ELECTRICAL AND THERMAL PROPERTIES OF SPINELS

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ABSTRACT

The properties of spinel oxides were studied in an effort to identify a potential solid oxide fuel cell (SOFC) interconnect coating which can hinder chromium oxide growth and evaporation as well provide acceptable electrical conductivity. Transition metal spinels based on aluminum, chromium, manganese and iron were examined. The electrical conductivities were measured in air from 500 to 800°C by the standard four-probe DC method. Additionally, the thermal expansion coefficients of some samples were measured in air from room temperature to 1000°C. The stoichiometric aluminates, chromites and manganites have thermal expansion coefficients that lie consistently in the 7-9 ppm/K range. Thermal expansion coefficients of the ferrites are in the 11-13 ppm/K range, and their conductivities are generally 0.1-10 S/cm. Conductivities of the aluminates are all less than 10^{-2} S/cm. Among the potential candidates for SOFC interconnect coatings, Co_2MnO_4 has a conductivity of 55 S/cm at 800°C and a thermal expansion coefficient of 9.7 ppm/K and CuFe_2O_4 has a conductivity of 9.1 S/cm at 800°C and a thermal expansion coefficient of 11.2 ppm/K. The ternary spinel oxides of CuMn_{2-x}Cr_xO_4 (x = 0.2, 0.6, 0.8 and 1.0) and Co_2Mn_{0.5}Cr_{0.5}O_4 are also acceptable in terms of their electrical conductivities and thermal expansion coefficients.

INTRODUCTION

Ferritic stainless steels used for the interconnect of solid oxide fuel cells (SOFCs) are protected from high temperature corrosion by a chromium oxide (Cr_2O_3) scale. However, scale growth and chromium poisoning of the cathode can lead to rapid performance degradation of the SOFC (1,2). Spinel oxides are readily formed as a contact layer on ferritic stainless steels under SOFC operating conditions. Earlier research results have shown growth of a pure spinel oxide or a spinel oxide on top of an inner chromia layer through suitable alloying addition (3-6). In this study, a systematic investigation of high temperature electrical and thermal properties of transition metal spinel oxides is reported.

EXPERIMENTAL

Samples of spinel oxides with different compositions were prepared by solid state reaction. The starting powders were Co_3O_4 (99.7%), CuO (99.99%), NiO (99.0%), MgO (99.95%), ZnO (99.5%), MnO_2 (99.9%), Fe_3O_4 (99.9%), Cr_2O_3 (99.0%) and Al_2O_3 (99.99%). The proportional amounts of starting oxide powders were thoroughly mixed, pressed into...
pellets, and then sintered at temperatures of 1100-1500°C for 5-30 hours using a heating rate of 70-90ºC per hour and a cooling rate of 100ºC per hour. The reacted pellets were crushed and reground, and the same sintering procedure was repeated. Different spinel oxides require different sintering conditions. The specific sintering temperature, time and atmosphere for each sample were determined from the respective phase diagrams and are given in Table 1.

To identify the phases of spinel samples, room temperature X-ray powder diffraction was carried out using Cu-Kα radiation. The electrical conductivities were measured by the standard four probe DC method in air from 500 to 800°C. The thermal expansion coefficients of some samples were measured in air from room temperature to 1000°C.

### Table 1. Sintering temperature, time and atmosphere for spinel samples.

| Spinel oxide  | Sintering temperature | Sintering time | Atmosphere |
|---------------|-----------------------|----------------|------------|
| CoFe₂O₄       | 1100                  | 5/5            | Air        |
| CuFe₂O₄       | 1150                  | 5/5            | Air        |
| MgFe₂O₄       | 1200                  | 5/5            | Air        |
| NiFe₂O₄       | 1200                  | 8/8            | Air        |
| ZnFe₂O₄       | 1200                  | 5/5            | Air        |
| Co₂MnO₄       | 1200                  | 6/6            | Air        |
| CoMn₂O₄       | 1000                  | 8/8            | Air        |
| CuMn₂O₄       | 1200                  | 5/5            | Oxygen     |
| CuMn₁₈O₄      | 1000                  | 5/5            | Air        |
| MgMn₂O₄       | 1150                  | 8/8            | Air        |
| Mn₁₂Cr₁₈O₄    | 1450                  | 24/24          | Argon      |
| CoCr₂O₄       | 1350 / 800            | 24/24          | Air        |
| ZnCr₂O₄       | 1300                  | 10/10          | Air        |
| MnAl₂O₄       | 1200                  | 10/10          | Nitrogen   |
| CuAl₂O₄       | 1100                  | 10/10          | Air        |
| CuMn₂₋₅Cr₋₅O₄| 1200                  | 10/10          | Air        |
| Co₂Mn₀₋₅Cr₀₋₅O₄| 1200                  | 10/10          | Air        |

