CHROMIUM VAPORIZATION FROM METALLIC INTERCONNECT AND RETENTION BY PEROVSKITE LAYERS

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ABSTRACT

Chromium-based alloys like the oxide-dispersion-strengthened (ODS) alloy Cr5Fe1Y2O3 are suitable materials for the metallic interconnect of solid oxide fuel cells (SOFCs). The vaporization of volatile chromium species from chromium-containing alloys (such as Cr5Fe1Y2O3) on the cathode side of the SOFC leads to a rapid degradation of the electrical properties of the cell. Acceptor-doped perovskites based on LaCrO3 are considered as coating materials in order to prevent chromium vaporization from metallic interconnects. In the present paper, the chromium evaporation rate of the uncoated ODS alloy Cr5Fe1Y2O3 is compared with the amount of chromium vaporizing from the La0.9Sr0.1CrO3-coated sample. Chromium vaporization rates were determined by the transpiration method under cathodic SOFC conditions (T = 950 °C, p[H2O] = 0.02 bar, p[O2] = 0.21 bar). Moreover, chromium diffusion coefficients in perovskite layers (La0.9Sr0.1CrO3, La0.6Ca0.4CrO3) were derived by using a 53Cr tracer technique.

INTRODUCTION

Typical interconnector materials used in the planar solid oxide fuel cell design are chromium-based alloys and chromium-containing steels (1). Chromium-containing alloys used for metallic interconnects are protected from corrosion by a chromia scale, which is formed under cathodic SOFC conditions (T = 950 °C, p[H2O] = 0.02 bar, p[O2] = 0.21 bar). Depending on temperature and the partial pressures of H2O and O2, volatile chromium species are formed by the Cr2O3 layer (2, 3):

\[
\begin{align*}
\text{Cr}_2\text{O}_3(s) + 1.5 \text{O}_2(g) &= 2 \text{CrO}_3(g) \quad [1] \\
\text{Cr}_2\text{O}_3(s) + 1.5 \text{O}_2(g) + 2 \text{H}_2\text{O}(g) &= 2 \text{Cr}_2\text{O}_3(\text{OH})_3(g) \quad [2] \\
\text{Cr}_2\text{O}_3(s) + \text{O}_2(g) + \text{H}_2\text{O}(g) &= 2 \text{CrO}_2\text{OH}(g) \quad [3]
\end{align*}
\]

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The vaporization of gaseous chromium oxides and chromium oxyhydroxides (Eqs. 1-3) at the cathode side of the fuel cell causes a rapid degradation of the electrical properties of an SOFC (2, 4). The reduction of volatile Cr(VI) species to solid Cr(III)oxide at the cathode-electrolyte interface is considered to be the reason for the observed degradation of cell performance. Metallic interconnect materials are coated with ceramic layers to reduce chromium evaporation in order to prevent the degradation processes. In the Siemens planar SOFC concept the ODS alloy Cr5Fe1Y2O3 is coated with a protective perovskite scale of La0.9Sr0.1CrO3 (4, 5). The thickness of the vacuum plasma sprayed (VPS) perovskite layer is between 25-30 μm.

In this paper the chromium vaporization from the surface of Cr5Fe1Y2O3 is determined by transpiration experiments. The evaporation rates of uncoated and coated (La0.9Sr0.1CrO3) ODS samples are compared to find suitable protection layers with maximum chromium retention. In addition chromium diffusion coefficients in acceptor-doped LaCrO3 ceramics are measured by 53Cr tracer experiments. The investigation of chromium solid-state diffusion in protective scales is necessary to estimate the value of perovskite layers for chromium retention. Using the chromium diffusion coefficients, breakthrough times for chromium in La_xSr_yCrO_3 and La_xCa_yCrO_3 scales are calculated.

**EXPERIMENTAL**

**Transpiration Experiments**

Chromium vaporization rates were determined by the use of a transpiration apparatus (6). In a heated quartz tube volatile chromium species vaporize from the sample surface. The gas stream transports the volatile species from the reaction tube to the condensing tube outside the furnace. The reaction and condensing parts of the quartz tube are connected by a joint, a capillary is used to separate the two compartments of the tube. The temperature in the reaction tube is monitored by a Pt13%Rh/Pt30%Rh thermocouple. All experiments were carried out at a temperature of 950 °C. A quartz filter between the gas inlet and the reaction tube is used to minimize backstream diffusion. The reaction gases pass a mass flow controller before entering the humidifier. To maintain non-equilibrium conditions a gas flow rate of 1.8 l/min was selected. For all experiments synthetic air with p[H2O] = 0.02 bar was used. The water vapour pressure was controlled by the temperature of a condenser.

