EFFECT OF Pt ADDITIONS ON THE RESISTANCE OF La$_{0.9}$Sr$_{0.1}$MnO$_3$ CATHODE

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ABSTRACT

The effect of platinum additions to La$_{0.9}$Sr$_{0.1}$MnO$_3$ on the electrical conductivity and cathodic properties were studied with a view to reduce ohmic polarization loss of SOFC. The electrical conductivity at 1000°C rose from 5.3 S cm$^{-1}$ to 12 S cm$^{-1}$ by increasing platinum content from 0 vol% to 41.8 vol%. Platinum additions reduced the ohmic polarization of SOFC from 1.1 ohm to 0.8 ohm and the current density of SOFC rose from 0.48 A/cm$^2$ to 0.63 A/cm$^2$ at 0.5 V. Other results suggested that this improvement is attributed to not only increasing the electrical conductivity of cathode but also reducing the contact resistance between cathode and electrical collector.

1. INTRODUCTION

Recently, solid oxide fuel cells (SOFC) have attracted much attention. The 3kW pilot plant of tubular type cell made by Westinghouse Electric Corporation has been running for more than 3000 hours in Osaka Gas Co., Ltd. (1). Many other solid oxide fuel cell configurations, for example monolithic, honeycomb and planar, have also been proposed.

On account of high operating temperature, selection of materials for SOFC is restricted. La$_{0.9}$Sr$_{0.1}$MnO$_3$ has been used as a cathode for Westinghouse tubular cell (2) and Argonne National Laboratory monolithic cell (3). A perovskite oxide, especially Sr doped LaMnO$_3$, is used as a cathode for SOFC nowadays (4). These materials have high catalytic activity for dissociation of oxygen molecules, relatively high electrical conductivity, and thermal and chemical stability. The cathodic properties of LaMO$_3$ (M=Mn, Co) have been examined (5,6). The electrical conductivity and its temperature dependence of perovskite oxides have also been studied (7,8,9). According to these studies the electrical conductivity of Sr doped LaMnO$_3$ at 1000°C reaches more than 100
Scm$^{-1}$, and is sufficient for cathode of a SOFC. However, the electrical conductivity of an actual perovskite cathode is expected to be much lower than such values because of its porosity and pore shape\cite{10}. Therefore, ohmic polarization loss of cathode forms a large part of total ohmic polarization loss of a SOFC\cite{11}. It is, therefore, important to improve the electrical conductivity of porous perovskite cathode. On the other hand, platinum has less activity for dissociation of oxygen molecules but high electrical conductivity compared with those of perovskite oxides. In this paper, the effect of platinum additions on the electrical conductivity and the cathodic properties of La$_{0.9}$Sr$_{0.1}$MnO$_3$ were studied with a view to reduce ohmic polarization loss of SOFC.

2. EXPERIMENTAL

 Powders of the composition La$_{0.9}$Sr$_{0.1}$MnO$_3$ and platinum were mixed in an agate mortar and dispersed in a binder solution. These slurries were painted on 1cm wide alumina substrates for the electrical conductivity measurements. Four platinum wires were put on each specimen as probes for four probe D.C. method, and the slurries were painted on the four platinum wires again. After that, specimens were dried in an oven at 90°C. The distance between two potential probes was 1cm and the thicknesses of the cermets were 0.35-0.45mm. The samples were heated in a tubular furnace in flowing oxygen gas and the electrical conductivities were measured with a HOKUTO DENKO potentiostat/galvanostat.

 The morphologies of these specimens were observed by a JEOL JSM-820 scanning electron microscope and the X-ray mapping images of all elements were obtained by an energy dispersive X-ray microscopy (EDX), KEVEX DELTA CLASS ANALYZER. The crystalline structures were analyzed and identified by a PHILIPS PW-1700 XRD system. The porosities of cermets were measured by a mercury penetration method with a MICROMERITICS porosimeter, AUTO PORE 9200.

