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## Method Development to Evaluate the Oxygen Reduction Activity of High-Surface-Area Catalysts for Li-Air Batteries

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This study presents a new method to quantitatively determine the electrocatalytic activity of Vulcan carbon and Vulcan-supported Au nanoparticles, dispersed as catalyst thin films on glass carbon, for oxygen reduction in an aprotic electrolyte using rotating disk electrode measurements. The ORR activity of Vulcan carbon can be described by a Tafel slope of 120 mV/dec and Levich-Koutecky analysis of Vulcan carbon suggests that solvated LiO<sub>2</sub> is the initially formed O<sub>2</sub> reduction product. Discharge voltages extrapolated from this thin-film method are in excellent agreements with those of Li-oxygen batteries demonstrating its validity to serve as an effective technique for catalyst screening.

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Rechargeable Li-air batteries have the potential to provide gravimetric energy three or four times that of conventional Li-ion batteries.<sup>1</sup> The discharge reaction in an Li-air battery is the reduction of oxygen with lithium ions to form lithium (per)oxide: (1)  $2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$  at 2.96 V<sub>Li</sub> (Refs. 1 and 2), (2)  $4\text{Li} + \text{O}_2 \leftrightarrow 2\text{Li}_2\text{O}$  at 2.91 V<sub>Li</sub> (Refs. 1 and 2) (V<sub>Li</sub> refers to the potential measured vs. metallic lithium in the same electrolyte). During charge, these oxides need to be decomposed electrochemically to regenerate lithium and oxygen. There are a number of challenges that need to be overcome in order to make rechargeable Li-air batteries practical, which include increasing round-trip efficiency [best values in the range of ~70% (Ref. 3) to ~75% (Ref. 4)], rate capability (typically 0.1–1.0 mA/cm<sup>2</sup>),<sup>5,6</sup> and cycle life (at best 10–100 cycles).<sup>3,7,8</sup> etc. Very recently, it has been shown that catalyzed high-surface-area carbon (e.g., Pt/C) in the air electrode can greatly influence the discharge and charge voltages of rechargeable Li-O<sub>2</sub> batteries.<sup>1,4,9</sup> The search for new catalysts<sup>1,3,4,9–11</sup> with improved activity for the oxygen reduction reaction (ORR) during discharge and for the oxygen evolution reaction (OER) during charge is crucial to further enhance the round-trip efficiency of Li-air batteries. Effective catalyst development, however, requires the experimental ability to quantitatively determine the electrocatalytic activity of high-surface-area catalysts. The conventional way to evaluate catalyst activity is to fabricate carbon-based porous electrodes and to measure the discharge voltage profiles in a Li-O<sub>2</sub> single cell configuration.<sup>10</sup> However, the evaluation of the intrinsic electrocatalytic activity of high-surface-area catalysts from such single-cell tests is often complicated by the presence of unquantifiable transport resistances, which can be caused by poor oxygen, lithium-ion, and electron transport across thick air electrodes (typically 20–50 μm). In addition, the presence of solid discharge products in the case of Li-air batteries using organic electrolytes (i.e., Li<sub>2</sub>O, Li<sub>2</sub>O<sub>2</sub>, and probably LiO<sub>2</sub> surface films) can poison the active catalyst surfaces for the ORR. For example, Aurbach and co-workers<sup>12</sup> suggested that O<sub>2</sub> reduction in the presence of Li<sup>+</sup> ions leads to the formation of lithium superoxide and lithium peroxide precipitates that block the electrode surface, where a charge of 200 μC/cm<sup>2</sup> per monolayer (ML) of adsorbed LiO<sub>2</sub> can be assumed.

In order to determine the intrinsic electrocatalytic activity of high-surface-area catalysts for rechargeable Li-air batteries, we have developed a method for the quantitative evaluation of the electrocatalytic activity of high-surface-area catalysts dispersed as a thin-film layer (~1 to ~5 μm) on a glassy carbon rotating disk electrode (RDE), analogous to that developed for ORR activity measurements in aqueous electrolytes.<sup>13,14</sup> Employing such thin films to study ORR

kinetics essentially eliminates all undefined mass-transport resistances. In addition, this technique reduces the amount of catalyst required for testing and simplifies the testing procedure. Here we utilize pure Vulcan carbon (Vulcan XC 72) and 40 wt % Au/Vulcan to demonstrate the experimental approach and to outline the analysis procedure. ORR activity values of pure Vulcan and 40 wt % Au/Vulcan obtained by the described method are then compared quantitatively with the discharge voltages measured in Li-O<sub>2</sub> single-cells. The Levich-Koutecky analysis of RDE data collected from non-catalyzed Vulcan carbon at suitably high catalyst loadings (0.1 mg<sub>carbon</sub>/cm<sup>2</sup>; ~3 μm thickness) suggests one-electron oxygen reduction having solvated LiO<sub>2</sub> as the initially formed O<sub>2</sub> reduction product.

