CHROMIUM INTERACTIONS WITH CATHODE MATERIALS

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ABSTRACT

Chromium poisoning of cathodes has been reported by several groups developing solid oxide fuel cells (SOFCs) with metallic bipolar plates. Typically, chromium is presumed to migrate from the bipolar plates into the cathode via a volatile oxyhydroxide species. In this paper we report results of experiments in which cells measuring 2.5 cm by 2.5 cm were operated with Crofer 22 APU bipolar plates and with three different cathode materials, \( \text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3 \), \( \text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3 \), and \( \text{La}_{0.7}\text{Sr}_{0.2}\text{FeO}_3 \). Chromium deposits were observed at the cathode electrolyte interfaces but also across the entire cathode. The chromium levels were highest in the most active cathodes. We also measured the weight loss of chromium oxide, lanthanum chromium perovskite, and manganese chromium spinel by thermogravimetry in air with various water vapor pressures and verified that the weight loss correlated with vapor pressure of water. The weight loss was about an order of magnitude lower for the two ternary oxides than for the binary compound. We tested cathodes with up to 10% chromium substituted on the B site and noticed significant increases in the area specific resistance, suggesting that chromium affects the electronic properties of the cathodes.

INTRODUCTION

Chromium contamination of SOFC cathodes has been observed by several groups of researchers developing cells with metallic bipolar plates. These cells exhibited significant performance declines leading to speculation that chromium contamination may "poison" the cathode performance. Hilpert et al. have attributed the chromium transport to the formation of volatile oxyhydroxide species that form when chromium-containing steels are exposed to oxygen and water at elevated temperatures (1,2). The volatile oxyhydroxide, \( \text{CrO}_2(\text{OH})_2 \), can form either by reaction of the surface oxide with oxygen and water, or by direct reaction of metallic chromium (3). It has also been shown that \( \text{CrO}_2(\text{OH})_2 \) is the dominant species in the gas phase when water is present (4), and that the cathode acts as a nucleation site for the deposition of chromium (5). Quadakkers et al. provide an overview of this and other issues related to metallic-based interconnects (6). There is also work that indicates that both the cathode and electrolyte composition can play a role in chromium poisoning (7). In an earlier publication, we presented cell degradation data for two types of steel (8). In this paper we present results with Crofer 22. We also measured the vapor loss of chromium oxyhydroxide from chromium oxide and two ternary compounds.
As discussed by Hilpert and others (7, 9) the chromium oxyhydroxide is presumed to be reduced to chromium trioxide at the triple phase boundaries in the cathode as shown:

\[
2\text{CrO}_2(\text{OH})_2 + 6e^- + 3\text{V}^- = \text{Cr}_2\text{O}_3 + 2\text{H}_2\text{O} + 3\text{O}_2^- \tag{1}
\]

It is further presumed that the oxide deposits block the access of oxygen to the electrochemically active sites and cause the performance decay of the cell. However, one may ask whether the chromium trioxide may interact with the cathode and form lanthanum chromite or perhaps the mixed perovskite \((\text{La}_{0.8}\text{Sr}_{0.2})\text{Mn}_x\text{Cr}_{1-x}\text{O}_3\). The latter would be expected to have diminished oxide ion conductivity, and perhaps that is the reason for the performance decline of the cells. To test this hypothesis, we deliberately added chromium to cathodes and determined cell performance.

**EXPERIMENTAL PROCEDURE**

SOFCs of 2.5 cm x 2.5 cm and similar-sized samples of Crofer 22 APU were operated at constant voltage of 0.7 V for 50-200 hr. To further enhance the chromium poisoning effect, we placed particles of the metal interconnect on top of the cathode. Next, a Pt current collector was placed on top of the cathode and particles. A plate of interconnect, with slits cut in it, was then placed on top of the Pt current collector. Separate cells with lanthanum ferrite (LSF), lanthanum manganite (LSM), or an A-site-deficient LSF cathode were operated at 700°C and 800°C. The air contained 2% humidity. The cells were operated until only 50% of the initial current was supported at 0.7 V. Post-operation analysis was done by scanning electron microscopy (SEM) and Cr distribution was determined by energy dispersive x-ray spectroscopy (EDS).

Weight loss from ~100-mg fine powder samples of \(\text{Cr}_2\text{O}_3\), \(\text{LaCr}_2\text{O}_3\), and \(\text{MnCr}_2\text{O}_4\) were determined using a ThermoCahn thermogravimetric analyzer. The powders were prepared by a solid state synthesis reaction. Alumina powder was used as standard. Runs were carried out using various combinations of temperature, 700°C and 800°C, and between 0 mol% and 25 mol% \(\text{H}_2\text{O}\) in a carrier gas of 20.1% \(\text{O}_2\) in Ar. A flow rate of 50 sccm was used. The materials were allowed to reach temperature and given 1 hr to equilibrate.

