Electronic Supplementary Information (ESI) for

Third-body effects of native surfactants on Pt nanoparticle electrocatalyst

in proton exchange fuel cells

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S1. Experimental details

S1.1. Preparation of oleylamine-modified platinum nanoparticles (cPt-OA)

To compare with the unmodified carbon-supported platinum electrocatalysts (cPt), oleylamine-modified platium (cPt-OA) was prepared by simply mixing cPt and oleylamine in an organic solvent. All chemicals were analytic grade and were treated without purification. The detailed procedure is as follows: commercial Pt/C (20 wt %, Johnson Matthey, 500 mg) was dispersed in ethanol (100 mL, > 99.5 %, anhydrous, Sigma –Aldrich). After 10 min sonication, oleylamine (1.7 μ L, C₁₈H₃₇N, TCI) was added to the solution with vigorous stirring. After stirring overnight, the solution was filtered and the obtained particles were dried in a vacuum oven.

S1.2. Synthesis of platinum nanoparticles using oleylamine as a surfactant (sPt-OA)

The carbon-supported platinum nanoparticles (sPt-OA) were synthesized by the colloidal reduction method using oleylamine as the capping agent. The detail procedure is as follows: carbon black (0.15 g, Vulcan XC-72) and oleylamine (184 μ L, 0.57 mmol) were dispersed in ethanol (200 mL). After sonication, platinum (IV) chloride (0.064 g, 0.19 mmol, PtCl₄, > 99.99 %, Sigma-Aldrich) was added to the solution with magnetic stirring for 2 h. The reducing agent, sodium borohydride (0.1500 g, NaBH₄, 99.99%, Aldrich), was introduced to the above solution and stirred overnight for complete reduction. The mixture was filtered with ethanol and dried in a vacuum oven.

S.1.3. Characterization

Near edge X-ray absorption fine structure (NEXAFS) spectra of the C K edge were measured using the 4D beamline of the Pohang Light Source-II (PLS-II, 3 GeV). High-resolution transmission electron microscopy (HR-TEM) images were obtained with a Titan 80-300 (300 kV, FEI) and analyzed by the Gatan DigitalMicrograph software package. X-ray absorption near-edge structure (XANES) spectra of the Pt L_3 edge (E₀ = 11,564 eV) were measured using the 8C beamline of PLS-II. Data analysis was conducted using ATHENA program. X-ray diffraction (XRD, D/Max 2500, Rigaku) measurements were carried out in the 2 θ scan range of 20 ~ 90° at a scan rate of 0.5° min⁻¹. Thermogravimetric analysis (TGA) was performed with a

Q50 (TA Instruments) with a heating rate of 5 °C min⁻¹. X-ray photoelectron spectroscopy (XPS, Al K_{α}) spectra were obtained using a PHI 5000 (VersaProbe, UIvac-PHI) and calibrated against the C 1*s* peak as 284.6 eV. The Pt 4*f* spectrum was deconvoluted using the XPSPEAK4.1 software package.

S.1.4. Electrochemical measurements: half-cell

Electrochemical measurements were carried out using a three electrode system: i) a glassy carbon electrode (0.196 cm², working), ii) a saturated calomel electrode (SCE with saturated KCl, reference), and iii) a platinum wire electrode (counter). We prepared electrocatalyst inks: the electrocatalysts (0.015 g), 2-propanol (1200 μ L, Junsei), and a Nafion solution (85.8 μ L, 5 wt%, Aldrich). The catalyst ink (5 μ L) was dropped onto working electrode and pre-potential cycling was conducted until a stable curve was obtained. We used various electrolytes to confirm the third-body effect of the proposed catalysts, *i.e.*, 0.1 M HClO₄ (70%, Sigma-Aldrich), 0.1 M HClO₄ + 0.01M H₃PO₄ (85%, Sigma-Aldrich), and 0.1 M HClO₄ + 0.1 M H₃PO₄. Cyclic voltamograms (CVs) were obtained with a scan rate of 20 mV s⁻¹ under saturated Ar. Polarization curves for the oxygen reduction reactions (ORRs) were measured using a rotating disc electrode (RDE) technique with rotating speed of 1600 rpm and scan rate of 5 mV s⁻¹ under an O₂-saturated atmosphere. All electrochemical measurements were conducted using AUTOLAB potentiostat (Eco Chemie, PGSTAT) at room temperature, and the potentials were standardized with respect to a reversible hydrogen electrode (RHE).

S1.5. Electrochemical measurements: single-cell

To perform the single-cell measurements, membrane electrode assemblies (MEAs) were fabricated using a home-made H_3PO_4 doped para-polybenzimidazole (p-PBI) membrane with a gas diffusion electrode (GDE, 4 cm²).¹ For comparison, we utilized the different cathode electrocatalysts (1.5 mg cm⁻²), *i.e.*, cPt and sPt-OA using the spraying method on the gas diffusion layer (Sigracet 10BC, SGL Co.). To negate any contributions from the anode, commercial Pt/C (46 wt%, Tanaka Kikinzoku Kogyo, KK) was used as an anode electrocatalyst in both MEAs (2.2 mg cm⁻²). The electrochemical measurements were conducted using a PEMFC test station (CNL Energy Co.) at 160 °C. The gas feeds of the anode and cathode were non-humidified H_2 (55 sccm) and air (196 sccm), respectively. After an activation process (0.2 A cm⁻²), electrochemical impedance spectroscopy

(EIS, HCP 803, Bio-logic) was performed at different currents in the frequency range from 50 kHz to 30 MHz. Durability tests were carried out at a constant current density (0.2 A cm⁻²) over 150 h.



S2. Supplementary electrochemical data for cPt-OA

Fig. S1 CVs of cPt and cPt-OA in 0.1M HClO₄ + 0.1M H₃PO₄.

S3. X-ray diffraction spectra of sPt-OA



Fig. S2 XRD pattern of sPt-OA (black line) and a typical *fcc* structure of Pt (red line).

S4. Pt 4f spectrum of X-ray photoelectron spectroscopy (XPS) for sPt-OA



Fig. S3. The Pt 4*f* XPS spectrum for sPt-OA.

S5. Thermogravimetric analysis (TGA) of sPt-OA



Fig. S4 The TGA curve of sPt-OA.

S5. Current densities in a single cell scale



Fig. S5 Current densities normalized by Pt mass of the cPt and sPt-OA electrocatalysts (cathode: 0.30 and 0.26 mg_{Pt} cm⁻², respectively) at 0.6 V in a single cell using the H₃PO₄-doped PBI membrane without iR compensation. All measurements were conducted with H₂/air feeds at 160 °C.

S6. Reference

1 H.-J. Lee, B. G. Kim, D. H. Lee, S. J. Park, Y. Kim, J. W. Lee, D. Henkensmeier, S. W. Nam, H.-J. Kim, H. Kim and J.-Y. Kim, *Int. J. Hydrogen Energy*, 2011, **36**, 5521.