### Experimental

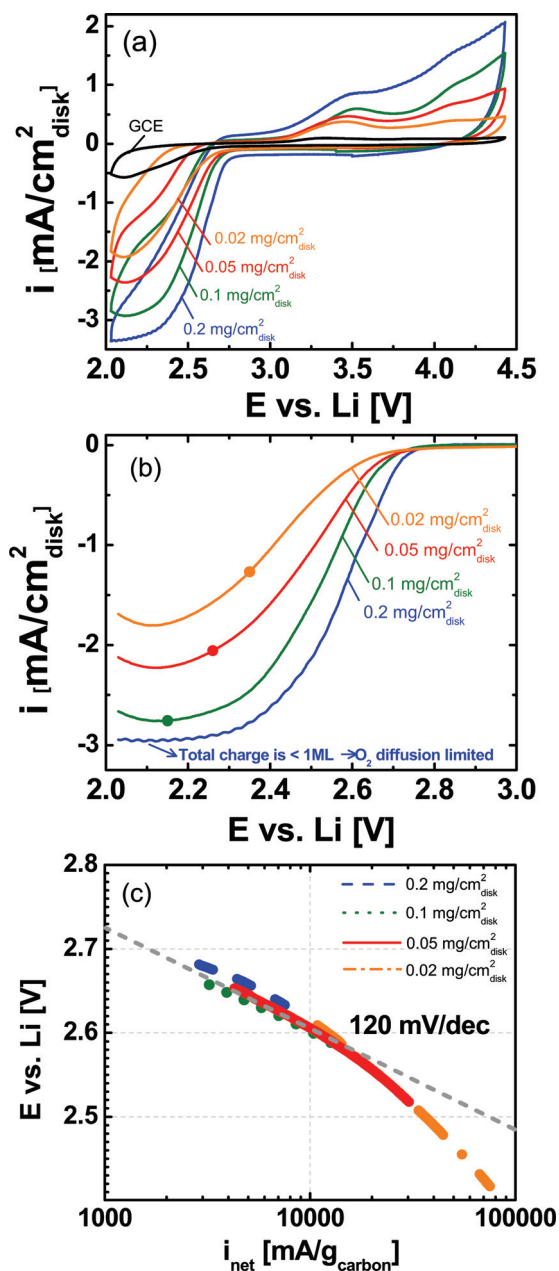
All experiments were conducted in 1 M LiClO<sub>4</sub> in PC:DME (1:2 v/v) electrolyte, prepared from lithium perchlorate, propylene carbonate, and 1,2-dimethoxyethane from Sigma-Aldrich (all <50 ppm H<sub>2</sub>O) at room temperature. It should be noted that PC has been reported to be react with superoxide ions.<sup>8,12</sup> However, PC solvent or co-solvent has been used in most Li-air studies to date<sup>3,5,6,10,15–20</sup> due to its low volatility, its high solubility for lithium salts (i.e., LiPF<sub>6</sub> and LiClO<sub>4</sub>), and its consequently high conductivity. The latter is critical to enable the RDE experiments presented in this work in order to minimize the ohmic losses associated with the large currents obtained with high-surface-area catalysts.

Catalyst thin films and three-electrode cells were prepared as following. Glassy carbon disks (0.196 cm<sup>2</sup> disks; Pine, USA) were polished to a 0.05 μm mirror-finish before each experiment. Thin films of pure Vulcan XC-72 or 40 wt % Au/Vulcan (Premetek, USA) were prepared by drop-casting catalyst inks with a Nafion/carbon weight ratio of 0.5/1 onto a glassy carbon disk, yielding carbon loadings ranging from 0.2 to 0.02 mg<sub>carbon</sub>/cm<sup>2</sup><sub>disk</sub>. The catalyst inks were composed of Vulcan or Au/Vulcan, lithiated Nafion (LITHion dispersion, Ion Power, USA), and 20% 2-propanol (Sigma-Aldrich) in deionized water. The catalyst thin-films were subsequently dried in air for 24 h before testing. The description of the three-electrode cell used for RDE measurements was reported recently<sup>9</sup>; it consists of a lithium-foil counter electrode embedded into nickel foam (INCOFOAM), a reference electrode based on a silver wire immersed into 0.1 M TBAPF<sub>6</sub> (Sigma-Aldrich) and 0.01 M AgNO<sub>3</sub> (BASi) in PC:DME (1:2 v/v) which was calibrated against Li metal (0 V<sub>Li</sub> ≈ −3.53 ± 0.02 V vs. Ag/Ag<sup>+</sup>), and a catalyst-covered glassy carbon disk as the working electrode. The working electrode was immersed into the Ar or O<sub>2</sub>-purged electrolyte for 30 min prior to each cyclic voltammetry (CV) experiment. The first scan CV in this study is defined as follows: after steady-state CVs were obtained in Ar, the cell was purged with O<sub>2</sub> for 20 min, and then the potential was scanned from 3.5 V<sub>Li</sub> to the low voltage limit (2.0 V<sub>Li</sub> for Figs. 1 and 2; 2.5 V<sub>Li</sub> for Fig. 3), followed by a voltage scan to the upper

