

Short Communication

Surface treatment of alloy separator in a planar-type solid oxide fuel cell

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Abstract

In the process of improving the performance of planar-type solid oxide fuel cells it is found necessary to apply an appropriate surface treatment to the alloy separator that can diffuse chromium to the cathode. Cathode polarization shows a correlation with the intensity of the chromium. With heat treatment and polishing to remove the surface oxide layer, the amount of chromium diffusing from the alloy is suppressed and cell performance is raised. Accordingly, a 150 mm² single cell has been operated stably for about 3000 h.

Introduction

Planar-type solid oxide fuel cells (SOFCs) have received much attention because of their simple manufacturing process and the promise of a higher power density than that available from tubular designs.

The authors have conducted [1] research into composite electrodes in order to improve electrode performance, and have worked on developing a melt-sealing technology. The composite electrode has both electronic and ionic conductivity; this provides high performance and high reliability. The melt-sealing method is a new technique that combines a flexible seal with melted glass. As a consequence, a sealing efficiency of over 98% was obtained, as well as an output power of 415 W with a 125 cm² × 20-cell stack [2]. A stack is now under development with a high fuel utilization and a stable performance.

In the process of improving cell performance, it was found necessary to apply an appropriate surface treatment to the alloy separator, in addition to decreasing other sources of internal resistance.

For the separator material, a heat-resisting alloy must offer good performance in terms of electrical conductivity, heat conductivity, gas-tightness, mechanical strength, and ease of manufacturing. It has been pointed out, however, that chromium diffuses from the alloy to the cathode at the operating temperature of 1000 °C and subsequently degrades the properties of the electrode [3, 4]. To deal with this problem, an investigation has been made of the alloy surface treatment. As a result, it has been found that cell performance can be improved with an alloy that has been heat treated and polished.

In this paper, a report is given of the effect of this surface treatment for the alloy separator, as well as a description of the long-range performance of 150 mm² single cell.

Experimental

Alloy separator surface treatment

The specifications of the test cell are shown in Table 1. The cells were made by the following method. The anode material (NiO 1 μm , 56 wt.% + YSZ (8mol% Y_2O_3 -92mol% ZrO_2) 0.5 μm , 44 wt.%) was painted on the surface of the electrolyte and sintered at 1250 °C for 2 h. The cathode material ($\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ 1 μm , 80 wt.% + YSZ 0.5 μm , 20 wt.%) was painted on the other side and sintered at 1100 °C for 4 h. The electrode sizes for the test cells were 4 mm \times 12.5 mm. Current was collected by a platinum mesh. Separator test pieces of Inconel 600 alloy (16wt.%Cr-8wt.%Fe-76wt.%Ni) were made by a machining process. The size of these pieces was 2 mm \times 2 mm \times 12.5 mm.

The following three surface treatments were applied to these alloy test pieces:

- (i) sample A: heat treated at 1050 °C for 48 h in air followed by removal of the surface oxide layer by polishing;
- (ii) sample B: heat treated at 1050 °C for 48 h in air, and
- (iii) sample C: untreated.

In order to evaluate the effect of the chromium that diffused from the alloy to the cathode, the test pieces were put on the surface of the cathode of the test cells.

The test cells were operated at a constant current density of 300 mA/cm² at 1000 °C with air (cathode) and H_2 +3% H_2O (anode) gas. Cell performance was evaluated in terms of cell voltage at 300 mA/cm², and its change with time was monitored. Ohmic loss and polarization were measured simultaneously by the current-interruption method.

The distribution of chromium in the cathode and in the alloy was measured by electron probe microanalysis (EPMA).