### RESULTS AND DISCUSSION

**Phase Identification and Porosity of Spinel Samples**

Among the ferrite spinels, the samples of MgFe₂O₄, CoFe₂O₄, NiFe₂O₄ and ZnFe₂O₄ were found to be single phase cubic spinel, while the sample of CuFe₂O₄ showed a mixture of tetragonal and cubic spinel phases. For the manganite spinels, the samples of Co₂MnO₄ and CuMn₁₂O₄ were found to be single phase, while the sample of MgMn₂O₄ showed mixed phases of MgMn₂O₄ (85%) – Mg₂MnO₄ (15%), and the CoMn₂O₄ sample contained a minor amount of Co₂MnO₄. Copper manganite could only be obtained as a single phase.
with non-stoichiometric CuMn$_{1.8}$O$_4$. The sample of CuMn$_2$O$_4$ contained 20% Mn$_3$O$_4$ phase, despite its superior conductivity. All the chromite and aluminate samples formed single phase spinel except CoCr$_2$O$_4$, which contained approximately 20% Co$_3$O$_4$ phase.

In addition to the phase purity, porosity also has an effect on the electrical conductivity. Listed in Table 2 are the phase purity and density data of the samples. The values of bulk density were calculated from the dimensions and weight, while the theoretical densities were obtained from the lattice parameters. For samples with mixed phases, the calculation was based on the major component phase. For example, the theoretical density of CuFe$_2$O$_4$ was calculated based on the tetragonal structure, while the theoretical densities of the other four single ferrite spinels were based on the cubic structure.

Table 2. Phase purity and percent theoretical density of spinel oxide samples obtained from X-ray analysis.

| Spinel oxide  | Phase purity | Measured density (g/cm$^3$) | Theoretical density from lattice parameters (g/cm$^3$) | Percent theoretical density |
|---------------|--------------|------------------------------|------------------------------------------------------|-----------------------------|
| CoFe$_2$O$_4$ | Pure         | 4.86 0.01                    | 5.274                                                | 92.2%                       |
| CuFe$_2$O$_4$ | Pure         | 5.36 0.01                    | 5.390                                                | 99.5%                       |
| MgFe$_2$O$_4$ | Pure         | 3.76 0.01                    | 4.523                                                | 83.0%                       |
| NiFe$_2$O$_4$ | Pure         | 5.16 0.01                    | 5.370                                                | 96.1%                       |
| ZnFe$_2$O$_4$ | Pure         | 5.56 0.01                    | 5.325                                                | 104.4%                      |
| Co$_2$MnO$_4$ | Pure         | 5.23 0.01                    | 5.564                                                | 93.9%                       |
| CoMn$_2$O$_4$ | 90% Pure     | 5.25 0.01                    | 5.084                                                | 103.2%                      |
| CuMn$_2$O$_4$ | 80% Pure     | 5.72 0.01                    | 5.496                                                | 104.1%                      |
| MgMn$_2$O$_4$ | 85% Pure     | 3.99 0.01                    | 4.293                                                | 92.9%                       |
| Mn$_{1.2}$C$_{1.8}$O$_4$ | Pure | 3.96 0.01                    | 4.931                                                | 80.3%                       |
| CoCr$_2$O$_4$ | 80% Pure     | 5.04 0.01                    | 5.210                                                | 96.7%                       |
| ZnCr$_2$O$_4$ | Pure         | 4.84 0.01                    | 5.368                                                | 90.1%                       |
| MnAl$_2$O$_4$ | Pure         | 3.50 0.01                    | 4.160                                                | 84.2%                       |
| CuAl$_2$O$_4$ | Pure         | 3.90 0.01                    | 4.579                                                | 85.3%                       |

