ELECTRICAL CONDUCTIVITY OF SrCrO₄ AND Sr₃Cr₂O₈ AT ELEVATED TEMPERATURES IN RELATION TO THE HIGHLY CONDUCTIVE CHROMIA SCALE FORMED ON AN ALLOY SEPARATOR IN SOFC

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ABSTRACT

A metallic separator of a nickel based alloy coated with (La, Sr)CoO₃ has been successfully demonstrated to maintain high conductivity during long term operation in a planer type SOFC. The chromia scale formed on the alloys at the cathode is highly conductive and the scale contains the oxide particles of the Sr-Cr-O system. The electrical conductivity of SrCrO₄ and Sr₃Cr₂O₈ was measured at 1273~1373 K as a function of oxygen pressure. The measured conductivity of the two compounds is much higher than that of Cr₂O₃.

INTRODUCTION

Calcium-doped lanthanum chromite, (La, Ca)CrO₃, has been used as a separator in a solid oxide fuel cell (SOFC). Among the cell components of SOFC, the separator is only one component which can be substituted by metallic materials, because the separator should be highly electrical conductive and free from the leakage of gases. A chromia-forming alloy is a potential alternative for a separator. Alloys are completely dense not to permit the gas leakage and are highly conductive. Formation of conductive chromia scale is the key issue to the application. The high performance of the cell with Ni-based chromia-forming alloy has been proved when the (La, Sr)CoO₃ was coated on the alloy [1]. The chromia scale was formed between the coating and the alloy and the oxidation resistance was as same as the non-coated alloy. The chromia scale was highly conductive and the scale contained oxide precipitates of the Sr-Cr-O system [2].

In available literatures, there is few information on phase relations and the electrical conductivity of the Sr-Cr-oxides. To elucidate the origin of the high conductivity of the chromia scale, the thermodynamic and transport properties of the oxides should be determined in equilibrium with Cr₂O₃. The present authors have determined the Gibbs energy of formation of SrCrO₄ and Sr₃Cr₂O₈ [3]. In the present
study, the electrical conductivity of the oxides was measured at 1273~1373 K as a function of oxygen pressure.

EXPERIMENTAL

Materials

The powders of SrCO$_3$ and Cr$_2$O$_3$ were mixed in molar ratio of 2 to 1, pressed at 160 MPa and heated at 1273 K for 170 ks in air. The following reaction,

$$2\text{SrCO}_3 + \text{Cr}_2\text{O}_3 + (3/2)\text{O}_2 = 2\text{SrCrO}_4 + 2\text{CO}_2 \quad (1)$$

gives SrCrO$_4$. The same procedure using the mixture of SrCO$_3$ and Cr$_2$O$_3$ with the ratio of 3 to 1 provides Sr$_3$Cr$_2$O$_8$.

$$3\text{SrCO}_3 + \text{Cr}_2\text{O}_3 + \text{O}_2 = \text{Sr}_3\text{Cr}_2\text{O}_8 + \text{CO}_2 \quad (2)$$

The resulting samples were pulverized and subjected to X-ray diffraction in order to confirm the completion of the reactions.

Figure 1 shows the phase relation among Cr$_2$O$_3$, SrCrO$_4$ and Sr$_3$Cr$_2$O$_8$ [3]. In the present study, the electrical conductivity was measured on the following two samples; (a) SrCrO$_4$ equilibrated with Cr$_2$O$_3$, and (b) SrCrO$_4$ equilibrated with Sr$_3$Cr$_2$O$_8$. These samples give the electrical conductivity of SrCrO$_4$ whose composition is at the phase boundary of the single phase. The sample (a) was prepared by mixing powders of SrCrO$_4$ and Cr$_2$O$_3$ (1.5 vol. %). The mixture was pressed into tablet at 160 MPa and sintered at 1273 K for 86 ks in air. From the sintered tablet, the sample was cut into 6.0 x 2.0 x 7.8 mm for the measurement. The sample (a) was referred to SrCrO$_4$ (Cr$_2$O$_3$). The sample (b) was prepared by the same procedure using SrCrO$_4$ and Sr$_3$Cr$_2$O$_8$ (4.4 vol. %). The size was 6.4 x 2.2 x 7.3 mm and referred to SrCrO$_4$ (Sr$_3$Cr$_2$O$_8$). The relative densities of both samples after sintering were 95 %.

Fig. 1 Tentative phase diagram in the Sr-Cr-O system [3].
Measurements

The electrical conductivity was measured by the D.C. four probe technique using the apparatus as shown in Fig. 2. The sample was placed as close as the oxygen sensor of stabilized zirconia. The oxygen partial pressure was controlled using argon-oxygen mixture. The electrical conductivity was measured at 1273–1373 K under the oxygen partial pressure between 1 and $10^{-3}$ atm.

