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*The Influence of Catalysts on Discharge and Charge Voltages of Rechargeable Li–Oxygen Batteries*

# The Influence of Catalysts on Discharge and Charge Voltages of Rechargeable Li–Oxygen Batteries

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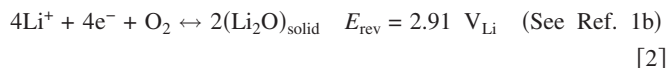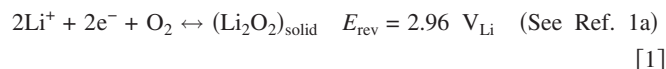
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This study revealed the strong influence of carbon, Au/C, and Pt/C catalysts on the charge and discharge voltages of rechargeable Li–O$_2$ batteries. Li–O$_2$ single-cell measurements showed that Au/C had the highest discharge activity, while Pt/C exhibited extraordinarily high charging activity.
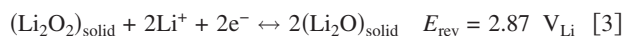© 2010 The Electrochemical Society. [DOI: 10.1149/1.3363047] All rights reserved.

Rechargeable Li-air battery performance with aprotic organic electrolytes is limited by cathode kinetics, viz., the formation and decomposition of lithium (per)oxide

$$2\text{Li}^+ + 2e^- + \text{O}_2 \leftrightarrow (\text{Li}_2\text{O}_2)_{\text{solid}} \quad E_{\text{rev}} = 2.96 \text{ V}_{\text{Li}} \quad \text{(See Ref. 1a)}$$
[1]

$$4\text{Li}^+ + 4e^- + \text{O}_2 \leftrightarrow 2(\text{Li}_2\text{O})_{\text{solid}} \quad E_{\text{rev}} = 2.91 \text{ V}_{\text{Li}} \quad \text{(See Ref. 1b)}$$
[2]

with reversible cell voltages, $E_{\text{rev}}$, referenced vs Li/Li$^+$ (as all potentials throughout this article). Although $E_{\text{rev}}$ for Li$_2$O$_2$ is often reported as $\approx$3.1 V$_{\text{Li}}$,[2,3] no references to the thermodynamic database underlying its derivation were provided. $E_{\text{rev}}$ for the (Li$_2$O$_2$)$_{\text{solid}}$ formation derived from published Gibbs free energy values is 2.96 V$_{\text{Li}}$ ($E_{\text{rev}} = -\Delta G/nF$, where $\Delta G$ is the Gibbs free energy of the reaction, $n$ is the number of electrons transferred, and $F$ is the Faraday constant).[1a] Single-cell Li-air battery tests followed by ex situ Raman spectroscopy[2,4] have revealed Li$_2$O$_2$ as the major discharge product, while oxygen consumption measurements during discharge suggest a partial formation of Li$_2$O.[5] The latter could also form as a secondary product during discharge[1]

$$(\text{Li}_2\text{O}_2)_{\text{solid}} + 2\text{Li}^+ + 2e^- \leftrightarrow 2(\text{Li}_2\text{O})_{\text{solid}} \quad E_{\text{rev}} = 2.87 \text{ V}_{\text{Li}} \quad [3]$$

Not only can Li-air battery cathode catalysts determine the current-dependent charge/discharge potentials (i.e., the roundtrip efficiency) but they also affect whether Li$_2$O$_2$ vs Li$_2$O is formed because $E_{\text{rev}}$ for Li$_2$O$_2$ and Li$_2$O formation is very similar. Unfortunately, the effect of catalysts on the reaction kinetics of the oxygen reduction reaction (ORR) during discharge and the oxygen evolution reaction (OER) during charging in rechargeable Li-air batteries using aprotic electrolytes is poorly understood, hindering the progress of this technology. The ORR mechanism in aprotic electrolytes is complex and poorly understood. Hummelshøj et al.[6] suggested that oxygen can be reduced by lithium via a one-electron transfer process forming LiO$_2$ (adsorbed on the surface). This is followed by another one-electron reduction forming Li$_2$O$_2$ (solid). Alternatively, Laoire and co-workers[7] proposed that LiO$_2$ could chemically decompose to Li$_2$O$_2$ and O$_2$ through a disproportionation reaction. The further reduction of Li$_2$O$_2$ to Li$_2$O is also thermodynamically possible in the typical discharge potential range of Li–O$_2$ batteries (2.8–2.0 V$_{\text{Li}}$).[1]