Electrical Conductivity Studies

According to the octahedral site preference energies of Fe$^{3+}$, Cr$^{3+}$, Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ (7-9), it is well established that most ferrite spinels have inverse structure, most chromite spinels have normal structure, and most manganite spinels have partially inverse structure. The electrical conduction of spinels is associated with the presence of ions of different valences in crystallographically equivalent positions. It has been suggested that the electrical conductivity of the spinel is due to the movement of charge carriers between different valence cations on octahedral sites (10). However, some spinel oxides, such as Cu$_x$Mn$_{3-x}$O$_4$, have a mixed cation distribution, and there are also cations with different valences on the tetrahedral sites. Thus, the conduction mechanism is not simply explained by the charge carrier transitions on octahedral sites only, but a contribution from the tetrahedral cations with mixed valence states must also be taken into consideration.
**Ferrite Spinels.** Among the samples investigated, ZnFe$_2$O$_4$ and MgFe$_2$O$_4$ had relatively low conductivities of 0.06-0.07 S/cm at 800°C, probably due to the single valence state for Mg and Zn and the low density of MgFe$_2$O$_4$, while the values for CoFe$_2$O$_4$ and NiFe$_2$O$_4$ were 0.83 S/cm and 0.25 S/cm (0.2 S/cm for NiFe$_2$O$_4$ was reported in ref. 11), respectively. The sample of CuFe$_2$O$_4$ showed the highest conductivity of 9.1 S/cm at 800°C among these ferrite spinels. The temperature dependence of the electrical conductivity for the ferrite spinels in air is shown in Fig. 1. The conductivities of some ferrite spinels can be changed with non-stoichiometric compositions or doping with other elements (10-12). For example, it has been reported (12) that the conductivity of CoFe$_2$O$_4$ can be increased with iron excess or cobalt excess.

![Graph showing the temperature dependence of the electrical conductivity for ferrite spinels](image)

**Figure 1.** Plot of log$_{10}$ conductivity vs. 1000/T for the ferrite spinels measured in air; (a) CuFe$_2$O$_4$ : log $\sigma = -1617.6/T + 2.409$; (b) CoFe$_2$O$_4$ : log $\sigma = -945.9/T + 0.801$; (c) NiFe$_2$O$_4$ : log $\sigma = -4615.3/T + 3.729$; (d) ZnFe$_2$O$_4$ : log $\sigma = -2133.3/T + 0.805$; (e) MgFe$_2$O$_4$ : log $\sigma = -6797.3/T + 5.091$.

**Manganite Spinels.** Among the manganite spinels investigated, copper manganites had the highest conductivities of over 100 S/cm at 800°C. The conductivities of cobalt manganites depend on the crystal structure: cubic Co$_2$MnO$_4$ had a conductivity of 55 S/cm at 800°C, while the conductivity of tetragonal CoMn$_2$O$_4$ was only 6 S/cm at 800°C. MgMn$_2$O$_4$ (85%) showed a relatively low conductivity of 0.86 S/cm at 800°C (0.8 S/cm was reported in ref. (13). The temperature dependence of the electrical conductivity for the manganite spinels in air is shown in Fig. 2.

The cation distribution and electrical conductivity in the copper manganite system have been widely investigated by various researchers (8,14-16). In this study, the sample of CuMn$_2$O$_4$ showed the highest conductivity among the spinels investigated – 138.2 S/cm at 800°C in air despite having a high fraction (20%) of Mn$_3$O$_4$ impurity phase. The high fraction of impurity phase is a result of phase equilibria at the high sintering temperature. Judging from the Cu-Mn-O phase diagram (17), a lower sintering temperature, such as 900°C, is recommended in order to avoid the second phase. A non-stoichiometric copper manganite composition, CuMn$_{1.8}$O$_4$, showed single spinel phase after sintering at 1000°C for 5 hours in air and a conductivity of 100 S/cm at 800°C.
Figure 2. Plot of log₁₀ conductivity vs. 1000/T for the manganite spinels measured in air; (a) CuMn₂O₄: log σ = -756.8/T + 2.845 (HT); (b) Co₂MnO₄: log σ = -2789.7/T + 4.332; (c) CoMn₂O₄: log σ = -2891/T + 3.462; (d) MgMn₂O₄: log σ = -884.1/T + 0.750.

