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Platinum-Gold Nanoparticles: A Highly Active Bifunctional Electrocatalyst 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 Erev = 2.96 VLi and/or (2) 4Li+ + 4e− + O2 ↔ 2(Li2O)solid having Erev = 2.91 VLi.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) (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 Li2O2 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 dry air to remove the nanoparticle surfactant before battery assembly (see Supporting Information for details). Transmission electron microscopy (TEM) shows that PtAu nanoparticles are uniformly distributed on carbon (Figure 1), having a number-averaged particle size of 6.8 ± 1.4 nm (Supporting Information Figure S2) and a volume-averaged diameter of 7.3 nm (yielding a dispersion of 40 m2/gPtAu). In addition, X-ray diffraction data of PtAu/C indicate that Pt and Au atoms form a solid-solution (Figure 1a), which is in agreement with previous reported powder diffraction file (PDF#01-074-5396) database for Pt5Au5Sb1.6 This is further supported by energy-dispersive X-ray (EDX) mapping by scanning transmission electron microscopy revealing Pt and Au atoms distributed uniformly within individual particles (Supporting Information Figure S3).

As electrocatalytic activity is dominated by nanoparticle surface compositions, we use well-established cyclic voltammetry (CV) methods7 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 Li2O2 cells, which was compared with those of pure carbon (Vulcan XC-72), Pt/C and Au/C (Premeetek, 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,8 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 ¾ 360 – 150 mV. During charge (OER), the charge voltages of PtAu/C fell in the range from 3.4 VLi to 3.8 VLi (with an average of ¾ 3.6 VLi), which is substantially lower (by 900 mV) than that of pure carbon (with an average voltage of ¾ 4.5 VLi). In order to verify that the charging current of voltages lower than 4 VLi is not

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Figure 1. (a) A representative TEM image (top right) and X-ray diffraction data of PtAu/C. (b) Cyclic Voltammograms of PtAu/C 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).
a result of electrolyte decomposition, cells were charged under both Ar and O₂. The charge associated with electrolyte decomposition on PtAu/C became significant only above 4.0 V_Li,
proving that PtAu/C catalyzes the oxidation of lithium (per)oxide discharge products at voltages as low as 3.4 V_Li. The round-trip
efficiency of the PtAu/C cathode in Li-O₂ cells was 73%, which is
much improved relative to 57% found for the pure carbon
cathode. Interestingly, the PtAu/C catalyst exhibits considerably
lower charging voltages than MnOₓ/C and α-MnO₂ nanotubes,α and C₀₃O₄
at a comparable
current density of 70 mAh/g_carbon. Moreover, PtAu/C shows higher
OER activity than pyrolyzed cobalt phthalocyanine supported on
Pt/C and Au/C while charging voltages with PtAu/C at the same rate, as shown in Figure 3a.
In order to understand the roles of surface Pt and Au atoms of
PtAu/C in catalyzing ORR and OER kinetics, first discharge and
charge voltages of Li-O₂ cells with PtAu/C were compared with
those with Pt/C and Au/C at the same rate, as shown in Figure 3a.
The discharge voltages with PtAu/C are comparable to those with
Pt/C while charging voltages with PtAu/C are comparable to those with Pt/C. This result indicates that surface Pt and Au atoms
on PtAu/C are responsible for ORR and OER kinetics, respectively. Therefore, PtAu/C demonstrates bifunctional
catalytic activity for ORR and OER in Li-O₂ cells. Interestingly,
the charging voltages of PtAu/C became lower than Pt/C in
subsequent cycles (Figure 2 and Supporting Information Figure S4), which were reproducible over multiple cells. The physical
origin of the enhanced OER activity and lowered charging potentials of PtAu/C compared to Pt/C are not understood and
will be investigated in future studies.

We further examine the effect of current density on the
discharge and charge voltages of Li-O₂ cells with PtAu/C. With
decreasing current densities, the difference between discharge and
charge voltages was further reduced considerably, as shown in
Figure 3b. Remarkably, at 50 mAh/g_carbon Li-O₂ cells with PtAu/C
can deliver ≈50% (=1000 mAh/g_carbon) of the discharge capacity
above 2.7 V_Li and ≈50% (=1000 mAh/g_carbon) of the charge capacity below 3.5 V_Li, rendering a round-trip efficiency of ≈77%.
While it is not surprising to observe increased discharge capacity with decreasing current densities as reported in several previous studies,α β, it is interesting to note that charging voltages are
lowered by a few hundreds of milli-volts with decreasing current
densities by a factor of five, which cannot be explained simply by

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**Figure 2.** (a) Li-O₂ cell discharge/charge profiles of carbon (black) and
PtAu/C (red) in the third cycle at 0.04 mA/cm²_electrode (100 mA/g_carbon
for PtAu/C, 85 mA/g_carbon for carbon) (b) Background measurement
during charging at 100 mA/g_carbon of an Ar and O₂-filled cell (charging
first) for PtAu/C.

**Figure 3.** (a) Li-O₂ cell 1st discharge/charge profiles of carbon at
85 mA/g_carbon, Pt/C, and PtAu/C at 100 mA/g_carbon. (b) Li-O₂ cell
discharge/charge profiles (1st cycle) of PtAu/C at 50 mA/g_carbon,
100 mA/g_carbon, and 250 mA/g_carbon (see Figure S5 for background
measurements)

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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 $\text{xLi}^+ + \text{O}_2 + \text{xe}^- \rightarrow \text{Li}_x\text{O}_2$), the discharge voltage with PtAu/C is considerably higher than pure carbon and comparable to Au/C. During charge (OER via $\text{Li}_x\text{O}_2 \rightarrow \text{xLi}^+ + \text{O}_2 + \text{xe}^-$), the charge voltages with PtAu/C fell in the range from 3.4 $\text{V}_\text{Li}$ to 3.8 $\text{V}_\text{Li}$, 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.