

## An Intermediate-Temperature Fuel Cell Using a Proton-Conducting $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ Electrolyte

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Performance of a fuel cell using  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  and Pt/C as the electrolyte and electrodes, respectively was evaluated in the temperature range of 150-300°C under unhumidified conditions. The cell performance was improved by forming an intermediate layer consisting of  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  and Pt/C catalyst powders at the interface between the electrolyte and cathode, which significantly reduced the cathode polarization. As a result, the peak power density reached 152 mW cm<sup>-2</sup> at 250°C using the 1.0-mm-thick electrolyte. The present fuel cell also showed high stability at low relative humidities ( $P_{\text{H}_2\text{O}} \approx 0.0075$  atm) and 10% CO concentration. We also tested performance of a fuel cell using Mo<sub>2</sub>C-ZrO<sub>2</sub>/C as the anode between 150 and 300°C. It was found that at 250°C or higher, the Mo<sub>2</sub>C-ZrO<sub>2</sub>/C anode showed a cell performance comparable to that of the Pt/C anode.

Key words:  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  electrolyte, intermediate-temperature fuel cells, high proton conductivities, performance of a fuel cell, alternative catalysts to Pt

### 1. INTRODUCTION

Proton exchange membrane fuel cells (PEFCs) have received increasing interest in recent years because of their high efficiency and environmentally friendly characteristics. Proton-conducting fluoropolymers such as Nafion are commonly used as the electrolytes. Since protons attach themselves to water and diffuse as  $\text{H}_3\text{O}^+$  ions through the electrolyte, the operating temperature of PEMFCs is limited to the dehydration temperature of ~100°C, causing serious CO poisoning of the anode electrocatalysts.[1] The electrolytes also need to be operated in highly humidified conditions, resulting in complicated water management. More importantly, the use of the expensive Pt catalyst is required to catalyze the electrode reactions at such low temperatures. These challenges would be overcome by using a proton conductor capable of operating above 100°C under low humidity or dry conditions. Thus, considerable efforts have been devoted to developing such proton conductors worldwide.[2-4]

We have recently reported a promising anhydrous proton conductor, 10 mol% In<sup>3+</sup>-doped  $\text{SnP}_2\text{O}_7$  ( $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ ), which shows high proton conductivities above 0.1 S cm<sup>-1</sup> between 150 and 350°C under unhumidified conditions.[5] The electromotive force values of a hydrogen concentration cell with this material were very near the theoretical values calculated from Nernst's equation, indicating that the ionic transport number was 0.97. Thus,  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  was found to be an almost purely ionic conductor in hydrogen atmospheres.

In present study, intermediate-temperature fuel

cells using  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  as electrolyte material were investigated. Fuel cell tests were conducted in unhumidified hydrogen and air in the temperature range of 150-300°C. The tolerance of the fuel cell for CO was evaluated in the presence of 5 and 10% CO. Furthermore, we report the Mo<sub>2</sub>C-ZrO<sub>2</sub>/C anode catalyst as a promising alternative to Pt/C at the intermediate temperatures.

### 2. EXPERIMENTAL

*Electrolyte Preparation:*  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  was prepared as described in our previous study.[5] The corresponding oxides ( $\text{SnO}_2$  and  $\text{In}_2\text{O}_3$ ) were mixed with 85%  $\text{H}_3\text{PO}_4$  and ion-exchanged water and then held at 300°C with stirring until the mixture turned into a paste with a high viscosity. After calcinating at 650°C for 2.5 h, the compound was ground with a mortar and pestle. The compound powders were pressed into a pellet under a pressure of  $2 \times 10^3$  kg cm<sup>-2</sup>. The measured density of the obtained pellet was 3.065 g cm<sup>-3</sup>, with a relative density of 79.3%.

*Fuel Cell Tests:* The anode and cathode (area: 0.5 cm<sup>2</sup>) were attached on opposite sides of the  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  electrolyte (1.0 mm thickness unless otherwise specified). Two gas chambers were set up by placing a cell between two alumina tubes. Each chamber was sealed with an inorganic adhesive. The fuel and air chambers were supplied with unhumidified hydrogen and air, respectively, at a flow rate of 30 mL min<sup>-1</sup> between 150 and 300°C. The electrode polarizations were analyzed by the current interruption method. In this case, a Pt reference electrode was attached on the surface of the side

of the electrolyte. The voltage-current density curves were measured by the four-probe method between 150 and 300°C.

