Electronic Supplementary Information

Pt/C Trapped in Activated Graphitic Carbon Layers as a Highly Durable Electrocatalyst for Oxygen Reduction Reaction

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The State Key Laboratory of Power Transmission Equipment & System Security and New Technology, College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China **Synthesis of Pt/C@NGC Catalyst**: 80 mg of aniline monomer (distilled before use) were dissolved in 60 ml of 0.5 M H₂SO₄ aqueous solution, after ultrasonic blending for 10 min, 80 mg of 20% Pt/C catalyst (E-TEK) were dispersed in it. The mixture was then stirred magnetically at room temperature for 10 h to achieve homogeneous dispersion, and then 20 ml of 0.5 M H₂SO₄ aqueous solution containing 246.7 mg of (NH4)₂S₂O₈ (ammonium peroxydisulfate, APS) and appropriate amount of FeCl₃·6H₂O and Co(NO₃)₂·6H₂O was added dropwise with vigorous stirring (the molar ratio of APS to aniline was controlled at 1.25:1, while the molar ratio of iron and cobalt salts was 3:1). The polymerization was conducted in an ice bath (<5°C) for 24 h. After evaporating the water from the suspension, the remaining solid phase was dried under vacuum at 80°C for 12 h and then subjected to heat treatment at 900°C in an inert atmosphere of a nitrogen gas for 1 h. The heat-treated product was then preleached in 0.5 M H₂SO₄ at 80°C for 8h to remove unstable species from the catalysts and thoroughly washed in deionized water and then dried under vacuum at 80°C for 24 h.

For comparison, pure PANI-derived NGC supported on Vulcan XC-72 was prepared under conditions similar to those mentioned above. The weight ratio of aniline to Pt/C or Vulcan XC-72 was controlled at 1:1.

Electrochemical tests: The electrochemical properties of the catalysts were characterized using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques. All the electrochemical experiments were performed in 0.1 M HClO₄ using a Princeton Parstst 4000 potentiostat, a platinum wire counter electrode and an Ag/AgCl (saturated KNO₃) reference electrode. All potentials in this study, however, are given relative to the reversible hydrogen electrode (RHE). A rotating disk electrode (RDE) with a glassy carbon (0.19625cm²) was used as the working electrode. The catalyst ink was prepared by blending the catalyst powder (Pt/C@NGC or commercial Pt/C catalysts from E-TEK Co.) with ethanol in an ultrasonic bath. For comparison of the electrochemical surface areas (ECSAs), cyclic voltammograms recorded in nitrogen were used to obtain the ECSA using the following relation:

$$ECSA = Q_H / (Q_{ref} m)$$

where Q_H (mC) is the charge due to the hydrogen adsorption and desorption in the hydrogen region (0.05-0.40 V) of the CVs, $Q_{ref} = 0.21$ mC is the electrical charge associated with a monolayer adsorption of hydrogen on Pt, and m is the loading of Pt on the working electrode.

Oxygen reduction reactions were conducted in a 0.1 M HClO₄ aqueous solution. The polarization curves were obtained by sweeping the potential from 1.1 to 0.32 V at a scan rate of 10 mV s-1 and a rotation rate of 1600 rpm. The current density was normalized in reference to the ECSA of the catalyst. Based on the ORR polarization curves, the kinetic current density (ik) was calculated using the Koutecky-Levich equation:

$$1/J = 1/J_{K} + 1/J_{D}$$

where J is the measured current density, J_{K} and J_{D} are the kinetic and diffusionlimiting current densities, respectively.

The electrochemical stability and performance of the Pt/C@NGC and commercial Pt/C catalysts were examined using an accelerated durability test (ADT) by continuously cycling the potential between 0 and 1.2 V in nitrogen-saturated 0.1M $HCIO_4$ at a scan rate of 50 mV s⁻¹



Fig.S1 Thermal gravimetric analysis (TGA) of Pt/C@NGC. When the temperature <200 °C, the weight loss is assigned to the loss of chemically adsorbed water molecules. PANI starts decomposition at 270 °C.



Fig.S2 XPS surveys of Pt/C and Pt/C@NGC; inset in Figure S1 shows the surface atomic concentrations of each element.



Fig .S3 (a)Mass activities and specific activities at 0.95V for Pt/C@NGC and Pt/C catalysts. (b) The Tafel plots for Pt/C@NGC and Pt/C catalysts.



Fig.*S4* (a) Cyclic voltammograms for NGC/C catalyst in N₂-saturated 0.1M HClO₄ solution at room temperature with a sweep rate of 50mV/s. Catalyst loading was 0.6mg/cm². (b) Polarization curves for NGC/C catalyst at a rotating speed of 1600rpm in an O₂-saturated 0.1M HClO₄ solution at 60 °C with a sweep rate of 10mV/s, Catalyst loading was 0.6mg/cm².