The electrical properties of a high-chromium alloy proposed for use as an interconnect material for intermediate temperature solid oxide fuel cells were studied by impedance spectroscopy and four-point resistance techniques. The increasing resistance with time complicated measurement of the resistance in air at moderate temperatures. Even at temperatures as low as 200 °C, the resistance of the metal noticeably increased with time. Two samples were heated at 1000 °C for 75 hours in air in an effort to simulate the effect of a long-term exposure at 500 °C. The samples developed a semiconducting film with a resistance sufficiently large, even at 500 °C, to prevent this alloy from being used as an interconnect material by itself. It is possible that a coating may be able to maintain a low contact resistance throughout the lifetime of the cell.

INTRODUCTION

Fuel cells are comprised of several components, each with different physical, chemical, and electrical requirements: an anode, an electrolyte, and a cathode. In addition, an electronically-conducting material, or interconnect, is used to make electrical contact with the anode in one cell to the cathode in the other, if the cells are placed in series. The electrical properties of a high-chromium alloy interconnect material were studied to evaluate its use in an intermediate (500 °C) temperature solid oxide fuel cell (SOFC) capable of using methanol as the fuel.

Interconnect materials must possess a rather unusual combination of properties: chemical stability and low electronic resistivity in the presence of both reducing and oxidizing environments, low porosity, and a thermal expansion coefficient matched to the ceramic electrolyte in order to avoid excessive stresses (particularly tensile) in the electrolyte as it is heated from ambient to operating temperatures. Good oxidation resistance is generally found for materials with highly resistive oxide films; therefore, oxidation resistance and low electronic resistivity are mutually exclusive in most cases.

Typically, the thermal expansion of SOFC electrolytes, such as yttria-stabilized zirconia (10 μ °C⁻¹) and gadolinia-doped ceria (12 μ °C⁻¹) is lower than most metallic materials that could be used as interconnects. This type of mismatch can result in the ceramic experiencing a tensile stress as the temperature is increased above room
temperature; therefore, it is important that any interconnect material have a thermal expansion coefficient equal to or less than that of the electrolyte. In addition, the need for flexible sealing materials is reduced if the thermal expansion of all the components is matched.

Previous work on chromium oxidation is often contradictory. It was generally believed that the diffusion rate of chromium was greater than that of oxygen in chromia films. However, in a series of articles by Sabioni, et al. (1-4), it was demonstrated through the use of Cr and O radiotracers in the same samples that the reverse is, in fact, true.

Whereas previous work (5, 6) has been primarily concerned with the mass-transport properties of chromia films, this work focused on the temperature dependence of the electrical properties, such as the resistance and impedance, of chromia films formed insitu. The goal was to determine whether a high-chromium alloy would be sufficiently electronically conductive at 500–800 °C to be able to support a current density of 500 mAcm⁻². The high-chromium alloy, reported to be 95% Cr, 4% Fe, and 1% Y₂O₃, with a thermal expansion coefficient of 10 μ °C⁻¹, was obtained from Siemens. Five samples were selected and are referred to as A, B, C, D, and E.

METHODS

The electrical properties of samples A and B were studied in air from room temperature to 500 °C. Samples C and D were heated in air to 1000 °C for 75 hr before electrical measurements were begun to simulate the effect of a long-term exposure at 500 °C. Sample E was used by itself to determine the temperature dependence of the electronic resistivity.

A Schlumberger SI 1286 Electrochemical Interface (potentiostat/galvanostat) was used to determine the dc-resistance using either a constant potential (±10 mV) for oxidized samples or a constant current (±100 mA) for the unoxidized sample. A Schlumberger 1260 Impedance Analyzer was used to obtain the impedance over a range of frequencies, typically from 10 mHz to 10 MHz.

