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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) $2\text{Li}^+ + 2\text{e}^- + \text{O}_2 \leftrightarrow (\text{Li}_2\text{O}_2)_{\text{solid}}$ having $E_{\text{rev}} = 2.96 \text{ V}_{\text{Li}}$ ² and/or (2) $4\text{Li}^+ + 4\text{e}^- + \text{O}_2 \leftrightarrow 2(\text{Li}_2\text{O})_{\text{solid}}$ having $E_{\text{rev}} = 2.91 \text{ V}_{\text{Li}}$.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 Li-O₂ 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 $6.8 \pm 1.4 \text{ nm}$ (Supporting Information Figure S2) and a volume-averaged diameter of 7.3 nm (yielding a dispersion of $40 \text{ m}^2/\text{g}_{\text{PtAu}}$). 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 Pt_{0.5}Au_{0.5}.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

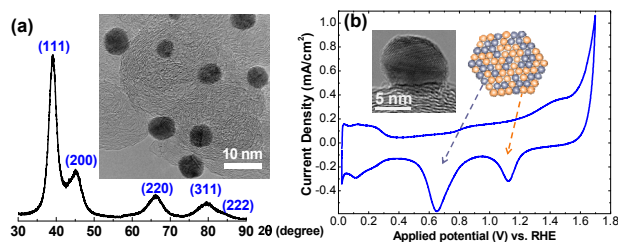


Figure 1. (a) A representative TEM image (top right) and X-ray diffraction data of PtAu/C. (b) Cyclic voltammograms of PtAu/C collected in Ar-saturated 0.5 M H₂SO₄ between 0.05 V-1.7 V vs. RHE (room temperature and 50 mV/s). Inset: (Left) HRTEM image of PtAu/C. (Right) Schematic representation of PtAu with arrows indicating the CV signatures for Pt (gray) and Au (yellow).

on Pt and the oxide desorption on Au from CV data in Figure 1b, respectively. The specific ESA is $38 \pm 4 \text{ m}^2/\text{g}_{\text{PtAu}}$, which is in reasonable agreement with the dispersion estimated from TEM data. Surface atomic ratio of Pt/Au was found to be $(60 \pm 2\%)/(40 \pm 2\%)$ which is in good agreement with the average particle composition obtained from EDX (Pt $56 \pm 5\%$ and Au $44 \pm 5\%$) (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 $0.50 \pm 0.02 \text{ mg}$. Pure carbon electrodes have carbon-loadings of $0.65 \pm 0.11 \text{ mg}$ over an area of 1.27 cm^2 . The thicknesses for all the air electrodes are $14 \mu\text{m} \pm 2 \mu\text{m}$. 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 Li_xO₂ storage, and thus similar specific capacities.

The discharge and charge voltages of Li-O₂ cells can be influenced greatly by PtAu nanoparticles used in the air electrode. While Figure 2a shows that Li-O₂ cells of PtAu/C and pure carbon exhibited similar specific capacities ($\approx 1200 \text{ mAh}/\text{g}_{\text{carbon}}$), 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 $\approx 360 - 150 \text{ mV}$. During charge (OER), the charge voltages of PtAu/C fell in the range from $3.4 \text{ V}_{\text{Li}}$ to $3.8 \text{ V}_{\text{Li}}$ (with an average of $\approx 3.6 \text{ V}_{\text{Li}}$), which is substantially lower (by 900 mV) than that of pure carbon (with an average voltage of $\approx 4.5 \text{ V}_{\text{Li}}$). In order to verify that the charging current of voltages lower than 4 V_{Li} is not

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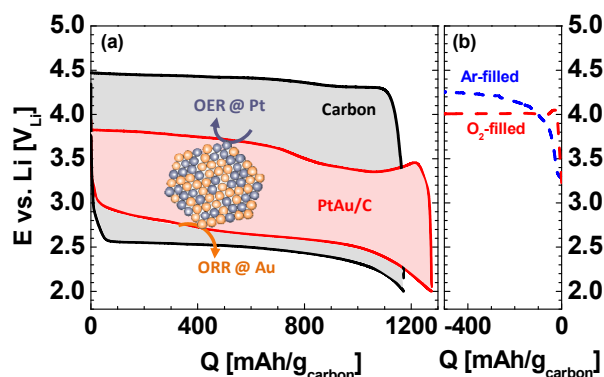