![Fig. 2 Apparatus for electrical conductivity measurement.](image)

RESULTS AND DISCUSSION

Figure 3 shows the electrical conductivity of the SrCrO$_4$ (Cr$_2$O$_3$). The vertical broken lines denoted the dissociation pressure of SrCrO$_4$ to Sr$_3$Cr$_2$O$_8$, which was previously determined by a thermodynamic measurement [3]. With decreasing the oxygen pressure, the electrical conductivity increases and is proportional to $1/5$ of the oxygen pressure. The temperature dependence of the conductivity indicated the semiconducting behavior. In this sample where SrCrO$_4$ is equilibrated with Cr$_2$O$_3$, the dissolution-precipitation of Cr$_2$O$_3$ occurs in the following manner.

$$2\text{SrCrO}_4 = 2\text{Sr}^{**} + \text{Cr}_2\text{O}_3 + (5/2)\text{O}_2 + 4\text{e}'$$

where $\text{Sr}^{**}$ is the doubly charged interstitial strontium ion and $\text{e}'$ is the excess electron in SrCrO$_4$. The equilibrium constant ($K_3$) is

$$K_3 = a_{\text{Sr}^{**}}^{-2} a_{\text{Cr}_2\text{O}_3} P_{\text{O}_2}^{5/2} a_{\text{e}'}^{-4} / a_{\text{SrCrO}_4}^2$$

where $a$ is the activity. In the Eq. (4), $a_{\text{Cr}_2\text{O}_3}=a_{\text{SrCrO}_4}=1$ and one can reasonably assume that the defect concentration is dilute enough ($a_{\text{Sr}^{**}} \propto [\text{Sr}^{**}]$ and $a_{\text{e}'} \propto [\text{e}']$).

$$K_3 \propto [\text{Sr}^{**}]^2 P_{\text{O}_2}^{5/2}[\text{e}']^4$$

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The electrical neutrality condition \( (2[Sr^{**}]=[e']) \) gives
\[ [e'] \propto P_{O_2}^{-5/12} \quad (6) \]
The electrical conductivity is proportional to the electron concentration so that it has the same oxygen pressure dependence.

Below the dissociation pressure, \( \text{SrCrO}_4 \) decomposes to \( \text{Sr}_3\text{Cr}_2\text{O}_8 \) and \( \text{Cr}_2\text{O}_3 \), \( \text{Sr}_3\text{Cr}_2\text{O}_8 (\text{Cr}_2\text{O}_3) \).
\[ 3\text{SrCrO}_4 = \text{Sr}_3\text{Cr}_2\text{O}_8 + (1/2)\text{Cr}_2\text{O}_3 + (5/4) \text{O}_2 \quad (7) \]
The electrical conductivity of the \( \text{Sr}_3\text{Cr}_2\text{O}_8 (\text{Cr}_2\text{O}_3) \) is high and to be about 3 S cm\(^{-1}\), although the volume fraction of \( \text{Cr}_2\text{O}_3 \) is increased to be 13.4 vol.%. The conductivity is independent of oxygen pressure and the temperature dependence is extremely small. This fact suggests that \( \text{Sr}_3\text{Cr}_2\text{O}_8 \) is semimetallic conductor.

Figure 4 shows the electrical conductivity of \( \text{SrCrO}_4 (\text{Sr}_3\text{Cr}_2\text{O}_8) \). The conductivity of \( \text{SrCrO}_4 (\text{Sr}_3\text{Cr}_2\text{O}_8) \) is independent of oxygen pressure and that of \( \text{Sr}_3\text{Cr}_2\text{O}_8 (\text{Cr}_2\text{O}_3) \) which is formed by the decomposition of \( \text{SrCrO}_4 \) is as same as in Fig. 3. In this sample where \( \text{SrCrO}_4 \) is equilibrated with \( \text{Sr}_3\text{Cr}_2\text{O}_8 \), the dissolution-precipitation reaction is
\[ \text{Sr}_3\text{Cr}_2\text{O}_8 = Sr^{**} + 2\text{Sr}_x^X + 2\text{Cr}_4\text{O}_4^X + 2e' \quad (8) \]
The dissolution of \( \text{Sr}_3\text{Cr}_2\text{O}_8 \) into \( \text{SrCrO}_4 \) increases the interstitial strontium ion and excess electron, and the concentration is always fixed at the solubility which is
Fig. 4 Electrical Conductivity of the Sr\textsubscript{3}Cr\textsubscript{2}O\textsubscript{8} (Sr\textsubscript{3}Cr\textsubscript{2}O\textsubscript{8}).

Fig. 5 Electrical Conductivity of SrCr\textsubscript{4} and Sr\textsubscript{3}Cr\textsubscript{2}O\textsubscript{8}.
independent of oxygen pressure.

For the clarity, Figs. 3 and 4 are merged into Fig. 5. The interesting point is that the electrical conductivities of SrCrO₄ (Cr₂O₃) and SrCrO₄ (Sr₃Cr₂O₈) coincide at the point where SrCrO₄ decomposes. This evidence agrees with the Gibbs phase rule. At the dissociation pressure, SrCrO₄ exists with Sr₃Cr₂O₈ and Cr₂O₃ in equilibrium, and the composition of SrCrO₄ is fixed.

REFERENCES

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