Li-air battery specific capacities, however, are dominated by the electrode porosity required to provide Li$_2$O$_x$ storage[8] and by oxygen diffusion through the electrolyte-flooded pores.[5] Thus, using high oxygen pressures and electrolytes with high oxygen solubility increases specific activities,[9] which is consistent with current distribution modeling.[10] Conventionally, specific capacities for carbon-based Li-air cathodes are normalized to carbon weight, with values reported as high as 2500–5000 mAh/g$_{\text{carbon}}$.[4,11,12] For cathodes based on high surface area carbon blacks with a carbon volume fraction of $\approx$15%,[13] the maximum specific capacities can be estimated by assuming a required electrolyte volume fraction of 25% (capacities calculated this way were experimentally verified for the ice filling of fuel cell cathodes[14] discharged at $-$20°C and 10 mA/cm$^2$). While these estimated maximum capacities shown in Table I agree well with capacities reported at low discharge rates (e.g., 5000 mAh/g$_{\text{carbon}}$ at 0.01 mA/cm$_{\text{electrode}}^2$),[11] lower capacities are obtained at higher discharge rates[3,9,10] having a lower degree of electrode pore filling with Li$_2$O$_x$.[10] To compare cathode capacities of Li-air with those of Li-ion batteries, capacities must be normalized to the lithiated (discharged) cathode mass, including carbon in Li-air cathodes due to its high mass fraction. Table I shows that $>$5-fold higher specific capacities and $>$4-fold higher specific energies are projected for Li-air cathodes compared to state-of-the-art LiCoO$_2$, whereby a considerably higher capacity could be obtained by catalysts selective for Li$_2$O formation during discharge and active for electro-oxidizing Li$_2$O upon charging.

Although catalysts should affect discharge (ORR) and charge (OER) potentials, very similar average discharge voltages of $\approx$2.6 V$_{\text{Li}}$ have been shown for a wide range of catalysts (carbon, Pt, and transition-metal oxides),[15] identical with values reported for $\lambda$-MnO$_2$,[5] $\alpha$-MnO$_2$ nanowires,[4] MnO$_x$/C,[12] and carbon-supported pyrolyzed Co macrocycles[2] at comparable discharge currents (70 mA/g$_{\text{carbon}}$ or 0.1 mA/cm$_{\text{electrode}}^2$). This could either be explained by assuming that the ORR in a Li-air cathode is not a catalytically sensitive reaction or by assuming that the ORR activity of added carbon itself is sufficiently high to mask the ORR activity of catalysts of interest (most Li-air battery catalyst studies use cathodes with 60–75 wt % carbon).[4,15] Conversely, the charging (OER) activity of carbon is poor, with an average voltage plateau of $\approx$4.7 V$_{\text{Li}}$[15] vs $\approx$4.2 V$_{\text{Li}}$ on MnO$_x$/C[12] and $\approx$4.0 V$_{\text{Li}}$ on $\lambda$-MnO$_2$,[5] $\alpha$-MnO$_2$ nanowires,[4] and Co$_3$O$_4$[15] (70 mA/g$_{\text{carbon}}$ or 0.1 mA/cm$_{\text{electrode}}^2$). The lowest charging voltage reported so far was $\approx$3.6 V$_{\text{Li}}$ for pyrolyzed cobalt phthalocyanine supported on carbon,[2] which was measured, however, at a lower rate of 0.05 mA/cm$_{\text{electrode}}^2$. Clearly, catalyst development is needed to reduce the ORR/OER potential losses and to increase the Li-air battery roundtrip efficiency.

Here, we compare the effect of catalyzed (40 wt % Au/C or 40 wt % Pt/C) and pure Vulcan-XC72 carbon cathodes on the discharge and charge voltages of single-cell Li–O$_2$ batteries. The discharge and charge voltage profiles of Li–O$_2$ cells reveal that 40 wt % Au/C is most active for the ORR while 40 wt % Pt/C has remarkable activity for charging (OER). These findings agree well with the oxidative current densities obtained from potentiostatic measurements of Li/Li$_2$O$_2$ cells, reflecting the activity associated with the electro-oxidation of Li$_2$O$_2$ on these catalysts.