TABLE 1

Specifications of test cells

	Test cell	Single cell
Active area (cm ²)	0.5	130
Material		
Anode	NiO/YSZ slurry coat, sinter 100 μm	NiO/YSZ screen print, sinter 70 μm
Cathode	$\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ /YSZ slurry coat, sinter 100 μm	$\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ /YSZ screen print, sinter 70 μm
Electrolyte	PSZ (3mol% Y_2O_3 -97mol% ZrO_2) self-support type 200 μm	PSZ (3mol% Y_2O_3 -97mol% ZrO_2) self-support type 200 μm
Alloy separator	Inconel 600 (16wt.%Cr-8wt.%Fe-76wt.%Ni)	Inconel 600 (16wt.%Cr-8wt.%Fe-76wt.%Ni)

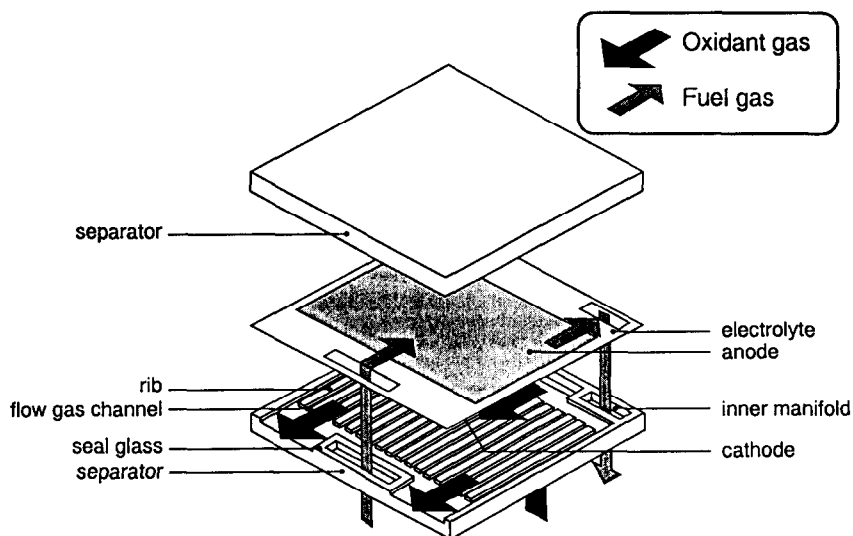


Fig. 1. Construction of single planar-type solid oxide fuel cell.

Single-cell performance

A 150 mm² single cell was tested to investigate long-range performance. Table 1 shows the specifications of the cell components. Figure 1 shows the construction of the single cell. The separators were given the surface treatment described below. An inner manifold was used for the gas supply. The oxidant and fuel gas were sealed by melting glass around the separators. Nickel felts were used for the current-collector of the anodes.

Results and discussion

Alloy separator surface treatment

Figure 2 presents the cross-sectional distribution of chromium in the alloy prepared for this study. Each line represents the intensity of chromium as measured by EPMA. After the heat treatment, the alloy was covered with a Cr₂O₃-rich layer. Inside the alloy near this Cr₂O₃-rich surface layer, the amount of chromium decreased. Accordingly, after removing the Cr₂O₃-rich surface layer by polishing, the amount of chromium in the surface layer was decreased, i.e., sample A.

Figure 3 shows the change in cell voltage with time for samples A, B and C. The increase in polarization for samples A, B and C compared with the cell performance obtained in the absence of the alloy is given in Fig. 4. The untreated sample C caused a deterioration in the cell performance after a few hundred hours. This deterioration was due to an increase in polarization (Fig. 4). EPMA measurements detected the presence of chromium in the cathode after 300 h (Fig. 5). This appeared to diminish the cathode activity.

The cell performance with sample B was much worse than that with untreated sample C because of a marked increase in polarization (Fig. 4). This appears to be due to an increase in the amount of chromium that diffuses from the alloy, especially from the Cr₂O₃-rich surface layer.

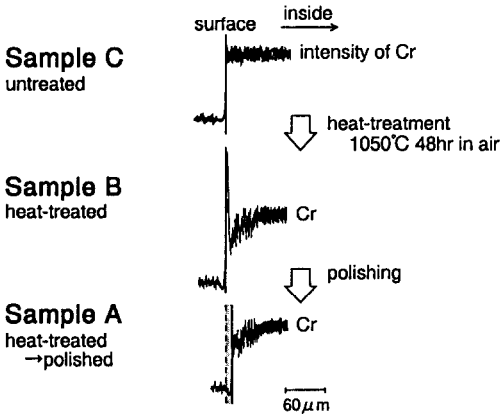


Fig. 2. Cross-sectional distribution of chromium in alloy after heat treatment and polishing.