Chromite and Aluminate Spinels. Most chromite spinel samples showed intermediate conductivities within the range of 10⁻² S/cm to 1 S/cm. For aluminate spinels, since the aluminum ion cannot exist in a valence state other than +3, the charge carrier exchange is limited, and thus conductivities of aluminates are all less than 10⁻² S/cm. CuAl₂O₄ has the highest conductivity among aluminates of 0.04 S/cm at 800°C. The temperature dependence of the electrical conductivity for the chromite and aluminate spinels in air is shown in Fig. 3.

Figure 3. Plot of log₁₀ conductivity vs. 1000/T for the chromite and aluminate spinels measured in air; (a) CoCr₂O₄ : log σ = -3463.7/T + 4.016; (b) CuAl₂O₄ : log σ = -8531.2/T + 6.564; (c) Mn₁₀₂Cr₁₈O₄ : log σ = -6697.1/T + 4.394; (d) ZnCr₂O₄ : log σ = -3464.9/T + 1.113; (e) MnAl₂O₄ : log σ = -6444.9/T + 3.453.

Manganese chromite plays an important role in SOFC applications. Under SOFC operating conditions, a Mn-Cr spinel may form at the interface between the Cr-containing alloy interconnect and the LSM cathode (18). However, it is difficult to sinter manganese chromite to high density because of the volatility of chromium oxide at high temperature. Table 3 gives the information for the three manganese chromite samples investigated under different conditions.
Table 3. Sintering conditions and electrical conductivities of manganese chromite samples.

| Composition       | Sintering conditions | Phase identification | Percent theoretical density | Electrical conductivity at 800°C (S/cm) |
|-------------------|----------------------|-----------------------|-----------------------------|----------------------------------------|
| MnCr$_2$O$_4$     | 1450°C, Air          | Pure phase            | 62.1%                       | 2.5E-03                                |
| MnCr$_2$O$_4$     | 1450°C, Argon        | Pure phase            | 73.3%                       | 4.0E-03                                |
| Mn$_{1.2}$Cr$_{1.8}$O$_4$ | 1450°C, Argon | Pure phase            | 80.3%                       | 1.4E-02                                |

Clearly, sintering in argon gives higher density. However, since chromites are naturally very difficult to be sintered dense, even when high temperature and argon atmosphere were used, the highest density obtained was only 80%. Among the three manganese chromites investigated, Mn$_{1.2}$Cr$_{1.8}$O$_4$ showed the highest conductivity of 0.014 S/cm and it is reasonable that composition should also have an effect on conductivity. Lu (19) reported that Mn$_x$Cr$_{3-x}$O$_4$ spinels have electrical conductivity of 4x10$^{-3}$ to 0.4 S/cm at 800°C depending on the ratio of Mn/Cr.

CoCr$_2$O$_4$ was also very difficult to be sintered dense, and the density of the stoichiometric sample investigated was only around 50%. However, almost fully dense CoCr$_2$O$_4$ (96.7% theoretical density) was obtained by adding excess Co$_3$O$_4$. The high conductivity (7.1 S/cm at 800°C) of the mixed phase CoCr$_2$O$_4$ compared with other chromite spinels is proposed to originate from the presence of Co$_3$O$_4$, which has a conductivity of around 7 S/cm at 800°C.

**Ternary Spinels: CuMn$_{2-x}$Cr$_x$O$_4$ and Co$_3$Mn$_{0.5}$Cr$_{0.5}$O$_4$.** Under SOFC operating conditions, a spinel coating on a chromium alloy will react with the growing Cr$_2$O$_3$ scale and form ternary spinel oxides. In this study, the electrical properties of CuMn$_{2-x}$Cr$_x$O$_4$ (x = 0.2, 0.6, 0.8 and 1.0) and Co$_3$Mn$_{0.5}$Cr$_{0.5}$O$_4$ were investigated (Fig. 4). Table 4 gives the measured conductivities of the CuMn$_{2-x}$Cr$_x$O$_4$ system.