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**Table I. Maximum specific capacity and energy for Li-air cathodes compared to LiCoO$_2$ intercalation cathodes in current Li-ion batteries. Underlying assumptions for carbon black (e.g., Vulcan-XC72) based Li-air cathodes: (*i*) carbon packing density of 0.36 g/cm$^3$ with $\approx$15% carbon volume fraction,[13] (*ii*) 25% electrolyte volume fraction, and (*iii*) complete filling of the 60% void volume fraction with Li$_2$O$_x$ product.**

|  | Li$_2$O$_2$ | Li$_2$O | LiCoO$_2$ |
|---|---|---|---|
| Specific capacity with respect to carbon (mAh/g$_{carbon}$) | 4600 | 6000 | Not applicable |
| Specific capacity with respect to C + Li$_2$O$_x$ or LiCoO$_2$ (mAh/g$_{cathode}$) | 900 | 1350 | 160 |
| Average discharge voltage (V$_{Li}$) | 2.75 | 2.75 | 3.9 |
| Specific energy density with respect to C + Li$_2$O$_x$ or LiCoO$_2$ (mWh/g$_{cathode}$) | 2450 | 3700 | 620 |

## Experimental

All experiments were conducted at room temperature in 1 M LiClO$_4$ in a propylene carbonate (PC):1,2-dimethoxyethane (DME) (1:2 v/v) electrolyte, prepared from LiClO$_4$, PC, and DME from Sigma-Aldrich (all <30 ppm H$_2$O). The solvent system was chosen because most Li-air battery data in the literature used either PC[4,12,15,16] or PC with co-solvents.[3,5,9] Figure 1a shows the Li–O$_2$ battery configuration used in this study, consisting of a lithium foil (15 mm diameter), two pieces of Celgard separator (C480, 17 mm diameter), and a Nafion-bonded cathode (12.7 mm diameter) coated on a Celgard C480 using either pure Vulcan XC-72 carbon, 40 wt % Au/C (Vulcan), or 40 wt % Pt/C (Vulcan) from Premetek. High metal loading catalysts were used to ensure that the performance of cathodes with Au/C and Pt/C in Li–O$_2$ cells reflected differences in the intrinsic catalytic activity of Au and Pt relative to C. Due to the high electronic conductivity of Vulcan carbon in the Nafion-bonded electrodes ($\approx$1 S/cm[13]), electron conduction resistances in all cathodes were negligible. Au/C and Pt/C dispersions estimated from X-ray powder diffraction line broadening were $\approx$13 m$^2$/g$_{Au}$ and $\approx$80 m$^2$/g$_{Pt}$, respectively. Cathodes with a Nafion/carbon weight ratio of 0.5/1 were prepared by coating ultrasonicated inks composed of carbon or catalyst, Nafion dispersion (DE2020, Ion-Power), and 2-propanol (Sigma-Aldrich) onto the separator. After air-drying at 20°C for about 20 min and subsequent vacuum-drying for 3 h, the cathodes were weighed and then soaked in excess electrolyte, yielding lithium-ion-exchanged Nafion. All cathode carbon loadings were within 0.65 $\pm$ 0.15 mg (0.51 $\pm$ 0.12 mg/cm$^2_{electrode}$). Li–O$_2$ cells were assembled in the following order: (*i*) placing a lithium foil onto the cell's stainless steel current collector, (*ii*) adding 10 $\mu$L of electrolyte, (*iii*) placing two pieces of the separator onto the lithium foil, (*iv*) adding 10 $\mu$L electrolyte, (*v*) placing the cathode-coated separator onto the separator, (*vi*) adding on top a cathode current collector (316 stainless steel mesh and spring), and (*vii*) purging the cell with PC/DME-saturated oxygen for 10 min. Afterward, the cells were sealed and tested galvanostatically (Solartron 1470) at 0.1 mA/cm$^2_{electrode}$ with a low voltage limit of 2.0 V$_{Li}$ and with upper limits of 4.5 V$_{Li}$ (pure carbon, subsequently held at 4.5 V$_{Li}$ for 5 h before the next discharge), 4.4 V$_{Li}$ (Au/C, no holding), and 4.0 V$_{Li}$ (Pt/C, no holding) to avoid electrolyte decomposition.

