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Effect of Coating by Perfluorosulfonated Ionomer Film on Electrochemical Behaviors of Pt(111) Electrode in Acidic Solutions

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Electrochemical behaviors of bare and perfluorosulfonated ionomer (PFSI) film-coated Pt(111) electrodes in perchloric and sulfuric acid solutions were investigated. While current peaks corresponding to specific adsorption and desorption of anions were clearly observed at the bare electrode, no such peaks were observed at the PFSI-coated electrode, showing that anions do not reach the electrode surface because of the cation-selective nature and/or adsorption of PFSI film. Although no structural change was observed by repetitive potential cycling as far as positive potential limit was more negative than that of oxide formation, significant structural change was noticed during potential cycling if the anodic potential limit was made more positive than oxide formation potential.

Fuel cells, particularly polymer electrolyte membrane fuel cells (PEMFCs), have attracted much attention because they can directly convert chemical energy, e.g., hydrogen, to electrical energy with very high theoretical conversion efficiency.[1] The main component of PEMFC is a membrane–electrode assembly (MEA), which is a PEM sandwiched by carbon-supported Pt catalyst layer coated by perfluorosulfonated ionomer (PFSI). Degradation of fuel cell performance is considered to be affected by PFSI. Thus, understanding of electrochemical properties and stability of PFSI-coated Pt electrodes is very important for the development of fuel cell catalysts.

Nafion®, a PFSI, is the most widely used PEM in MEA[2–5] because of its excellent proton conductivity and chemical durability. Electrochemical behavior of Nafion-coated Pt electrodes has been investigated using polycrystalline Pt, and it was found that recast Nafion film is electrochemically stable in the potential range between the onsets of H_2 and O_2 evolution.[6–9]

In this paper, we investigated the electrochemical behavior of a single-crystal Pt(111) electrode coated with Nafion film so that more detailed information on ion transport, interaction between Nafion and Pt, and potential dependent stability can be obtained.

A single-crystal platinum bead prepared by the Clavilier method[10] was cut and polished with diamond slurries down to 0.5 µm. The sample was annealed using an induction heater (AMBRELL, HOTSHOT 2 Ext.FF V4) at about 1600 °C for 10 h under Ar/H_2 flow.[11] Prior to each experiment, the sample was annealed under the same conditions for 30 min. The sample was cooled for 2 min in Ar/H_2 flow and then quenched in water saturated with Ar/H_2 gas. After surface water was removed by blowing N_2 gas, 15 µL of 10% Nafion solution (DE2020 CS, polymer content: 20–22 wt %, water: 34 wt %, 1-propanol: 44 wt %) was placed onto the sample surface. The sample was dried in air for 4 h before being baked in an oven for 1 h at 100 °C. The film thickness was determined by using a home-built laser microscope to be 300 µm. X-ray crystal truncation rod measurement confirmed that the Pt(111) surface was not affected by these treatments.[12]

Ultrapure reagent grade $HClO_4$ and H_2SO_4 were purchased from Wako Pure Chemicals. Water was purified by a Milli-Q system (Yamato, WQ-500).

The electrochemical measurements were carried out in a three-electrode cell in hanging meniscus configuration. A reversible hydrogen electrode (RHE) and a Pt wire were used as a reference and a counter electrode, respectively. All measurements were carried out at room temperature. For the measurements at a bare Pt electrode, the electrode was cleaned by potential cycling between 0.07 and 0.9 V vs. RHE in a 0.1 M $HClO_4$ solution or 0.07 and 1.1 V in a 0.1 M H_2SO_4 solution with a scan rate of 50 mV s^{-1} until reversible peaks were observed before recording a steady state cyclic voltammogram (CV). The CVs of the Nafion-coated electrodes were recorded after the electrode was held in a hanging meniscus configuration for 1 h at open circuit.

Figure 1 shows CVs of the bare (a, b) and Nafion-coated (c, d) Pt(111) electrodes in a 0.1 M $HClO_4$ solution between 0.07 and 0.9 V (a, c) and in a 0.1 M H_2SO_4 solution between 0.07 and 1.1 V (b, d). The CVs of the bare Pt(111) electrodes are identical to those reported previously.[10,13] The shapes of CVs did not change during successive potential cycling, showing that both the bare and Nafion-coated Pt(111) electrodes are stable within these potential regions.

The CVs of the Nafion-coated electrodes (c, d) are totally different from those of the bare Pt(111) electrode. Peaks

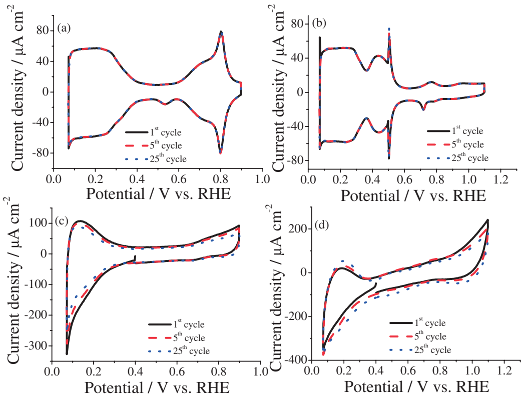

Figure 1. CVs of the bare (a, b) and Nafion-coated (c, d) Pt(111) electrodes in 0.1 M $HClO_4$ (a, c) and 0.1 M H_2SO_4 (b, d) solutions of the 1st, 5th, and 25th successive potential cycling. Scan rate: 50 mV s^{-1}.