Cathodes containing 1, 5, and 10% chromium were prepared by the glycine nitrate combustion process and tested in a half-cell configuration. AC impedance measurements were used to determine the resistance of the cathode using a CH Instruments impedance analyzer.

**RESULTS**

**Full Cell Tests**

Figure 1 provides SEM cross-section images of three different cathodes; all placed in contact with a Crofer 22 APU interconnect. Figure 1a shows an LSM cathode after 200 hr of operation; Figures 1b and 1c show a similar analysis of two different LSF cathodes after 50 hr. The length of time the cells were run was determined by how long
it took to lose half their initial current at 0.7 V. The data indicate that the LSM cathode contained the least amount of chromium in the bulk of the cathode but a significant accumulation at the electrolyte interface. The LSF cathodes contained a higher chromium content that had accumulated more rapidly.

Figure 1. SEM of (a) LSM cathode, (b) LSF cathode, and (c) A-site-deficient LSF operated at 800°C with a Crofer 22 APU interconnect. The charts to the right correspond to the chromium content determined by EDS for points 1 through 5 for each cathode.

Thermogravimetric Analysis

Shown in Figure 2 are the mass losses of chromium trioxide powder measured by thermogravimetric analysis in flowing air at 800°C with 0, 3, 10, 20, and 25 mol% water in air. Chromia reacts with oxygen and water to form a volatile species, and the weight loss is clearly related to the water content in the air, as one would expect for the formation of CrO$_2$(OH)$_2$.  

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Unlike most steels, Crofer 22 APU does not form a chromium oxide coating on the surface, but instead the manganese chromium spinel, MnCr$_2$O$_4$. Figure 3 shows the weight loss from the spinel along with chromia and the lanthanum chromium perovskite. From thermodynamic data one would have anticipated a difference in mass loss due to the volatility of the oxyhydroxide of about two orders of magnitude; however, only one order was observed.

Figure 2. Mass loss for Cr$_2$O$_3$ at 800°C with various levels of water content.

Figure 3. Mass loss at 800°C, air with 3 mol% water, normalized relative to moles of chromium in the compound.
**Electrochemical Properties of Cr-Doped LSF**

The effects of deliberately doping chromium into a cathode are seen in Figure 4. The area specific resistances are plotted versus temperature for lanthanum ferrite doped with 0, 1, 5, and 10% chromium on the B site. One percent doping does not seem to have an effect, but 5 and 10% do.

![Graph showing effects of chromium doping on LSF for various concentrations and temperatures.](image)

**DISCUSSION**

The electrochemical reduction of chromium oxyhydroxide as shown in Equation 1 requires oxide ion vacancies in addition to electrons. In a comparison of the chromium concentrations and profiles in the three different cathode materials in Figure 1, it is readily apparent that the material with the lowest oxide ion conductivity (LSM) has also the lowest chromium content, which is largely concentrated at the electrolyte interface. Conversely, the substoichiometric LSF, which should have the largest number of oxide ion vacancies, has the highest chromium content. Further, chromium is distributed across the entire cathode, because the oxide ion formed by the reduction of the oxyhydroxide can be readily transported through the LSF to the electrolyte.

It is tempting to correlate the volatility from the thermogravimetric measurements with the deposits in the cathodes. Using the surface area of the oxide in the thermogravimetric experiment and the surface area of the Crofer in the electrochemical cells, we project a total chromium volatization in the cells to be very roughly 5000 µg. We estimate the chromium contents in the cathodes to be approximately 150 µg in LSM, 800 in stoichiometric LSF, and 1200 in substoichiometric LSF. This suggests that only a small fraction of the available chromium is actually reduced on the less active cathodes.
As mentioned, all the cathodes discussed here had lost approximately half their current density at a fixed potential of 0.7 V, when the cells were shut down, but the LSF cathodes contained obviously more chromium than the LSM cathode. Therefore, they appear to be more tolerant to chromium contamination. Since the LSF cathodes have more active sites for oxygen reduction, it is conceivably that the loss of activity is caused by blockage of active sites. Alternatively, it is also possible that the number of oxide ion vacancies in the cathodes is decreased by chromium ions entering the cathode lattice and going into a plus four oxidation state. Figure 4 is consistent with such a mechanism. More work will have to be done to clarify the issue.

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