The activity of the Vulcan-XC72 (40 wt % Au/C and 40 wt % Pt/C) catalysts for the electro-oxidation of Li$_2$O$_2$ (OER) was measured in argon-filled cells (Tomcell type TJ-AC) with a lithium anode and two Celgard 2500 separators. Kynar-bonded cathodes with and without Li$_2$O$_2$ were prepared from ultrasonicated inks containing carbon or catalyst, poly(vinylidene fluoride) (PVDF, Kynar) dissolved in *N*-methyl pyrrolidone (<50 ppm H$_2$O, Alfa Aesar), and ground Li$_2$O$_2$ (Aldrich 90%) for Li$_2$O$_2$-filled electrodes. Inks were coated onto aluminum foil (0.019 mm thick, McMaster), vacuum-dried at 70°C, and cut (15 mm diameter). Cathode carbon loadings were within 0.85 $\pm$ 0.15 mg (0.48 $\pm$ 0.08 mg/cm$^2_{electrode}$) at a PVDF/carbon weight ratio of 3.6/1. The Li$_2$O$_2$/carbon weight ratio was 1/1, equating to an estimated charging capacity of 1050 mAh/g$_{carbon}$ for Li$_2$O$_2 \leftrightarrow$ 2Li + O$_2$ (considering 90% Li$_2$O$_2$ sample purity). Potentiostatic tests were performed at 4.0–4.5 V$_{Li}$ for 10 h after an initial 30 min rest following cell assembly. Net Li$_2$O$_2$ electro-oxidation currents were obtained by subtracting carbon-mass normalized currents of Li$_2$O$_2$-free electrodes from those filled with Li$_2$O$_2$. While Al current collectors were used in Li-air cathodes previously,[16] some minor Al corrosion was reported to occur at 4.5 V$_{Li}$ in LiClO$_4$-based electrolytes (15 $\mu$A/cm$^2$).[17] We thus examined the background current densities from Li$_2$O$_2$-free electrodes, which were 1–2 orders of magnitude lower than those from Li$_2$O$_2$-filled electrodes measured at 4.5 V$_{Li}$ (>150 $\mu$A/cm$^2_{electrode}$ or >300 mA/g$_{carbon}$). This agrees with the observation that no apparent change for the Al current collectors was found after any measurements of electrodes without or with Li$_2$O$_2$.

## Results and Discussion

Galvanostatic discharging and charging tests under oxygen (Fig. 1b) reveal pronounced catalytic effects for both ORR and OER. The ORR activity trends are obtained by comparing the discharge voltage profiles of Li–O$_2$ cells with different catalysts. 40 wt % Au/C demonstrated an onset voltage of $\approx$2.8 V$_{Li}$, and its average voltage plateau of $\approx$2.7 V$_{Li}$ (only $\approx$0.3 V lower than the estimated equilibrium voltage of 2.96 V$_{Li}$ for Li$_2$O$_2$ formation) is higher than those of manganese-oxide-based cathodes at lower (70 mA/g$_{carbon}$)[4,12,15] or equal discharge currents
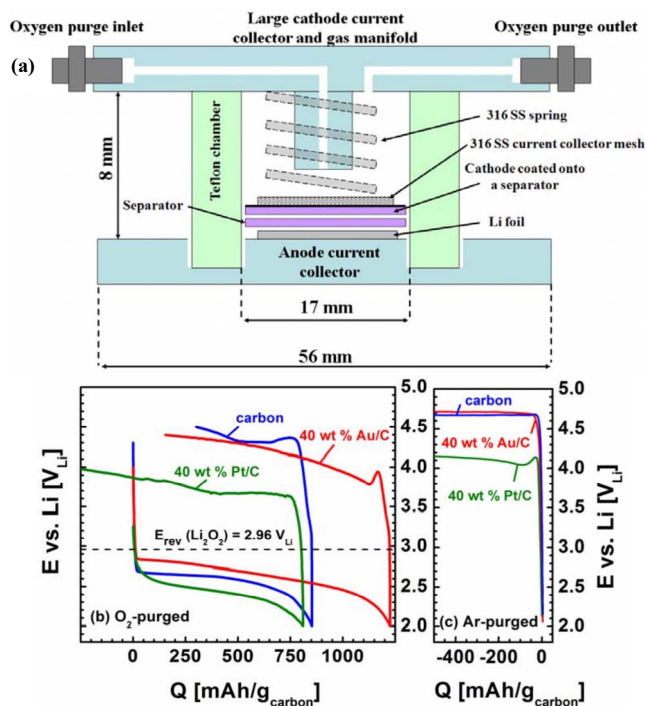