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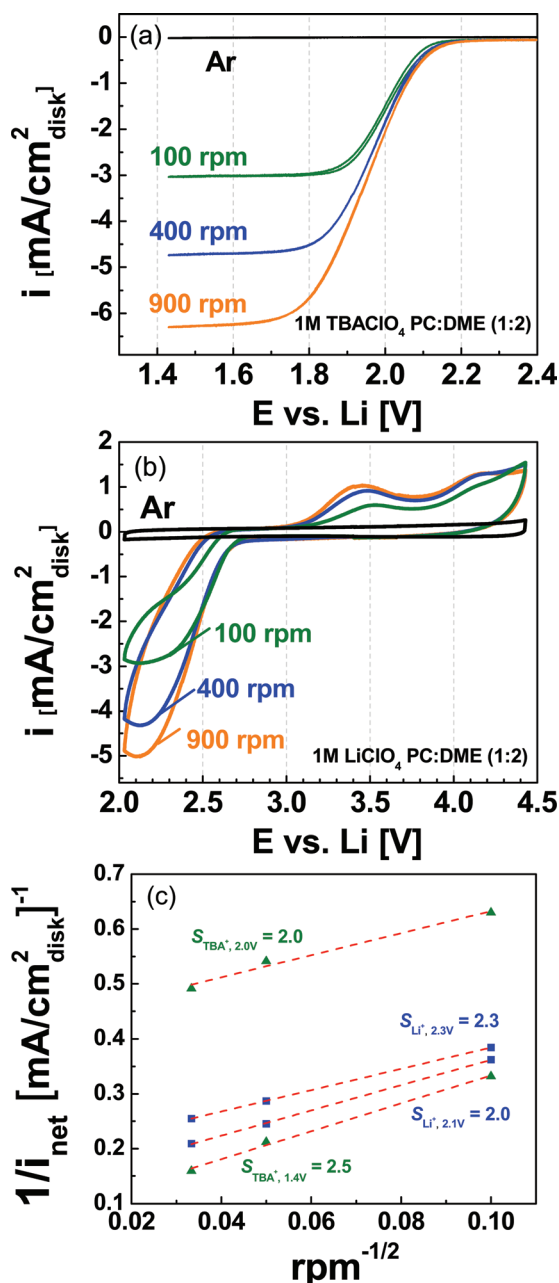
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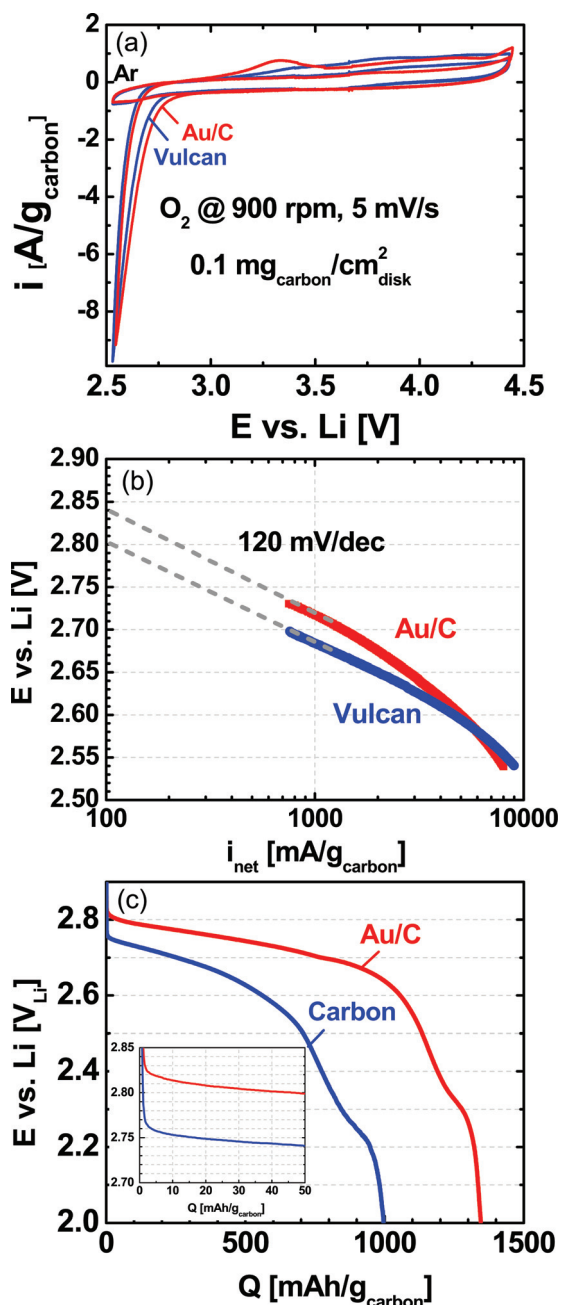
**Figure 1.** (Color online) (a) First CV scan (50 mV/s) at a rotation rate of 100 rpm between 2.0 and 4.4  $V_{Li}$  (see Experimental section for definition) on glassy carbon and pure Vulcan carbon electrodes with various loadings (0.02–0.2  $\text{mg}_{\text{carbon}}/\text{cm}^2_{\text{disk}}$ ) in oxygen-saturated PC:DME (1:2 v/v) with 1 M  $\text{LiClO}_4$ . (b) Capacitive-corrected net ORR current densities during the negative-going scan based on the data in Fig. 1a. The solid-dots indicate the voltage at which the accumulated charge reaches a one-monolayer equivalent of  $\text{LiO}_2$  (200  $\mu\text{C}/\text{cm}^2_{\text{carbon}}$ ) for each carbon loading; for 0.2  $\text{mg}_{\text{carbon}}/\text{cm}^2_{\text{disk}}$ , the total accumulated charge remains less than one monolayer down to the negative potential limit. (c) Capacitance-corrected,  $\text{O}_2$  mass transport-corrected ( $i_d = 3 \text{ mA}/\text{cm}^2_{\text{disk}}$ ), and IR-corrected Tafel plots for the ORR on pure Vulcan carbon electrodes, whereby the maximum IR-correction is  $\sim 12 \text{ mV}$ .

