Pd-Ti and Pd-Co-Au electrocatalysts as a replacement for platinum for oxygen reduction in proton exchange membrane fuel cells

SUPPORTING INFORMATION

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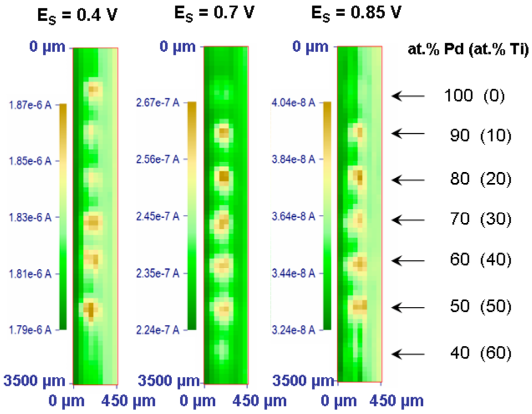

Figure S1 SECM images of oxygen reduction activity measured on a binary Pd-Ti array in 0.5 M H_2SO_4 by scanning a 25 µm tip generating oxygen above an array of different compositions at different potentials. Tip-substrate distance = 30 µm, tip current = -171 nA, and scan rate = 50 µm each 0.2 s. Potentials are vs. the hydrogen reference electrode. The image is a color-map graph of substrate current vs. tip position (X, Y).

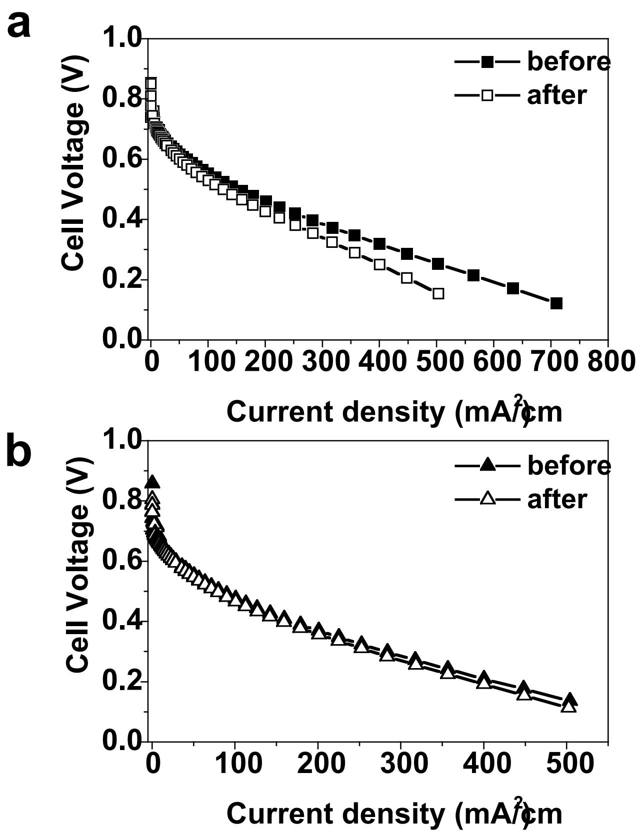

Figure S2 Comparison of steady-state polarization curves of the carbon supported catalysts: (a) 750 ^{o}C Pd(70)Co(20)Au(10) and (b) 900 ^{o}C Pd(50)Ti(50) for ORR in single cell PEMFC at 60 ^{o}C with a metal(s) loading of 0.2 mg/cm^2 before and after polarizing the cell at 200 mA/cm^2 for 12 h. The performance of the Pd-Ti/C sample is maintained even after polarizing the cell at 200 mA/cm^2 for 12 h, whereas the Pd-Co-Au/C sample was found to degrade, indicating the former is more stable than the latter. The current density values given are with respect to geometric electrode area.

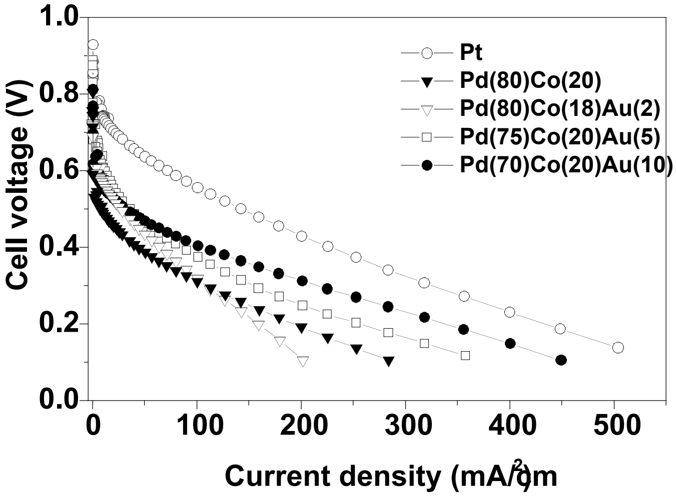

Figure S3. Comparison of the steady-state polarization curves of the carbon supported Pd-Co-Au catalysts with various Au contents (after heat treating at 500 °C) for ORR in single cell PEMFC with that of a commercial (Johnson-Matthey) Pt catalyst at 60 °C with a metal(s) loading of 0.2 mg/cm^2. The data were collected with Nafion 115 membrane, Pt anode catalyst loading of 0.2 mg/cm^2, humidifier temperature of 60 °C, and a hydrogen and oxygen pressures of, respectively, 18 and 20 psi. The Pd-Co/C catalyst shows poor performance compared to the Au incorporated Pd-Co-Au/C samples, suggesting that the incorporation of Au improves the ORR activity significantly. However, the electrocatalytic activity depends on the amount of Au in the sample. The Pd-Co-Au sample with 10-atom % Au shows the best performance with low polarization loss similar to that of a commercial Pt catalyst. The current density values given are with respect to geometric electrode area.