**Figure 1.** (Color online) (a) Li–O$_2$ single-cell configuration. (b) Li–O$_2$ single-cell discharge/charge (second cycle) at 0.1 mA/cm$^2_{electrode}$, corresponding to $\approx$150 mA/g$_{carbon}$ (carbon) or $\approx$250 mA/g$_{carbon}$ (Au/C and Pt/C). (c) Background measurement during charging at 0.1 mA/cm$^2_{electrode}$ of an argon-filled cell for pure carbon, 40 wt % Pt/C, and 40 wt % Au/C.

$(0.1 \ \mathrm{mA/cm^2_{electrode}})$.[5] The pure Vulcan carbon provides an onset voltage of $\approx 2.7 \ \mathrm{V_{Li}}$ and an average voltage plateau of $\approx 2.6 \ \mathrm{V_{Li}}$, while 40 wt % Pt/C shows a lower discharge voltage of $\approx 2.5 \ \mathrm{V_{Li}}$, which may thus be rationalized by blocking of the Vulcan carbon surface by Pt having lower activity (estimated $> 25\%$ of the Vulcan surface for 40 wt % Pt/C based on $\approx 30 \ \mathrm{m^2_{Pt}/g_{catalyst}}$ and $\approx 60 \ \mathrm{m^2_{carbon}/g_{catalyst}}$ using the external surface areas of Pt and Vulcan). This order of activity is consistent with a cyclic voltammetry study on the ORR activity of flat model electrodes in the same electrolyte, yielding an intrinsic ORR activity trend of Au > glassy carbon > Pt.[18] Therefore, no measurable difference in the discharge voltages of cathodes with different catalysts reported previously[15] can be attributed to the reasonably high intrinsic ORR activity of carbon and its large mass fraction in these cathodes ($\approx 60$ to 75 wt %).[15] Lastly, although solid $Li_2O_x$ products are formed during discharge, the discharge voltage of Au/C is higher than that of Pt/C and C, suggesting that the $Li_2O_x$ formation is catalyzed by the Au surface throughout most of the discharge process, analogous to what is found for the water–ice formation reaction during oxygen reduction in a fuel cell at $-20°C$.[14]

Specific discharge capacities of $Li–O_2$ cells at $0.1 \ \mathrm{mA/cm^2_{electrode}}$ or $250 \ \mathrm{mA/g_{carbon}}$ (Fig. 1b) with Au/C were $\approx 1500 \ \mathrm{mAh/g_{carbon}}$, which is roughly 2–3 times lower than that reported for $MnO_x$-based cathodes discharged at a lower rate of $70 \ \mathrm{mA/g_{carbon}}$.[4,12] The difference is likely due to the generally observed increase in specific capacity with decreasing current densities.[3,9,10] However, only $\approx 800 \ \mathrm{mAh/g_{carbon}}$ was observed for pure Vulcan and Pt/C electrodes. Because all our cathodes have the same carbon loading and thickness and because the void volume fraction of catalyzed and noncatalyzed Vulcan-carbon electrodes is essentially the same (the metal volume fraction is negligible),[13] all of our cathodes should have the same available volume for $Li_xO_2$ storage. Because the latter strongly affected specific discharge capacities,[8] one would expect to obtain similar specific capacities for our cathodes, independent of the catalyst. Although it is relatively straightforward to relate the enhanced ORR kinetics of Au/C to increased discharge voltages, the substantially higher discharge specific capacity for Au/C (reproducible over three cells) compared to carbon and Pt/C is not understood. We suggest that different catalysts may yield different reaction products ($LiO_2$, $Li_2O$, or $Li_2O_2$), analogous to the ORR in aqueous electrolytes with predominantly $H_2O_2$ on Au and C, in contrast to $H_2O$ on Pt. Thus, variation in discharge product formation/distribution in the cathode may affect the discharge capacity, which needs to be examined in future studies.

