Electronic Supplementary Information

High Performance Pt-free Cathode Catalyst for Polymer Electrolyte Membrane Fuel Cells Prepared from Widely Available Chemicals

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Experimental

Polyimide particles

PMDA and ODA were purified by sublimation before use. A solution of PMDA in acetone was added to a solution of ODA and iron(III) acetylacetonate (Fe(acac)₃, >98.0% ,Dojindo) in acetone (>99.0 %, Wako). The amount of Fe species was 2 wt% with relative to resulting polyimide. The mixture was stirred for 30 min, typically at 0 °C. The solvent was removed with a rotary evaporator to collect poly(amic acid). The curing reaction was conducted by heating the poly(amic acid) at 200°C under evacuation, to obtain polyimide fine particles.

Carbonization protocols

The polyimide particles were converted into carbon based catalysts by a pyrolysis protocols called multi-step pyrolyses. Fe/PI-600-I-N₂ was prepared by single step pyrolysis of the Fe containing polyimide at 600 °C for 5 h. Fe/PI-800-II-NH₃ was prepared by pyrolyzing Fe/PI-600-I-N₂ at 800°C under a NH₃ flow (50 %) for 1 h. Fe/PI-1000-III-NH₃ was prepared by pyrolyzing Fe/PI-800-II-NH₃ at 1000 °C under a NH₃ flow (50 %) for 1 h. Acid washing with conc. HCl was carried out after the first and second pyrolysis steps.

Characterization

The specific surface area and meso-pore volume of the catalysts were determined by N₂ adsorption using a volumetric adsorption measurement instrument (Bel Japan, Belsorp-mini II). The BET surface area and mesopore surface area were determined by the BET method and BJH method, respectively. The C, H and N contents of the catalysts were determined using a CHN elemental analyzer (Perkinelmer, 2400-II). The Fe content was determined by wavelength dispersive spectrometry (WDS) using an electron probe micro analyzer (EPMA; JXA-8100, JEOL). A LiFH crystal was used for Fe detection. The EPMA measurement was carried out by analyzing a pellet prepared from the catalyst powder without any binder. X-ray diffraction (XRD) was

measured at room temperature using an X-ray diffractometer (Rigaku, Ultima IV) with Cu Kα radiation. Scanning electron microscopy (SEM) and transition electron microscopy (TEM) were carried out using a VE9800 spectrometor (Keyence) and a 200 kV FE-TEM (2010F, JEOL), respectively.

Half cell testing

The catalytic activity of the samples was tested by linear sweep voltammetry (LSV, 5 mV sec⁻¹) with a rotating disk electrode (RDE). The catalyst powder was dispersed in a mixture of Nafion solution (5wt%, Aldrich), ethanol and water and applied onto the surface of a glassy carbon electrode. The amount of loaded catalyst was 0.2 mg cm⁻². The rotation speed of the RDE was kept at 1500 rpm with a RDE system (Nikko Keisoku, RDE-1) and the electrochemical data were collected with a potentiostat (ALS, 2323). The LSV was first carried out in N₂ saturated H₂SO₄ (0.5 M), and then in O₂ saturated H₂SO₄. The ORR current was determined by subtracting the N₂ current from the O₂ current.

Fuel cell testing

A MEA (Membrane Electrode Assembly) was fabricated by decal transfer method. The cathode catalyst powder was dispersed in a mixture of Nafion solution (20wt%, Aldrich), ethanol and ethyl acetate. The concentration of catalyst was 20 wt% and the catalyst/nafion ratio was 5/3. Anode ink was prepared by a similar manner using a PtRu/carbon catalyst (TEC61E54, Tanaka Kikinzoku Kogyo). These inks were coated on poly(ethylene terephthalate) films using an Auto Film Applicator (Tester Sangyo). The coated catalysts were transferred onto a Nafion NR211 electrolyte membrane (du Pont) by pressing them at 150 °C and 30 kg cm⁻² for 2 min. GDL25BC (SGL) was used as the gas diffusion layers for both sides of the MEA.

The I-V polarization curves were measured at 80 °C using a 1 cm² scale cell by flowing fully humidified hydrogen (300 mL min⁻¹) into the anode side and fully humidified oxygen or air into the cathode side (300 mL min⁻¹). The absolute pressures of the anode and cathode compartments were maintained at 0.2 MPa. The curves were measured by recording the cell voltages after holding the current density at each value for 5 min with an electronic load (Kikusui, PLZ164WA).

Durability tests were carried out using a 25 cm² scale cell by holding the current density at 30 or 250 mA cm⁻² and recording the cell voltage. The anode gas was fully humidified hydrogen (flow rate: 52 and 62 mL min⁻¹ for 30 and 250 mA cm⁻², respectively). The cathode gas was fully humidified air (flow rate:207 and 259 mL min⁻¹ for 30 and 250 mA cm⁻², respectively).

Results and Discussion

Preparation of polyimide fine particles

Although there had been several reports about size-controlled polyimide synthesis, most of them resulted in larger particle sizes than those desired as fuel cell catalysts; therefore, the polymerization condition was optimized to obtain fine polyimide particles before investigating the pyrolysis of them. This optimization was carried out without Fe addition. Figure S1 shows the effect of polymerization temperature on the particle size of

polyimide. In the range of 0-30 °C, the lower temperature resulted in the lower particle size. Even lower temperature below 0 °C did not resulted in any lower particle size in the current polymerization condition. Figure S2 shows the effect of monomer concentration on the particle size of polyimide. The higher monomer concentration resulted in the smaller particle size. Even higher concentration cannot be tested because of the solubility limit. The tendency on the particle size seems to be reasonable. The important factor for small particle size is to enhance the precipitation before the polymer grows too much by keeping fairly low temperature and high concentration of the monomer.

Figure S3 shows the FT-IR spectra of the prepared polymer before and after the curing. Poly(amic acid) derived peaks at 1413 (C=O, acid), 1532 (C-N-H) and 1665 cm⁻¹ (C=O, amide) disappeared and polyimide derived peaks at 1378 (C-N-C) and 1726 (C=O) appeared.



Fig. S1 SEM images of the polyimide samples prepared with different polymerization temperatures.



Fig. S2 SEM images of the polyimide samples prepared with different monomer concentration.



Fig. S3 FT-IR spectra of the Fe containing poly(amic acid) before and after the curing at 200 $^{\circ}$ C