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Electrical conductivity in \( \text{Li}_2\text{O}_2 \) and its role in determining capacity limitations in non-aqueous \( \text{Li}-\text{O}_2 \) batteries

V. Viswanathan, K. S. Thygesen, J. S. Hummelshøj, J. K. Nørskov, G. Girishkumar, B. D. McCloskey, and A. C. Luntz

1Department of Chemical Engineering, Stanford University, Stanford, California 94305-5025, USA
2Center for Atomic-scale Materials Design (CAMD), Department of Physics, Technical University of Denmark, Fysikvej 1, 28000 Kgs Lyngby, Denmark
3SUNCAT, SLAC National Accelerator Laboratory, Stanford, California 94025-7015, USA
4Almaden Research Center, IBM Research, 650 Harry Rd., San Jose, California 95120, USA

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Non-aqueous Li-air or Li-O\(_2\) cells show considerable promise as a very high energy density battery couple. Such cells, however, show sudden death at capacities far below their theoretical capacity and this, among other problems, limits their practicality. In this paper, we show that this sudden death arises from limited charge transport through the growing \( \text{Li}_2\text{O}_2 \) film to the \( \text{Li}_2\text{O}_2\)-electrolyte interface, and this limitation defines a critical film thickness, above which it is not possible to support electrochemistry at the \( \text{Li}_2\text{O}_2\)-electrolyte interface. We report both electrochemical experiments using a reversible internal redox couple and a first principles metal-insulator-metal charge transport model to explore the electrical conductivity through \( \text{Li}_2\text{O}_2 \) films produced during Li-O\(_2\) discharge. Both experiment and theory show a “sudden death” in charge transport when film thickness is \( \sim 5 \) to \( 10 \) nm. The theoretical model shows that this occurs when the tunneling current through the film can no longer support the electrochemical current. Thus, engineering charge transport through \( \text{Li}_2\text{O}_2 \) is a serious challenge if Li-O\(_2\) batteries are ever to reach their potential.

I. INTRODUCTION

Over the past couple of years, there has been feverish research activity into non-aqueous Li-air (or Li-O\(_2\)) batteries with the hope that a successful Li-air battery could ultimately be developed to give a safe and cost effective secondary battery with \( \sim 5 \) to \( 10 \) times the specific energy of current Li-ion batteries. If successfully developed, such a battery would fully enable electric vehicle transportation without range anxiety. In this battery, the net electrochemical reaction is \( 2\text{Li} + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2 \), with the forward direction describing discharge of the battery and the reverse direction describing charge.\(^1\) The (possible) large increase in specific energy, compared to Li-ion batteries, arises from two sources: (i) one of the reactants, \( \text{O}_2 \), is not stored in the battery but comes from breathing air as in a fuel cell and (ii) \( \text{Li} \) metal would be used as the anode rather than \( \text{Li} \) intercalated graphite (\( \text{LiC}_6 \)) as in Li-ion batteries. However, despite their great promise, many scientific and technical challenges must be overcome if a practical Li-air battery is to ever become a reality.\(^2\)

One of the important challenges for Li-O\(_2\) batteries is the limited capacity (mA h) in discharge relative to that theoretically possible from the pore volume of the cathode. Since the reaction product Li\(_2\)O\(_2\) is completely insoluble in the non-aqueous electrolyte, it builds up as a solid in the porous C cathode where it is formed. It has previously been argued\(^3\) that the limited cell capacity is a consequence of electrical passivation of the cathode by the discharge products rather than pore clogging or \( \text{O}_2 \) transport limitations as claimed by others.\(^4, 5\)

The suggestion that electrical passivation was a central issue resulted from comparing the discharge capacity of typical Li-O\(_2\) batteries with large surface area porous C cathodes to that observed with low surface area glassy carbon (GC) electrodes, where clogging and \( \text{O}_2 \) transport issues were negligible. Although the absolute magnitudes of the capacity were different in the two cases, both showed the same qualitative discharge behavior, i.e., a relatively stable discharge potential at \( \sim 2.6 \) V to a certain discharge capacity, followed by a sudden decrease in output potential to \( < 2.0 \) V (defined as death of the cell). Using an empirically defined electrical resistance through the deposited film as a function of average discharge product thickness fit to the discharge behavior of cells with the GC electrodes, a continuum model (including thermodynamics, transport, and kinetic processes) also described the capacity limitations of Li-O\(_2\) batteries with porous cathodes.\(^5\) In these early experiments, carbonate based electrolytes were used, so that the reaction products were undoubtedly predominately insoluble carbonates rather than Li\(_2\)O\(_2\).\(^5\)