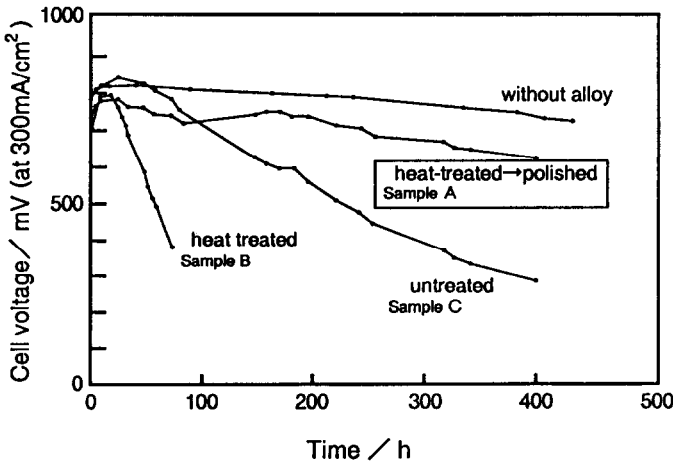


Fig. 3. Cell voltage for samples A, B and C. Each cell was operated at a constant current density of 300 mA/cm² at 1000 °C with H₂+3% H₂O (anode) gas and air (cathode).

By contrast, the heat-treated and polished sample A exerted less influence on the cell voltage, and the cell performance was improved. The increase in polarization with sample A was small and did not increase much after 700 h (Fig. 4).

A comparison of the cross-sectional distribution of chromium in the cathode between samples A and C is given in Fig. 5. The amount of chromium diffused from the alloy was suppressed in the case of sample A, and the intensity did not increase much after 700 h. This result was consistent with the observed cell performance.

The relationship between the intensity of chromium in the cathode and the increase in polarization is presented in Fig. 6. The horizontal axis shows the average intensity of chromium at the interface between the electrolyte and the cathode. When the intensity of chromium increased, polarization increased and the cell performance became unstable. With a high chromium content at the interface, the polarization increased from the time the current was applied. In Fig. 6, the open circles give the

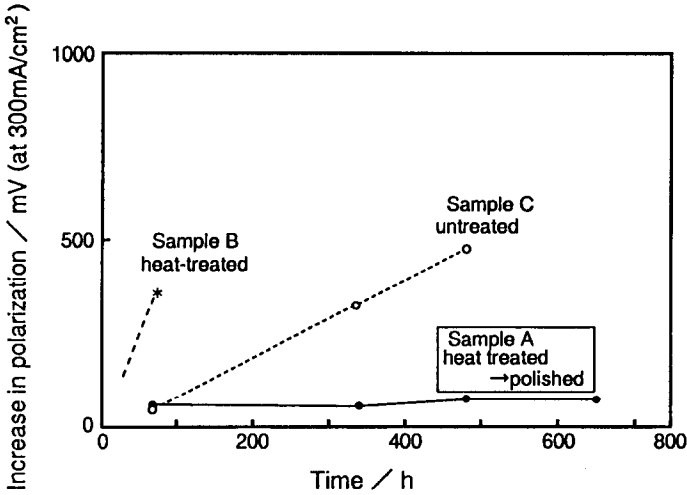


Fig. 4. Increase in polarization for samples A, B and C compared with cell performance without the alloy. Each cell was operated at a constant current density of 300 mA/cm² at 1000 °C with H₂+3% H₂O (anode) gas and air (cathode).

