

Supplementary Information

**Controlled synthesis and characterization of carbon-supported Pd₄Co nanoalloy
electrocatalysts for oxygen reduction reaction in fuel cells**

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Synthesis of the electrocatalysts by the modified polyol process

Carbon-supported Pd₄Co electrocatalysts with a metal(s) loading of 20 wt% were prepared by a modified polyol process described below. Required amounts of (NH₄)₂PdCl₄ (Aldrich) and CoCl₂·6H₂O (Alfa Aesar) to obtain 100 mg of Pd₄Co/C were dissolved in 40 mL of a mixed solution containing ethylene glycol (EG, a polyol) and water in the volume ratio of 2:1 by magnetic stirring. 25 mg of poly(vinylpyrrolidone) (PVP, MW = 40,000), which is much lower than that used in conventional polyol processes, was then dissolved in the above solution by sonication and magnetic stirring. After vigorous stirring for 1 h, a freshly prepared solution of NaBH₄ (Alfa Aesar) containing 200 mg of NaBH₄ in 40 mL of water was added dropwise to the above solution under stirring. The mixture was then refluxed at 130 °C for 2 h under a flowing nitrogen atmosphere and cooled to room temperature. To the dark brown or black colloidal solution thus formed, an appropriate amount of carbon (Vulcan XC 72R) was added to give a metal(s):C weight ratio of 20:80. The mixture was then kept under constant stirring for 2 h, and the slurry was filtered, washed copiously with ethanol and deionized water, and dried in an oven overnight at 100 °C. The as-prepared powders thus obtained were then examined by a Perkin Elmer FT-IR System (Spectrum BX) to detect if any PVP is present. The as-prepared powder is denoted hereafter as Pd₄Co/C-Ap. The sample was then heated at 350 and 500 °C in a flowing mixture of 10 % H₂-90 % Ar for 2 h and cooled to room temperature with a cooling rate of 5 °C/min, which are denoted

hereafter as Pd₄Co/C-350 and Pd₄Co/C-500 respectively. For a comparison, Pd/C and Pt/C electrocatalysts were also prepared by a similar process and denoted as Pd/C-Ap, Pd/C-350, Pd/C-500, Pt/C-Ap, Pt/C-350 and Pt/C-500.

Electrochemical characterization of the electrocatalysts

Cyclic voltammetry. The stability of the catalyst samples was assessed by cyclic voltammetry (CV) using a glassy carbon (GC) micro-electrode in a classical three-electrode system with 0.5 M H₂SO₄ or 0.5 M H₂SO₄ + 1 M methanol electrolyte solution. In the three-electrode test cell, the GC micro-electrode was taken as the working electrode and a Pt net and a saturated calomel electrode (SCE) were used, respectively, as the counter and reference electrodes. The GC micro-electrode was prepared as described below. 5 mg of the carbon-supported electrocatalyst synthesized was mixed with 1 mL of ethanol and ultrasonicated for 25 min to form an ink. 5 μL of the ink was then cast onto the GC electrode surface to form a thin film of electrocatalyst, followed by the application of 2 μL of 5% Nafion solution (Du Pont) to the thin film surface and drying the coating at 100 °C. The CV curves were obtained with a sweep rate of 20 mV s⁻¹ in the potential window of -0.24 to 1.1 V vs. SCE. Nitrogen gas was bubbled through the electrolyte solution to keep a clean reaction atmosphere.

Single cell evaluation. The electrocatalytic activity for ORR was assessed by single

cell measurements in PEMFC. The electrodes of PEMFC consisted of gas-diffusion and catalyst layers. The anode catalyst was a commercial 20 wt.% Pt/C (E-TEK) and the cathode catalysts were the synthesized Pt/C, Pd/C and Pd₄Co/C samples. The electrodes were impregnated with Nafion solution (5 wt.% solution, DuPont Fluoro-products) by a spray technique and dried at 90 °C under vacuum for 30 min. The metal or alloy loadings in both the anode and cathode were 0.4 mg cm⁻², and the Nafion loading for both the anode and cathode catalysts were 0.5 mg cm⁻². The membrane-electrode assemblies (MEAs) were fabricated by uniaxially hot-pressing the anode and cathode onto a Nafion 112 membrane (DuPont) at 140 °C for 2 min. The electrochemical performances in PEMFC of the MEAs were evaluated with a single-cell fixture having an active area of 5 cm² and by feeding humidified hydrogen into the anode at a flow rate of 100 mL min⁻¹ with a back pressure of 14 psi and humidified oxygen into the cathode at a flow rate of 200 mL min⁻¹ with a back pressure of 15 psi. The temperatures of the humidified hydrogen and oxygen were same as that of the cell temperature (60 °C).

The electrocatalytic activity for ORR was also assessed in single cell DMFC. In this case, the anode catalyst was a commercial 40 wt.% Pt–Ru (1:1) in carbon (E-TEK) and the cathode catalysts were Pd/C-350, Pt/C-350, Pd₄Co/C-350, and a commercial 20 wt.% Pt in carbon (Alfa Aesar). The electrodes were prepared by the same procedure as that for PEMFC. The metal or alloy loadings for the anode and

cathode were, respectively, 0.8 and 0.25 mg cm⁻², and the Nafion loading for both the anode and cathode catalysts were 0.35 mg cm⁻². The electrochemical performances in DMFC of the MEAs fabricated with Nafion 112 membrane (DuPont) were evaluated by feeding a preheated 1 M methanol solution into the anode at a flow rate of 2.5 mL min⁻¹ by a peristaltic pump without back pressurization and humidified oxygen into the cathode at a flow rate of 200 mL min⁻¹ with a back pressure of 20 psi. The temperatures of the preheated methanol solution and humidified oxygen were same as that of the cell temperature (65 °C).

Linear polarization measurements. To assess the electrocatalytic activity for ORR further and for extracting kinetic parameters, linear polarization (LP) measurements using a rotating disk electrode (RDE) were carried out with the same three-electrode system as that for the CV tests with 0.5 M H₂SO₄ electrolyte solution saturated with oxygen in the potential range of 1.0 to 0.1 V vs. NHE with a sweep rate of 5 mV s⁻¹. A 5 mm diameter glassy carbon rotating disk micro-electrode was taken as the working electrode and the micro-electrode was prepared by the same procedure described above for the CV tests. While the LP-RDE tests were carried out with 10 μL of the sample ink, the LP tests for extracting the electrochemical parameters were carried out with 5 μL of the sample ink. The rotating rate was fixed at 1600 rpm. All the electrode potential values attained in the LP tests were treated with iR correction.