In this paper, we investigate electrical conductivity through films of Li\(_2\)O\(_2\) both experimentally and theoretically and demonstrate conclusively that electrical conductivity is responsible for the capacity limitation of Li-O\(_2\) batteries. In the experiments, we use cyclic voltammetry and impedance measurements of a well known redox couple (ferrocene/ferrocenium) to probe electron (or hole) transport through films of Li\(_2\)O\(_2\) grown on flat GC electrodes at various stages of Li-O\(_2\) discharge using dimethoxyethane as the electrolyte solvent (which produces principally Li\(_2\)O\(_2\) on

\(^{a)\text{Author to whom correspondence should be addressed. Electronic mail: acluntz@pachell.net.}}\)
discharge\(^6\)). These experiments show that the electrical conductivity through the film mirrors the capacity behavior and demonstrates a critical thickness of the Li\(_2\)O\(_2\) deposit, above which electron transport to the Li\(_2\)O\(_2\)-electrolyte interface is inhibited, and hence, electrochemistry cannot be supported. Using a metal-insulator-metal (MIM) representation for the electrochemistry at the cathode of a Li-O\(_2\) cell, first principles transport calculations give a deep understanding of how this critical thickness arises. These calculations show that a mechanism of hole tunneling through the electrically insulating Li\(_2\)O\(_2\) film determines the capacity limitations. When the tunneling current is sufficient to drive the electrochemistry, the cell discharge potential \(U\) is determined principally by the kinetic overpotential \(\eta\). However, as discharge progresses and the Li\(_2\)O\(_2\) film thickness grows large enough, an exponentially increasing bias across the film is necessary to maintain a tunneling current sufficient to drive the electrochemistry. This bias no longer appears as an output voltage at the cathode. In other words, the cell suddenly fails at a critical Li\(_2\)O\(_2\) film thickness.

II. EXPERIMENT

The basic experimental concept is outlined in Fig. 1. A hermetically sealed 3-electrode bulk electrolysis cell containing a 1 M non-aqueous Li salt electrolyte and dissolved O\(_2\) gas allow Li\(_2\)O\(_2\) films to be deposited on a smooth glassy carbon cathode during discharge. In addition, the electrolyte contains 3 mM Ferrocene which generates an outer sphere reversible redox couple ferrocene/ferrocenium (Fc/Fc\(^+\)) at \(\sim 3.4\) V relative to Li/Li\(^+\). Since the oxidation/reduction of the Fc/Fc\(^+\) couple only depends upon electron (or hole) transport through the Li\(_2\)O\(_2\) film to the solution, the current of this reaction provides a direct measurement of charge transport through the film. This current is followed at various stages of discharge corresponding to different average thickness \(d\) of the Li\(_2\)O\(_2\) film. It should be pointed out that because the Fc/Fc\(^+\) redox couple is centered at \(\sim 3.4\) V (Li/Li\(^+\)), that some small fraction of the Li\(_2\)O\(_2\) film is undoubtedly removed during the oxidation of Fe so that the values of \(d\) obtained from the total discharge coulometry may be underestimated.