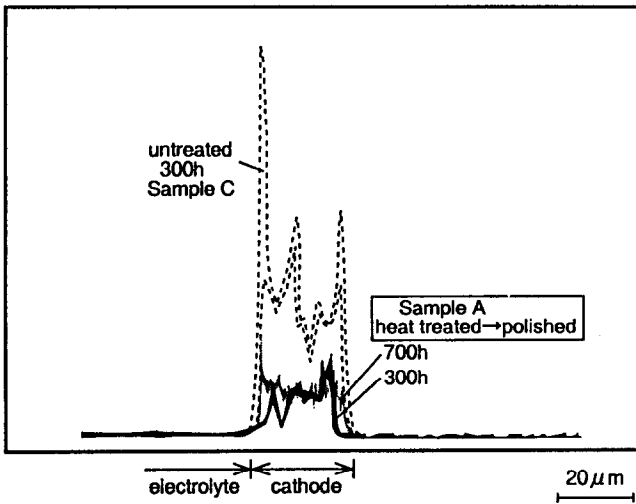


Fig. 5. Comparison of chromium intensity in cathode for samples A and C after 300 h and 700 h at 1000 °C. EPMA measurement condition: 20 kV, 0.02 μA, crystal LiF(Cr), full scale 2000 counts per s).

value just after the current was applied and the closed circles indicate the value 1 h later. The chromium distribution was affected by the current: the intensity at the cathode/electrolyte interface increased considerably. This phenomenon will be reported elsewhere. The surface treatment suppressed the amount of chromium that diffused from the alloy and, thereby, decreased the polarization.

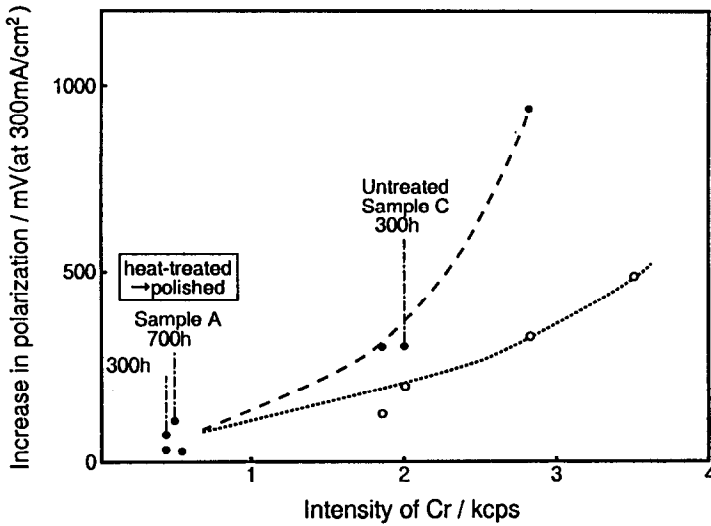


Fig. 6. Relationship between intensity of chromium (at cathode/electrolyte interface) and increase in polarization. Cell performance was measured at 1000 °C with H₂+3% H₂O (anode) gas and air (cathode). EPMA measurement condition: 20 kV, 0.02 μA, crystal LiF(Cr). Open circles indicate the value just after current was applied and closed circles indicate value 1 h later.

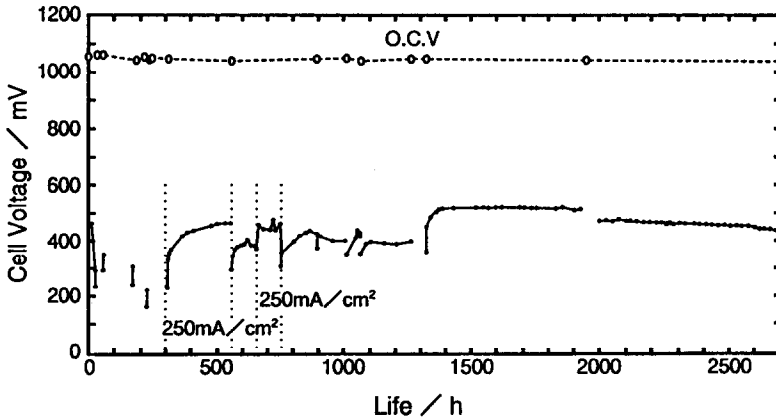


Fig. 7. Endurance of a 150 mm² single cell. The cell was operated at a constant current density of 300 mA/cm² at 982 °C with H₂+3% H₂O (at 40% fuel utilization) and air (at 25% oxidant utilization).

