Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Material

Triple phase boundary and power density enhancement in PEMFC of Pt/C electrode with double catalyst layers

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Additional experimental section

Chemicals. All chemicals were of analytical grade, and were used as such without any further purification. Pt/C composite catalyst powder (40 wt.% Pt) was purchased from E-TEK Co. The 2-propanol (99.5 %), methanol (CH_3OH, 99.8 %), sulfuric acid (H_2SO_4, 98.08 %), nitric acid (HNO_3, 63.01 %), hydrochloric acid (HCl, 37 %), and trisodium citrate hydrate ($C_6H_5Na_3O_7.2H_2O$, 98 %) were supplied by Showa Chemicals. Hydrogen hexachloroplatinate (IV) hydrate ($H_2PtCl_6.6H_2O$, 99.9 %) was obtained from Kojima Chemicals.

Preparation of the Pt/C catalyst slurry. Initially, 160 mg of commercial Pt/C (40 wt.% Pt) catalyst powder was introduced into a 20 mL glass vial. Next, 1.31 mL of distilled water, 3.41 mL of 2-propanol, and 1.02 mL of Nafion (5 wt.%, Dupont) solution were added to the above vial, respectively. Then, the suspension was ultrasonicated at room temperature for 1 h, to make sure that the black catalyst slurry was uniformly obtained (Fig. S1a).

Preparation of the Pt colloid. Pt catalyst nanoparticles were synthesized by a chemical reduction method using the reflux setup. First, 5 mL of aqueous stock solution containing Pt^{4+} (0.1 M) was dissolved into 405 mL distilled water in a 3-neck flask (500 mL in volume) connecting with the reflux, which was then heated to 90 °C with vigorous stirring. The temperature of reaction was tightly controlled by the sensor. Next, 90 mL of warm reducing agent solution (Na_3-citrate 0.034 M) was added to the yellow solution above. After continuous stirring for about 5 min, the temperature of the reaction system was again reached to 90 °C, and maintained for 4 h, to make sure that all Pt^{4+} ions had been totally reduced to metal nanoparticles. Finally, the synthesized Pt colloid was cooled to room temperature naturally. The solution had already turned to dark brown (Fig. S1b), and the pH value was found to be around pH = 5.7.

Preparation of Pt-dispersed catalyst electrode. 35 cm^2 of carbon cloth substrate was firstly dried at 60^oC for 1 h in electric oven, then was uniformly sprayed an amount of 1.0 mL the Pt/C catalyst slurry on its

surface. Next, the obtained electrode was dried at 60^{o}C for overnight before the use. An area 1 cm x 1 cm was cut for the electrochemical property testing.

Preparation of Pt-concentrated catalyst electrode. Before the EPD of the synthesized Pt catalyst nanoparticles, 6.25 cm^2 of carbon cloth substrate was dried at 60^{o}C for 1 h in electric oven, then sprayed by the mixture of active carbon black and Nafion ionomer. The obtained electrode was dried overnight. Next, depositing Pt catalyst nanoparticles on the surface of electrode using the EPD method with the times was 10 min. After that, the electrode was dried at 60^{o}C for 1 h, and washed by warm distilled water for 20 min, then dried at 60^{o}C for overnight before the use.

Table S1. Experimental conditions, Pt loading weight, and electrode denotation of the as-prepared Pt/c catalyst electrodes.

Area of carbon cloth (cm^2)	Volume of Pt/C slurry (mL)	EPD time (min)	Pt loading weight by ICP (mg/cm^2)			Weight ratio of Pt in dispersed and concentrated layer	Catalytic electrode denotation
			Dispersed layer	Concentrated layer	Total		
35	1.00	0	0.125	0.000	0.125	1:0	Sprayed
35	0.53	4*	0.062	0.068	0.130	1:1	DCL
5	0.00	10	0.000	0.135	0.135	0:1	EPD

* For EPD, 5 cm^2 electrode area was cut from the sprayed electrodes.