The bulk electrolysis electrochemical cell has high purity 250 \(\mu\)m thick electrochemical grade Li metal discs as counter and reference electrodes (FMC Corp., Charlotte, NC, USA) and a flat electrochemical grade GC disc for the cathode (Tokai Carbon USA, Hillsboro, OR, USA). All electrodes are \(\sim 1.1\) cm\(^2\) area. The GC electrode underwent standard cleaning procedures involving polishing with successive grades of alumina paste to a smooth finish followed by sonication in acetone. The electrolyte consisted of \(\sim 15\) ml of 1 M lithium-bis(trifluoromethanesulfonimide) [LiTFSI] dissolved in dimethoxyethane (DME). The salt and solvent were both high purity electrochemical grade (Novolyte Corp., Cleveland, OH, USA) with <20 ppm H\(_2\)O as measured by Karl-Fischer titration. 3 mM high purity ferrocene (Sigma Aldrich, St. Louis, MO, USA) is added to the electrolyte. The air tight cell has both O\(_2\) inlet and outlet ports which allow bubbling of ultrahigh purity O\(_2\) at a pressure of \(\sim 1\) bar through the electrolyte during discharge to insure that the electrolyte remains saturated with O\(_2\). This also gives considerable stirring action during discharge. The cell and all components are assembled in an Ar glove box (<0.1 ppm H\(_2\)O and O\(_2\)) and special care is taken to never expose the cell contents to ambient air from beginning to end of the experiments. All electrochemical experiments were performed using a BioLogic VMP3 Multichannel Workstation (Bio-Logic, Knoxville, TN, USA). Previous experiments using high surface area C cathodes have shown that the dominant detectable product formed during discharge is Li\(_2\)O\(_2\) with LiTFSI/DME as the electrolyte.\(^6\) XPS and scanning Auger measurements of deposits formed on the GC during discharge are also consistent with this conclusion.

The Li\(_2\)O\(_2\) films on the GC are grown using galvanostatic discharge at \(\sim 1\) mA/cm\(^2\) current density. Prior to the Li\(_2\)O\(_2\) cell reaching its end of life (defined as an output voltage \(U = 2.0\) V), the discharge is periodically interrupted every 10–15 min to analyze charge transfer at the Li\(_2\)O\(_2\)-electrolyte interface. During interruption, the cell is initially open circuited for \(\sim 2\) min and O\(_2\) bubbling stopped, after which an oxidation and then reduction cyclic voltammetry (CV) of the Fc/Fc\(^+\) couple is performed. Immediately following the reduction cycle while there is a quasi-equilibrium of Fe and Fc\(^+\) at the electrode-solution interface, electrochemical impedance spectroscopy (EIS) is performed to measure the charge transfer resistance of the Fc/Fc\(^+\) redox reaction corresponding to this state of Li–O\(_2\) discharge. The galvanostatic discharge producing Li\(_2\)O\(_2\) is then continued for another 10–15 min, followed by interruption to measure the Fc/Fc\(^+\) redox, etc. The procedure is repeated until the cell’s end of life. The CV over the Fc/Fc\(^+\) couple are run at a scan rate of 100 mVs\(^{-1}\). The EIS is measured using a 10 mV amplitude sine wave applied to the GC/Li\(_2\)O\(_2\) electrode under open circuit conditions and scanned over the frequency range of 0.005 Hz to 100 kHz. The charge transfer resistance \(R_{CT}\) for the Fc/Fc\(^+\) redox reaction is obtained by measuring the diameter of the charge transfer semicircle along the real axis in a Nyquist plot. The raw impedance data corresponding to the various states
of discharge are given in Fig. 2. C labels the total number of Coulombs of discharge Q prior to the EIS experiment. At Q = 0 before the cell is subjected to discharge, a well defined oxidation/reduction peak corresponding to ferrocene redox chemistry is obtained in the CV. However, as the cell is subjected to Li–O2 discharge, and the CVs are intermittently recorded, several key things happen: (1) The peak separation between Fc → Fc⁺ and Fc⁺ → Fc redox reactions, ∆Eₚ, increases, consistent with an increase in R_CT (or decrease in exchange current density) and (2) the currents in the redox peaks decreases progressively. After discharging for Q = 0.006 C, the redox peaks disappear completely. Since the current in the Fc/Fc⁺ redox CV depends only upon charge transfer, this demonstrates qualitatively that the Li₂O₂ film becomes increasingly electrically insulating as it grows. EIS is used to probe the charge transport quantitatively for various stages of discharge.

Figure 3(a) shows a typical discharge curve, cell output voltage U vs discharge capacity Q (Coulombs), at a current density j ≈ 1 μA/cm². Also included is the estimated average thickness d of the Li₂O₂ film obtained from Q, the projected area of the electrode, and the bulk density of Li₂O₂ of 2.3 gm/cm³. This discharge curve shows an immediate drop from the open circuit potential (OCV) to ~2.65 V due to the overpotential for discharge η, then a gently decreasing output potential until the sudden death of the cell, similar to that observed previously in cells with GC electrodes and carbonate based electrolytes. Since employing DME as a solvent has been shown to principally produce Li₂O₂ deposits during discharge, while carbonate solvents produce complex carbonate deposits on discharge, the nature of the capacity limitation is not related to any specific cathode chemistry, but rather only that the deposits be electrically insulating.

