

**Supporting Information  
for**

**Remarkably Stable CO tolerance of PtRu Electrocatalyst Stabilized by Nitrogen**

**Doped Carbon layer**

Zehui Yang<sup>a\*</sup>, Xinxin Yu<sup>a</sup> and Quan Zhang<sup>a</sup>

*<sup>a</sup>Sustainable Energy Laboratory, Faculty of Materials Science and Chemistry, China University of Geosciences Wuhan, 388 Lumo RD, Wuhan, 430074, China*

To whom correspondence should be addressed:

Tel/Fax: +86 186-7237-4372; E-mail: yeungzehui@gmail.com

**Experimental**

**Materials**

Poly(vinyl pyrrolidone) (PVP, K-30), Methanol, isopropanol, and N,N-Dimethylacetamide (DMAc) 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/NC/PtRu**

Briefly, 20 mg of CB was wrapped by PVP (20 mg) using sonication (Yamato 5510, Branson) for 1 h in water. The composite was then collected by filtration, and then dried under vacuum at 80 °C. 20 mg of CB/PVP was dispersed in EG aq. (v/v=3:2). The PtRu loading was carried out by reduction of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (53 mg) and RuCl<sub>3</sub>

(20 mg) in EG aq. (v/v=3:2, 100 mL) at 140 °C for 6 h under N<sub>2</sub> atmosphere. The obtained product was filtered, washed, and then dried overnight under vacuum at 80 °C to completely remove solvent. The solid product was then carbonized at 500 °C under N<sub>2</sub> atmosphere.

### **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<sup>-2</sup>. The obtained GDE was dried overnight under vacuum at 25 °C to remove isopropanol. The anode GDE was prepared using commercial CB/PtRu or synthesized CB/NC/PtRu with 2 mg<sub>Pt</sub> cm<sup>-2</sup>.

### **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<sup>2</sup>.

### **Characterization**

The XPS spectra were measured using an AXIS-ULTRADLD (Shimadzu). The TGA measurements were conducted by an EXSTAR 6000, Seiko Inc. at the heating rate of 5 °C min<sup>-1</sup> under 100 mL min<sup>-1</sup> 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 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<sup>2</sup> 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<sup>-2</sup>). 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<sup>-1</sup> were carried in an N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25 °C), 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<sup>-1</sup>, while holding the working electrode

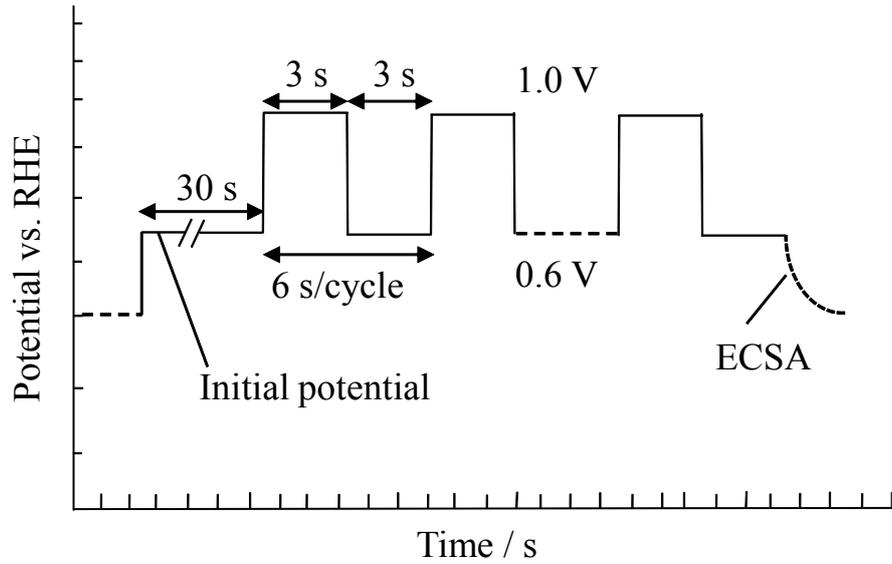
potential at 0.2 V vs. RHE. After the adsorption, the CO was removed from electrode and changed to N<sub>2</sub> bubbling for 50 min. CO stripping voltammogram was recorded with scan rate of 50 mV s<sup>-1</sup>.

### **Methanol oxidation (MOR)**

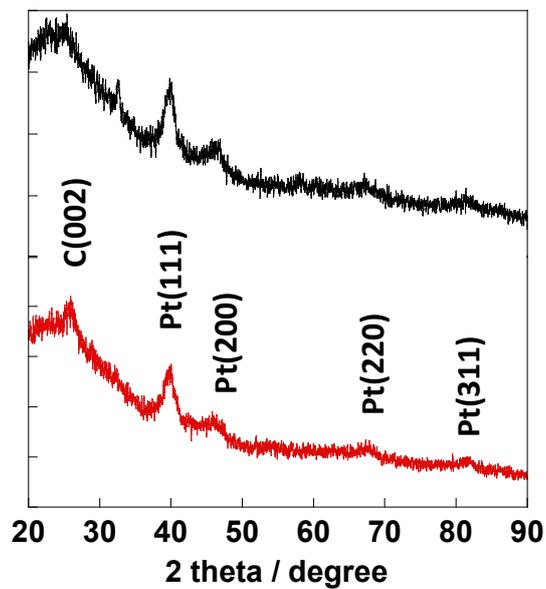
The methanol oxidation reaction (MOR) was evaluated before and after the durability test using N<sub>2</sub>-saturated 1M methanol and 0.5 M H<sub>2</sub>SO<sub>4</sub> at the scan rate of 50 mV s<sup>-1</sup> at room temperature without rotation (The electrode was the same one used for the ECSA measurement. The Pt loading amount was controlled at 14 μg cm<sup>-2</sup>). Before the measurement, 50 cycles were carried out to active the catalyst.