potential limit of 4.4  $V_{Li}$  and then back to 3.5  $V_{Li}$ . The IR-correction to remove ohmic losses was performed by considering a total cell resistance of  $\sim 60 \Omega$  measured by AC impedance. The capacitive-corrected ORR currents were obtained by subtracting the current measured under Ar from that found in pure oxygen under identical scan rates, rotation speeds, and catalyst loadings. Kinetic currents,  $i_k$ , were obtained by correcting the net ORR currents,  $i_{\text{ORR}}$ , for a known value of the  $\text{O}_2$  diffusion-limited current,  $i_d$ , using the Levich equation for a first order reaction ( $i_k = i_d \times i_{\text{ORR}}/[i_d - i_{\text{ORR}}]$ ).



**Figure 2.** (Color online) (a) Steady-state CVs of a glassy carbon RDE in PC:DME (1:2 v/v) with 1 M  $\text{TBAClO}_4$  at 20 mV/s between 2.0 and 4.4  $V_{Li}$  in Ar (900 rpm) and in pure  $\text{O}_2$  (100, 400, and 900 rpm). (b) First voltammetric scans (see Experimental section) of a Vulcan carbon electrode (0.1  $\text{mg}_{\text{carbon}}/\text{cm}^2_{\text{disk}}$ ) in PC:DME (1:2 v/v) with 1 M  $\text{LiClO}_4$  at 50 mV/s between 2.0 and 4.4  $V_{Li}$  in pure  $\text{O}_2$  (100, 400, and 900 rpm); the Ar steady-state CV at 900 rpm is also shown for reference. (c) Levich-Koutecky plots from the ORR data shown in Figs. 2a and 2b, whereby the values of the slopes,  $S$ , indicated in the figure are given in units of  $\text{cm}^2_{\text{disk}} \cdot \text{rpm}^{0.5} / \text{mA}$ .

$\text{Li-O}_2$  single-cells consisted of a lithium metal anode (15 mm in diameter and  $\sim 0.45 \text{ mm}$  thickness) and a Nafion-bonded cathode (12.7 mm diameter) using either pure Vulcan XC-72 or 40 wt % Au/Vulcan. Cathodes with a Nafion/carbon weight ratio of 0.5/1 were prepared by coating ultrasonicated inks composed of catalyst, lithiated Nafion (LITHion dispersion, Ion-Power, USA), and 2-propanol onto the separator (Celgard C480). After air-drying at  $20^\circ\text{C}$  for 20 min, the cathodes were then subsequent vacuum-drying at  $60^\circ\text{C}$  for 3 h. The carbon loading for pure Vulcan and 40 wt % Au/Vulcan electrode was 0.5  $\text{mg}_{\text{carbon}}$  (0.39  $\text{mg}_{\text{carbon}}/\text{cm}^2_{\text{electrode}}$ ) and 0.45  $\text{mg}_{\text{carbon}}$  (0.35  $\text{mg}_{\text{carbon}}/\text{cm}^2_{\text{electrode}}$ ), respectively. The detailed