 The cathodic properties of the La$_{0.9}$Sr$_{0.1}$MnO$_3$/platinum cermets were examined. 3 mol% yttria doped PSZ sheets from NIPPON SHOKUBAI KAGAKU were used as the solid oxide electrolyte. The thickness of the PSZ sheets is about 0.2mm. Ni/ZrO$_2$=10/1 cermet was used as an anode. The cathode and anode were painted on the PSZ sheets with a square active area of 1.0cm$^2$. Platinum mesh for the electrical collector covered the anode. The electrical collector on the cathode was a platinum wire for clarifying the effect of the electrical conductivity of cathode. This PSZ sheet was put between alumina tubes. The gas seal between the alumina tube and the PSZ sheet was made with a TEMPAX glass ring gasket. The cell was heated in air at a rate of 10°C/min and the
temperature was held at 1000°C. As feed gas, oxygen was supplied to the cathodic side of the cell and hydrogen to the anodic side, respectively. Voltage-current characteristics and the non-ohmic polarization properties were measured with the potentiostatic and the current interrupter method, respectively. SOLATRON 1286 ELECTROCHEMICAL INTERFACE was used for these measurements. The difference between the overall voltage-current characteristics and the non-ohmic polarization loss measured by the current interrupter method is thought to be an ohmic polarization loss.

3. RESULTS AND DISCUSSION

By the SEM image of the platinum powder used in this study, platinum grains looked spherical and the diameter of each grain was about 0.5 μm. The surface of platinum after calcining at 1000°C was much sintered, though no significant change was observed for that of La₀.₉Sr₀.₁MnO₃ of which grains were about 5μm in size.

SEM image and X-ray mapping image by EDX of La₀.₉Sr₀.₁MnO₃/platinum=76.5/23.5 vol% cermet after calcining at 1000°C, shown in Figs.1 and 2, revealed that platinum grains were sintered to larger grains. Some small grains of platinum were found between La₀.₉Sr₀.₁MnO₃ grains, and large platinum grains were unconnected with each other. Consequently, the electrical conduction mechanism of this sample was presumed not to be that of a metal. From the XRD pattern of this cermet, no reaction compound of La₀.₉Sr₀.₁MnO₃ and platinum was found.

In Fig.3, the electrical conductivities of painted La₀.₉Sr₀.₁MnO₃/platinum cermets at 1000°C are shown as a function of platinum content. The electrical conductivity of La₀.₉Sr₀.₁MnO₃ was 5.3 S/cm⁻¹. This value was about two orders of magnitude lower than that of other study, 133 S/cm⁻¹(8). It is considered that the difference of the electrical conductivities of painted La₀.₉Sr₀.₁MnO₃ from that of bulk La₀.₉Sr₀.₁MnO₃ depends on its porosity. The porosity of painted La₀.₉Sr₀.₁MnO₃ was very large as shown in Fig.4. The platinum additions improved the electrical conductivities of cermets and reduced the porosities. Drastic change was not observed for the electrical conductivities. This is different from the case of Ni/ZrO₂ cermet used as an anode of SOFC(12). Though the threshold of Ni content has been reported 30 vol% Ni, no threshold was found in La₀.₉Sr₀.₁MnO₃/platinum cermet up to 41.8 vol% platinum. Platinum grains used in this study are supposed to easily migrate and grow larger due to small diameter. The platinum grains were, therefore, dispersed in La₀.₉Sr₀.₁MnO₃ grains and were unable to make connections with each other as shown in Fig.2.

Fig.5 shows the temperature dependence of the electrical conductivities of
La_{0.5}Sr_{0.5}MnO_3/platinum cermets. The ln(\sigma T) versus 1/T curves of La_{0.5}Sr_{0.5}MnO_3/platinum cermets were almost straight. All curves were nearly parallel. As mentioned above, the temperature dependence of the electrical conductivity of these cermets was not that of metal. It has been reported that the electrical conduction mechanism of La_{1-x}Sr_xMnO_3 is small-polaron conduction mechanism because the ln(\sigma T) versus 1/T curve is straight line(7,8). Accordingly, it is thought that the conduction mechanism of these cermets is also governed by that of La_{0.5}Sr_{0.5}MnO_3. The electrical conductivity of perovskite oxides is said to decrease with increasing porosity(6). The cermets shrank by sintering of platinum grains and the porosities of the cermets decreased as shown in Fig.4. It is possible that the electrical conductivities of these cermets improved without changing the conduction mechanism. This is thought to be one of the effects of platinum additions.

