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A High-Performance Mo_2C-ZrO_2 Anode Catalyst for Intermediate-Temperature Fuel Cells

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Anode performance of non-Pt catalysts for hydrogen oxidation was investigated in intermediate-temperature proton exchange membrane fuel cells. Molybdenum carbide (Mo_2C) showed the highest catalytic activity among the transition metal carbides tested. Furthermore, the catalytic activity of Mo_2C was significantly improved by the addition of ZrO_2 to the anode. Transmission electron microscopy and X-ray diffraction measurements revealed that Mo_2C was more highly dispersed in the Mo_2C-ZrO_2/C than in the Mo_2C/C, suggesting that the particle growth of Mo_2C was suppressed by the addition of ZrO_2. We also tested the performance of a fuel cell using Mo_2C-ZrO_2/C and $Sn_{0.9}In_{0.1}P_2O_7$ as the anode and electrolyte materials, respectively, between 150 and 300°C. At 250°C or higher, the Mo_2C-ZrO_2/C anode showed a cell performance comparable to that of the Pt/Canode. However, cell performance was strongly dependent on the operating temperature, reflecting that the catalytic activity of Mo_2C-ZrO_2 was greatly lowered by the decrease in operating temperature. Thus it was concluded that the Mo_2C-ZrO_2 catalyst is a promising alternative anode material to Pt, especially at intermediate temperatures.
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Recently, proton exchange membrane fuel cells (PEMFCs) have received increasing attention as next generation alternative power sources because of their high efficiencies and environmentally friendly characteristics. Proton-conducting fluoropolymers such as Nafion are commonly used as electrolyte membranes. However, these electrolytes present some challenges regarding technology and materials costs for the commercialization of PEMFCs.[1] Because protons attach themselves to water and diffuse as H_3O^+ 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. 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.[2-7]

We recently found that an anhydrous proton conductor, 10 mol% In^{3+}-doped SnP_2O_7 ($Sn_{0.9}In_{0.1}P_2O_7$), showed high proton conductivities above 0.1 S cm^{-1} between 150 and 350°C under unhumidified conditions.[8-11] The electromotive force values of a hydrogen concentration cell using this material were very near the theoretical values calculated by Nernst's equation, indicating that the ionic transport number was 0.97. A hydrogen/air fuel cell with a 0.35 mm thick $Sn_{0.9}In_{0.1}P_2O_7$ electrolyte could yield a high power density of 264 mW cm^{-2} at 250°C. Furthermore, the fuel cell showed excellent tolerance toward 10% CO and good thermal stability under unhumidified conditions. However, there still remains the need to use Pt/C electrodes to achieve reasonable cell performance.

To date, low Pt loadings have been achieved by increasing the utilization of Pt and by alloying Pt with transition metals.[12,13] However, there are no alternative electrodes showing as high a performance as Pt-based electrodes. Transition metal carbides such as Mo_2C and WC have been reported as potential catalysts for many chemical reactions because of their Pt-like behavior at elevated temperatures.[14-23] Mo_2C has also been investigated as an anode catalyst for PEMFCs,[24,25] although its catalytic activity for electrochemical hydrogen oxidation is not high enough to meet the criteria for an alternative material. It is likely that the low catalytic activity of this material results from the low-temperature operation below 100°C.

In this paper, we report the anode performance of Mo_2C-based catalysts toward hydrogen oxidation at intermediate temperatures between 150 and 300°C. The overpotential of Mo_2C was compared with those of other transition metal carbides and a Pt catalyst. Moreover, the catalytic activity of Mo_2C was improved by the addition of different metal oxides to the anode. Performance of a fuel cell with the optimized Mo_2C catalyst was evaluated in the temperature range from 150 to 300°C.

