

Supporting Information

Ultrasonic Spray Pyrolyzed Iron-Polypyrrole Mesoporous Spheres for Fuel Cell Oxygen Reduction Electrocatalyst

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Material preparation

Ultrasonic spray pyrolysis and colloidal silica template methods were used to synthesize the target self-supported catalysts: 2.0 g pyrrole (Sigma-Aldrich) and 2.46 g potassium ferricyanide (Sigma-Aldrich) were dissolved in 300 ml of deionized (DI) water to form a solution. The potassium ferricyanide was chosen as an iron precursor because the cationic polypyrrole are facile to integrate with anions. As a synthetic template, 5.0 g commercially available colloidal silica (LUDOX[®]TM40, DuPont) was added to this solution, followed by 45 ml of 3.0 wt% H₂O₂. After 1.0 ml 0.01 M FeCl₃ was dropped in to activate the polymerization, the solution was stirred for 24 hours. In this way, the pyrrole could be gradually polymerized into polypyrrole colloids. The co-existing colloidal solution of polypyrrole and silica was then transferred to a homemade ultrasonic spray pyrolysis system, in which a 2.4 MHz ultrasonic atomizer turned this colloidal solution into aerosol mist. Then, this aerosol mist was carried into a tube furnace by a stream of high-purity nitrogen gas. In the tube furnace at 800 °C, the aerosol droplets were dried, condensed, polymerized, and carbonized. The black solid particles (FePPy-SiO₂ composite particles) that formed were then precipitated in a water bubbling collector. The silica component in these FePPy-SiO₂ composite particles was then removed by etching in 10% HF solution for 24 hours. The final sample was washed by DI water 3 times and acetone 3 times to remove the residual chemicals.

For comparison, a carbon black-supported FePPy catalyst was synthesized by the conventional heat-treatment method: 1.0 g carbon black (Vulcan XC72, Cabot Corp.) was added to a solution of 0.5 g pyrrole and 0.62 g potassium ferricyanide. After pyrrole polymerization initialized by H₂O₂, the solution was evaporated at 105 °C. The dried precursor was then heat-treated at 800 °C for 2 hours in a tube furnace with a nitrogen gas flow. In order to remove the acid-unstable iron residuals, the as-prepared carbon-supported FePPy powder was also rinsed in 10% HF solution for 24 hours.

Physical characterization

A scanning electron microscope (SEM, FEI Dual Beam Strata 235) with an EDAX analyzer was operated to observe the morphology and measure the composition of the prepared catalyst samples. Nitrogen sorption techniques (SA3100 surface area analyzer, Beckman Coulter) were applied at 77 K to measure the surface area and porosity of the prepared catalyst samples. Before the measurements of the nitrogen sorption isotherms, the samples were outgassed at 150 °C for 15 minutes. The surface areas were calculated by the BET (Brunauer-Emmett-Teller) method, and the pore size distribution was calculated from the adsorption isotherm branch by the BJH (Barrett-Joyner-Halenda) method. X-ray diffraction (XRD, Bruker D8-Discovery) was used to phase detection of the samples.

Electrochemical measurement

The electrochemical activities of the as-prepared catalysts were evaluated by cyclic voltammetry (CV) and rotating ring disk electrode (RRDE) techniques. The measurements were performed using a multi-potentiostat (Solartron 1480) and a single-compartment, three-electrode cell with an MSR rotator (Pine Research, Inc.). A glassy carbon disk-platinum ring electrode (disk diameter 4.57 mm, ring width 5.38–4.93 mm, Pine Research, Inc.) was used as the working electrode. Platinum wire was used as the counter electrode. Oxygen-saturated 0.5 M H₂SO₄ solution was used as the electrolyte. A

standard Hg/HgSO₄ reference electrode (CH Instruments, Inc.) was used as the reference electrode. The potentials presented in this work are referred with respect to a normal hydrogen electrode (NHE). The catalysts were applied onto the disk electrode by an ink coating technique. The catalyst ink (5.0 mg·ml⁻¹) was prepared by ultrasonically blending the mixture of catalyst powder and isopropanol for 10 minutes. 20 µl of the ink was coated onto the glassy carbon disk gradually by a micro-syringe. After the evaporation of the solvent, 10 µl of diluted Nafion solution (0.1 wt%, Aldrich) was added onto the top of the catalyst layer. The Nafion film was dried naturally at room temperature. The CVs were recorded by scanning the disk potential from 1.0 to 0 V versus NHE with a scan rate of 20 mVs⁻¹. Before recording the CV curves, several potential scanning cycles were carried out to rule out the effect of possible contamination of the electrode surface. For the RRDE measurements, the ring potential was fixed at 1.2 V versus NHE to oxidize any peroxide produced during the potential scan of the disk electrode from open circuit potential (OCP) to 0 V versus NHE at a rate of 5 mVs⁻¹. All the experiments were performed at room temperature and ambient pressure.