The unoxidized metallic alloy is expected to behave as a single resistance. However, as the alloy oxidizes, there is a possibility that the resultant film may develop a significant resistance and capacitance; therefore, in principle, impedance spectroscopy can be used to follow the changes in the various resistances and capacitances associated with the film. This knowledge can be used to better understand the mechanism of oxidation and can lead, ultimately, to better materials selection.
RESULTS AND DISCUSSION

The resistance of a single unoxidized sample (E) was measured from room temperature to about 120 °C to determine the temperature coefficient of the resistivity. The results are shown in Figure 1. The points on the left were obtained with increasing temperature and the points on the right with decreasing temperature. The slopes are comparable at about 30 μΩcm°C⁻¹. The offset is believed to be due to a small change in the contact resistance as the sample adjusted to changes in dimensions. The resistivity of the unoxidized metal at 500 °C should therefore be about 30 mΩcm.

![Figure 1. Variation of the resistivity of an unoxidized sample (E) from two different runs. The slopes are about 30 μΩcm°C⁻¹. The offset is likely due to slight variations in the contact resistance at different times.](image)

Samples A and B, which were used as-received, exhibited metallic behavior throughout the experiment, in spite of the development of a greenish film. The temperature dependence of the resistance after numerous temperature cycles is shown in Figure 2. If the resistance was measured at fixed increasing temperatures, the curvature was always concave up whereas if the resistance was measured at fixed decreasing temperatures, it was always concave-down. This behavior is due to the resistance increasing during the time of the measurement. Therefore, the actual temperature dependence of the sample’s resistance is closer to the dashed line.

It is not possible to assign a resistivity or area resistance to the samples at any given temperature since these properties constantly increased with time as the measurements were made at the various temperatures.
Two 0.5 cm$^2$ samples (C and D) were heated to 1000 °C in air for about 75 hr in order to obtain a thick film more representative of what would be found after 40,000 hr. of operation at 500 °C. The resulting films were dark green, suggesting the presence of doped chromium oxide.

Figure 3 shows the temperature dependence of the resistance as a function of inverse temperature from 271–982 °C at early times. The room temperature resistance is of the order of 10$^6$ higher than samples held at 500 °C, but only briefly exposed to 1000 °C. The area resistance is about 200 $\Omega$cm$^2$ at 500 °C, which is unacceptably large for an interconnect material.

The impedance of samples A and B, which had been held at 500 °C for several days, exhibited unusual frequency dispersion, as shown in Figure 4. As the frequency increased from 1 mHz to about 1 Hz, $Z''$ (-Im$Z$) remained approximately constant while $Z'$ (Re$Z$) increased as the frequency increased. There was no indication that there was a limit to the low frequency impedance.

Figure 2. Change in resistance of the original two samples (A and B) that had been repeatedly measured at temperatures of 500 °C and below.
Figure 3. The exponential dependence of the resistance of samples C and D with inverse temperature indicates that the film is semiconducting.

Figure 4. Nyquist plot showing the frequency dispersion of samples A and B in contact at 500 °C.
The apparent increase in resistance with increasing frequency was found to be an artifact, simply due to an ever-increasing sample resistance with time. Since the impedance at low frequencies was always measured first (when the film is apparently thinnest), the impedance at higher frequencies will be larger than it would have been if the sample had not changed.

The impedance of samples C and D, which had been heated to 1000 °C for 75 hr in air, is shown in Figure 5 at 500 °C. There appears to be two time constants in series, which can be fit to the equivalent circuit shown in Figure 6, consisting of three parts in series: an inductance (due to the cell), a parallel resistance and "constant phase element" or CPE, and another parallel resistance and CPE. The high-frequency CPE is essentially a capacitance since its exponent is 0.92—nearly unity. The low-frequency CPE has a frequency dependence (n) midway between that of a capacitor (1) and a Warburg impedance (0.5), or about 0.71.

However, the fit to this equivalent circuit over the entire temperature range was poor, which prevented the determination of the temperature dependence of individual circuit elements.