40 wt % Pt/C demonstrated an average charging plateau of $\approx 3.8 \ \mathrm{V_{Li}}$ in Fig. 1b, substantially below the onset voltage of electrolyte decomposition. To determine the influence of electrolyte decomposition on the OER current, the cells were first charged under argon at $0.1 \ \mathrm{mA/cm^2_{electrode}}$, revealing electrolyte decomposition on Pt/C at $\approx 4.1 \ \mathrm{V_{Li}}$ compared to $\approx 4.5 \ \mathrm{V_{Li}}$ on carbon and Au/C (Fig. 1c). The charging voltage of Pt/C is lower than the $\approx 4.0 \ \mathrm{V_{Li}}$ reported for manganese oxides and $Co_3O_4$ at lower ($70 \ \mathrm{mA/g_{carbon}}$)[4,12,15] or equal currents ($0.1 \ \mathrm{mA/cm^2_{electrode}}$).[5] Thus, the Pt/C catalyst (Fig. 1b) exhibits the lowest charging voltage reported so far, only matched by pyrolyzed carbon-supported cobalt macrocycles measured, however, at a lower rate ($0.05 \ \mathrm{mA/cm^2_{electrode}}$).[2] It is followed by the Au/C catalyst (half-capacity at $\approx 4.2 \ \mathrm{V_{Li}}$), which in turn is more active than high surface area ($240 \ \mathrm{m^2/g}$) Vulcan carbon (half-capacity at $\approx 4.4 \ \mathrm{V_{Li}}$). Vulcan is more active than Super-S with only $40 \ \mathrm{m^2/g}$ ($\approx 4.7 \ \mathrm{V_{Li}}$ at $70 \ \mathrm{mA/g_{carbon}}$) reported previously,[15] reflecting the importance of catalyst surface area on reaction rates and cell voltages.

As the charging voltage of $Li–O_2$ cells is influenced not only by the catalyst OER activity but also by catalyst-dependent discharge products ($Li_2O_2$ vs $Li_2O$), Fig. 1b only affords a qualitative OER activity comparison. Because $Li_2O_2$ is reported as the major discharge product in $Li–O_2$ cells,[2,4] we further compared the electro-oxidation activity (current densities) of $Li_2O_2$ with Au/C, C, and
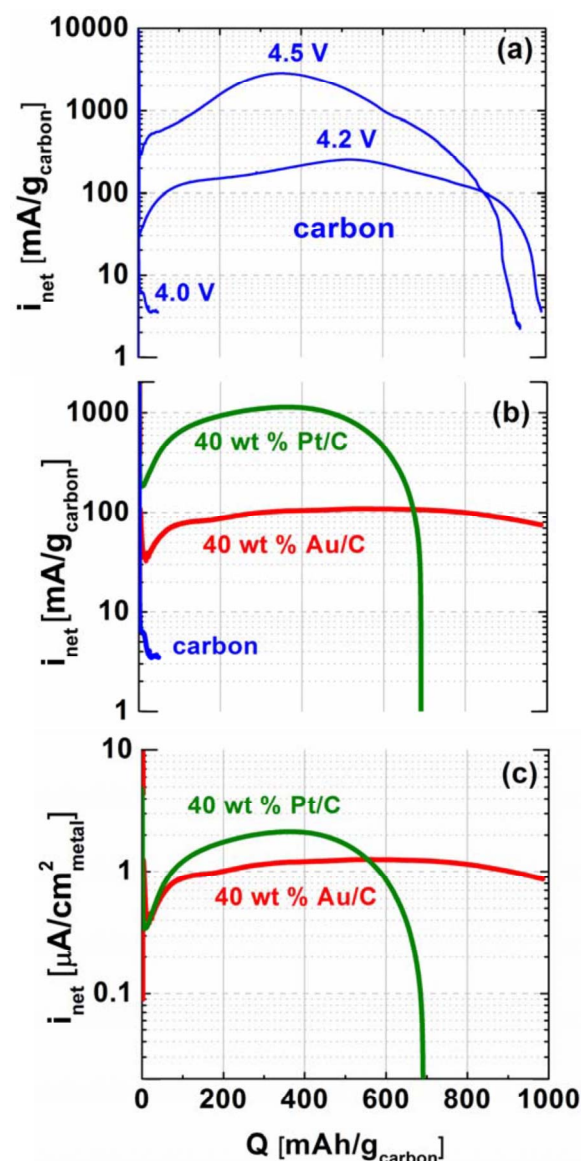