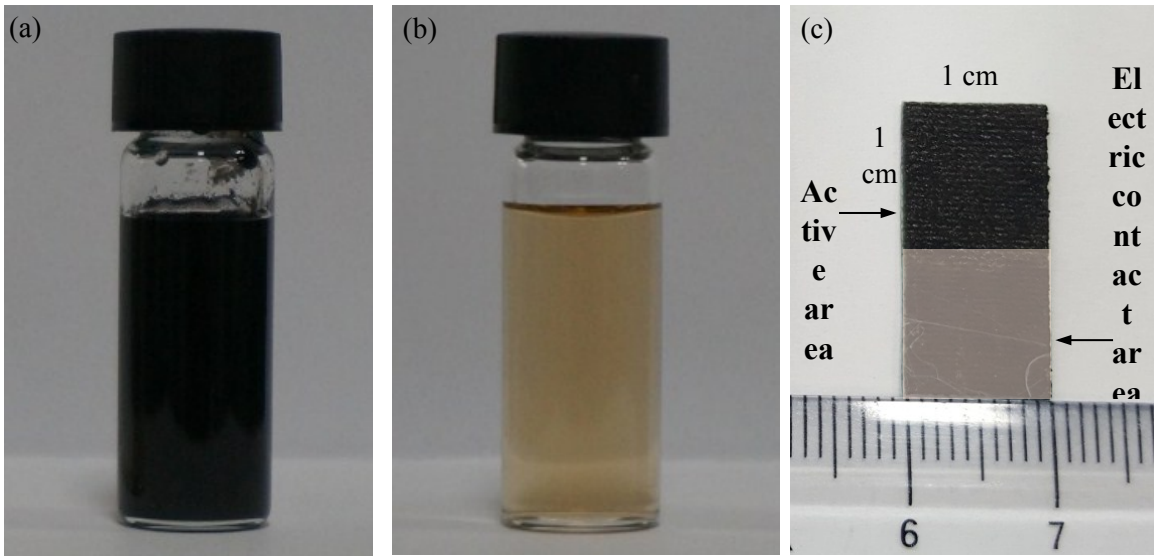

Fig. S1 Photographs of (a) Pt/C (wt. 40%) slurry, (b) synthesized Pt colloid, and (c) the obtained DCL electrode for CV and EIS testing.

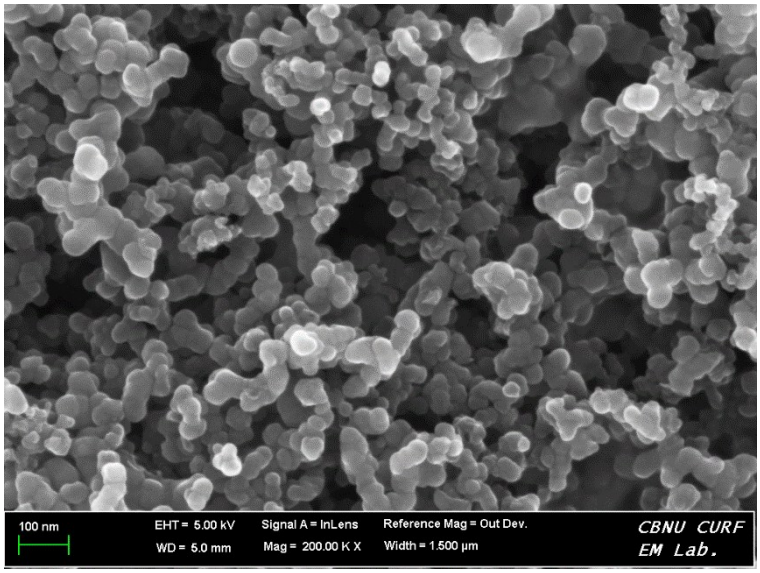

Fig. S2. FESEM surface image of carbon cloth with the microporous layer.

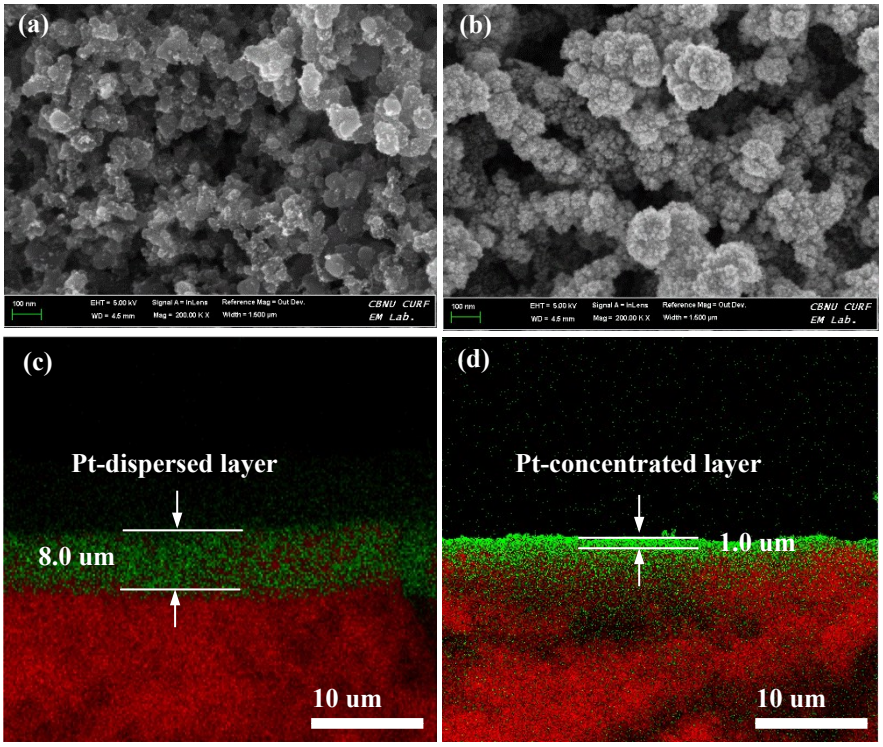

Fig. S3. FESEM surface and cross-sectional images of (a,c) the sprayed and (b,d) EPD catalyst electrodes.

