

Supporting Information

“Pt-free cathode catalysts prepared via multi-step pyrolysis of Fe phthalocyanine and phenolic resin for fuel cells”

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Experimental

Catalysts preparation. The catalysts studied in this work were prepared by pyrolyzing mixtures of Fe phthalocyanine (Tokyo Kasei) and phenolic resin (PSK-2320, Gunei Chemical) (FePc/PhRs). PhRs was dissolved in acetone, and then FePc was dispersed into the solution under ultrasonication. The solvent was removed with a rotary evaporator to obtain powdery mixtures of the precursors. The amount of Fe in the mixture was 3 wt%. For single-step pyrolysis, the FePc/PhRs mixture was pyrolyzed at 600°C under a flow of nitrogen gas for 5 hours, and then washed by conc. HCl to remove accessible Fe species. The resulting powder was rinsed with Millipore water, and then dried at 80 °C under vacuum for several hours. This catalyst was named 600-I-N₂. For multi-step pyrolysis, 600-I-N₂ was heat-treated at 800 °C for an extra 1 hour, and then washed with HCl in the same manner. Two kinds of gas, N₂ and NH₃, were used for this step of treatment and the resulting catalysts were named

800-II-N₂ and 800-II-NH₃, respectively. 800-II-NH₃ was heat-treated at 1000 °C for an extra 1 hour in NH₃, and then washed with HCl in the same manner, to obtain 1000-III-NH₃.

Characterization. Transition electron microscopy (TEM) was carried out using a FE-TEM (2010F, JEOL) operated with an acceleration voltage of 200 kV. The C, H and N contents of the catalysts were determined using a CHN elemental analyzer (Yanaco, CHN corder MT-6). 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. The specific BET surface area was 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.

Catalyst ink and membrane electrode assembly (MEA). Cathode catalyst ink was prepared by thoroughly blending the cathode catalysts with alcohol and recast Nafion ionomer (20 wt% Nafion suspension in alcohol and pure water, Nafion equivalent weight: 1100, Aldrich). The catalyst was dispersed in alcohol and then the Nafion suspension was added. The mass ratio of Nafion to catalyst was 1:3. The mixture was ultrasonically stirred for 3 minutes in a cool water bath, which was used to minimize evaporation of solvents. The anode ink was prepared from Pt/carbon catalyst (45.7 wt%, Tanaka Precious Metal), *n*-butyl acetate and the recast Nafion ionomer in a similar manner. The ratio of Nafion to Pt/XC-72 was 1:2.

The cathode catalyst layer was fabricated on a Nafion membrane via the catalyst decal transfer method.^[i] The cathode ink was printed on a PTFE film using a screen-printer (MEC-2400, Mitani Electronics), and baked at 125 °C in dry air. Additional layers were added in the same manner to achieve a desired catalyst loading

of 4 mg/cm^2 . The cathode catalyst layer was transformed from the PTFE film to a Nafion 115 membrane (Dupont) by hot-pressing at $140 \text{ }^\circ\text{C}$ and 3 MPa for 10 minutes. The anode ink was directly screen-printed (0.5 mg-Pt/cm^2) onto the hydrophobic gas diffusion layer (GDL) (H120H, Chemix), and then baked at $125 \text{ }^\circ\text{C}$ in dry air. A MEA was fabricated by hot-pressing a cathode GDL (H60H, Chemix), the catalyst-coated Nafion membrane and the Pt catalyst-coated anode GDL at $120 \text{ }^\circ\text{C}$ and 1.5 MPa for 2 minutes.

Fuel cell testing. The MEA with GDL was installed in a small scale unit cell (PEM-004, Chemix). The geometric surface area of the electrodes was 1 cm^2 . The cell performance was tested at $80 \text{ }^\circ\text{C}$ using a fuel cell testing system (Chino) equipped with an electrochemical measurement system (1287, Solartron). The initial activities of the fuel cells were tested in fully humidified flowing hydrogen and oxygen. The absolute pressures of the anode and cathode compartments were maintained at 0.2 MPa . Durability tests were carried out by operating the fuel cells at 0.1 A/cm^2 current density, in flowing Air at atmospheric pressure and at $80 \text{ }^\circ\text{C}$.

Results

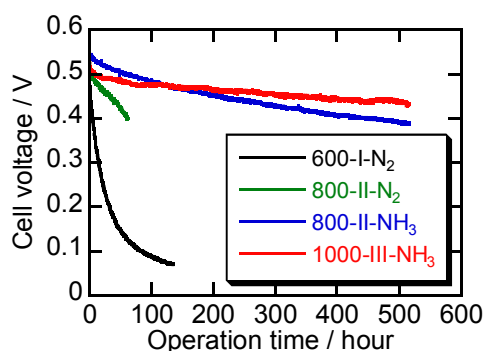


Fig. S1 Time courses for cell voltages measured at 0.4 A/cm^2 with (black) 600-I-N₂, (green) 800-II-N₂, (blue) 800-II-NH₃ and (red) 1000-III-NH₃ cathode catalysts. Cathode: Air 0.1 MPa . Anode: H₂ 0.1 MPa . T : $80 \text{ }^\circ\text{C}$.

References for the Supporting Information

[i] M. S. Wilson S. Gottesfeld, *J. Appl. Electrochem.*, **1992**, 22, 1.