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Preparation and Evaluation of Boundary between Polymer Electrolyte and Platinum over Functionalized Proton-Conductive Carbon

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Abstract**—**Platinum nanoparticles have been reported with mean size of between 1.5 and 7 nm supported on carbon. The contact between Pt nanoparticles and C has rarely been controlled and monitored nanoscopically. In this paper, stable Pt nanoparticles with mean size of 1.2 nm were synthesized embedded on/in C matrix produced from ethyne over the Pt nanoparticles. The replica-Pt-C composite was synthesized inside the ordered mesopores (2.7 nm) of Al-MCM-41 followed by removal of silica. In polymer electrolyte fuel cells (PEFCs), it is important to secure proximate diffusion paths of reactants and electrons. The approach is to optimize the boundary between polymer electrolyte and Pt nanoparticle surface. Based on synchrotron X-ray absorption fine structure to monitor directly the status of catalysts of PEFCs, it was found that Pt sites of replica Pt–C were reduced to Pt^0 by alcohols contained in polymer electrolyte dispersion solution during the preparation of cathode of PEFC. As in membrane electrolyte assembly, only the Pt sites not covered by polymer electrolyte reoxidized to $Pt^{2+/4+}$. Based on this information, the interface between Pt and polymer electrolyte was optimized.

Keywords**—**Ordered mesoporous silica, Polymer electrolyte fuel cell, Platinum, Replica synthesis, XANES

I. INTRODUCTION

FOR polymer electrolyte fuel cells (PEFCs), active site exists at the triple phase boundary in the catalysts [1]. The solid, liquid, and gas phases play the roles of electron conduction, proton diffusion, and reactant gas diffusion, respectively. However, coincidence of the three factors depends on luck during preparation conditions of membrane electrolyte assembly (MEA), and triple phase boundary is in general very limited as points. Thus, it is important to extend the two-phase boundary from line to face to maximize the active sites of PEFC at the triple phase boundary.

The approach is to maximize the boundary between active platinum nanoparticles and proton-conducting polymer. It is still a difficult task to evaluate how much the surface of metal nanoparticle is covered with light and soft constituent, e.g. polymer electrolyte. In this work, the contact of Pt with C was controlled based on the idea of catalytic acetylene decomposition over Pt nanoparticles in narrow size distribution centered at 1.2 nm formed inside Al-exchanged ordered mesoporous silica Al-MCM-41 to produce Pt-C composites in mesopores. The replica-Pt-C composite was separated via the removal of Al-MCM-41 using hydrofluoric acid. Furthermore, the boundary formation between Pt nanoparticles and proton conducting polymer was monitored as the electronic state change of Pt sites by Pt L_3-edge X-ray absorption fine structure (XAFS). The electronic state is quite sensitive to the surrounding environment, i.e. proton conducting polymer and oxidative/reductive gas. Pt L_3-edge XAFS was recently applied to probe the one monolayer of Pt single crystal surface [2].

II. EXPERIMENTAL SECTION

Ten milliliters of 8.4 mM aqueous solution of tetraammineplatinum(II) hydroxide hydrate $Pt^{II}(NH_3)_4(OH)_2{\bullet}2H_2O$ (Strem Chemicals) and 1.0 g of Al-MCM-41 (molar ratio SiO_2/Al_2O_3 = 0.9875/0.0125, 1.11 wt% Al; Aldrich) were mixed and stirred at 353 K for 2 days. The suspension was filtered, washed, and heated in vacuum at 573 K for 2 h. Obtained powder (Pt-Al-MCM-41, 1.3 wt% Pt) was in 30 mL min^{-1} of H_2 (> 99.99%; 101 kPa) flow at 573 K for 2 h and then in 200 mL min^{-1} of C_2H_2 (> 98%) + N_2 (> 99.999%) flow (molar ratio 1:9, total 101 kPa) at 973 K for 1 h. The obtained black powder (0.72 wt% Pt) was treated with 30 mL of hydrofluoric acid (15%; Special Grade, Wako Pure Chemical) to give replica-Pt-C composite (0.84 wt% Pt). Amorphous C dissolves in hydrofluoric acid and Pt-graphite was preferably obtained [3,4]. Similar synthesis to this replica Pt–C was also reported using SBA-15 as a template for Pt–C [5] and Pt/Ru–C [6].

Nitrogen adsorption measurements were performed at 77 K with the pressures between 1.0 and 90 kPa in a vacuum system connected to diffusion and rotary pumps (10^{-6} Pa) and equipped with a capacitance manometer (Models CCMT-1000A and GM-2001, ULVAC). The samples were evacuated at 393 K for 2 h before measurements. High-resolution TEM images were taken using field-emission-type TEM equipment (JEOL, Model JEM-4000FX) with an accelerating voltage of 400 kV. Samples were dispersed in ethanol (>99.5%, Wako Pure Chemical) and mounted on amorphous C-coated copper mesh

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(CU150 Mesh, JEOL).

