electrochemical impedance spectroscopy measurements, corrected for the low OCV, showed that electrode polarization resistances at OCV in hydrogen at 800°C varied little for 2-20 wt% Ni, ranging from ≈ 0.08 to 0.28 Ωcm² for anodes fired at 1100°C.

5. These anodes have potential to provide high power densities if used in cells with thin electrolytes. However, it will be necessary to develop processing techniques for making thin electrolyte SOFCs with these anodes. The present results suggest that this would work best in cathode-supported cells, where anode firing temperatures could be kept relatively low to optimize electrochemical properties.

6. More work is needed to better understand these anodes, improve their properties, evaluate their long-term stability, determine their performance in different fuels, evaluate redox cycling performance, and observe effects of sulfur contamination.
ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the Department of Energy SECA Program during this work. In addition, a NSF Graduate Fellowship supported Brian Madsen. This work made use of central facilities supported by the MRSEC program of the NSF (DMR-0076097) at the Materials Research Center of Northwestern University.

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