Experimental

Electrode preparation.— The Mo_2C/C anode was fabricated as follows. A $MoCl_5$ precursor was impregnated onto a carbon support (Black Pearls, Brunauer-Emmett-Teller surface area = 1500 m^2 g^{-1}). The impregnated sample was reduced in a 10 vol % H_2/Ar mixture at 500°C for 2 h and then carburized in a 20 vol % CH_4/H_2 mixture at 700°C for 3 h. Other transition metal carbides, MxC/C (M = W, Ni, Co), were prepared in a similar manner, although their carburization temperatures ranged from 700 to 1000°C, depending on the materials. The loading of all the carbides was 30 mg cm^{-2}. The Mo_2C/C anode was also modified by impregnating $MoCl_5$ along with various other metal chlorides or oxychlorides, such as $ZrCl_2O{\cdot}8H_2O$. Subsequent treatments were the same as those for Mo_2C. A Pt/C catalyst (30 wt % Pt/C, Tanaka Kikinzoku Kogyo) was used for comparison. The catalyst powder was mixed with 10% poly(vinylidene fluoride) (PVdF) binder in 1-methyl-2-pyrrolidinone (NMP) solvent using a mortar and pestle. However, because there is a possibility that PVdF melts above 200°C, the use of a more thermal-resistant binder would be necessary for practical applications. The mixture was coated on a carbon paper (Toray TGPH-090). This sample was then dried for 1 h at 90°C, followed by 1 h at 130°C. A commercial Pt/C cathode (10 wt % Pt/C, 0.6 mg Pt cm^{-2}) was purchased from E-TEK, Inc. The microstructure of the catalysts was analyzed using X-ray diffraction (XRD, Shimazu XRD-600) and transmission electron microscopy (TEM, Hitachi H-800).

Electrolyte preparation.— $Sn_{0.9}In_{0.1}P_2O_7$ was prepared as described in our previous study.[9] The corresponding oxides (SnO_2 and In_2O_3) were mixed with 85% H_3PO_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 1.0 mm thick and 14.0 mm in diam under a pressure of 2×10^3 kg cm^{-2}.

Fuel cell tests.— The anode and cathode (area = 0.5 cm^2) were attached on opposite sides of the $Sn_{0.9}In_{0.1}P_2O_7$ electrolyte. 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

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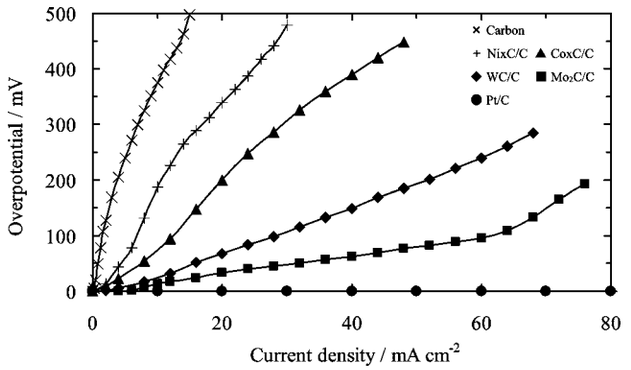

Figure 1. Anodic overpotentials of various carbon-supported transition metal carbide catalysts at 250°C. For comparison, the results obtained for Pt/C and carbon anodes are shown as well.

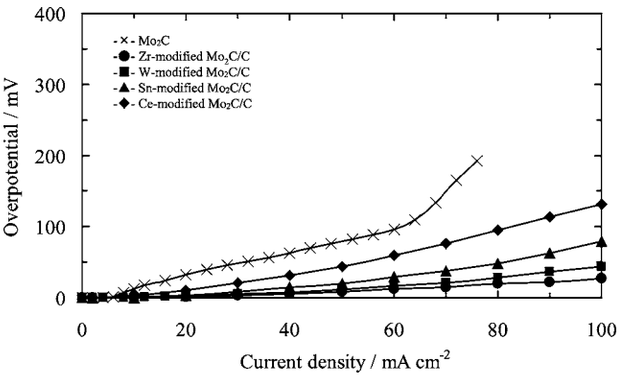

Figure 2. Anodic overpotentials of modified Mo_2C/C anodes at 250°C.

air chambers were supplied with unhumidified hydrogen and air, respectively, at a flow rate of 30 mL min^{-1} between 150 and 300°C. The anodic overpotentials 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.