![Figure 4. Plot of log$_{10}$ conductivity vs. 1000/T for the Cu-Mn-Cr ternary spinels and Co$_3$Mn$_{0.5}$Cr$_{0.5}$O$_4$ measured in air; (a) CuMn$_{1.4}$Cr$_{0.6}$O$_4$ : log $\sigma$ = -36.7/T + 2.368; (b) CuMn$_{1.2}$Cr$_{0.8}$O$_4$ : log $\sigma$ = -45.5/T + 2.281; (c) CuMn$_{1.0}$Cr$_{1.0}$O$_4$ : log $\sigma$ = -69.3/T + 2.240; (d) Co$_2$Mn$_{0.5}$Cr$_{0.5}$O$_4$ : log $\sigma$ = -426.4/T + 5.217.](image)
Table 4. Electrical conductivities of CuMn$_{2-x}$Cr$_x$O$_4$ at 800°C.

| CuMn$_{2-x}$Cr$_x$O$_4$ | x = 0 | x = 0.2 | x = 0.6 | x = 0.8 | x = 1.0 |
|------------------------|-------|---------|---------|---------|---------|
| Conductivity at 800°C (S/cm) | 138.2 | 106.8 | 104.9 | 72.1 | 39.3 |

The increasing substitution of Cr ions results in lower conductivity because of electron–hole compensation caused by Cr$^{4+}$ - electron pairs produced from Cr$^{3+}$ ions. The main conduction mechanism of copper manganites is due to small polaron hopping of electron holes (p-type) between Mn$^{4+}$ and Mn$^{3+}$ ions on octahedral sites. With the substitution of Mn by Cr, the concentration of Cr$^{3+}$ increases, Cr$^{4+}$ - electron pairs are created and the concentration of holes is decreased by electron – hole compensation. Thus, lower charge carrier concentration leads to lower conductivity. However, even when x = 1.0, the conductivity of the CuMnCrO$_4$ sample is around 40 S/cm at 800°C, which may be acceptable for SOFC application. Similar to the case for CuMn$_{2-x}$Cr$_x$O$_4$, Co$_2$Mn$_{0.5}$Cr$_{0.5}$O$_4$ has a conductivity of 17.8 S/cm at 800°C, which is lower than that of Co$_3$Mn$_4$O$_4$.

**Thermal Expansion Studies**

The thermal expansion coefficients of the spinels investigated were measured from room temperature to 1000°C in air. Basically, thermal expansion coefficients of ferrite spinels and ternary spinels of Co$_2$Mn$_{0.5}$Cr$_{0.5}$O$_4$ (12.9 ppm/K) and CuMn$_{2-x}$Cr$_x$O$_4$ (11.6 ppm/K for CuMnCrO$_4$) fall within the range of 11-13 ppm/K, matching well with that of YSZ electrolyte, whereas, manganite, chromite and aluminate spinels have thermal expansion coefficients within the range of 7-9 ppm/K.

**CONCLUSIONS**

High temperature electrical and thermal properties of transition metal spinel oxides based on aluminum, chromium, manganese and iron were investigated. Among the spinels surveyed, Co$_3$Mn$_4$O$_4$ has a conductivity of 55 S/cm at 800°C and a thermal expansion coefficient of 9.7 ppm/K; CuFe$_2$O$_4$ has a conductivity of 9.1 S/cm at 800°C and a thermal expansion coefficient of 11.2 ppm/K; ternary spinel oxides of CuMn$_{2-x}$Cr$_x$O$_4$ (x = 0.2, 0.6, 0.8 and 1.0) and Co$_2$Mn$_{0.5}$Cr$_{0.5}$O$_4$ also have acceptable conductivities and thermal expansion coefficients. These spinels have the greatest potential for application as protective coatings for SOFC ferritic stainless steel interconnects.

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