The catalyst activity was also evaluated in a real PEM fuel cell (in-house 5.0 cm² single H₂-air fuel cell). Membrane electrode assemblies (MEAs) were fabricated by a spray method. The catalyst ink, which contained an appropriate amount of catalyst, ionomer, and solvent of water/isopropanol, was uniformly deposited onto the carbon paper by a homemade automatic pressurized spray deposition (PSD) system. The cathode catalyst layer had a catalyst loading of 5.0 mg·cm⁻² of either FePPy-MS or FePPy-VC, and the anode catalyst layer contained 0.3 mg·cm⁻² of Pt-Ru (20 wt% Pt-Ru/C, ETEK). Nafion® 112 membrane was used as the proton exchange membrane. The MEAs were hot-pressed at 135 °C using a Carver hydraulic press machine. The single-cell testing was carried out in a Fideris™ fuel cell test station. The single cell was operated at a temperature of 80 °C, a relative humidity of 100%, and a backpressure of 30 psig. Hydrogen with a flow rate of 20 ml·min⁻¹ and air with a flow rate of 100 ml·min⁻¹ were used as the fuel and oxidant feeds, respectively.

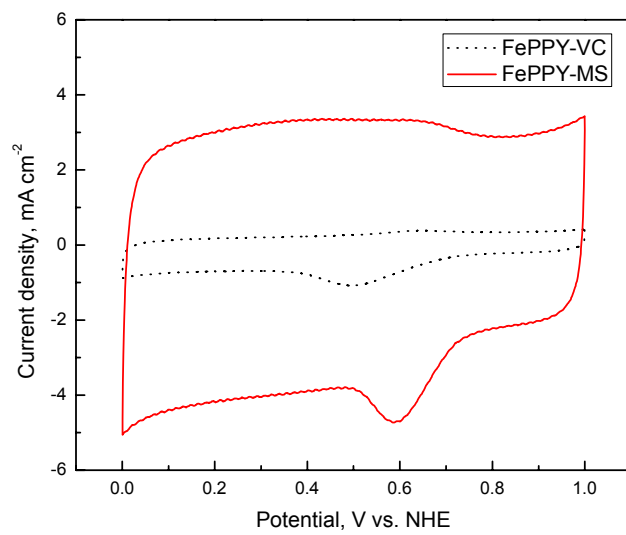
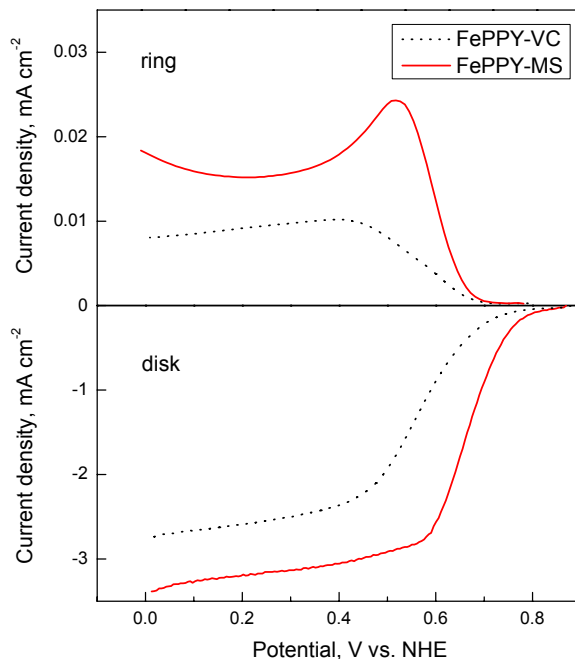
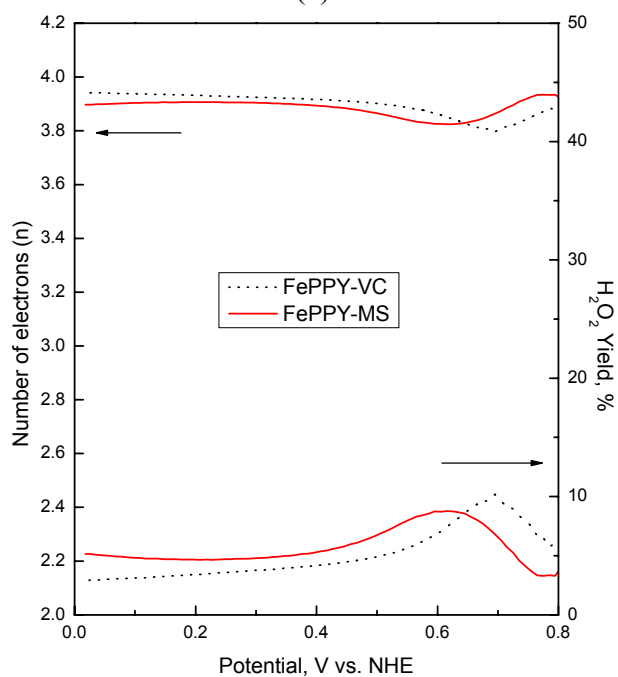


Figure S1. Cyclic voltammograms of carbon-supported FePPy (FePPy-VC) and self-supported FePPy mesoporous sphere (FePPy-MS) catalysts with a potential scan rate of $20 \text{ mV}\cdot\text{s}^{-1}$ in oxygen-saturated $0.5 \text{ M H}_2\text{SO}_4$.



(a)



(b)

Figure S2. RRDE results of carbon-supported FePPy (FePPy-VC) and self-supported FePPy mesoporous sphere (FePPy-MS) catalysts: (a) potential-current curves of disk and ring electrodes under a rotation rate of 900 rpm; (b) potential-reaction electron number and hydrogen peroxide yield curves.