Samples for the transpiration experiments were made of Cr5Fe1Y2O3. The coating material for the coated samples was La0.9Sr0.1CrO3. The perovskite layers of 25-30 μm thickness were prepared by Siemens using VPS. Chemical composition and morphology of the protective scales were controlled by SEM, XRD and laser profilometry. The size of coated and uncoated specimens was 80x30x5 mm³. Uncoated samples were pre-oxidized in air for 200 h at a temperature of 1000 °C. In the transpiration apparatus samples were kept in a quartz sample holder. After completion of the transpiration experiment, the condensing part of the quartz tube was removed and washed with distilled water and conc. HNO3. The chromium content of the solution was analysed by atom absorption spectroscopy (AAS).
**53Cr Tracer Experiments**

Chromium diffusion coefficients in protective perovskite scales were derived by 53Cr tracer experiments (7). The perovskite coatings were deposited by VPS on a sample area of 1x1 cm². The substrate material was Al₂O₃, and the scale thickness was 25-30 μm. Tracer experiments were carried out with three different compositions of perovskite layers: La₀.₉Sr₀.₁CrO₃, La₀.₈Sr₀.₂CrO₃, and La₀.₆Ca₀.₄CrO₃. The perovskite surfaces were polished to a roughness of less than 1 μm. After polishing the scale morphology and chemical composition of the perovskite layers were determined by laser profilometry, SEM and EDX. A solution of 53Cr nitrate was used to prepare the tracer spots on the polished perovskite surfaces. After the water of the tracer solution had evaporated another polished sample was used as the top of a sandwich. The sample sandwiches were annealed in a furnace in an air atmosphere at a temperature of 1000 °C and 1107 °C. After annealing the specimen was analysed by secondary ion mass spectrometry (SIMS) to derive the 53Cr concentration profile. Diffusion coefficients are calculated by fitting these curves using a thin film model of diffusion into semi-infinite space.

**RESULTS**

**Transpiration Experiments**

To maintain non-equilibrium conditions in the reaction tube of the transpiration apparatus it is necessary to study the chromium transport rate with respect to the gas flow rate (8). Figure 1 shows the variation of the chromium transport rate as function of the flow rate for the coated ODS sample in air of T = 950 °C and p[H₂O] = 0.02 bar. For flow rates of more than 1.5 l/min the plateau region of the curve is reached.

![Figure 1. Chromium vaporization rate, k, of ODS in air of 950 °C using different gas flow rates, v.](image_url)
In this part of the curve the transport rate is independent of the gas flow rate and is, therefore, determined by kinetics. For the transpiration experiments with the coated and uncoated ODS samples a flow rate of 1.8 l/min was selected. According to Figure 1, at a flow rate of 1.8 l/min a chromium transport rate of 8.6 µg/h was obtained. The results of the transpiration experiments with the La\textsubscript{9}Sr\textsubscript{1}CrO\textsubscript{3}-coated samples are shown in Table I.

| Sample number | Annealing time t/h | Evaporation rate k/(µg h\textsuperscript{-1}) | Chromium Retention |
|---------------|-------------------|---------------------------------------------|-------------------|
| 1             | 1159              | 0.4                                         | 95 %              |
| 2             | 391               | 0.3                                         | 96 %              |

Compared to the evaporation rates of the uncoated ODS alloy Cr\textsubscript{5}Fe\textsubscript{1}Y\textsubscript{2}O\textsubscript{5} (k = 8.6 µg/h) the experiments demonstrate a chromium retention of around 95 % for the La\textsubscript{9}Sr\textsubscript{1}CrO\textsubscript{3} scale. The experimental conditions for the measurement of evaporation rates with coated samples were the same as for uncoated specimens (p[H\textsubscript{2}O] = 0.02 bar, T = 950 °C, v = 1.8 l/min).

\textbf{\textsuperscript{53}Cr Tracer Experiments}

The \textsuperscript{53}Cr tracer experiments with protective perovskite scales were carried out at an oxygen partial pressure of p = 0.21 bar and temperatures of 1000 °C and 1107 °C. Annealing times between 154200 s and 922800 s were used. As described in Table II, three different perovskite compositions were examined. The diffusion coefficients D\textsubscript{Cr} were derived by fitting the SIMS profiles with Eq. 4, following a thin film model. Equation 4 is a solution of Fick's second law for the tracer diffusion into a semi-infinite space (9). It describes the dependence of the chromium concentration from the penetration depth x of the tracer and the annealing time t. The constant M is the initial amount of tracer substance on the sample surface.

\[
C_{Cr}(x, t) = M (\pi D_{Cr} t)^{0.5} \exp (-x^2/4 D_{Cr} t) \tag{4}
\]

In Figure 2 the measured diffusion profile for the La\textsubscript{9}Sr\textsubscript{1}CrO\textsubscript{3}-coated sample is shown together with the fitted curve.

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The results of all $^{53}$Cr tracer experiments are listed in Table II. To compare the values of the chromium diffusion coefficients of the three different perovskite layers it is necessary to extrapolate $D_C[\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3]$ from 1107 °C to 1000 °C.