**Electrode and intermediate layer preparation:** Both the anode and cathode were made from a catalyst (10 wt% Pt/C, E-TEK) and carbon paper (Toray TGPB-090), in which the Pt loading was about  $0.6 \text{ mg cm}^{-2}$ .

An intermediate layer was prepared by mixing  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  and Pt/C catalyst powders with a 10% poly(vinylidene fluoride) (PVdF) binder in 1-methyl-2-pyrrolidinone (NMP) solvent using a mortar and pestle. The Pt/C catalysts (10-40 wt% Pt) was prepared via precipitation method using chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) solution and sodium boron-hydride ( $\text{NaBH}_4$ ) solution.

The  $\text{Mo}_2\text{C}/\text{C}$  anode catalyst was fabricated as follows. A  $\text{MoCl}_5$  precursor was impregnated onto a carbon support (Black Pearls, BET surface area =  $1500 \text{ m}^2\text{g}^{-1}$ ). The impregnated sample was reduced in a 10 vol%  $\text{H}_2/\text{Ar}$  mixture at 500°C for 2 h and then carburized in a 20 vol%  $\text{CH}_4/\text{H}_2$  mixture at 700°C for 3 h. The loading of all the carbides was  $30 \text{ mg cm}^{-2}$ . The  $\text{Mo}_2\text{C}/\text{C}$  anode was also modified by impregnating  $\text{MoCl}_5$  along with various other metal chlorides or oxychlorides, such as  $\text{ZrCl}_2 \cdot 8\text{H}_2\text{O}$ . Subsequent treatments were the same as those for  $\text{Mo}_2\text{C}$ . The mixture was coated on a carbon paper (Toray TGPB-090). This sample was then dried for 1 h at 90°C, followed by 1 h at 130°C.

Microstructure of  $\text{Mo}_2\text{C}$ -based catalyst was analyzed using X-ray diffraction (XRD) and transmission electron microscopy (TEM).

### 3. RESULTS AND DISCUSSION

The conductivities of non- and  $\text{In}^{3+}$ -doped  $\text{SnP}_2\text{O}_7$  at different temperatures in an unhumidified air ( $P_{\text{H}_2\text{O}} \approx 0.0075 \text{ atm}$ ) are shown in Fig. 1. The substitution of  $\text{In}^{3+}$  for  $\text{Sn}^{4+}$  enhanced the conductivity, and an impurity phase formed at the  $\text{In}^{3+}$  contents of more than 10 mol% deteriorated the conductivity. 10 mol%  $\text{In}^{3+}$ -doped  $\text{SnP}_2\text{O}_7$  ( $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ ) with the highest conductivity of  $1.95 \times 10^{-1} \text{ S cm}^{-1}$  at 250 °C was used in subsequent experiments.

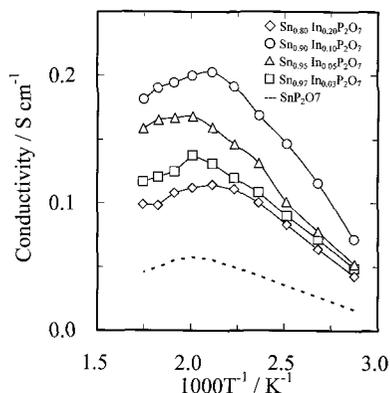


Figure 1. Temperature dependence of conductivity of non- and  $\text{In}^{3+}$ -doped  $\text{SnP}_2\text{O}_7$ . The samples were maintained in unhumidified air ( $P_{\text{H}_2\text{O}} \approx 0.0075 \text{ atm}$ ).

Figure 2 plots the cell voltage and power density versus the current density at various temperatures using 10 wt% Pt/C (E-TEK) as the cathode under unhumidified conditions ( $P_{\text{H}_2\text{O}} \approx 0.0075 \text{ atm}$ ). The open circuit voltages (OCVs) were about 920 mV, which were lower than the theoretical value of  $\sim 1.1 \text{ V}$ . As reported earlier[5],  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  was an almost purely ionic conductor in reducing atmospheres ( $P_{\text{O}_2} = 10^{-22}\text{-}10^{-3} \text{ atm}$ ), but showed mixed proton and electron-hole conduction in oxidizing atmospheres ( $P_{\text{O}_2} = 10^{-3}\text{-}1 \text{ atm}$ ). Thus, the low OCVs are attributable to the partial electron-hole conduction in the electrolyte, causing an internal short circuit in the cell. Another possible explanation is physical leakage of gas through the electrolyte since the OCVs increased with increasing electrolyte thickness. The fuel cell yielded the peak power density of  $85 \text{ mW cm}^{-2}$  at 250°C. However, this power density value was much lower when compared to that expected from the AC conductivity ( $1.95 \times 10^{-1} \text{ S cm}^{-1}$ ) of Fig. 1.

