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

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Abstract: PtAu nanoparticles (NPs) were shown to strongly enhance the kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in rechargeable $Li−O_2$ cells. $Li−O_2$ cells with PtAu/C were found to exhibit the highest round-trip efficiency reported to date. During ORR via $xLi^+ + O_2 + xe^- \rightarrow Li_xO_2$, the discharge voltage with PtAu/C was considerably higher than that of pure carbon and comparable to that of Au/C. During OER via $Li_xO_2 \rightarrow xLi^+ + O_2 + xe^-$, the charge voltages with PtAu/C fell in the range from 3.4 to 3.8 V_{Li}, which is slightly lower than obtained with 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 $Li−O_2$ cells, respectively.

Figure 1. (a) Representative TEM image (top right) and XRD data of PtAu/C. (b) Cyclic voltammograms of PtAu/C collected in Ar-saturated 0.5 M H_2SO_4 between 0.05 and 1.7 V vs RHE (room temperature and 50 mV/s). Insets: (left) HRTEM image of PtAu/C and (right) schematic representation of PtAu, with arrows indicating the CV signatures for Pt (gray) and Au (yellow).

Lithium−air batteries have promise to reach over 3-fold greater energy density than lithium−ion batteries at 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) $2Li^+ + 2e^- + O_2 \rightleftharpoons (Li_2O_2)_{solid}$, having $E_{rev} = 2.96$ V_{Li},[2] and/or (2) $4Li^+ + 4e^- + O_2 \rightleftharpoons 2(Li_2O)_{solid}$, 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 for both ORR and OER, namely a bifunctional electrocatalyst.

Our recent work[4] has shown that catalysts can greatly influence the discharge and charge voltages of $Li−O_2$ batteries, where Au is the most active for ORR and Pt is the most active for OER among Pt, Au, and C in bulk and nanoparticle (NP) forms. In this report, we combine Au and Pt onto the surfaces of individual PtAu NPs and examine the ORR and OER activity of such particles supported on carbon in $Li−O_2$ cells. We show that a PtAu/C bifunctional catalyst gives rise to the highest round-trip efficiency (the ratio of discharge to charge voltages) of rechargeable $Li−O_2$ batteries reported to date.

PtAu NPs[5] were synthesized by reducing $HAuCl_4$ and H_2PtCl_6 in oleylamine (Supporting Information (SI), 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 NP surfactant before battery assembly (see SI for details). Transmission electron microscopy (TEM) shows that PtAu NPs are uniformly distributed on carbon (Figure 1), having a number-averaged particle size of 6.8 ± 1.4 nm (SI, Figure S2) and a volume-averaged diameter of 7.3 nm (yielding a dispersion of 40 m^2/g_{PtAu}). In addition, X-ray diffraction (XRD) data of PtAu/C indicate that Pt and Au atoms form a solid-solution (Figure 1a), which is in agreement with the previously reported powder diffraction file (PDF
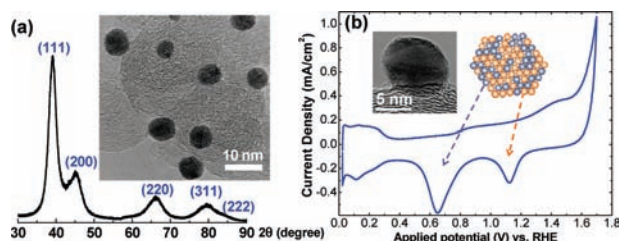
no. 01-074-5396) database record for $Pt_{0.5}Au_{0.5}$.[6] This is further supported by energy-dispersive X-ray (EDX) mapping in a scanning TEM, revealing Pt and Au atoms distributed uniformly within individual particles (SI, Figure S3).

As electrocatalytic activity is dominated by NP surface compositions, we use well-established cyclic voltammetry (CV) methods[7] to obtain the electrochemical surface area (ESA) of Pt and Au of PtAu NPs, from which surface atomic fractions can be estimated. The ESAs 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 m^2/g_{PtAu}, which is in reasonable agreement with the dispersion estimated from TEM data. The 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, $56 \pm 5\%$; Au, $44 \pm 5\%$) (see SI for details).

The electrocatalytic activity of PtAu/C for ORR and OER was examined in $Li−O_2$ cells and compared with those of pure carbon (Vulcan XC-72), Pt/C, and Au/C (Premetek, 40 wt % on Vulcan XC-72). The cell configuration and assembly of air electrodes are described in the SI. All air electrodes had very comparable carbon loadings. Catalyzed carbon catalysts (i.e., 40 wt % Pt/C, 40 wt % Au/C, and 40 wt % PtAu/C) had carbon loadings of 0.50 ± 0.02 mg. Pure carbon electrodes had carbon loadings of 0.65 ± 0.11 mg over an area of 1.27 cm^2. The thickness for all the air electrodes was 14 $\mu m \pm 2$ μm. As the metal volume fraction was negligible and the void volume fraction of catalyzed and noncatalyzed air electrodes was essentially the same,[8] all our air electrodes were expected to have similar void volumes for Li_xO_2 storage, and thus similar specific capacities.