Figure 2. (a) Li-O₂ cell discharge/charge profiles of carbon (black) and PtAu/C (red) in the third cycle at 0.04 mA/cm²_{electrode} (100 mA/g_{carbon} for PtAu/C, 85 mA/g_{carbon} for carbon) (b) Background measurement during charging at 100 mA/g_{carbon} of an Ar and O₂-filled cell (charging first) for PtAu/C.

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 MnO_x/C⁹ (≈4.2 V_{Li}), λ-MnO₂,^{3d} α-MnO₂ nanotubes,^{3f} and Co₃O₄^{3b} (≈4.0 V_{Li}) at a comparable current density of 70 mA/g_{carbon}. Moreover, PtAu/C shows higher OER activity than pyrolyzed cobalt phthalocyanine supported on carbon reported previously,^{3c} where below 3.6 V_{Li}, PtAu/C has a charging capacity of ~500 mAh/g_{carbon} (at 0.04 mA/cm²_{electrode}) while the cobalt-based catalyst delivers ≈60 mAh/g_{carbon} at similar conditions (0.05 mA/cm²_{electrode}; rate in mA/g_{carbon} not reported).

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 Au/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 mA/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,^{3d,3e,10} 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

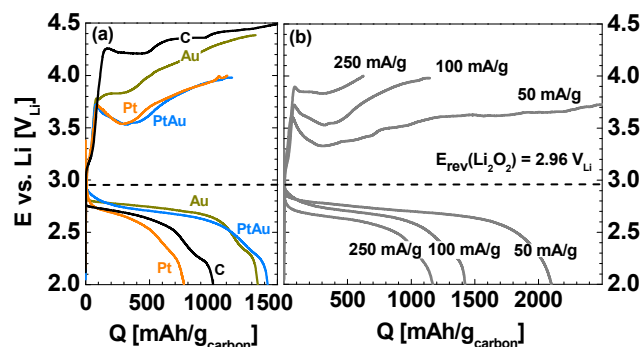


Figure 3. (a) Li-O₂ cell 1st discharge/charge profiles of carbon at 85 mA/g_{carbon}, Au/C, Pt/C, and PtAu/C at 100 mA/g_{carbon}. (b) Li-O₂ cell discharge/charge profiles (1st cycle) of PtAu/C at 50 mA/g_{carbon}, 100 mA/g_{carbon}, and 250 mA/g_{carbon} (see Figure S5 for background measurements)

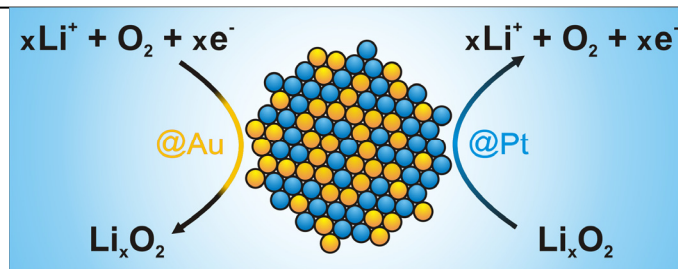
lowered surface kinetics overpotentials. However, it is believed that the natures of product formation/distribution could also affect the reaction voltages, which requires further studies.

In summary, we show that PtAu/C exhibits bifunctional catalytic activity, where it is hypothesized that surface Au and Pt atoms are primarily responsible for ORR and OER kinetics in Li-O₂ cells, respectively. To our knowledge, PtAu/C reported here demonstrates the lowest charging voltage and highest round-trip efficiency of Li-O₂ cells reported to date.^{3b,3c,3f} This work shows that placing select atoms (such as Pt and Au) on nanoparticle surfaces can be a promising strategy to develop highly active bifunctional catalysts for Li-air batteries.

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

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PtAu nanoparticles (NPs) were shown to strongly enhance the kinetics 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_{Li} to 3.8 V_{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.