Table II: $^{53}$Cr tracer experiments with different perovskite compositions.

| Perovskite composition | Annealing time t/s | Temperature T/°C | Cr Diffusion coefficient $D_C/(\text{cm}^2\text{s}^{-1})$ |
|------------------------|--------------------|------------------|--------------------------------------------------|
| $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$ | 732300 | 1000 | 2.59 $10^{16}$ |
| $\text{La}_{0.9}\text{Sr}_{0.2}\text{CrO}_3$ | 154200 | 1107 | 1.51 $10^{15}$ |
| $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ | 922800 | 1000 | 6.60 $10^{15}$ |

For this extrapolation Eq. 5 was used and $D_C[\text{La}_{0.9}\text{Sr}_{0.2}\text{CrO}_3] = 5.49 \ 10^{16} \text{ cm}^2/\text{s}$ was calculated for a temperature of 1000 °C. The temperature $T_1$ corresponds to the diffusion coefficient $D_1$.

$$\ln D_2 - \ln D_1 = a \ (T_1 - T_2) (T_1 \ T_2)^{-1}$$  \[5\]

The factor $a$ in Eq. 5 was derived by temperature dependence studies of $D_C$ in $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$ scales. Of the three scale compositions, $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$ seems to be the best diffusion barrier for chromium. The calcium-doped LaCrO$_3$ shows the highest chromium diffusion coefficient.

Figure 2. Fitting for $^{53}$Cr diffusion profile in $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$ scale.
Figure 3 shows an optical microscope image of the cross section of a La₀.₉Sr₀.₁CrO₃ protective scale on Al₂O₃ substrate. The porosity of the perovskite layer is closed, the diameter of the biggest pores is about 5 µm. The surface roughness of the sample after polishing is about 0.5 µm as is visible in Figure 4. The chromium diffusion coefficients measured in perovskite layers are similar to the values given by Sakai et al. (10) for bulk-diffusion in LSC and LCC.

Figure 4. Surface roughness of polished La₀.₉Sr₀.₁CrO₃ sample

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Short Stack Test Experience

Short stack tests with uncoated metallic interconnector plates show high degradation rates mainly due to chromium penetration into the active cathode areas (interface of cathode and electrolyte). These problems can be reduced (a) by perovskite coatings on the interconnect surface as described above, (b) by the use of cathodes with a composite structure (LSM/YSZ) which increase the electrochemical active volume, and (c) the decrease of the operating temperature. The decrease of the chromium release by the reduction of the operating temperature is, however, small (2).

The cell degradation of an operating cell due to chromium release can be detected by impedance measurements. Former short stack tests using uncoated interconnector plates and MEAs with pure LSM cathodes showed unstable cathode polarisation resistances. The values increased by a factor >10 during a time period of 100 h stack operation, see Figure 5. Short stack long term tests, which contain the mentioned improvements (a), (b), and (c), showed low and very stable cathode polarization resistances, see Figure 6.

Figure 5. Cathode polarisation resistance without protective interconnect coating.
SUMMARY AND CONCLUSIONS

The chromium vaporization rates from uncoated and La$_{0.8}$Sr$_{0.1}$CrO$_3$-coated ODS samples were investigated under cathodic SOFC conditions. The transpiration experiments with coated Cr$_5$Fe$_1$Y$_2$O$_3$ specimens showed a 95 % reduction of the chromium evaporation rate compared to the uncoated ODS sample. In combination with a decrease of operating temperature of 100°C from 950 °C to 850 °C, a chromium retention of 98-99 % should be possible.

Chromium diffusion coefficients in three different protective perovskite scales (La$_{0.8}$Sr$_{0.2}$CrO$_3$, La$_{0.8}$Sr$_{0.2}$CrO$_3$, La$_{0.9}$Ca$_{0.1}$CrO$_3$) were determined. In $^{53}$Cr tracer experiments with strontium- and calcium-doped LaCrO$_3$ layers, chromium diffusion coefficients between $6.60 \times 10^{-15}$ and $2.59 \times 10^{-16}$ cm$^2$/s were obtained. Of the three perovskite compositions the La$_{0.9}$Sr$_{0.1}$CrO$_3$ scale showed the lowest chromium tracer diffusion coefficient. Assuming a scale thickness of 30 μm for La$_{0.8}$Sr$_{0.2}$CrO$_3$ a breakthrough time of 550 a can easily be estimated using the equation $x = (2Dt)^{0.5}$. A breakthrough time of 22 a was calculated for the La$_{0.9}$Ca$_{0.1}$CrO$_3$ layer under the same conditions. It is obvious that chromium transport via bulk diffusion through the protective VPS layer is not considered as the rate-determining step.

Short stack long term tests with La$_{0.8}$Sr$_{0.1}$CrO$_3$-coated interconnects and a composite LSM/YSZ cathode showed no indication of a degradation due to chromium vaporization from interconnect.
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