**Figure 2.** (Color online) Net $Li_2O_2$ decomposition currents, $i_{net}$, vs integrated charge of $Li_2O_2$-filled cathodes under argon: (a) Carbon cathodes at various potentials; (b) carbon, 40 wt % Au/C, and 40 wt % Pt/C at $4.0 \ \mathrm{V_{Li}}$; and (c) same as (b), but currents are normalized to Pt and Au surface areas.

Pt/C catalysts with the trend in the charging voltage of $Li–O_2$ cells shown in Fig. 1b. The activity for the electro-oxidation of $Li_2O_2$ on these three catalysts was measured by the potentiostatic charging of $Li_2O_2$-filled cathodes. For carbon cathodes, net currents of $\approx 150 \ \mathrm{mA/g_{carbon}}$ were obtained at $4.2 \ \mathrm{V_{Li}}$ (Fig. 2a) and the current was negligible at $4.0 \ \mathrm{V_{Li}}$, which is consistent with the $Li–O_2$ cell data in Fig. 1b (background currents in $Li_2O_2$-free electrodes were negligible; see the Experimental section). Furthermore, the accumulated charge agrees, within experimental error, with the estimated charging capacity (see the Experimental section). The same was observed for galvanostatically charged $Li_2O_2$-filled Super-S carbon-based cathodes,[16] even though their charging voltage ($\approx 4.5 \ \mathrm{V_{Li}}$ at $10 \ \mathrm{mA/g_{carbon}}$) is substantially higher than that of the Vulcan-based cathodes shown in Fig. 2a ($4.2 \ \mathrm{V_{Li}}$ at $\approx 100 \ \mathrm{mA/g_{carbon}}$), probably due to the faster reaction rates per gram of carbon obtained for Vulcan with a higher surface area ($240 \ \mathrm{m^2/g}$) than Super-S ($40 \ \mathrm{m^2/g}$). While the charging current density clearly must decrease with increasing time (specific capacity) as $Li_2O_2$ is depleted by oxi-

dation (Fig. 2a), the origin of the initial increase in current density is not understood, which might be related to the increase in available surface reaction sites during the initial stages of $Li_2O_2$ oxidation. At 4.0 $V_{Li}$, the $Li_2O_2$ electro-oxidation current density was found the highest for Pt/C, then for Au/C, and lowest for carbon, which mirrors the trend in the charging voltage of Li–$O_2$ cells (Fig. 1b). The Pt/C cathode can provide a charging rate $> 200$ mA/$g_{carbon}$ at 4.0 $V_{Li}$, which is more active for the electro-oxidation of $Li_2O_2$ than the manganese oxide having 10 mA/$g_{carbon}$ at $\approx 4.3$ $V_{Li}$ in similar experiments.[16] The intrinsic $Li_2O_2$ electro-oxidation activities on Au/C and Pt/C were obtained by normalizing current densities to the metal surface area in the cathode, as shown in Fig. 2c. It shows that Pt/C and Au/C have a comparable intrinsic $Li_2O_2$ decomposition activity; consequently, Au/C catalysts with higher dispersion than 13 $m^2/g_{Au}$ should yield a similarly high charging activity as the Pt/C catalyst ($\approx 80$ $m^2/g_{Pt}$) used in this study.

## Conclusions

This study shows the strong influence of carbon, Au/C, and Pt/C catalysts on the charge and discharge potentials of rechargeable Li–$O_2$ batteries. A single-cell Li–$O_2$ battery reveals that Au/C is the most effective ORR catalyst in comparison to a Vulcan carbon and Pt/C (Au/C $\gg$ C $>$ Pt/C). Conversely, Pt/C is the most effective catalyst for the charging of Li–$O_2$ cells, i.e., providing one of the lowest reported charging voltages ($\approx 3.8$ $V_{Li}$ at 250 mA/$g_{carbon}$), which agrees well with its high electro-oxidation activity in $Li_2O_2$-filled cathodes at 4.0 $V_{Li}$.

## Acknowledgments

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