Electrochemical Impedance Study of Carbon-Supported Pt/Mo-Oxide for CO-Tolerant Anode Catalyst

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The CO-tolerance of a carbon-supported Pt/Mo-oxide (Pt/MoOx/C) anode in proton-exchange membrane fuel cells was examined by electrochemical impedance spectroscopy. A pseudo-inductive loop was clearly observed only for a Pt/MoOx/C anode at low anodic polarizations, which indicates the onset of the electro-oxidation of adsorbed CO (CO_{ad}) on the Pt/MoOx/C catalyst. The CO-tolerance of Pt/MoOx/C at low anodic polarizations is mainly ascribed to the combination of the electro-oxidation of CO_{ad} and the removal of CO by the water-gas shift reaction depending on the operating conditions.

Key Words : PEMFC, Electrocatalyst, Molybdenum Oxide, Carbon Monoxide

1 Introduction

The poisoning of an anode catalyst by carbon monoxide (CO) is a main cause of anodic voltage loss in reformate-feed PEMFCs.¹⁾ To overcome this loss due to CO-poisoning, many Pt-based catalysts including alloys and oxides have been proposed.²⁾ Although carbon-supported PtRu alloys (PtRu/C) are state-of-the-art anode catalysts, the CO-tolerance of PtRu is still unsatisfactory for higher CO concentrations. In addition, the limited availability of Ru may become a significant problem before the mass production of PEMFC systems can be realized.

As alternatives to a PtRu catalyst, PtMo alloy catalysts have attracted considerable attention due to their high catalytic activity in the anodic oxidation of H₂ under CO/H₂ feed.³⁾ Previously, we reported the improved CO-tolerance of a carbon-supported nano-sized Pt/Mo-oxide (Pt/MoOx/C) heterogeneous catalyst.^{4,6)} Polarization measurements combined with gas analyses at the anode outlet revealed that Pt/MoOx/C shows better CO-tolerance than PtRu/C for CO/H₂ mixtures and they have different mechanisms for the toleration of CO at low potentials (< 100 mV vs RHE); the CO-tolerance of Pt/MoOx/C is mainly due to the higher catalytic activity for the water-gas shift (WGS) reaction (eq.1) and the electro-oxidation of CO (eq.2).

Electrochemical impedance spectroscopy (EIS) is a useful tool for analyzing electrochemical processes at a steady state by using an alternating signal of small magnitude to perturb the cell. EIS has the advantage of separating different rate processes in the frequency domain, and this technique has been demonstrated to provide valuable information for processes that involve the

adsorption of CO on the catalyst surface in a PEMFC.^{7,8)} In this paper, the anodic reaction on a Pt/MoOx/C anode under CO/H₂ feed in PEMFC was examined by EIS measurements, and the intrinsic CO-tolerance properties of Pt/MoOx/C at low anodic polarizations are discussed.

2 Experimental

The Pt/MoOx/C electrocatalyst was prepared in-house by following the procedure described in previous reports.^{4,6)} Briefly, MoCl₅ (Aldrich, reagent grade) was used as a Mo source for MoOx deposition. The carbon support material (Vulcan XC-72R, Cabot) was dispersed in MoCl₅ solution to give 9 wt.% Mo content (nominal), and the pH of the solution was then adjusted to 7-8 by the addition of 2.5% (CH₃)₄NOH (Wako, reagent grade) solution to precipitate hydrous MoOx on the support. After filtering, drying and washing, the Mo-deposited carbon was heated at 400 °C for 6 h under flowing N₂ to obtain stable MoOx/C catalyst. For Pt deposition on the MoOx/C catalyst, Pt(NO₂)₂(NH₃)₂ solution was used. The Pt-impregnated MoOx/C was reduced at 250 °C for 5 h under flowing H₂ atmosphere to give Pt/MoOx/C catalyst. The catalyst metal (Pt) loading density was 30 wt.% for Pt/MoOx/C throughout this study. To compare the CO-tolerance properties of the prepared Pt/MoOx/C catalysts with the state-of-the-art PtRu/C catalyst, 45 wt.% PtRu(1:1)/C supplied from Johnson Matthey Inc. (HiSPEC7000 Fuel Cell Catalyst) was used as a standard anode catalyst. As a cathode catalyst, we used 40 wt.% Pt/C (Johnson Matthey Inc., HiSPEC4000 Fuel Cell Catalyst).

The CO-tolerance properties of the catalysts were examined by testing the performance of a small-scale single cell (active area of 2 or 10 cm²). Membrane electrode assemblies (MEAs) were prepared by the “decals method”. Catalyst “ink” was prepared by mixing catalyst

material, ionomer solution (5 wt.% Nafion, Aldrich) and 2-propanol (Wako, reagent grade). Ionomer/carbon weight ratios were *ca.* 0.5/1. The catalyst slurry-coated PTFE films for the anode and cathode were placed on both sides of a pre-treated Nafion112 membrane and then hot-pressed at 140 °C for 2 min to form MEA. Specific catalyst loadings for anode and cathode are given in the figure captions.

