Platinum-Gold Nanoparticles: A Highly Active Bifunctional Electrocatalyst for Rechargeable Lithium-Air Batteries

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Platinum-Gold Nanoparticles: A Highly Active Bifunctional Electro catalyst for Rechargeable Lithium-Air Batteries

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Lithium-air batteries have promise to reach over 3-fold greater energy density than lithium-ion batteries in the fully-packed cell level.1 During discharge of a lithium-air battery, oxygen is reduced by lithium ions to form lithium (per)oxides via: (1) 2Li+ + 2e- + O2 ↔ (Li2O)x solid having E(rev) = 2.96 V Li and/or (2) 4Li+ + 4e- + O2 ↔ 2(Li2O)solid having E(rev) = 2.91 V Li.2 Critical challenges that limit the practical use of this technology include the sluggish oxygen reduction reaction (ORR) (during discharge) and oxygen evolution reaction (OER) kinetics (during charging) in Li+- containing aprotic electrolytes.3 Therefore, it is vital to develop an effective electrocatalyst to catalyze both ORR and OER, namely a bifunctional electrocatalyst.

Our recent work4 has shown that catalysts can greatly influence the discharge and charge voltages of Li-O2 batteries, where Au is most active for ORR and Pt is the most active for OER among Pt, Au and C in bulk and nanoparticle forms. In this report, we combine Au and Pt onto the surfaces of individual PtAu nanoparticles, and examine the ORR and OER activity of such particles supported on carbon in Li-O2 cells. We show that a PtAu/C bifunctional catalyst gives rise to the highest round-trip efficiency (the ratio of discharge to charge voltage) of rechargeable Li2O2 batteries reported to date.

PtAu nanoparticles5 were synthesized by reducing HAuCl4 and H2PtCl6 in oleylamine (Supporting Information Figure S1) and then loaded onto Vulcan carbon (XC-72) to yield 40 wt% PtAu/C. The catalyst was thermally treated at 250 °C in Ar-saturated 0.5 M H2SO4 between 0.05 V-1.7 V vs. RHE (room temperature and 50 mV/s). Inset: (Left) HRTEM image of PtAu/C. (Right) Schematic representation of PtAu with arrows indicating the CV signatures for Pt (gray) and Au (yellow).

Pt and the oxide desorption on Au from CV data in Figure 1b, respectively. The specific ESA is 38 ± 4 m2/gPtAu which is in reasonable agreement with the dispersion estimated from TEM data. Surface atomic ratio of Pt/Au was found to be (60 ± 2%)/(40 ± 2%) which is in good agreement with the average particle composition obtained from EDX (Pt 56 ± 5% and Au 44 ± 5%) (Supporting Information for details).

As electrocatalytic activity is dominated by nanoparticle surface compositions, we use well-established cyclic voltammetry (CV) methods6 to obtain the electrochemical surface area (ESA) of Pt and Au of PtAu nanoparticles, from which surface atomic fractions can be estimated. The ESA of Pt and Au were estimated from the charge associated with hydrogen adsorption/desorption on Pt and the oxide desorption on Au from CV data in Figure 1b, respectively. The specific ESA is 38 ± 4 m2/gPtAu which is in reasonable agreement with the dispersion estimated from TEM data. Surface atomic ratio of Pt/Au was found to be (60 ± 2%)/(40 ± 2%) which is in good agreement with the average particle composition obtained from EDX (Pt 56 ± 5% and Au 44 ± 5%) (Supporting Information for details).

The electrocatalytic activity of PtAu/C for ORR and OER were examined in Li-O2 cells, which was compared with those of pure carbon (Vulcan XC-72), Pt/C and Au/C (Premetek, 40wt% on Vulcan XC-72). Cell configuration and the making of air electrodes are reported in the Supporting Information. All air electrodes have very comparable carbon-loadings. Catalyzed-carbon catalysts (i.e., 40 wt% Pt/C, 40 wt% Au/C and 40 wt% PtAu/C) have carbon-loadings of 0.50 ± 0.02 mg. Pure carbon electrodes have carbon-loadings of 0.65 ± 0.11 mg over an area of 1.27 cm2. The thicknesses for all the air electrodes are 14 μm ± 2 μm. As the metal volume fraction is negligible and the void volume fraction of catalyzed and non-catalyzed air electrodes is essentially the same,9 all our air electrodes are expected to have similar void volume for Li2O2 storage, and thus similar specific capacities.

The discharge and charge voltages of Li2O2 cells can be influenced greatly by PtAu nanoparticles used in the air electrode. While Figure 2a shows that Li2O2 cells of PtAu/C and pure carbon exhibited similar specific capacities (∼1200 mAh/gcarbon), air electrodes with PtAu/C had a higher round-trip efficiency than that with carbon only. During discharge (ORR), the discharge voltage of PtAu/C is consistently higher than pure carbon by ∼360 – 150 mV. During charge (OER), the charge voltages of PtAu/C fell in the range from 3.4 V Li to 3.8 V Li (with an average of ∼3.6 V Li), which is substantially lower (by 900 mV) than that of pure carbon (with an average voltage of ∼4.5 V Li). In order to verify that the charging current of voltages lower than 4 V Li is not

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Figure 1. (a) A representative TEM image (top right) and X-ray diffraction data of PtAuC. (b) Cyclic Voltammograms of PtAuC collected in Ar-saturated 0.5 M H2SO4 between 0.05 V-1.7 V vs. RHE (room temperature and 50 mV/s). Inset: (Left) HRTEM image of PtAu/C. (Right) Schematic representation of PtAu with arrows indicating the CV signatures for Pt (gray) and Au (yellow).
Remarkably, at 50 mA/g carbon, Li-O2 cells with PtAu/C can deliver lower charging voltages than MnOx/C9 (4.2 V Li), whereas 57% was found for the pure carbon electrode; rate in mA/g carbon not reported). The authors thank J. Suntivich and J. Kim for the fruitful discussion on CV measurement/interpretation.

Supporting Information Available: PtAu/C synthesis and characterization, electrode preparation, electrochemical measurements.

8. (b) Bruce, P. G. J. Power Sources 2007, 174, 1177-1182.
PtAu nanoparticles (NPs) were shown to strongly enhance the kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in rechargeable Li-O₂ cells. Li-O₂ cells with PtAu/C were found to exhibit the highest round-trip efficiency reported to date. During discharge (ORR via $x\text{Li}^+ + \text{O}_2 + xe^- \rightarrow \text{Li}_x\text{O}_2$), the discharge voltage with PtAu/C is considerably higher than pure carbon and comparable to Au/C. During charge (OER via $\text{Li}_x\text{O}_2 \rightarrow x\text{Li}^+ + \text{O}_2 + xe^-$), the charge voltages with PtAu/C fell in the range from 3.4 $V_{\text{Li}}$ to 3.8 $V_{\text{Li}}$, which is slightly lower than Pt. It is hypothesized that PtAu NPs exhibit bifunctional catalytic activity having surface Au and Pt atoms primarily responsible for ORR and OER kinetics in Li-O₂ cells, respectively.