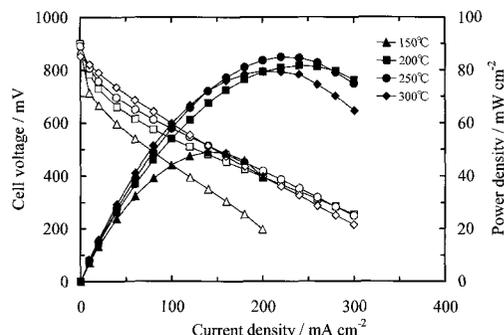


Figure 2. Cell voltage and power density vs. current density of the fuel cells using  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  as the electrolyte between 150 and 300°C.

To better understand the above low cell performance, the electrode polarization was measured between 150 and 300°C. The anodic and cathodic overpotentials as a function of the current density are shown in Fig. 3. The cathodic overpotentials were much larger than the anodic overpotentials over the whole temperature range. Moreover, the cathodic overpotential showed a strong temperature dependence, suggesting that the cathode had a high activation energy for the reduction of oxygen. Clearly, the development of a more active cathode is required to improve the cell performance.

It is useful to increase the area of the three-phase boundary for promotion of the cathode reaction. Thus, intermediate layers of  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  and Pt/C catalyst powders were applied at the interface between the electrolyte and electrode. As a result of the optimization of both the Pt content in the Pt/C catalyst and the weight ratio of the  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  electrolyte to the Pt/C catalyst, the cathodic overpotential could be the most improved when Pt content = 30 wt% and  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  : Pt/C catalyst = 10:1. It is believed that the intermediate layer provides

proton conduction to the cathode, enhancing the frequency of contact between proton and oxygen.

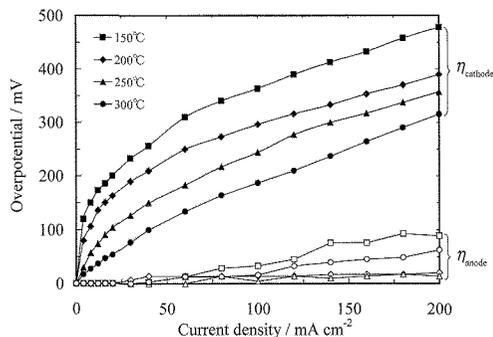


Figure 3. Anodic and cathodic overpotentials between 150 and 300°C.

Performance of the fuel cell with the intermediate layer was evaluated under unhumidified conditions (Fig. 4). The voltage drop during discharge was less dependent on the temperature between 200 and 300°C, which is responsible for the small difference in the proton conductivity of the electrolyte under such conditions. The peak power density ranged from 120 mW cm<sup>-2</sup> at 150°C to 152 mW cm<sup>-2</sup> at 250°C; these values are considerably higher than those obtained without using the intermediate layer shown in Fig. 1. This indicates that the intermediate layer effectively improved the cell performance.

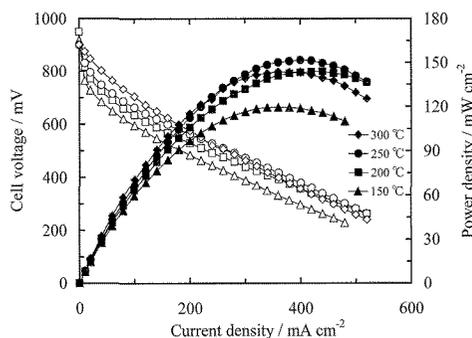


Figure 4. Cell voltage and power density vs. current density of the fuel cells with an intermediate layer of Sn<sub>0.9</sub>In<sub>0.1</sub>P<sub>2</sub>O<sub>7</sub> and 30 wt% Pt/C catalyst between 150 and 300°C.