Evaluations of cell performance and CO-tolerance were conducted using a custom in-house test bench. As anode reactants, pure hydrogen and CO(80 or 100 ppm)/H₂ were used to examine the poisoning effect of CO in the fuel stream. As a cathode reactant, pure oxygen was supplied in large excess (100 mL min⁻¹) to avoid any instability associated with mass transport in the cathode. During fuel cell testing, the cell was maintained at 80 °C and at atmospheric pressure. The reactants were humidified by bubbling the gases through water in stainless steel bottles thermostated at 80 °C. The current-voltage relationships (polarization curves) of the cells were obtained galvanostatically using a PC-controlled electronic load system (Scribner Associates Inc., Model890CL). All of the electrochemical impedance spectra were recorded using a Solartron SI1260 frequency response analyser/SI1287 potentiogalvanostat system. The impedance spectra were measured in the frequency range of 5 kHz to 10 mHz under the constant current mode, and the applied amplitude was set to 10 % of DC current. To obtain impedance spectra of the anode and cathode separately, a small auxiliary electrode was placed beside the anode to serve as a reference electrode.

3 Results and Discussion

Figure 1 shows typical steady-state polarization curves of single cells using Pt/MoOx/C catalyst as an anode on pure H₂ and CO(80 ppm)/H₂ with a fuel utilization factor (*U_f*: a inverse of fuel stoichiometry) of 0.7 along with that using PtRu/C catalyst. While the cell performances are

Fig. 1 Polarization curves of a single cell with Pt/MoOx/C and PtRu/C anodes under pure H₂ and CO(80 ppm)/H₂. Cell operating conditions; cell temperature: 80 °C, reactant gases: humidified at 80 °C without back-pressure. Catalyst loadings; anode: *ca.* 0.3 mg-Pt cm⁻² (0.4 mg-PtRu cm⁻²), cathode: 0.5 mg-Pt cm⁻².

very similar under feeding with pure H₂, the effects of 80 ppm CO on cell voltage vary depending on the anode catalyst; Pt/MoOx/C showed a smaller voltage loss on CO(80 ppm)/H₂ than PtRu/C, as shown in a previous paper.⁶⁾

The impedance spectra of Pt/MoOx/C and PtRu/C under the same operating condition (0.3 A cm⁻², 80 ppmCO/H₂, *U_f* = 0.05) are compared in Fig. 2. There is an apparent difference in the impedance plots in the low frequency range. The impedance plot of PtRu/C anode for CO/H₂ oxidation is a usual capacitive arc, whereas that of Pt/MoOx/C anode consists of a usual capacitive semi-circle followed by an additional pseudo-inductive semi-circle in the lower frequency range. Similar pseudo-inductive behavior has been reported for Faradaic processes involving adsorbed intermediates such as anodic corrosion reactions of metals.⁹⁾ Conway *et al.*⁹⁾ showed by the electrode kinetic model approach that a negative slope in plots of adsorbate coverage vs. electrode potential is associated with the pseudo-inductive behavior. For a PEMFC system, such pseudo-inductive impedance plots have also been reported for CO/H₂^{7,8)} and methanol¹⁰⁾ oxidation reactions on Pt/C or PtRu/C anodes at relatively high anodic polarizations (> 0.3-0.55 V, depending on the experimental conditions). Ciureanu *et al.*⁷⁾ reported that the appearance of the characteristic inductive loop for the anode fed with CO/H₂ is an indication of the onset of electro-oxidation of the adsorbed CO on Pt/C or PtRu/C. Considering the similarity of the Pt-based catalyst between Pt/C and Pt/MoOx/C, it is reasonable to expect that the origin of the pseudo-inductive behavior of Pt/MoOx/C should also be the electro-oxidation of CO_{ad}.

Figure 3 shows the Tafel plots of anodic polarizations (η_a) of Pt/MoOx/C and PtRu/C anodes. At the cell operating condition of Fig. 2 (current density of 0.3 A cm⁻², *U_f* = 0.05), both Pt/MoOx/C and PtRu/C anodes show similar low anodic polarizations; η_a are *ca.* 60 and 40 mV vs RHE at 0.3 A cm⁻², respectively. These anodic polarizations are much lower than the reported onset potential

Fig. 2 Impedance plots of Pt/MoOx/C and PtRu/C anodes at 0.3 A cm⁻², *U_f* = 0.05 under CO(80 ppm)/H₂ feed. The numbers in the diagram indicate the frequency (Hz). Cell operating conditions; see Fig. 1.

of pseudo-inductive loops for Pt/C or PtRu/C anodes ($E > 0.3$ – 0.55 V),⁷⁾ as described above.

