Supporting Information
for

Facile Enhancement in durability and CO tolerance of CB/PtRu by Poly(2,5-benzimidazole) Coating *via* In-situ Polymerization

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Experimental

Materials

Methanol, isopropanol, *N,N*-Dimethylacetamide (DMAc), 3,4-diaminobenzoic acid (DABA), sulphuric acid, and polyphosphoric acid (PPA) were purchased from Sinopharm Chemical Reagent Co., Ltd. The commercial CB/PtRu (Pt: 40 wt%, Ru: 20 wt%) and CB/Pt (40 wt%) electrocatalysts were purchased from Alfar Aesar. Nafion solution (5 wt%) were offered by Sigma-Aldrich. Aqueous solutions were prepared using Milli-Q water and all chemicals were used as received without further purification.

Synthesis of CB/PtRu/ABPBI

100 mg of CB/PtRu and 10 mg of DABA were mixed in 100 g of PPA by stirring, and then increase the temperature to 200 ^{o}C under stable N_2 follow and

the polymerization was terminated after 5 h. The resultant solution was condensed in Milli-Q water and NaOH was added to neutralize the solution to remove PPA. The composite was collected by filtration, washing with DMAc to remove monomer and dried at 80 ^{o}C under vacuum.

Gas diffusion electrode (GDE) preparation

GDE was prepared as follows. Three different electrocatalysts were used to prepare GDEs for cathode sides. The electrocatalyst was dispersed in 20 mL of isopropanol aqueous solution (*v*/*v*=4:1) by sonication for 30 min, and then filtered using gas diffusion layer (GDL) as filter paper. The Pt loading amount on the GDL was controlled at 2 mg cm^{-2}. The obtained GDE was dried overnight under vacuum at 25 ^{o}C to remove isopropanol. The anode GDE was prepared using commercial CB/PtRu or synthesized CB/PtRu/ABPBI with 1 mg_{Pt} cm^{-2}.

Membrane electrode assembly (MEA) preparation

MEA was prepared by hot pressing the prepared GDEs and Nafion 117 membrane. The geometrical area of the MEA was 5 cm^{2}.

Characterization

The XPS spectra were measured using an AXIS-ULTRA^{DLD} (Shimadzu). The TGA measurements were conducted by an EXSTAR 6000, Seiko Inc. at the heating rate of 5 ºC min^{-1} under 100 mL min^{-1} of air. The TEM micrographs were measured using a JEM-2010 (JEOL, acceleration voltage of 120 kV) electron microscope.

Electrochemical measurements

The electrochemical measurements were performed using a glassy carbon electrode electrode attached to CHi640e potentiostat with a conventional three-electrode configuration in a vessel at room temperature. A GCE with a geometric surface area of 0.196 cm^2 was used as the working electrode. A Pt wire and an Ag/AgCl were used as the counter and reference electrodes, respectively. The catalyst ink was typically prepared as follows. The composites (1.0 mg) were ultrasonically dispersed in an 80% aqueous isopropanol solution (2.0 mL) to form a homogeneous suspension. A portion of the electrocatalyst suspension was then cast onto a GCE to form a uniform catalyst layer (the loading amount of Pt was controlled at 14 μg cm^{-2}). Finally, the cast films on the electrodes were air-dried. The cyclic voltammetry (CV) measurements of the electrocatalysts at the scan rate of 50 mV s^{-1} were carried in an N_2-saturated 0.5 M H_2SO_4 solution in order to determine the electrochemical surface area (ECSA) values.

Durability testing

The Pt stability was tested using the protocol of the Fuel Cell Commercialization Conference of Japan (FCCJ) (measured in N_2-saturated 0.5 M H_2SO_4 at 25 ^oC), in which the potential was kept at 0.6 V *vs*. RHE for 3 s, then applied up to 1 V *vs*. RHE for another 3 s. The procedure was cycled, and the CV measurement was carried out after every 600 cycles (see Supporting Information, **Figure S1**).

CO stripping

CO stripping voltammetry was performed by feeding the work electrode with CO gas for 10 min with flow rate of 100 mL min^{-1}, while holding the working electrode potential at 0.2 V *vs*. RHE. After the adsorption, the CO was removed from electrode and changed to N_2 bubbling for 50 min. CO stripping voltammogram was recorded with scan rate of 50 mV s^{-1}.

Methanol oxidation (MOR)

The methanol oxidation reaction (MOR) was evaluated before and after the durability test using N_2-saturated 1M methanol and 0.5 M H_2SO_4 at the scan rate of 50 mV s^{-1} at room temperature without rotation (The electrode was the same one used for the ECSA measurement. The Pt loading amount was controlled at 14 μg cm^{-2}). Before the measurement, 50 cycles were carried out to active the catalyst.

Fuel cell test

The FC performance of the fabricated MEAs was evaluated at 70 ºC using a computer-controlled fuel cell testing system (Model 850e, Scribner Associate, Inc.). The polarization and power density curves were obtained at atmospheric pressure by flowing 1M methanol (flow rate= 3 mL min^{-1}) and 100% humidified air (flow rate= 100 mL min^{-1}) to the anode and cathode, respectively.