CO poisoning of the present fuel cell was investigated by supplying hydrogen or a mixture of 5 or 10% CO and hydrogen to the fuel chamber at 250°C. The cell performance was clearly not influenced by the presence of CO (Fig. 5). Similar results were observed in AC impedance spectra, which maintained a constant polarization resistance regardless of the presence of CO. Such a negligibly small CO poisoning effect is roughly in agreement with theoretical studies on CO tolerance at high temperatures.[6] These results indicate that the present fuel cell has excellent CO tolerance for actual applications, in which the CO concentration in the outlet gases from conventional reformers is usually 10%.[7]

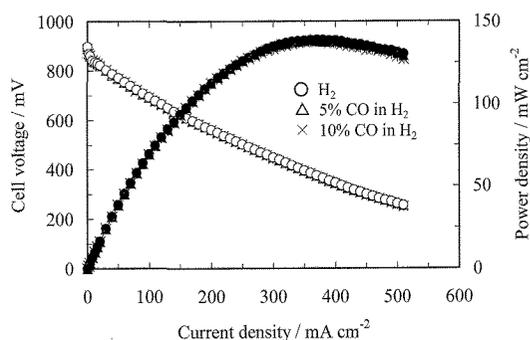


Figure 5. Cell voltage and power density vs. current density of the fuel cell using H<sub>2</sub> and a mixture of 5 or 10% CO + H<sub>2</sub> as the fuel gas at 250°C.

However, there still remains the need to use Pt/C electrodes to achieve reasonable cell performance. Transition metal carbides such as Mo<sub>2</sub>C and WC have been reported as potential catalysts for many chemical reactions because of their Pt-like behavior at elevated temperatures.[8-10]

Figure 6 shows the anodic overpotentials of the unmodified and modified Mo<sub>2</sub>C/C anodes at 250°C. All the modified Mo<sub>2</sub>C/C anodes, in particular Mo<sub>2</sub>C-ZrO<sub>2</sub>/C, showed considerably lower overpotentials compared to the unmodified Mo<sub>2</sub>C/C anode. The polarization resistance was 0.28 Ω cm<sup>2</sup>, which was approximately one order of magnitude lower than that of the unmodified Mo<sub>2</sub>C/C anode.

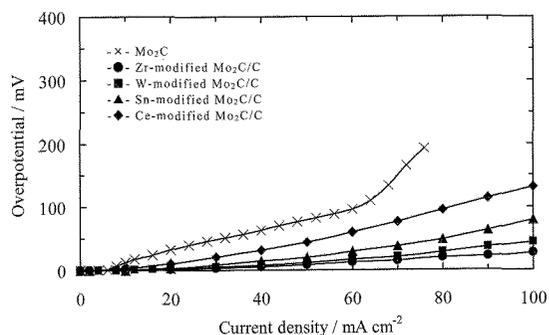


Figure 6. Anodic overpotentials of unmodified and modified Mo<sub>2</sub>C/C anodes at 250°C.

The microstructure of the Mo<sub>2</sub>C-ZrO<sub>2</sub>/C catalyst was characterized by XRD and TEM measurements. From XRD results of the Mo<sub>2</sub>C/C and Mo<sub>2</sub>C-ZrO<sub>2</sub>/C catalysts, the estimated particle sizes of the catalysts were 28 and 13 nm for Mo<sub>2</sub>C/C and Mo<sub>2</sub>C-ZrO<sub>2</sub>/C, respectively. A similar difference was observed in the particle size of Mo<sub>2</sub>C, as revealed by TEM measurements of the two catalysts. As shown in Fig. 7, the TEM images indicated that the particle sizes of Mo<sub>2</sub>C were 16-34 nm and 10-16 nm for Mo<sub>2</sub>C/C and Mo<sub>2</sub>C-ZrO<sub>2</sub>/C, respectively. These results indicate that the Mo<sub>2</sub>C particles showed a higher dispersion with ZrO<sub>2</sub> than without ZrO<sub>2</sub>. It is likely that excessive sintering of Mo<sub>2</sub>C during

carburization is inhibited in the presence of  $\text{ZrO}_2$ , resulting in the significantly improved catalytic activity of  $\text{Mo}_2\text{C}$  toward hydrogen oxidation.

