Supporting Information

Monodisperse PtRu Nanoalloy on Carbon as a High Performance DMFC Catalyst†

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Experimental

Synthesis of Colloidal PtRu Nanoalloy: A slurry of platinum acetylacetonate (0.25 mmol, 98%, Strem), ruthenium acetylacetonate (0.25 mmol, 99%, Strem), 1,2-hexadecanediol (0.75 mmol, 90%, Aldrich), and octyl ether (10 mL, 99%, Aldrich) was prepared in a 100 mL two necked round-bottom flask, and the mixture was heated at 100 °C under Ar atmosphere. To this solution were added oleylamine (1.25 mmol, 70%, Aldrich) and oleic acid (1.25 mmol, 99+%, Aldrich) via a syringe, and the reaction mixture was slowly heated to reflux for 100 min and allowed to reflux for 30 min to give a black solution. The solution was cooled to room temperature, and the black powders were precipitated by adding 12.5 mL of ethanol to give a colloidal PtRu (1:1) nanoalloy. The resulting colloids were easily dispersed in various hydrocarbon solvents, such as hexane, octane, and toluene.

Catalyst Preparation: A suspension of colloidal PtRu nanoalloy (191.5 mg) and Vulcan carbon (191.5 mg, Vulcan XC-72R, Carbot) in 100 mL toluene was vigorously stirred at 45 °C for 10 h. After solvent evaporation, the dark powder was dried in air for 1 h. In order to remove stabilizing surfactants on the nanoalloy, the colloidal PtRu/Vc catalyst precursor was vigorously stirred in 50 mL of acetic acid (99.0%, Junsei) at 80 °C for 10 h. The resulting PtRu/Vc catalyst was collected by centrifugation, washed with a copious amount of ethanol, and then dried at room temperature in air for 24 h. The obtained PtRu/Vc catalyst had a metal loading of 26.9 wt % by ICP measurement. The PtRu nanoalloy and PtRu/Vc catalyst were characterized by XRD (Rigaku D/MAX-RC, Cu-Kα radiation), TEM (Omega EM912 V; Philips F20Tecnai) with SAED and EDX.

Electrochemical Measurement: Linear sweep voltammetric and chronoamperometric data were collected using a platinum wire counter electrode and a Ag/AgCl (in saturated KCl) reference electrode in a three-electrode cell at room

temperature. All the potentials are reported with respect to the saturated calomel electrode (SCE). The solutions were purged with Ar prior to use for 30 min. Potential control and sweeps were established using an Autolab potentiostat (Eco chemie, Netherlands). The glassy carbon (GC) electrode with 3 mm diameter of a GC core (Bioanalytical Systems, Inc.) was polished with 0.05 mm Al_2O_3 paste and washed with ultrapure water (Modulab, US Filters, MA, >18 MΩ). For the preparation of electrode, 10 mg of catalyst was dispersed ultrasonically in a mixed solution of a 200 μL diluted Nafion alcohol solution (Fluka, 5.0 wt %) and 50 mL ultrapure water. The suspension of 30 μL was pipetted onto a working electrode surface. The coated electrode was carefully dried in an oven at 70 °C for 30 min so that catalyst could be uniformly coated over the entire cross-section of the 6 mm diameter area. The geometric area of GC was 0.0706 cm^2, and the electrode had a catalyst loading (metal base) of 22.86 $\mu g/cm^2$. The chronoamperometry experiment identified linear sweep voltammetric measurement except the potential positions. The working electrode was treated at the potential of 0.8 V for 2 s, followed by sudden decrease of the potential to -0.27 V for 2 s to remove any oxides and hydroxides adsorbed on the surface. The current transients were recorded at 0.2 V for 550 s.

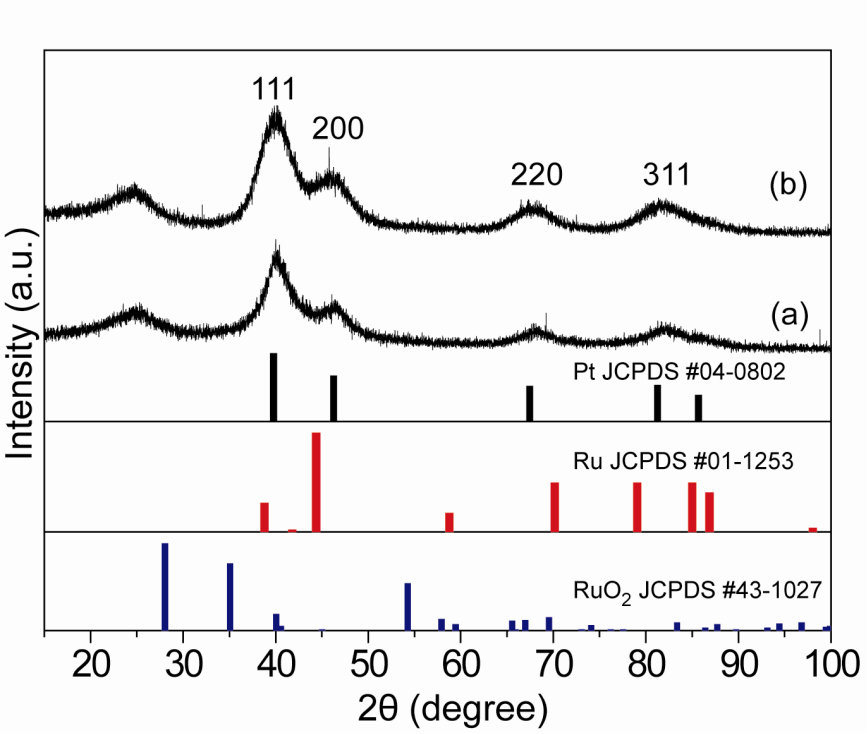

Figure S1. XRD spectra of (a) 30 wt % commercial E-TEK catalyst, (b) 26.9 wt % PtRu/Vc catalyst.

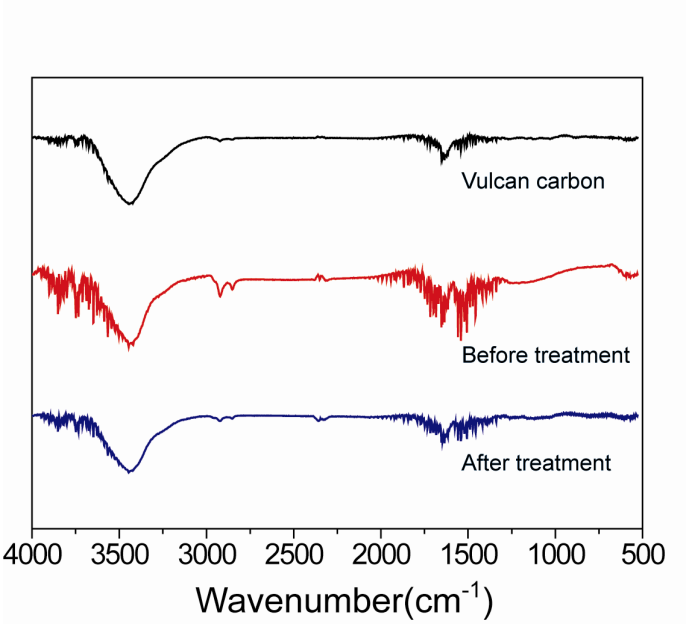

Figure S2. FTIR spectra of raw Vulcan carbon and after and before acid treatment of the colloidal PtRu/Vc with acetic acid.