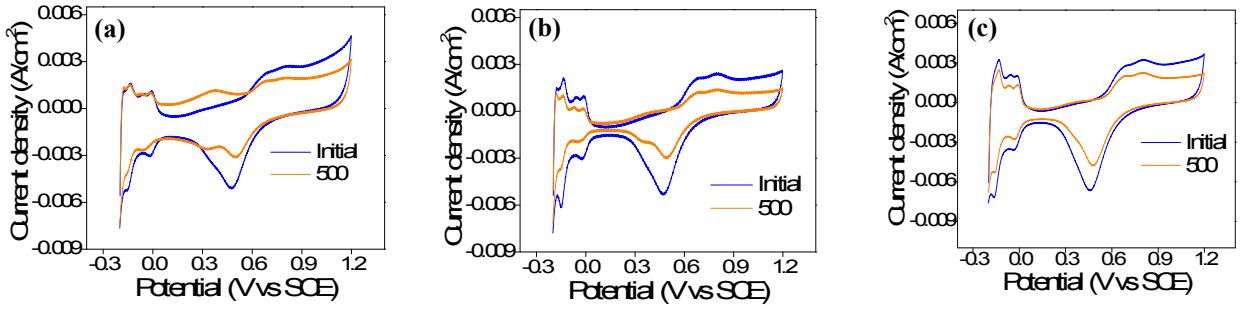

Fig. S4. CVs of the ECSA durability test of (a) Sprayed, (b) EPD, and (c) DCL electrodes after 500 sequential cycles.

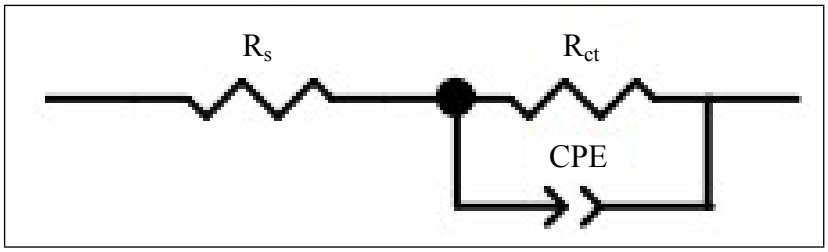

Fig. S5. An electrical equivalent circuit used to fit the Nyquist plots: R_s indicates the solution resistance R_{ct} presents the charge transfer resistance, and CPE is a constant phase element.

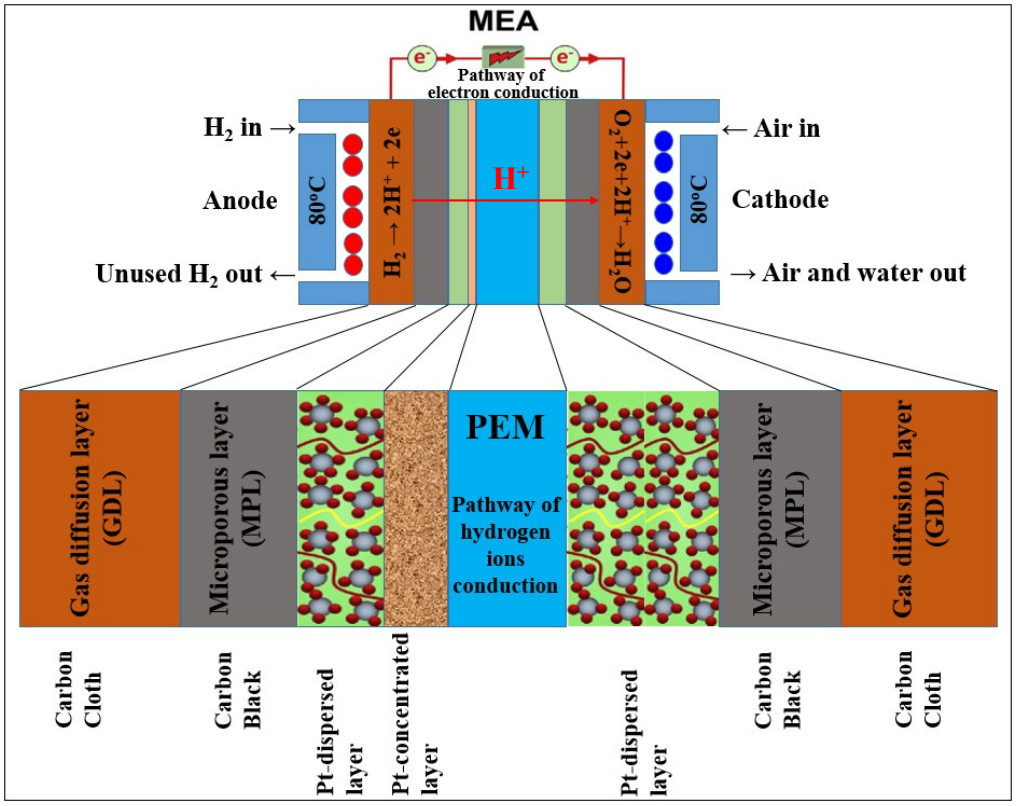

Fig. S6. The structural simulation of MEA containing the Pt/C DCL electrode at anode and Pt/C sprayed electrode at cathode.