**Figure 3.** (Color online) (a) First voltammetric scans at 5 mV/s (see Experimental section) of a pure Vulcan carbon and a 40 wt % Au/Vulcan electrode (both 0.1 mg<sub>carbon</sub>/cm<sup>2</sup><sub>disk</sub>) in PC:DME (1:2 v/v) with 1 M LiClO<sub>4</sub> between 2.5 and 4.4 V<sub>Li</sub> in pure O<sub>2</sub> (900 rpm); CVs in Ar are steady-state CVs at 900 rpm. (b) Capacitive- and IR-corrected Tafel-plots for the ORR on a pure Vulcan carbon electrode and a 40 wt % Au/Vulcan electrode; to extrapolate the activities to lower currents, a Tafel-slope of 120 mV/dec was used (dashed line). (c) Li-O<sub>2</sub> single cells: Discharge profiles (first discharge) of pure Vulcan carbon and 40 wt % Au/Vulcan at 0.04 mA/cm<sup>2</sup> corresponding to ~100 mA/g<sub>carbon</sub> for pure carbon and ~110 mA/g<sub>carbon</sub> for 40 wt % Au/Vulcan. Insert: initial discharge region below 50 mAh/g<sub>carbon</sub> (~1 monolayer of LiO<sub>2</sub>). In contrast to Fig. 1b, Fig. 3b was obtained under a slower scan rate (5 mV/s) in order to reduce the contributions from capacitive currents, so that lower carbon mass-normalized current densities can be obtained compared.

Li-O<sub>2</sub> single-cells assembling method was reported elsewhere.<sup>1</sup> Li-O<sub>2</sub> cells were discharged galvanostatically (Solartron 1470) at 0.04 mA/cm<sup>2</sup><sub>electrode</sub> (corresponding to ~100 mA/g<sub>carbon</sub> for Vulcan and ~110 mA/g<sub>carbon</sub> for 40 wt % Au/Vulcan) with a low voltage limit of 2.0 V<sub>Li</sub>.

## Results and Discussion

RDE polarization curves with different carbon loadings were used to determine the oxygen diffusion limiting current density at a rotation rate of 100 rpm. Figure 1a shows the first cyclic voltammetric scan at 100 rpm of a glassy carbon RDE and of Vulcan thin-films supported on a glassy carbon RDE with loadings ranging from 0.02 to 0.2 mg<sub>carbon</sub>/cm<sup>2</sup><sub>disk</sub> in the presence of oxygen. As expected, the onset potential for the ORR shifts positively and the overall current normalized to geometric surface area increases with increasing carbon loading, simply related to the increase of electrochemically active surface area with increasing catalyst loadings. Corresponding capacitance-corrected ORR polarization curves (see experimental section) for the negative-going scans are shown in Fig. 1b, from which the charge associated with the ORR can be obtained. Assuming an external surface area of 100 m<sup>2</sup>/g<sub>carbon</sub> for Vulcan XC-72 (based on a spherical approximation for primary carbon particles having a diameter of ~30 nm and a carbon bulk density of ~2 g/cm<sup>3</sup>),<sup>21</sup> the potentials at which ~1 monolayer of LiO<sub>2</sub> (~200 μC/cm<sup>2</sup><sub>LiO2</sub>) (Ref. 12) is formed on the carbon surface in the negative-going scans can be estimated (see dots in Fig. 1b). As the carbon loading increases from 0.02 to 0.1 mg<sub>carbon</sub>/cm<sup>2</sup><sub>disk</sub>, the potential corresponding to the buildup of 1 ML of adsorbed LiO<sub>2</sub> shifts to more negative values. The fact that no apparent O<sub>2</sub> diffusion-limited ORR currents are observed for these electrodes, suggests that ORR discharge products accumulate on the carbon surface and poison its ORR activity. This hypothesis is consistent with the presence of a O<sub>2</sub> diffusion-limited current density of ~3.0 mA/cm<sup>2</sup><sub>disk</sub> below 2.2 V<sub>Li</sub> for the highest carbon loading of 0.2 mg<sub>carbon</sub>/cm<sup>2</sup><sub>disk</sub>, for which the total accumulated ORR charge never reaches the 1 ML equivalent on the carbon surface during the negative-going potential scan down to 2.0 V<sub>Li</sub> (see Fig. 1b). The decreasing ORR current densities (upward bending curves) below 2.1 V<sub>Li</sub> for carbon loadings of ≤0.1 mg<sub>carbon</sub>/cm<sup>2</sup><sub>disk</sub> can be attributed to poisoning of the ORR by the accumulation of adsorbed ORR discharge products.