Results and Discussion

The anodic overpotentials of carbon-supported transition metal carbide anodes at 250°C are plotted in Fig. 1, including the results for Pt/C and carbon anodes. While the Pt/C anode showed negligibly small overpotentials, the carbon anode had significantly large overpotentials. The polarization resistances estimated from the slope of the potential vs the current density were 0.16 Ω cm^2 for Pt/C and 33.13 Ω cm^2 for carbon. Clearly, the catalyst-free hydrogen oxidation proceeded at a very slow rate even at 250°C. On the other hand, all of the metal carbide anodes showed lower overpotentials than that of the carbon anode. In particular, the Mo_2C/C anode exhibited the best performance among the carbides tested; the polarization resistance was 2.13 Ω cm^2. It is known that Mo_2C shows significant catalytic activities toward hydrogenation,[18-20] dehydrogenation,[21] hydrodenitrogenation,[22] and water gas shift reactions,[23] compared with the other metal carbides. It is also reported that Mo_2C has catalytic characteristics similar to those of Pt-group metals. Choi et al. have explained the unique catalytic activity of Mo_2C by the change in the electron density of the d-band of Mo upon its carburization.[16] The introduction of C atoms into the Mo metal lattice leads to an increase in the lattice parameters, causing a contraction of the d-band and thus an enhanced d-electron density in the d-electron density levels of noble metals. However, Fig. 1 also shows that the performance of the Mo_2C/C anode was still considerably inferior to that of the Pt/C anode. In addition, there was an increase in the overpotential of the Mo_2C/C anode at high current densities, indicating a significant concentration overpotential based on mass transportation limitation. This may be due to an insufficient spill-over of hydrogen, causing a low hydrogen diffusion rate.

An attempt was made to improve the Mo_2C catalyst by the addition of various promoters to the catalyst. The chlorides or oxychlorides of Sn, Ce, W, and Zr were impregnated together with $MoCl_5$ onto a carbon support and then carburized at 700°C. As described below, the promoters were confirmed to be oxides rather than carbides after carburization. Figure 2 shows the anodic overpotentials of the unmodified and modified Mo_2C/C anodes at 250°C. All of the modified Mo_2C/C anodes, in particular Mo_2C-ZrO_2/C, showed considerably lower overpotentials compared to the unmodified Mo_2C/C anode. Moreover, there were no large increases in overpotential at high current densities. We chose ZrO_2, which showed the best performance, as a promoter for subsequent experiments.

Figure 3 shows the anodic overpotentials of the modified Mo_2C/C anodes with different weight ratios of Mo_2C to ZrO_2 at 250°C. The overpotential decreased with increasing amount of ZrO_2 and reached a minimum at a weight ratio of Mo_2C:ZrO_2 of 1:0.2. The polarization resistance was 0.28 Ω cm^2, which was approximately one order of magnitude lower than that of the unmodified Mo_2C/C anode. On the other hand, the overpotential of the ZrO_2/C anode was much higher than that of the Mo_2C/C anode; the polarization resistance was 9.7 Ω cm^2. This result indicates that the effect of ZrO_2 shown in Fig. 3 is not attributable to the catalytic activity of ZrO_2 itself toward hydrogen oxidation.

To better understand the above effect of ZrO_2, the microstructure of the Mo_2C-ZrO_2/C catalyst was characterized by XRD and TEM measurements. Figure 4 shows XRD profiles of the Mo_2C/C and Mo_2C-ZrO_2/C catalysts. In the XRD profile of Mo_2C/C, all the diffraction peaks were identical to those reported for Mo_2C in the literature[16] and no peaks of Mo metal and oxides were detected. The XRD profile of Mo_2C-ZrO_2/C revealed that the added Zr species was present as ZrO_2. In addition, the diffraction peaks of Mo_2C were not shifted by the addition of ZrO_2 to the catalyst, suggesting no incorporation of Zr into the crystalline lattice of Mo_2C. The Scherrer formula was used to estimate the particle size of Mo_2C. The estimated particle sizes were 28 and 13 nm for Mo_2C/C and Mo_2C-ZrO_2/C, respectively. A similar difference was observed in the particle size of Mo_2C, as revealed by transmission electron microscopy (TEM) measurements of the two catalysts. As shown in Fig. 5, the TEM images indicated that the particle sizes of Mo_2C were 16–34 nm and 10–16 nm for Mo_2C/C and Mo_2C-ZrO_2/C, respectively. These results indicate that the Mo_2C particles showed a higher dispersion with ZrO_2 than without ZrO_2. It is likely that excessive sintering of Mo_2C during carburization is inhibited in the

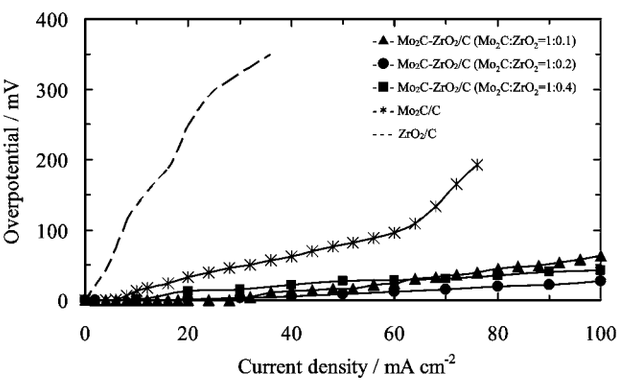

Figure 3. Anodic overpotentials of Mo_2C-ZrO_2/C anodes with different weight ratios of Mo_2C to ZrO_2 at 250°C.