X-ray diffraction (XRD) data were obtained using a Rigaku MiniFlex diffractometer at a Bragg angle of $2\theta_B = 2 - 10^\circ$. Condition involved 30 kV and 15 mA, Cu Kα emission, and a nickel filter. The replica-Pt-C powder and each intermediate composites during the synthesis were set in a dip of $18 \times 2 \times 1$ mm^3 on glass plate to measure the electric conductivity with two-point method [7].

50 mg of above obtained replica Pt–C powder (6.1 wt% of Pt; average Pt particle size 2.0 nm) was suspended in 0.2 mL Nafion dispersion solution [diluted to 2.8–1.5% by mixing 5% solution (DE521, Wako Pure Chemical) with ethanol] and dried (replica Pt–C–Nafion). Pt L_3-edge XAFS spectra were measured at 290 K in transmission mode in the Photon Factory at the High Energy Accelerator Research Organization (KEK, Tsukuba) on the beamlines of 7C, 9C, and 12C [8,9]. The storage ring energy was 2.5 GeV and the current was 180–450 mA. Si(111) double crystal monochromator was used. The data were analyzed using the software package XDAP [10].

III. RESULTS

The specific surface area (S_{BET}) 970 m^2 g^{-1} for Al-MCM-41 decreased by 21% upon impregnation of Pt (Table I). In contrast to this partial block of mesopores, the S_{BET} for Pt-Al-MCM-41 decreased by 95% after catalytic ethyne decomposition, suggesting nearly complete block of mesopores by C formed. The loss of S_{BET} was recovered to 540 m^2 g^{-1} with the acid treatment (Table I).

The regularity of MCM-41 framework was monitored by XRD during the synthetic step of replica-Pt-C. The distance between pore and neighboring pore (a_0 of unit cell) was 4.7 nm (d_{100} = 4.1 nm) for Al-MCM-41 (Table I) [3,11]. The value decreased to 4.5 nm (d_{100} = 3.9 nm) upon impregnation of Pt. In contrast, no peak was detected in XRD for Pt-C-Al-MCM-41 probably because the electron density of C formed in Al-MCM-41 mesopores was similar to that of Al-SiO_2 template. The lower angle peaks recovered at d = 3.7 and 3.2 nm for replica-Pt-C composite, but the intensity was weaker compared to peak for Pt-Al-MCM-41. No distinct peaks derived from Pt or C crystalline were observed throughout the synthetic step of replica-Pt-C. After fuel cell test as cathode in MEA for 3 h, the replica-Pt-C composite was re-examined by XRD. No peak was observed in the range of $2\theta_B = 10 - 75^\circ$, suggesting the Pt particle size remained small.

The intensity of whiteline peaks above the Pt L_3 absorption edge (11562 eV for Pt metal) was greater for replica Pt–C (Table IIa) under air (1.59) than 1.28 for Pt metal foil (e). The whiteline peak intensity for replica Pt–C–Nafion (b, c) was 1.28–1.27, weaker than 1.44 for replica Pt–C in air (a). Immersed in pure ethanol, the whiteline peak intensity for replica Pt–C (d) decreased to 1.26, that was the smallest intensity among replica Pt–C samples (a–d).

IV. DISCUSSION

The changes of whiteline peak intensity above the Pt L_3 absorption edge were explained due to the change of oxidation states of Pt sites by forming the boundary between Pt nanoparticles and Nafion (Figure 1). Under air, the valence of surface Pt sites was the mixture of 4+, 2+, and 0 (Figure 1A) [14]. Similar oxidation/reduction trends of surface sites were monitored based on peaks near the absorption edges of V, Cu, and Sn K and Au and Pb L_3 [12–19].

Next, the oxidic surface Pt sites were reduced to Pt^0 when the Pt–C catalyst was immersed in Nafion dispersion solution (Figure 1B). The reduction was found by the reaction not with Nafion but with alcohol(s). 14–26% of 1-propanol and 46–72% of ethanol were contained in Nafion dispersion solution used (2.8–1.5%). The Pt sites in replica Pt–C sample were totally reduced to Pt^0 in a blank test by just immersed in ethanol based on the whiteline intensity became smaller (1.26) to essentially the same as that for Pt metal (1.28; Table IId, e).

$$m\mathrm{C}_n\mathrm{H}_{2n+1}\text{–OH} + \mathrm{PtO}_m \rightarrow m\mathrm{C}_{n-1}\mathrm{H}_{2n-1}\text{–CHO} + m\mathrm{H_2O} + \mathrm{Pt}^0$$
$$(m = 1, 2;\ n = 2, 3, \cdots)$$