Single-cell performance

Figure 7 shows the long-range performance of a 150 mm² single cell in terms of the change in cell voltage with time. The current density was 300 mA/cm² and fuel utilization was 40%. Initially, the performance was not good but, after 1400 h, the cell voltage change was small and the cell performance was stable.

The results of an EPMA analysis for chromium in the cathode of this cell after 3000 h of operation are presented in Fig. 8. The intensity of chromium was measured along the interface between the electrolyte and the cathode. The chromium intensity

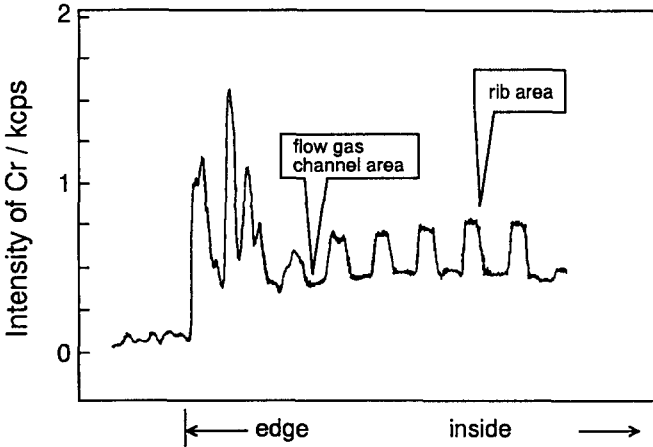


Fig. 8. EPMA chromium analysis of cathode of a 150 mm² single cell after 3000 h of operation. EPMA measurement condition: 20 kV, 0.02 μ A, crystal LiF(Cr).

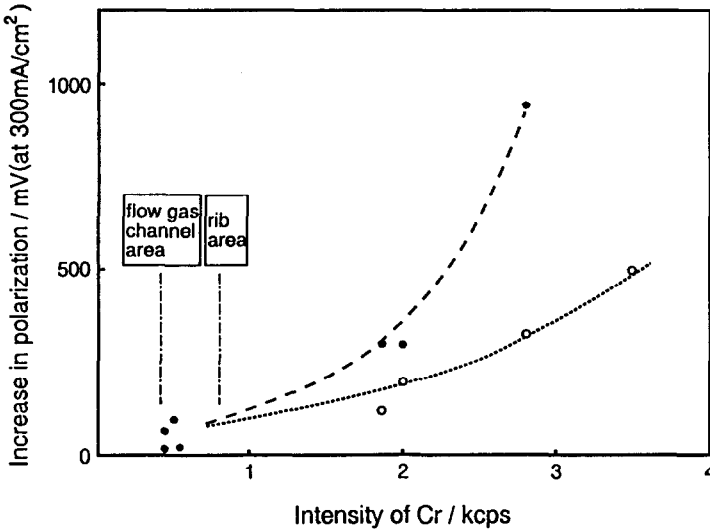


Fig. 9. Intensity of chromium in a 150 mm² single cell (after 3000 h of operation) and the corresponding cell performance (Fig. 6).

was higher in the rib area. The latter was in contact with the alloy bipolar plate. In the flow-gas channel area, which was not in contact with the alloy, the intensity of chromium was lower.

A comparison of the intensity of chromium in the single cell and the test cells is shown in Fig. 9. In the rib area, the chromium intensity was high and the corresponding increase in polarization was estimated to be about 100 mV at 300 mA/cm². In the flow-gas channel area, the increase in polarization was much smaller after 3000 h of operation. This result confirms that a long-range cell performance is improved by heat-treatment and polishing of the alloy separator.

Conclusions

With heat treatment and polishing to remove the surface oxide layer, the amount of chromium diffusing from the alloy to the cathode was suppressed and the cell performance was improved. By adopting this alloy surface treatment, a 150 mm² single cell was operated stably for about 3000 h.

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