The net ORR current densities of electrodes of various carbon loadings were used to extract the intrinsic mass activity of Vulcan carbon. To this purpose, the capacitance-corrected data shown in Fig. 1b were corrected both for ohmic losses (IR-correction) and for O<sub>2</sub> mass-transport resistances (i.e., using the Levich Equation with the observed limiting current of i<sub>d</sub> ~3.0 mA/cm<sup>2</sup><sub>disk</sub>). These kinetic ORR current densities were then normalized by the respective carbon loadings, yielding the *carbon mass activities* (in units of mA/g<sub>carbon</sub>), which is plotted vs. potential shown in Fig. 1c. It should be noted that the data in Fig. 1c are based only on ORR activity data for which the net ORR current density is two times larger than the corresponding capacitive current density and smaller than one-third of the observed oxygen diffusion limiting current density of 3 mA/cm<sup>2</sup><sub>disk</sub>, so that errors in the capacitive and O<sub>2</sub> mass-transport corrections are negligible. If one were to assume that the thin-film RDE method enables the extraction of the intrinsic carbon mass activity, one would expect that the ORR activities for all electrodes would superimpose, exactly as is observed in Fig. 1c. Furthermore, for carbon mass activities below ~15,000 mA/g<sub>carbon</sub>, the ORR activity can be described by a single Tafel slope of ~120 mV/dec (see dashed line in Fig. 1c). Above ~15,000 mA/g<sub>carbon</sub>, obtained only for electrodes with 0.02 and 0.05 mg<sub>carbon</sub>/cm<sup>2</sup> loadings (orange dashed-dotted and red solid lines in Fig. 1c), the ORR activity strongly deviates from the 120 mV/dec Tafel line, which can be explained by the fact that the poisoning by ORR discharge product(s) initiates at increasingly more positive potentials as the carbon loading is decreased (see Fig. 1b). The observed apparent Tafel slope of ~120 mV/dec in the region below ~15,000 mA/g<sub>carbon</sub> suggests a one-electron rate-limiting ORR having a Tafel-slope of  $2.303 \times R \times T / (n \times F \times \alpha)$ , where R is the gas constant, T is the temperature, n is the number of electron transfer in the rate-limiting step (equal to 1 for ~120 mV/dec), F is the Faraday constant (96,485 As/mol), and the transfer coefficient α is 0.5).<sup>22</sup> This one-electron reduction of oxygen is consistent with the



formation of lithium superoxide ( $\text{Li}^+ + \text{O}_2 + \text{e}^- \rightarrow \text{LiO}_2$ ) as proposed in our previous work<sup>9</sup> and Laoire et al.<sup>23</sup>

Since the poisoning of the ORR activity by discharge products becomes negligible with increasing carbon loadings as shown in Fig. 1, the Levich-Koutecky analysis can in principle be applied to determine the number of electrons,  $n$ , exchanged in the rate-limiting step (e.g.,  $n = 1$  for  $\text{LiO}_2$ ). Here, the slope of the Levich-Koutecky plot of the inverse of the ORR net current,  $i_{\text{net}}$ , versus the inverse of the square root of the rotation rate is described by<sup>22</sup>

$$\text{Slope} = (30/\pi)^{0.5} \cdot (0.62 \cdot n \cdot F \cdot D_{\text{O}}^{2/3} \cdot \nu^{-1/6} \cdot C_{\text{O}}^*)^{-1}$$

where  $F$  is the Faraday constant,  $D_{\text{O}}$  is the diffusion coefficient of  $\text{O}_2$ ,  $\nu$  is the kinematic viscosity of the solution, and  $C_{\text{O}}^*$  is the saturated  $\text{O}_2$  concentration in the electrolyte. Unfortunately, the precise values of the physical properties of the electrolyte (i.e.,  $D_{\text{O}}$ ,  $C_{\text{O}}^*$ ,  $\nu$ ) that are required to determine the value of  $n$ , are not known. These electrolyte properties, however, can be estimated, if the lithium cations are replaced by tetrabutyl ammonium (TBA) cations, under the reasonable assumption that the nature of the cation does not significantly affect  $D_{\text{O}}$ ,  $C_{\text{O}}^*$ , and  $\nu$ , as long as the total salt concentration is unchanged. Since the ORR in the presence of  $\text{TBA}^+$  cations in aprotic organic electrolytes exhibits a quasi reversible oxygen/superoxide-radical redox behavior ( $\text{O}_2 + \text{e}^- \leftrightarrow \text{O}_2^-$ ) (Ref. 24) with  $n = 1$ , the Levich-Koutecky slope (which is proportional to  $D_{\text{O}}^{2/3} \cdot \nu^{1/6} \cdot (C_{\text{O}}^*)^{-1}$ ) with  $\text{TBA}^+$  should provide a good estimate of the electrolyte properties when  $\text{TBA}^+$  is replaced by  $\text{Li}^+$ .

