

Electronic Supplementary Information for

Bottom-up Design of Carbon Nanotube-based Electrocatalysts and their Application in High Temperature Operating Polymer Electrolyte Fuel Cells

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Experimental Details

Materials. *N,N*-dimethylacetamide (DMAc), ethylene glycol, hydrogen hexachloroplatinate hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and sulfuric acid (H_2SO_4) were purchased from Wako Pure Chemical and used as received. Poly[2,2'-(2,6-pyridine)-5,5'-bibenzimidazole] (PyPBI) and MWNT/PyPBI/Pt were prepared according to the previously described method¹ Poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) was synthesized by the condensation reaction of isophthalic acid (TCI) and 3,3'-diaminobenzidine (TCI) in polyphosphoric acid (Wako chemical) as already reported². The MWCNTs were kindly supplied from the Nikkiso Co.

Measurements. IR spectra were recorded using a Spectrum 100 FT-IR (Perkin Elmer) spectrometer equipped with ATR. The TG curves were measured using an SSC 5200 (SII) operated in conditioned air at the heating rate of 5 °C/min.

Electrochemical Characterization. An MWNT/PyPBI/Pt composite was dispersed in *isopropanol*/water ($v/v=8/2$) by sonication (Branson, type 5510) for 10 min. The obtained suspension ($\sim 8 \mu\text{L}$) was placed on a polished glassy carbon (GC) disk electrode (diameter = 6.0 mm) of a RRDE (BAS) and then dried at room temperature. For the control sample, a suspension of a Pt/CB catalyst in *isopropanol*/water ($v/v=8/2$) containing Nafion (0.95 μg) was placed on a polished GC disk of a RRDE and then dried in air. The final metal loading on the GC disk electrodes was approximately 5.3 $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ for all the electrochemical experiments. The electrolyte solution was prepared using Milli-Q water (18 $\text{M}\Omega \text{ cm}$, Millipore) and HClO_4 (Suprapur, Merck). ECSA measurements for both the catalysts were carried out in 0.1 M HClO_4 solutions using an

electrochemical analyzer (BAS, Model 2323). The catalytic activities for the ORR were measured in an O₂-saturated 0.1 M HClO₄ solution using the RRDE at the scan rate of 10 mV s⁻¹ in various rotating rates. An Ag/AgCl and a platinum flag were used as the reference and counter electrodes, respectively. All of the potentials are given with respect to the reversible hydrogen electrode (RHE). The ring potential was kept at 1.3 V to oxidize H₂O₂ completely. The fraction of generated H₂O₂ (X) is calculated using the following equation (1)³:

$$X = \frac{2I_R/N}{I_D + I_R/N} \quad (1)$$

where N is the collection efficiency (estimated to be 0.356 by the reported method³), and I_D and I_R are the disk and the ring currents, respectively.

Koutecky-Levich Plots. The number of electrons transferred in the first order reduction reaction (n) can be calculated from the Koutecky-Levich equation (2)(3)^{4,5}:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_D} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$

(2)

$$B = 0.62nFD^{2/3}\nu^{-1/6}C_{O_2}$$

(3)

where j , j_k , and j_D are the measured, kinetic, and diffusion limited current densities, respectively, ω is the angular frequency of rotation, D is the O₂ diffusion coefficient (1.93×10^{-5} cm² s⁻¹),⁴ ν is the kinematic viscosity (8.93×10^{-3} cm² s⁻¹),⁴ and c_{O_2} is the oxygen concentration (1.22×10^{-6} mol cm⁻³).⁴

MEA Fabrication. An MWNT/PA-PyPBI/Pt was dispersed in *isopropanol*/water (v/v=8/2) mixture by sonication, and then deposited on a GDL (SIGRACET gas diffusion media GDL 25 BC, SGL Carbon Group) by a vacuum filtration method using the GDL as a filter to form the GDE. The same method was used to prepare a GDE of the MWNT/Pt. The Pt loading of the GDEs was controlled to be $0.45 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ in all cases. PA-doped PBI membranes were prepared as already reported[9], and the PA doping level of the membranes was estimated to be 5.3 mol per PBI repeat unit. The MEAs were fabricated by a hot pressing of the GDEs on PA-doped PBI membranes at $150 \text{ }^{\circ}\text{C}$ and 60 kg cm^{-2} for 3 min.

Single Cell Test. The polarization curves were measured under the following conditions: dry H_2 (flow rate: 100 mL min^{-1}) and dry air (flow rate: 200 mL min^{-1}) as fuel gases for the anode and cathode, respectively, and a cell temperature of $120 \text{ }^{\circ}\text{C}$.

References for Supplemental Information

1. T. Fujigaya, M. Okamoto and N. Nakashima, *Carbon*, 2009, **47**, 3227-3232.
2. T. Brock, D. C. Sherrington and H. G. Tang, *Polymer*, 1991, **32**, 353-357.
3. U. A. Paulus, T. J. Schmidt, H. A. Gasteiger and R. J. Behm, *J. Electroanal. Chem.*, 2001, **495**, 134-145.
4. R. R. Adzic, J. Wang and B. M. Ocko, *Electrochim. Acta*, 1995, **40**, 83-89.
5. J. Yang, J. Y. Lee, Q. Zhang, W. Zhou and Z. Liu, *J. Electrochem. Soc.*, 2008, **155**, B776-B781.