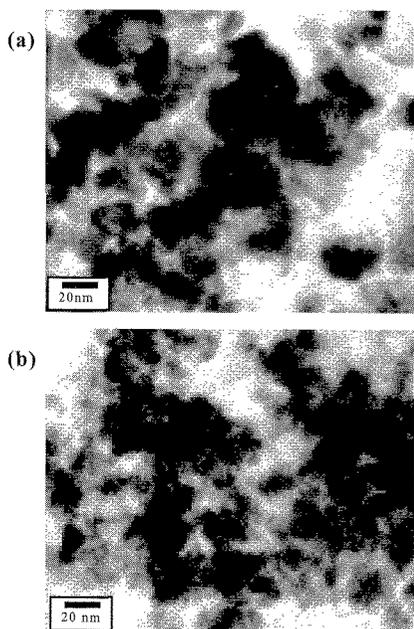


Figure 7. TEM images of (a)  $\text{Mo}_2\text{C}/\text{C}$  and (b)  $\text{Mo}_2\text{C}-\text{ZrO}_2/\text{C}$ . The catalysts and carbons are shown as black and gray, respectively.

Cell performance using the  $\text{Mo}_2\text{C}-\text{ZrO}_2/\text{C}$  anode was evaluated at  $250^\circ\text{C}$  under unhumidified  $\text{H}_2/\text{air}$  fuel cell conditions. Figure 8 compares the cell performance using the  $\text{Mo}_2\text{C}-\text{ZrO}_2/\text{C}$  anode with those using the  $\text{Mo}_2\text{C}/\text{C}$ , Pt/C, and carbon anodes at  $250^\circ\text{C}$ . It is important to note that while limiting current behavior was observed for the  $\text{Mo}_2\text{C}/\text{C}$  anode at high current densities, no change in the current-voltage slope was observed for the  $\text{Mo}_2\text{C}-\text{ZrO}_2/\text{C}$  anode, suggesting an enhanced hydrogen spill-over on the highly dispersed  $\text{Mo}_2\text{C}$ . More importantly, there is not a large difference in cell performance between the  $\text{Mo}_2\text{C}-\text{ZrO}_2/\text{C}$  anode and the Pt/C anode; the power density was  $67 \text{ mW cm}^{-2}$  for  $\text{Mo}_2\text{C}-\text{ZrO}_2/\text{C}$  and  $84 \text{ mW cm}^{-2}$  for Pt/C. This demonstrates that  $\text{Mo}_2\text{C}-\text{ZrO}_2/\text{C}$  has a high potential as an anode catalyst for PEMFCs.

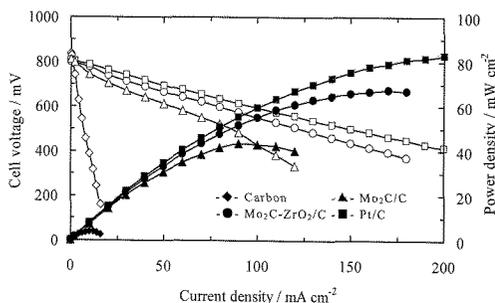


Figure 8. Cell voltage and power density vs. current density of fuel cells with  $\text{Mo}_2\text{C}/\text{C}$ ,  $\text{Mo}_2\text{C}-\text{ZrO}_2/\text{C}$ , Pt/C, and carbon anodes at  $250^\circ\text{C}$ .

#### 4. CONCLUSIONS

Performance of a fuel cell that employs  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  as the electrolyte was evaluated at low relative humidities and in the temperature range of  $150\text{--}300^\circ\text{C}$ . The cathodic polarization was significantly improved by applying an intermediate layer of  $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$  and 30 wt% Pt/C catalyst powders at the interface between the electrolyte and cathode. The resulting power density reached  $152 \text{ mW cm}^{-2}$  at  $250^\circ\text{C}$  with the 1.0-mm-thick electrolyte. More importantly, the present fuel cell showed excellent tolerance for 10% CO and good thermal stability in unhumidified conditions.

It was found that  $\text{Mo}_2\text{C}-\text{ZrO}_2/\text{C}$  anode catalyst is a promising alternative to Pt/C at the intermediate temperatures. The addition of  $\text{ZrO}_2$  to  $\text{Mo}_2\text{C}$  anode catalyst allowed the  $\text{Mo}_2\text{C}$  to become highly dispersed on the carbon support, so that the catalytic activity could be improved to the level of the Pt catalyst.

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