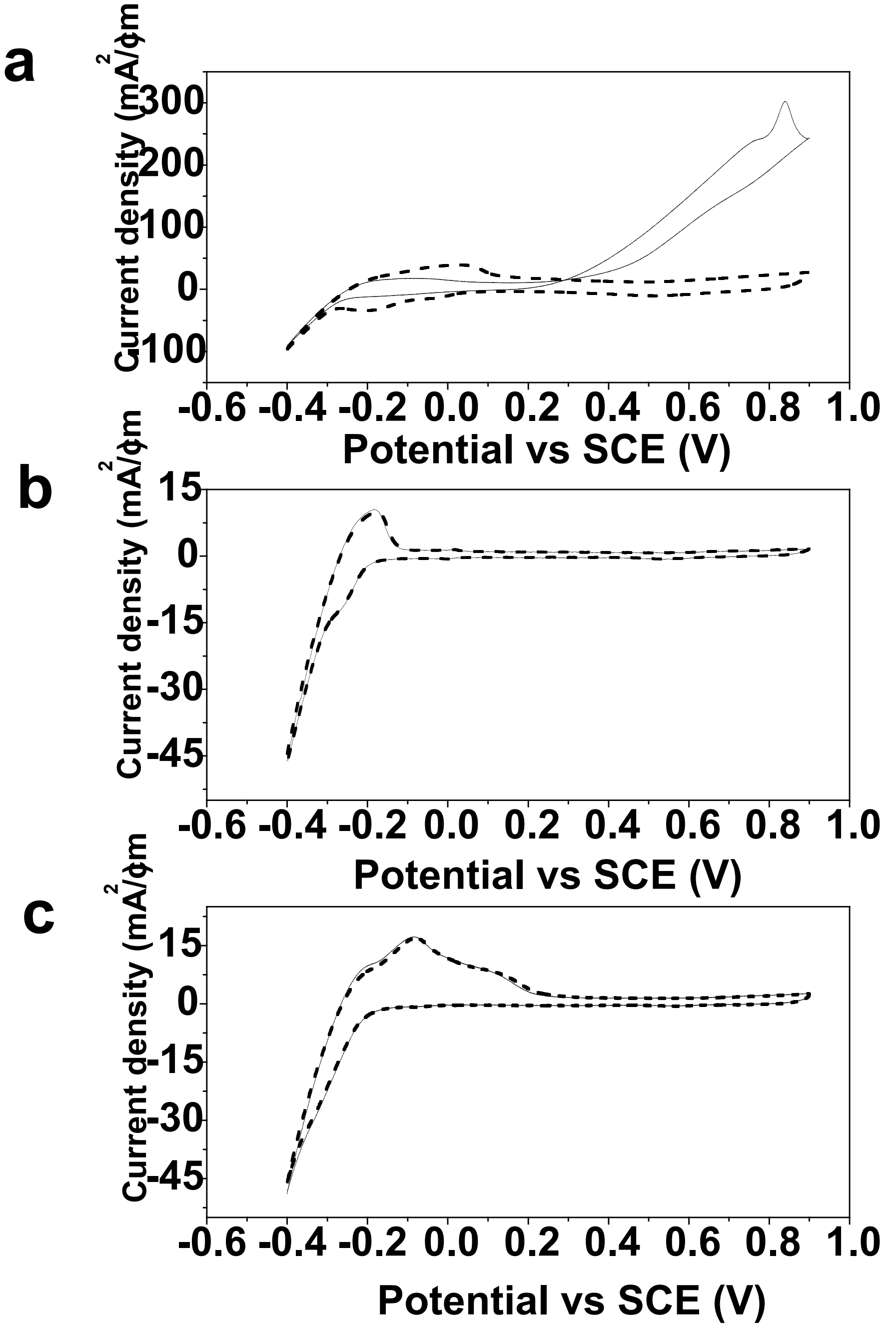

Figure S4. Cyclic voltammograms recorded in 1 M H_2SO_4 in the absence (----) and presence (—) of 1 M methanol with a scan rate of 25 mV/s at 25 °C: (a) commercial Pt, (b) 750 °C Pd-Co-Au, and (c) 900 °C Pd-Ti. Unlike the Pt catalyst, the Pd-Co-Au and Pd-Ti samples do not show any activity for methanol oxidation, indicating that the Pd-based electrocatalysts are more tolerant to methanol.