Fig.6 shows the effect of platinum additions on current density of SOFC. The current density rose from 0.48 A/cm² to 0.63 A/cm² at 0.5 V with increasing platinum content up to 23.5 vol% but drastically decreased in the case of the cathode involving 41.8 vol% platinum. In Fig.7, the effects of platinum additions on non ohmic and ohmic polarization are shown. The non ohmic polarization did not change with increasing platinum content. Using the cathode with 41.8 vol% platinum, it was observed that the surface of the cathode peeled off from the electrical collector after experiment. This is probably due to shrinkage of this cermet. Much ohmic polarization of this cell is attributed to this phenomenon.

The resistance of 3 mol% yttria doped PSZ sheet which is 0.2mm thick and 1.0cm² large is about 0.5 ohm. The electrical conductivity of the cermet involving 23.5 vol% platinum could not explain clearly a drastic decrease of ohmic polarization eliminating the resistance of PSZ sheet. It is suggested that a contact resistance exists between electrolyte and electrodes, or electrodes and electrical collectors. To confirm this, following experiment was carried out. After painting La_{0.5}Sr_{0.5}MnO_3 as cathode, a platinum wire was placed on it as the electrical collector and the cermet with 23.5 vol% platinum was painted around the platinum wire. Cell performance was measured. As shown in Table 1, the ohmic polarization decreased from 1.1 ohm to 1.0 ohm and the current density improved from 0.48 A/cm² to 0.53 A/cm². This result suggests that one of the effects of platinum additions is a reduction in the contact resistance between the cathode and the electrical collector. It is speculated that the apparent contact area of the electrical collector to the La_{0.5}Sr_{0.5}MnO_3 grains increased because of many platinum grains contact to the electrical collector. Generally, the resistances of an electrolyte and electrodes are reduced with increasing active area of cell. However, the contact resistances do not change. Consequently, the effect of platinum
additions is thought to be more important for the scale up of SOFC.

4. CONCLUSIONS

① The platinum grains used in this study sintered at 1000°C but La$_{0.5}$Sr$_{0.5}$MnO$_3$ was little sintered at this temperature.

② The electrical conductivity at 1000°C of painted La$_{0.5}$Sr$_{0.5}$MnO$_3$ improved by platinum additions. It is speculated that this improvement is due to reduced porosity of the cermet by platinum sintering.

③ The ohmic polarization of SOFC consisted of ohmic resistances of materials and contact resistances.

④ Platinum additions reduced the contact resistance between the cathode and the electrical collector and increased the current density of SOFC. This effect is thought to be more important for the scale up of SOFC.

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|                                | Ohmic polarization (ohm) | Current density (A/cm²) |
|--------------------------------|--------------------------|------------------------|
| La₀.₉Sr₀.₁MnO₃ cathode          | 1.1                      | 0.48                   |
| La₀.₉Sr₀.₁MnO₃ cathode with the |                          |                        |
| cermet containing 23.5 vol%    |                          |                        |
| platinum around the electrical |                          |                        |
| collector                      |                          |                        |
Fig. 1 Scanning electron micrograph of $\text{La}_0.9\text{Sr}_{0.1}\text{MnO}_3$/platinum=76.5/23.5 vol% cermet after calcination at 1000°C.

Fig. 2 Energy dispersive X-ray micrograph of platinum in $\text{La}_0.9\text{Sr}_{0.1}\text{MnO}_3$/platinum=76.5/23.5 vol% cermet after calcination at 1000°C.
Fig. 3 Relation between the electrical conductivities at 1000°C for painted La₀.₉Sr₀.₁MnO₃/platinum cermet and those platinum content.

Fig. 4 Relation between the porosities of painted La₀.₉Sr₀.₁MnO₃/platinum cermet and those platinum content.

Fig. 5 Temperature dependence of the electrical conductivities of painted La₀.₉Sr₀.₁MnO₃/platinum cermets. Platinum content (vol%): (○)0, (△)7.1, (●)23.5, (▲)41.8

Fig. 6 Effect of platinum additions to La₀.₉Sr₀.₁MnO₃ on the current densities at 0.5 volt of SOFC.
Fig. 7 Effect of platinum additions to La$_{0.8}$Sr$_{0.2}$MnO$_3$ on the polarization properties of SOFC: (○) non ohmic polarization, (●) ohmic polarization.