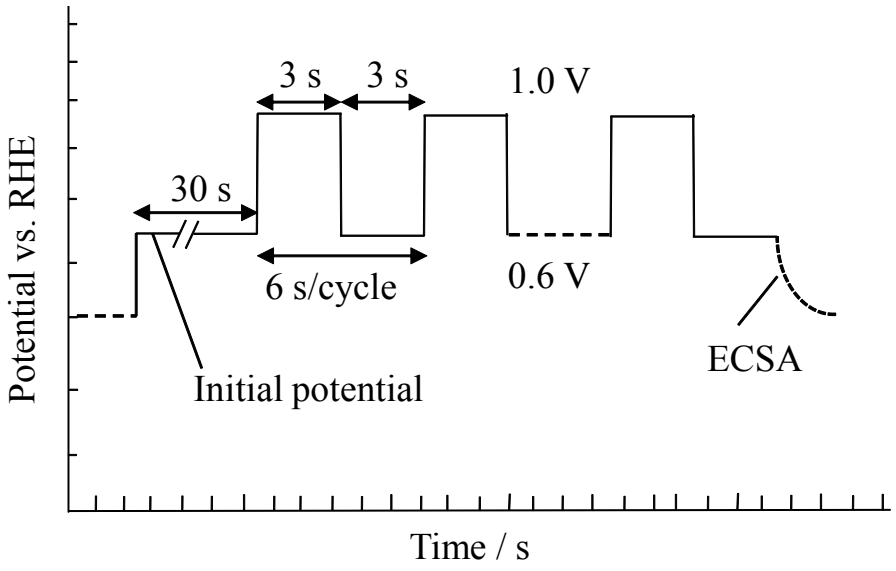

Figure S1 New test protocol of the Pt stability test in half-cell proposed by the Fuel Cell Commercialization Conference of Japan (FCCJ).

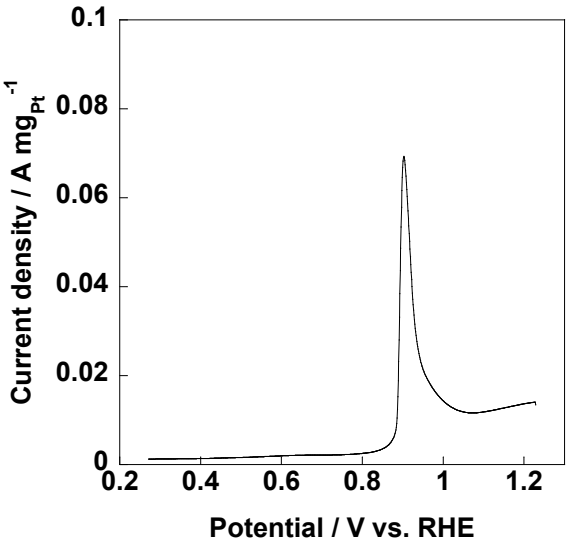

Figure S2 CO stripping curve of commercial CB/Pt measured in N_2-saturated 0.5 M H_2SO_4 electrolyte.

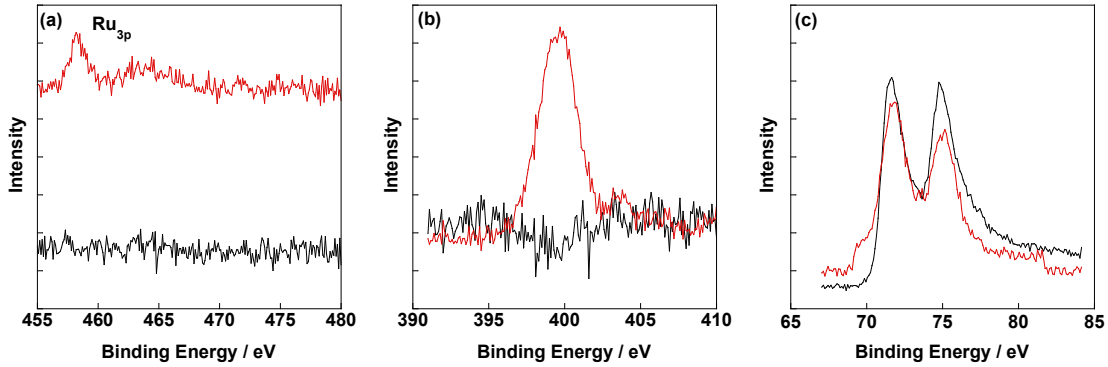

Figure S3 XPS narrow scan in Ru_{3p} (a), N_{1s} (b), Pt_{4f} (c) and regions of CB/PtRu (black line) and CB/PtRu/ABPBI (red line) after durability test, respectively.

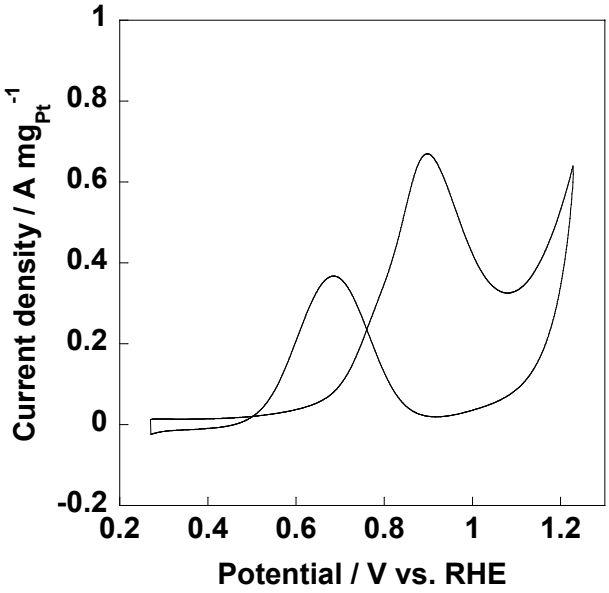

Figure S4 MOR curve of commercial CB/Pt measured in N_2-saturated 0.5 M H_2SO_4 with 1 M methanol in the electrolyte.