This approach is illustrated in Fig. 2. Figure 2a shows that well-defined  $\text{O}_2$  diffusion-limited currents are obtained for the ORR on a glassy carbon electrode in PC:DME (1:2 v/v) with 1 M  $\text{TBAClO}_4$ , analogous to that reported for acetonitrile with 1 M  $\text{TBAPF}_6$ .<sup>23</sup> The fact that the  $\text{O}_2$  diffusion-limited current density in PC:DME (1:2 v/v) with 1 M  $\text{TBAClO}_4$  at 100 rpm ( $i_{\text{d}} \sim 3 \text{ mA}/\text{cm}^2_{\text{disk}}$ ) is identical with that observed in Fig. 1a for 1 M  $\text{LiClO}_4$ -based electrolyte, already suggests that the initial ORR discharge product in the presence of lithium ions is  $\text{LiO}_2$ . The capacitance-corrected Levich-Koutecky plots in the presence of  $\text{TBA}^+$  obtained from Fig. 2a at  $2.0 \text{ V}_{\text{Li}}$  ( $\text{Slope} = 2.0 \text{ cm}^2_{\text{disk}} \cdot \text{rpm}^{0.5}/\text{mA}$ ) and  $1.4 \text{ V}_{\text{Li}}$  ( $\text{Slope} = 2.5 \text{ cm}^2_{\text{disk}} \cdot \text{rpm}^{0.5}/\text{mA}$ ) are shown in Fig. 2c.

Figure 2b shows the CVs of a Vulcan carbon electrode ( $0.1 \text{ mg}_{\text{carbon}}/\text{cm}^2_{\text{disk}}$ ) in PC:DME (1:2 v/v) with 1 M  $\text{LiClO}_4$  at various rotation rates, with a clearly pronounced rotation rate dependence of the ORR currents. Similarly the capacitance-corrected Levich-Koutecky slopes were obtained between 2.3 and  $2.1 \text{ V}_{\text{Li}}$  (see Fig. 2c), which has both significant rotation rate dependence of the ORR currents ( $\leq 2.3 \text{ V}_{\text{Li}}$ ) and negligible poisoning by ORR discharge products ( $\geq 2.1 \text{ V}_{\text{Li}}$ ; see Fig. 1b). The Levich-Koutecky slopes in the presence of  $\text{Li}^+$  ( $2.3$  and  $2.0 \text{ cm}^2_{\text{disk}} \cdot \text{rpm}^{0.5}/\text{mA}$ ) at  $2.3$  and  $2.1 \text{ V}_{\text{Li}}$ , respectively) are comparable to those in the presence of  $\text{TBA}^+$  within experimental errors (see Fig. 2c), which supports that the ORR in the presence of  $\text{Li}^+$  on Vulcan carbon first proceeds by an one-electron reduction to  $\text{LiO}_2$ , consistent with the ORR mechanism proposed in our recent work<sup>9</sup> and that from Laoire et al.<sup>23</sup> It should be noted that the slopes obtained for  $\text{Li}^+$  and  $\text{TBA}^+$  cations in 100%  $\text{O}_2$  ( $\sim 2.3 \text{ cm}^2_{\text{disk}} \cdot \text{rpm}^{0.5}/\text{mA}$ ) agree nicely with our previous work (translating  $8.1 \text{ cm}^2_{\text{disk}} \cdot \text{s}^{-0.5}/\text{mA}$  to  $25 \text{ cm}^2_{\text{disk}} \cdot \text{rpm}^{0.5}/\text{mA}$ ) in 10%  $\text{O}_2$ .<sup>9</sup> However, the observed slopes in Fig. 2c are roughly five times smaller than the value estimated based on published electrolyte properties ( $13.3 \text{ cm}^2_{\text{disk}} \cdot \text{rpm}^{0.5}/\text{mA}$ ),<sup>9</sup> which can be attributed to typically large errors in  $\text{O}_2$  diffusivity and solubility measurements. This highlights the need for more careful evaluation of electrolyte properties for Li-air battery development.

The approach presented here can provide insights into the initial ORR product formed for this self-poisoning reaction, but this approach can of course not resolve the subsequent reactions which might occur outside the analyzed potential window. It is believed that initially formed  $\text{LiO}_2$  will further react to form  $\text{Li}_2\text{O}_2$  ( $2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2$ ) (Refs. 9 and 23) and/or get further reduced to  $\text{Li}_2\text{O}_2$  at lower potentials ( $\text{LiO}_2 + \text{e}^- + \text{Li}^+ \rightarrow \text{Li}_2\text{O}_2$ ),<sup>25</sup> which both would equate to an overall  $2\text{e}^-$  reduction reaction.