The discharge and charge voltages of $Li−O_2$ cells can be influenced greatly by PtAu NPs used in the air electrode. While $Li−O_2$ cells of PtAu/C and pure carbon exhibited similar specific capacities (∼1200 $mA \cdot h/g_{carbon}$), air electrodes with PtAu/C were found to have a higher round-trip efficiency than that with carbon only, as shown in Figure 2a. During ORR, the discharge voltage of PtAu/C is consistently higher
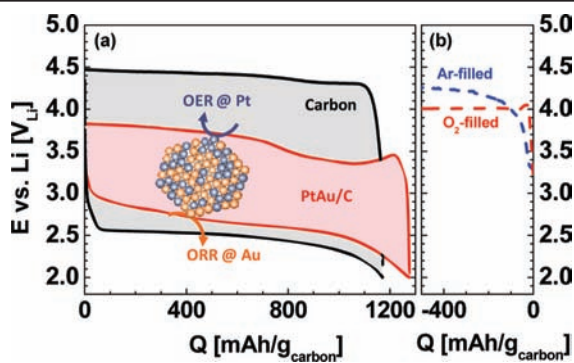
Figure 2. (a) Li−O$_2$ cell discharge/charge profiles of carbon (black, 85 mA/g$_{carbon}$) and PtAu/C (red, 100 mA/g$_{carbon}$) in the third cycle at 0.04 mA/cm$^2_{electrode}$. (b) Background measurement during charging at 100 mA/g$_{carbon}$ of Ar- and O$_2$-filled cells (charging first) for PtAu/C.

Figure 3. (a) Li−O$_2$ cell first discharge/charge profiles of carbon at 85 mA/g$_{carbon}$ and of Au/C, Pt/C, and PtAu/C at 100 mA/g$_{carbon}$. (b) Li−O$_2$ cell discharge/charge profiles (first cycle) of PtAu/C at 50, 100, and 250 mA/g$_{carbon}$. (See SI, Figure S5, for background measurements.)

than that of pure carbon by ∼150−360 mV. During OER, the charge voltage of PtAu/C fell in the range from 3.4 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 a result of electrolyte decomposition, cells were charged under both Ar and O$_2$. The charge associated with electrolyte decomposition on PtAu/C became significant only above 4.0 V$_{Li}$ (that on pure carbon and Au/C is ≥4.7 V$_{Li}$),[4] 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−O$_2$ cells was 73%, which is much improved relative to the 57% found for the pure carbon cathode. Interestingly, the PtAu/C catalyst exhibits considerably lower charging voltages than MnO$_x$/C[9] (∼4.2 V$_{Li}$), λ-MnO$_2$,[3d] α-MnO$_2$ nanotubes,[3f] and Co$_3$O$_4$[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 mA·h/g$_{carbon}$ (at 0.04 mA/cm$^2_{electrode}$), while the cobalt-based catalyst delivers ∼60 mA·h/g$_{carbon}$ at similar conditions (0.05 mA/cm$^2_{electrode}$; 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−O$_2$ 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−O$_2$ cells. Interestingly, the charging voltages of PtAu/C became lower than those of Pt/C in subsequent cycles (Figure 2 and SI, Figure S4), which was reproducible over multiple cells. The physical origin of the enhanced OER activity and lowered charging potentials of PtAu/C compared to Pt/C is 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−O$_2$ 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−O$_2$ cells with PtAu/C can deliver ∼50% (∼1000 mA·h/g$_{carbon}$) of the discharge capacity above 2.7 V$_{Li}$ and ∼50% (∼1000 mA·h/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,e,10] it is interesting to note that charging voltages are lowered by a few hundred millivolts with
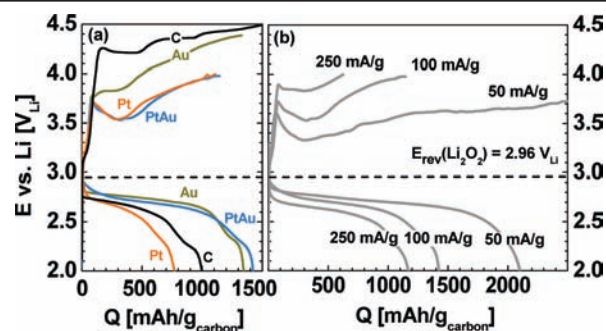
decreasing current densities by a factor of 5, which cannot be explained simply by lower surface kinetics overpotentials. It is believed that the nature of product formation/distribution could affect the reaction voltages, which requires further studies.

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−O$_2$ cells, respectively. To our knowledge, PtAu/C reported here demonstrates the lowest charging voltage and highest round-trip efficiency of Li−O$_2$ cells reported to date.[3b,c,f] 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.

Supporting Information Available: PtAu/C synthesis and characterization, electrode preparation, and electrochemical measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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