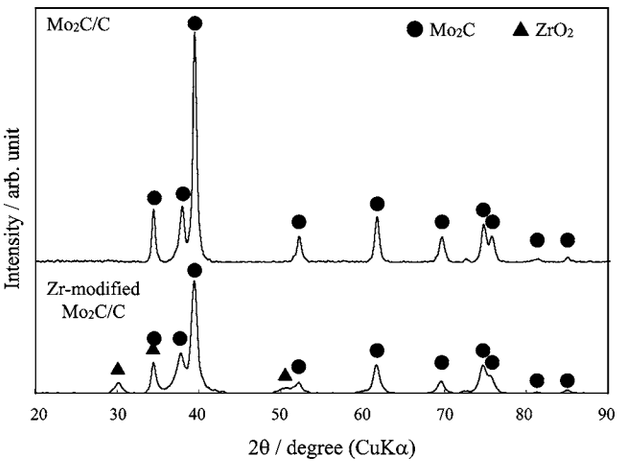

Figure 4. XRD profiles of Mo_2C/C and Mo_2C-ZrO_2/C.

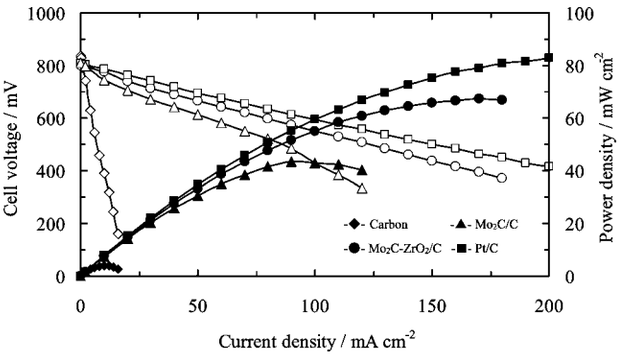

Figure 6. Cell voltage and power density vs current density of fuel cells with Mo_2C/C, Mo_2C-ZrO_2/C, Pt/C, and carbon anodes at 250°C. The thickness of the $Sn_{0.9}In_{0.1}P_2O_7$ electrolyte was 1 mm. The fuel and air chambers were supplied with unhumidified hydrogen and air, respectively, at a flow rate of 30 mL min^{-1}.

presence of ZrO_2, resulting in the significantly improved catalytic activity of Mo_2C toward hydrogen oxidation. Naito et al. have reported that ZrO_2 was an effective support for Mo_2C in the reforming of CH_4 by CO_2 compared to other support materials such as SiO_2, Al_2O_3, ZrO_2, TiO_2, and CeO_2.[19] XPS analysis revealed a strong electronic interaction between Mo_2C and ZrO_2 in the Mo_2C/ZrO_2 catalyst. This interaction may be another reason for the promotive effect of ZrO_2 on Mo_2C.

Cell performance using the Mo_2C-ZrO_2/C anode was evaluated at 250°C under unhumidified H_2/air fuel cell conditions. Figure 6 compares the cell performance using the Mo_2C-ZrO_2/C anode with those using the Mo_2C/C, Pt/C, and carbon anodes at 250°C. The open-circuit voltages (OCVs) of all the fuel cells tested were between 0.80 and 0.85 V, which are lower than the theoretical value of ~1.1 V. The low OCVs are due to the physical leakage of gas through the electrolyte and partial electron-hole conduction in the electrolyte, as reported in previous studies.[9] Note that while limiting current behavior was observed for the Mo_2C/C anode at high current densities, no change in the current-voltage slope was observed for the Mo_2C-ZrO_2/C anode, suggesting an enhanced hydrogen spill-over on the highly dispersed Mo_2C. More importantly, there is not a large difference in cell performance between the Mo_2C-ZrO_2/C anode and the Pt/C anode; the power density was 67 mW cm^{-2} for Mo_2C-ZrO_2/C and 84 mW cm^{-2} for Pt/C. This demonstrates that Mo_2C-ZrO_2/C has a high potential as an anode catalyst for PEMFCs. However, this is not applicable to operation below 250°C. It can be seen from Fig. 7 that the cell performance with the Mo_2C-ZrO_2/C anode was strongly dependent on the operating temperature; the peak power density reached 76 mW cm^{-2} at 300°C, but was significantly decreased at 200°C (35 mW cm^{-2}) and 150°C (28 mW cm^{-2}). The anodic overpotential measurements showed that the polarization resistance increased significantly with decreasing temperature, especially below 200°C; the polarization resistance was 1.57 Ω cm^2 at 200°C and 2.15 Ω cm^2 at 150°C. Thus, it is concluded that the Mo_2C-ZrO_2/C anode needs to be operated above 200°C for it to be an effective alternative to Pt-based anodes.