Figure 3a shows the CVs of a pure Vulcan and a 40 wt % Au/Vulcan electrodes with comparable loadings. First, the capacitive current of pure Vulcan was comparable to that of 40 wt % Au/Vulcan, since the carbon loadings were expected to be identical. The net ORR kinetic current densities (capacitance-corrected, mass-normalized, and IR-corrected (max. 10 mV)) are shown in Fig. 3b, which allows quantitative comparison of the catalyst's intrinsic mass activity. To extrapolate the data toward low mass activity values (i.e.,  $100 \text{ mA}/\text{g}_{\text{carbon}}$ ), a Tafel-slope of 120 mV/dec was used to extend the data toward lower currents. At  $100 \text{ mA}/\text{g}_{\text{carbon}}$ , the extrapolated potentials for Au/C ( $\sim 2.84 \text{ V}_{\text{Li}}$ ) and Vulcan ( $\sim 2.8 \text{ V}_{\text{Li}}$ ) were obtained, predicating that Au/C would exhibit a 40 mV higher discharge potential at this current density in Li- $\text{O}_2$  cells compared to Vulcan carbon.

To verify if this potential difference between Au/C and Vulcan can be realized in Li- $\text{O}_2$  cells at comparable mass-normalized currents, the discharge voltages of air electrodes with Vulcan carbon only and with 40 wt % Au/C were tested in Li- $\text{O}_2$  single-cells at a rate of  $0.04 \text{ mA}/\text{cm}^2_{\text{electrode}}$  are shown in Fig. 3c. The average discharge voltage of Au/C ( $\sim 2.77 \text{ V}_{\text{Li}}$ ) is higher than that of Vulcan ( $\sim 2.70 \text{ V}_{\text{Li}}$ ) by 70 mV. In order to examine the activity before significant self-poisoning, namely below the formation of a monolayer of  $\text{LiO}_2$  on the electrode surface, the voltages of the cells at discharge capacities of  $< 50 \text{ mAh}/\text{g}_{\text{carbon}}$  (corresponding to  $\sim 1$  monolayer of  $\text{LiO}_2$  by assuming Vulcan surface area of  $100 \text{ m}^2/\text{g}$  and  $\sim 200 \mu\text{C}/\text{cm}^2_{\text{LiO}_2}$  for 1 ML of  $\text{LiO}_2$ ), are compared in the inset of Fig. 3c. The discharge voltage at  $20 \text{ mAh}/\text{g}_{\text{carbon}}$  ( $< 0.5 \text{ ML}$ ) for Au/C was found to be  $\approx 2.81 \text{ V}_{\text{Li}}$ , which was 60 mV higher than that for pure Vulcan ( $2.75 \text{ V}_{\text{Li}}$ ). This voltage difference is comparable to that obtained by our thin-film RDE measurements ( $\sim 40 \text{ mV}$ ). The slightly higher activity for both Vulcan carbon and Au/C obtained from RDE measurements than that based on Li- $\text{O}_2$  cells is not surprising, since RDE measurements of thin-film catalyst layers represent ORR mass activities in the absence oxygen mass-transport losses, which can be considered one of the main sources of voltage loss from Li- $\text{O}_2$  cells. It should be noted that superoxide ions reacts with PC solvent in an irreversible process leading to continuous electrolyte decomposition,<sup>8,12</sup> which would of course be problematic if one were to study cycle-life. However, the catalyst activity presented in this work is expected not to be influenced by the side reaction, which is supported by RDE measurements in pure DME (having comparable kinetic currents at 100 rpm to those in PC:DME).

## Conclusion

In this study, we show a new method for the quantitative evaluation of the electrocatalytic activity of carbon-supported high-surface-area catalyst in a RDE configuration using pure Vulcan and 40 wt % Au/Vulcan catalysts. Tafel analysis shows that the ORR activity of Vulcan carbon can be described by a Tafel slope of 120 mV/dec and Levich-Koutecky analysis of the RDE data on Vulcan carbon suggests that the ORR in the presence of  $\text{Li}^+$  on Vulcan carbon first proceeds by an one-electron reduction to  $\text{LiO}_2$  in the rate-limiting step. The ORR activity difference between Vulcan carbon and supported Au nanoparticles on Vulcan obtained from the thin-film RDE method can be successfully translated into the discharge voltages of Li- $\text{O}_2$  cells at low discharge capacities (where the poisoning by the discharge products is negligible), which demonstrates that this method can serve as a quantitative tool to evaluate the catalysts for Li- $\text{O}_2$  batteries.

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