This trend is consistent with the dispersion of Pt on C. The average particle size of Pt was 1.2–4.8 nm [8], and essentially total reduction to Pt^0 immersed in ethanol is acceptable for replica Pt–C (average 2.0 nm of Pt). The Pt nanoparticles of replica Pt–C were more surrounded by C synthesized from ethyne gas decomposed over Pt for replica Pt–C and thus the interface sites cannot contact with Nafion/alcohol. The interface between Pt and C for replica Pt–C was intensively investigated by state-sensitive Pt L_3-edge XAFS spectroscopy [8].

When the samples immersed in 2.8–1.5% Nafion dispersion solution were dried (Table IIb, c), a part of Pt surface protected with Nafion thin film remained as Pt^0 and the other part of Pt surface in direct contact with air was reoxidized to Pt^{2+} and Pt^{4+} (Figure 3C). In summary, Pt L_3 whiteline peak intensity for Pt–C catalysts in contact with Nafion was a sensitive indicator of the Nafion coverage over the Pt surface and thus the formation of the boundary between Nafion and Pt surface sites.

V.CONCLUSIONS

Pt nanoparticles introduced by cation group exchange and formed by heating in vacuum at 573 K inside Al-MCM-41 catalyzed ethyne decomposition to form C. The Al-MCM-41 template was removed with HF acid solution. Pt nanoparticles with mean size of 1.2 nm were obtained embedded on/in C matrix. The Pt loading was 0.84 wt%. The replica-Pt-C synthetic procedure was supported by the changes of specific S_{BET} value from 767 m^2 g^{-1} for Pt-Al-MCM-41 to 35 m^2 g^{-1} for Pt-C-Al-MCM-41 then to 540 m^2 g^{-1} for replica-Pt-C. The Pt particles could not be monitored by XRD both before and after cathode catalytic tests in PEFC, suggesting the stability of 1.2

nm-Pt particles embedded on/in C matrix. It was possible to maximize the boundary between proton conducting polymer and surface Pt sites based on the synchrotron X-ray monitoring of Pt valence state change dependent on the amounts and concentrations of Nafion dispersion solutions used.

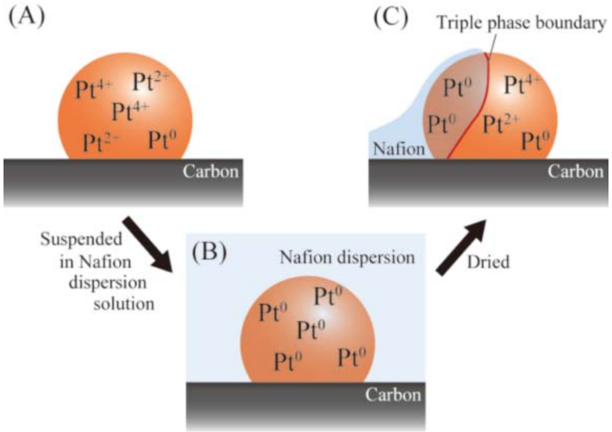

Fig. 1 Reduction and oxidation of surface Pt sites in Pt–C catalyst with Nafion. Pt was oxidized under air (A), reduced by alcohol in disperse medium (B), and partially re-oxidized under air (C).

TABLE I
PHYSICOCHEMICAL CHARACTERIZATION OF INTERMEDIATE AND FINAL MATERIALS IN THE REPLICA-PT-C COMPOSITE SYNTHESIS

SAMPLE	SPECIFIC SURFACE AREA (M^2 G^{-1})	PORE-PORE DISTANCE (NM)	PT LOADING (WT%)	PT–PT COORDINATION NUMBER	PT–O OR PT–C COORDINATION NUMBER	PT PARTICLE SIZE (NM)
Al-MCM-41	970	4.7				
Pt-Al-MCM-41	767	4.5	1.3			
Pt-C-Al-MCM-41	35		0.72	5.1	2.1	
Replica Pt-C	540		0.84	6.1	2.2	1.2

TABLE II
ENERGY POSITION (EV) AND NORMALIZED INTENSITY OF WHITELINE PEAK

SAMPLE	ENERGY (EV)	NORMALIZED INTENSITY
a Replica Pt–C under air	11566.7	1.59
b Replica Pt–C with 1.5% Nafion after dried	11566.8	1.28
c Replica Pt–C with 2.8% Nafion after dried	11566.8	1.27
d Replica Pt–C in ethanol	11566.7	1.26
e 5 μm thick Pt metal foil	11565.6	1.28
f PtO_2	11567.3	2.07

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