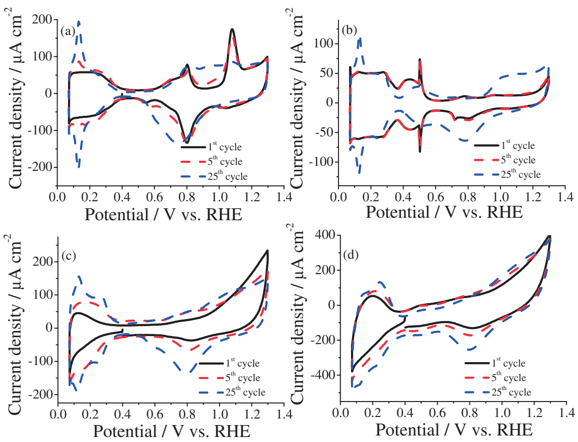

Figure 2. CVs of the bare (a, b) and Nafion-coated (c, d) Pt(111) electrodes in 0.1 M $HClO_4$ (a, c) and 0.1 M H_2SO_4 (b, d) solutions of the 1st, 5th, and 25th successive potential cycling. Scan rate: 50 mV s^{-1}.

corresponding to anion adsorption/desorption are absent, possibly due to strong adsorption of polymer chains on the Pt surface and/or the prevention of anion penetration into the Nafion film. The unique hydrogen adsorption/desorption waves at Pt(111) surface are also lost. This can be explained by the adsorption of polymer chains on the Pt surface, which was actually observed by ^{19}F NMR and AFM.[14] Hydrogen evolution reaction (HER) started at more positive potential than at the bare Pt(111) electrode due to lower pH within the Nafion film. HER proceeded smoothly, showing that proton is effectively transported through the Nafion film and that the adsorption of Nafion does not affect the HER kinetics.

Figure 2 shows CVs of the bare (a, b) and Nafion-coated (c, d) Pt(111) electrodes in 0.1 M $HClO_4$ (a, c) and 0.1 M H_2SO_4 (b, d) solutions when the positive potential limit was made more positive so that Pt oxide is formed. The CVs of the bare Pt(111) electrodes in both solutions at the first cycle show anion adsorption/desorption and oxide formation/reduction peaks, which are identical to those reported previously.[10,13] It has been reported that while Pt(111) electrode is oxidized via two steps in $HClO_4$, i.e., hydroxide adsorption at 0.8 V followed by Pt oxide formation at 1.1 V,[15] it is oxidized in one step and that oxide formation is suppressed to more positive potential in H_2SO_4 because of strongly adsorbed sulfate ion.[16] Successive potential cycling within this potential region leads to a loss of anion adsorption/desorption peaks and appearance of a new redox wave at 0.13 V in the hydrogen adsorption/desorption region, suggesting the formation of (110) substeps.[13,16,17] LEED pattern obtained after 25 potential cycles was still of (111) surface,[18] showing that the surface was composed of (111) terrace and (110) substeps. Not only hydrogen adsorption/desorption but also oxide reduction current increased, showing the increase of the electrochemically active surface area due to roughening of Pt(111) surface, with the number of potential cycles.

The CVs of the Nafion-coated Pt(111) electrodes in $HClO_4$ and H_2SO_4 solutions (c, d) in the 1st potential cycle are similar and show that anodic current started to flow around 1.0 V and that a relatively small cathodic peak was observed at 0.8 V. These behaviors in oxide formation/reduction region are similar to those observed at the bare Pt(111) electrode in H_2SO_4 solution and suggest that oxide formation takes place in one step in both solutions at the Nafion-coated Pt(111) electrode, since adsorbed Nafion polymer inhibits the adsorption of hydroxide species as is the case of sulfate anions at the bare Pt(111) surface in H_2SO_4 solution, although the less positive oxide formation potential at the Nafion-coated electrode suggests the weaker adsorption of Nafion.

Oxide reduction and hydrogen adsorption/desorption current increased with the number of potential cycles. However, the redox wave at 0.13 V corresponding to hydrogen adsorption/desorption at the (110) substep was not clear yet at the 5th cycle, suggesting that fluorocarbon backbones of Nafion polymer were detached from the surface Pt atoms by oxidation/reduction cycles leading to the simple increase of electrochemically active surface area at this stage. At the 25th potential cycle, new peaks were clearly observed at 0.13 and 0.28 V, corresponding to hydrogen adsorption/desorption at the (110) and (100) substeps, respectively,[13] showing the irreversible surface roughening of Pt surface as observed at the bare electrodes. Details of the structural change are now under investigation by quartz crystal microbalance, STM, LEED, and surface X-ray scattering.

In conclusion, electrochemical behaviors of the bare and Nafion-coated Pt(111) electrodes in $HClO_4$ and H_2SO_4 solutions were compared. Anion-dependent features observed at the bare electrode were not observed at the Nafion-coated electrode because anion penetration was prevented by permselectivity and/or strong adsorption of the Nafion layer. Although potential cycling in the double layer region did not cause any change, Nafion film was gradually detached from Pt surface by successive oxide formation/reduction cycles.

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