### **Fuel cell test**

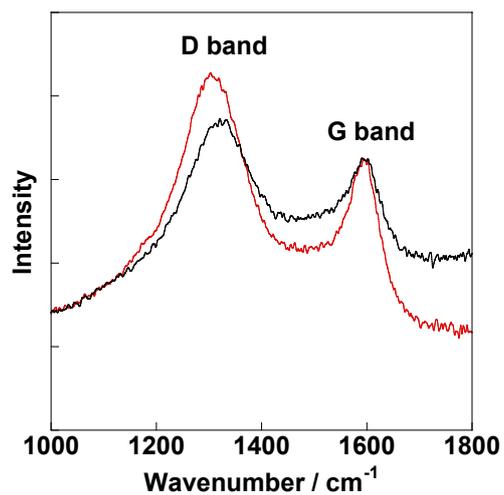
The FC performance of the fabricated MEAs was evaluated at 60 °C using a computer-controlled fuel cell testing system (Model 850e, Scribner Associate, Inc.). The polarization and power density curves were obtained at atmospheric pressure by flowing 1M methanol (flow rate= 3 mL min<sup>-1</sup>) and 100% humidified air (flow rate= 100 mL min<sup>-1</sup>) to the anode and cathode, respectively.



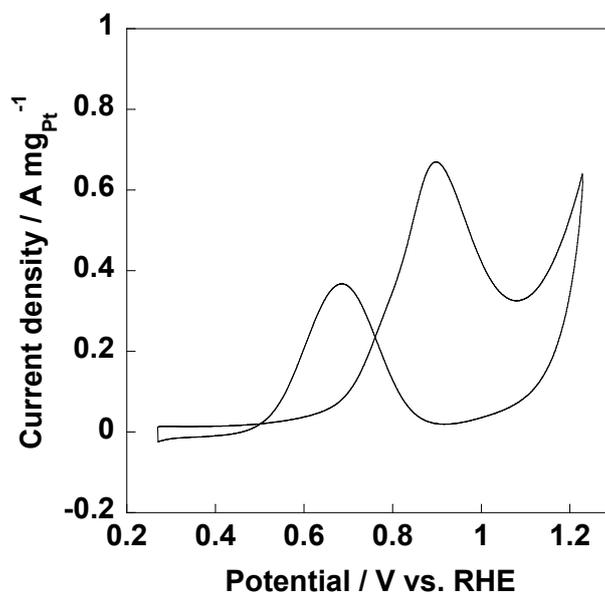
**Figure S1** New test protocol of the Pt stability test in half-cell proposed by the Fuel Cell Commercialization Conference of Japan (FCCJ).



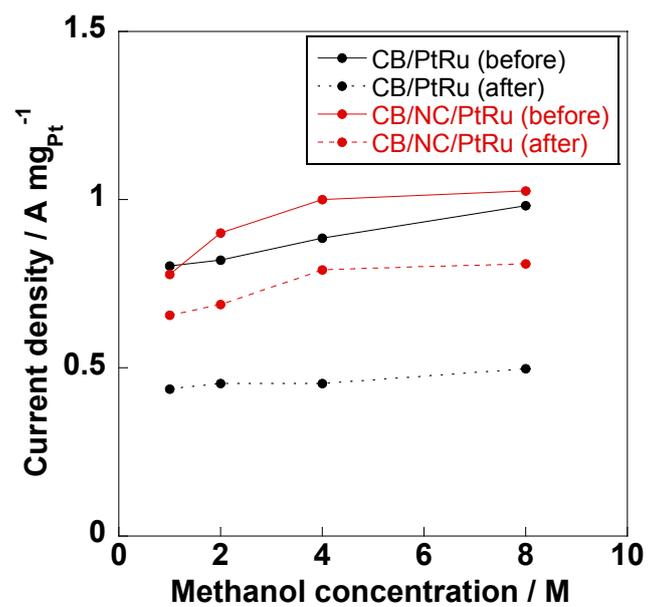
**Figure S2** XRD patterns of commercial CB/PtRu (black line) and CB/NC/PtRu (red line).



**Figure S3** Raman spectra of CB/PtRu (black line) and CB/NC/PtRu (red line), respectively.



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



**Figure S5** Comparison of mass activities of commercial CB/PtRu and CB/NC/PtRu before and after durability test.