The effect of the oxide/oxide interface on the frequency dispersion of the sample was removed by repeating the measurements using only sample D. The frequency response of sample D is shown in Figure 7 at 501 °C. Although the behavior appears to be similar to that found for C and D together, an analysis of the equivalent circuit revealed that the circuit could be simplified by replacing one of the CPEs with a Warburg impedance. In addition, the fit to the simplified circuit was much better, although the accuracy degraded at lower temperatures, particularly at the highest frequencies. The temperature dependence of the circuit elements is shown in Table I.

The Arrhenius behavior of the two resistances R1 and R2, shown in Figure 8, suggests that these model a thermally-activated process, such as: electron-hole promotion to the valence band, diffusion of ionic defects, or a mobility increase due to small polaron conduction by an electron hopping mechanism.

Since the Pt electrodes are blocking for ionic defects, the low-frequency resistance, R2, cannot be associated with ionic transport; therefore, R2 is attributed to electron holes. The activation energy of 0.58 eV, may be due either to an increase in charge carriers, an increase in mobility due to hopping, or both.

The high-frequency resistance, R1, with an activation energy of 0.51 eV, is also likely due to electron hole transport, perhaps across the Pt/film interface. The associated capacitance, represented by the constant phase elements Q and n, would then be that of the interface. The lower the value of n from unity, the greater the depression of the Nyquist semicircle below the real axis. Rougher interfaces tend to result in depressed semicircles, which is consistent with what is believed to be the nature of this film formed insitu, and agrees with $n \approx 0.65$. 

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Figure 5. Complex impedance of samples C and D at 500 °C that had been heated to 1000 °C for 75 hr.

Figure 6. Equivalent circuit used to model samples C and D in series, which is written as $L(RQ)(RQ)$ in the fitting program. At 200 °C, $L=1.4 \ \mu$H, $R_1=18 \ \text{k}\Omega$, $Q_1=4 \times 10^{-10} \ \Omega^{-1}$, $n_1=0.92$, $R_2=11 \ \text{k}\Omega$, $Q_2=1.3 \times 10^{-7} \ \Omega^{-1}$, and $n_2=0.71$. 
**Figure 7.** Impedance of sample D at 501 °C.

**Table I.** The variation of the circuit elements for sample D with temperature.

| Temperature °C | L (µH) | R1 (kΩ) | Q (nΩ⁻¹) | n | R2 (kΩ) | W (µΩ⁻¹) |
|---------------|--------|---------|----------|---|---------|---------|
| 501           | 5      | 0.338   | 30       | 0.66 | 0.0178 | 340     |
| 398           | 13     | 1.19    | 23       | 0.63 | 0.147  | 28      |
| 317           | 25     | 3.59    | 9.7      | 0.65 | 1.76   | 0.54    |
| 259           | 16     | 15.2    | 5.8      | 0.64 | 1.96   | 2.6     |
| 199           | 47     | 50      | 0.77     | 0.76 | 16.8   | 0.32    |
| 152           | 59     | 191     | 0.27     | 0.81 | 46.8   | 0.34    |
| 105           | 130    | 1070    | 0.081    | 0.87 | 237    | 0.44    |

**SUMMARY**

The formation of an extrinsic semiconducting film on the surface of this alloy does not bode well for the extended use of this alloy at moderate temperatures, such as 500 °C, due to the development of an increasing resistive film with time.

Even at 1000 °C the area resistance is several Ωcm² at 1000 °C, a value much larger than the target value of 0.1 Ωcm². Therefore, it does not appear as if this alloy will be able to support a current density of 500 mAcm⁻² after being exposed to air at 500 °C for a relatively short time. It may be possible, as discussed by Brückner, et al. (7), to use coatings to prevent the formation of resistive films.
Figure 8. Arrhenius behavior of the two resistances obtained from analysis of the Nyquist plots for sample, D. The activation energy for R1 and R2 is 0.51 and 0.58 eV, respectively.

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