Experimental Details

Chemicals. Vulcan XC-72R carbon was purchased from the Cabot Corporation (Bellerica, MA). $(NH4)_2PdCl_4$ (Aldrich, Milwaukee, WI), H_2AuCl_4 (Alfa Aesar, Ward Hill, MA), $Co(NO_3)_2\cdot 6H_2O$ (Aldrich), $(C_3H_7O)_4Ti$ (Fluka), $NaBH_4$ (Aldrich), ethylene glycol (Alfa), glycerol (Alfa Aesar), and sulfuric acid (98 %, Alfa Aesar) were all of reagent grade and were used as received. Reagent solutions were prepared using Milli-Q water (Millipore Co., Bedford, MA). Glassy carbon plates were purchased from Alfa Aesar.

Preparation of carbon supported Pd-Co-Au electrocatalysts. The carbon supported Pd-based catalysts (referred to as Pd-Co-Au/C) with a metal(s) loading of 20 wt % was prepared by a reverse microemulsion method using sodium dioctylsulfosuccinate (AOT) as the surfactant and heptane as the oil phase. Microemulsion I was prepared by mixing required amounts of ammonium hexachloropalladate, cobalt nitrate, dihydrogen tetrachloroaurate, AOT, deionized water, and heptane under constant stirring followed by ultrasonication for 20 min. Microemulsion II was prepared by mixing sodium borohydride, AOT, deionized water, and heptane under constant stirring followed by ultrasonication for 20 min. In both the microemulsion, the molar ratio of water to AOT was kept at 10:1. Microemulsion I and Microemulsion II were mixed together and ultrasonicated for 2 h. After that, an appropriate amount of carbon (Vulcan XC 72R) was added to the mixture to give a metal(s):C weight ratio of 20:80. The resultant slurry was kept under constant stirring for 2 h, filtered, washed copiously with acetone and deionized water, and dried in an air oven for 2 h. In order to study the effect of heat-treatment on the catalytic activity, the samples thus synthesized were heated at 500, 750 and 900 ^{o}C in a flowing mixture of 10 % H_2 – 90 % Ar for 1 h followed by cooling to room temperature at a rate of 5 ^{o}C/min.

Preparation of carbon supported Pd-Ti electrocatalyst. The carbon supported Pd-Ti catalyst (referred to as Pd-Ti/C) with a metal loading of 20 wt % was prepared by an impregnation method. The precursor solutions used were 0.4 M titanium isopropoxide and 0.4 M ammonium tetrachloropalladate in ethylene glycol. Required amount of Vulcan XC-72 R carbon was suspended into the ethylene glycol solution containing required amounts of the metal salts. To the suspension, 50 mL of acetone was added and ultrasonicated for 30 min, followed by evaporating the solvent on a hot plate. The resulting material was placed in a porcelain boat and heated at 550 ^{o}C for 1 h in H_2 atmosphere. Further heat treatment was carried out in a flowing mixture of 10 % H_2-90 % Ar at 900 oC for 2 h, followed by cooling to room temperature at a rate of 5 ^{o}C/min.

Sample characterization. The Pd-Co-Au/C and Pd-Ti/C samples were characterized by X-ray diffraction patterns recorded at a slow scan rate between 10 and 70^{o} with a counting time of 10 s per 0.02^{o}.

Membrane-electrode assembly fabrication. The electrodes for testing in single cell PEMFC consisted of gas diffusion and catalyst layers. A teflonized carbon cloth was employed as current collector and electrode support. The gas-diffusion layer was made by spraying a mixture consisting of carbon black powder (Vulcan XC-72R), 40 wt % polytetrafluoroethylene (PTFE), and a solvent (mixture of water and isopropyl alcohol) onto a teflonized carbon cloth and drying in vacuum at 300 ^{o}C for 2 h. On top of this gas diffusion layer, the catalyst layer was deposited by spraying a mixture of the required amount of carbon-supported metal(s) catalyst, solvent (mixture of water and isopropyl alcohol) and 33 wt % Nafion, followed by sintering in vacuum at 90 ^{o}C for 1 h; all the electrodes had a uniform catalyst metal loading of 0.2 mg/cm2. The membrane-electrode assembly (MEA) was then fabricated by uniaxially hot-pressing the anode and cathode onto a pretreated Nafion 115 membrane (C.G.Processing) at 130 ^{o}C for 2 min. Before fabricating the MEA, the Nafion membrane was treated with a 5 wt % solution of H_2O_2, washed with deionized water, and then treated with 1 M H_2SO_4.

Fuel cell electrochemical characterization. The performances of the MEAs in PEMFC with the Pd-based catalysts synthesized in this study as cathodes and commercial Pt/C (20 wt %

platinum on carbon, Johnson Matthey) as anodes were evaluated with a commercial fuel cell test system (Compucell GT, Electrochem) and a single cell test rig with 5 cm^2 active geometrical area. Galvanostatic polarization studies were conducted at 60 ^{o}C with humidified hydrogen and oxygen gas reactants; the hydrogen and oxygen pressures were 18 and 20 psi respectively. For a comparison, a commercial sample of platinized carbon (20 wt % platinum on carbon, Johnson Matthey) was also examined as cathode.

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