Previously, we reported the results of comparative evaluations of the CO-tolerance of Pt/MoOx/C and PtRu/C anodes by polarization measurement (0.3 A cm^{-2} , 80 ppm CO/H_2) combined with CO concentration analyses at the anode outlet.⁶⁾ For the Pt/MoOx/C anode, a decrease in the CO concentration was observed regardless of the anode potential, which indicates that Pt/MoOx/C catalyst facilitates CO oxidation by WGS reaction (eq. 1), and partly by electro-oxidation reaction (eq. 2). In contrast, a decrease in the CO concentration was not observed for PtRu/C anode, which indicates that PtRu/C catalyst does not proceed both WGS and electro-oxidation reactions at low anodic polarizations including open-circuit conditions. Therefore, appearance of the inductive loop for the impedance plot of Pt/MoOx/C in Fig. 2 clearly shows that the electro-oxidation of CO_{ad} proceeds even at such a low anodic polarization only for Pt/MoOx/C anode.

The CO-tolerance of Pt/MoOx/C catalyst depends on the operating condition such as current density, and U_i . Figure 4 shows the impedance spectra of the Pt/MoOx/C anode at different current loading conditions. A pseudo-inductive loop was observed for plots at a current density $\geq 0.2 \text{ A cm}^{-2}$, whereas an inductive loop disappeared at 0.1 A cm^{-2} ; this fact indicates that anodic polarization at 0.1 A cm^{-2} ($\eta_a \approx 20 \text{ mV}$ from Fig. 3) was not enough for the electro-oxidation of CO_{ad} on Pt/MoOx/C. Thus, the onset potential for CO_{ad} oxidation on Pt/MoOx/C should lie between 20 and 40 mV. This result agrees with that reported by Crabb *et al.*¹¹⁾ with PtMoOx/C catalyst in $1 \text{ M H}_2\text{SO}_4$ at 353 K , which showed CO oxidation activity at potentials above 25 mV vs RHE. The electro-oxidation of CO is thermodynamically possible reaction at H_2 -fed anode because the standard electrode potential $E^0(25^\circ\text{C})$ of the electro-oxidation of CO (eq. 2) is -0.106 V .¹²⁾ Thus, it appears that the activation of the electro-oxidation reaction of CO on the Pt/MoOx/C anode needs anodic polarization of *ca.* 0.13–

0.15 V. Therefore, at the potentials examined here (0–100 mV vs RHE), the Pt/MoOx/C anode shows two regions divided by the onset potential of the electro-oxidation of CO_{ad} ; the catalytic WGS reaction dominates below the onset potential, whereas both WGS and the CO_{ad} electro-oxidation reaction take place beyond this potential.

The impedance patterns of the Pt/MoOx/C anode at different U_i conditions are compared in Fig. 5. The anode was fed $\text{CO}(80 \text{ ppm})/\text{H}_2$ and the loading current was set at 0.5 A cm^{-2} . The electrode impedance decreased dramatically with an increase in U_i from 0.08 to 0.5, which suggests that CO-poisoning of the Pt/MoOx/C anode is alleviated under high U_i conditions. In fact, the anodic polarization of Pt/MoOx/C anode at high U_i condition is much smaller than that of low U_i as shown in Fig. 3. In addition, the pseudo-inductive loop for high U_i is much smaller than that for low U_i . Since WGS (eq. 1) is thermodynamically possible reaction at 80°C ($\Delta G_r^{\text{shift}} = -26.4 \text{ kJ/mol}$)¹³⁾ and the equilibrium of the WGS reaction lies much more to the right due to the small space velocity of fuel under high U_i conditions, the CO concentration

Fig. 4 Impedance plots of Pt/MoOx/C anode at different current densities (0.1, 0.2, 0.3 and 0.5 A cm^{-2}) under $\text{CO}(80 \text{ ppm})/\text{H}_2$ feed. Cell operating conditions; see Fig. 1.

Fig. 3 Anodic polarization vs. current density plots of Pt/MoOx/C and PtRu/C anodes at constant fuel flow rate (equivalent to $U_i = 0.05, 0.33$ at 0.3 A cm^{-2}) under $\text{CO}(80 \text{ ppm})/\text{H}_2$ feed. Cell operating conditions; see Fig. 1.

Fig. 5 Impedance plots of Pt/MoOx/C anode at different U_i conditions (0.08 and 0.5) under 0.5 A cm^{-2} loading and $\text{CO}(80 \text{ ppm})/\text{H}_2$ feed. The numbers in the diagram indicate the frequency (Hz). Cell operating conditions; see Fig. 1.

decreases significantly (≈ 20 ppm at the anode outlet).⁶⁾ This leads to the low anodic polarization and small pseudo-inductive loop at high U_f conditions.

4 Conclusions

The CO-tolerance of a Pt/MoOx/C anode was examined by electrochemical impedance analyses. Even at anodic polarizations as low as 40 mV vs. RHE, a characteristic pseudo-inductive loop was observed in the impedance plots for Pt/MoOx/C, which indicates that the electro-oxidation of CO_{ad} on the Pt/MoOx/C catalyst proceeds at such low potentials. This result shows that the electro-oxidation reaction of CO_{ad} plays an important role in the CO-tolerance of Pt/MoOx/C anode under practical operating conditions.

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