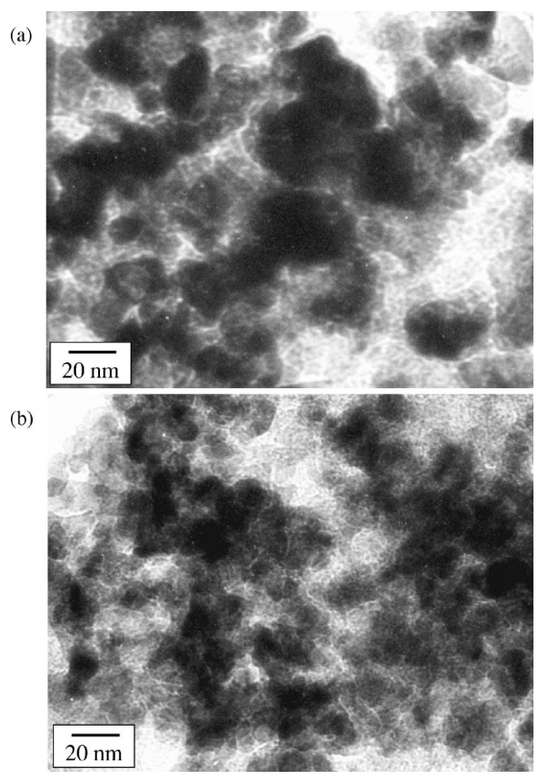

Figure 5. TEM images of Mo_2C/C and Mo_2C-ZrO_2/C. The catalysts and carbons are shown as black and gray, respectively.

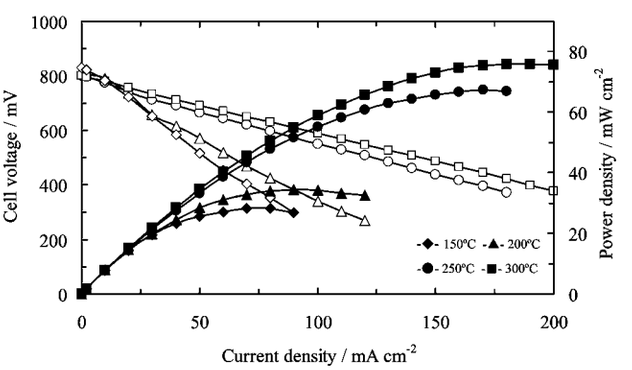

Figure 7. Cell voltage and power density vs current density of fuel cells with Mo_2C-ZrO_2/C anode at different temperatures. The experimental conditions are the same as those shown in Fig. 6.

Conclusions

Anode performance of Mo_2C-based catalysts was studied at intermediate temperatures between 150 and 300°C. Although the Mo_2C catalyst showed the lowest polarization resistance at 250°C among all the transition metal carbide catalysts tested, its performance was still insufficient compared to that of a Pt catalyst. However, the addition of ZrO_2 to the catalyst allowed the Mo_2C to become highly dispersed on the carbon support, so that the catalytic activity could be improved to the level of the Pt catalyst. A fuel cell using the Mo_2C-ZrO_2/C and $Sn_{0.9}In_{0.1}P_2O_7$ as the anode and electrolyte, respectively, yielded a peak power density of 67 mW cm^{-2} at 250°C, which was close to the peak power density of 84 mW cm^{-2} obtained using a fuel cell with the Pt/C anode. This high performance of the Mo_2C-ZrO_2/C anode was achieved by intermediate-temperature operation above 200°C.

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