Figure 3(a) suggests d ~ 4–5 nm as an average thickness of Li₂O₂ for cell death. Atomic force microscopy measurements of a GC cathode discharged under similar conditions gives an average thickness of d = 7 ± 3 nm at cell death and 3 ± 2 at half the Q required for cell death. These experiments used multiple contact mode scans with a boron doped diamond tip to erode the electrochemical deposit from a given area until a constant conductivity was obtained from the GC substrate (which does not erode under these forces). Tapping mode scans of the topology through the eroded and non-eroded regions give the average d of the electrochemical deposits. These experiments show that the electrochemical deposits fully covered the GC surface, albeit with a rms roughness of ~3 to 4 nm above that of the GC film. These experiments will be reported in detail elsewhere.

In a separate experiment, the cell was also discharged with the added ferrocene in the manner described above. Discharging at constant current density to electrodeposit Li₂O₂ by passing known charge Q and simultaneously following the electrochemistry of Fc/Fc⁺ allows us to probe charge transport at various points on the discharge curve. Figure 3(b) shows the exchange current density j₀ for the Fc/Fc⁺ redox reaction as a function of Q and d. j₀ is obtained from the charge transfer resistance R_CT from the analysis of the EIS according to j₀ = R_p T/2F R_CT, where R_p is the universal gas constant, T is the absolute temperature in degrees Kelvin, and F is the Faraday’s constant. The impedance scans from which
FIG. 3. (a) Discharge capacity of a Li-O₂ cell at ∼1 μA/cm² discharge current density, plotted as cell potential $U$ vs extent of discharge $Q$ (Coulombs) and average thickness $d$ of the Li₂O₂ film grown on the glassy carbon substrate. (b) Exchange current density $j_0$ for the charge transfer reaction Fc/Fc⁺ obtained from impedance spectroscopy as a function of $Q$ and $d$ for Li-O₂ discharge under similar conditions as in (a).

$R_{CT}$ is obtained are shown in Fig. 2. $j_0$ shows an immediate drop of approximately an order of magnitude with very minimal discharge, presumably due to scattering of charge carriers at the interface or partial passivation of electrochemically hyperactive defect sites. This is followed by a more gradual decrease in $j_0$ until a thickness of ∼5 nm, after which $j_0$ falls rapidly to values of ∼10⁻⁷ A/cm² at larger $d$. At large $d$, the impedance is almost exclusively capacitive so that it is difficult to extract meaningful values of $R_{CT}$. Thus, the value at 8 nm should only be considered as an upper bound to $j_0$. The sharp decrease in $j_0$ at $d$ ∼ 5 nm defines a critical thickness of Li₂O₂ above which it no longer supports electrochemistry at its electrolyte interface. Since $j_0$ depends only upon electrical conductivity through the film, this critical thickness arises solely from charge transport issues. In addition, since the capacity behavior in the Li-O₂ cell is so similar to that of $j_0$ for the Fc/Fc⁺ redox couple, this demonstrates that sudden cell death arises from the existence of the critical film thickness for electrical conductivity.

Figure 4 shows a schematic of a typical Li-O₂ electrochemical cell during discharge. This schematically indicates the path of the three reactive components necessary for electrochemistry: Li⁺, O₂, and e⁻. Figure 4 schematically indicates the electron energies within the different elements of the cell. At the equilibrium potential $U_0$ of a redox couple, e.g., Fc/Fc⁺ or Li-O₂, the Fermi energy $E_F$ is constant throughout the cell. The energy of vacuum zero, $E_0$, is indicated by the dotted lines. The energy for Li relative to vacuum zero (1.6 V) is taken from the potential of the standard hydrogen electrode (4.5 V) and the Li/Li⁺ potential relative to the standard hydrogen electrode in the non-aqueous solvent (2.9 V). Neglecting any Schottky barriers, $E_0 – E_F$ at the GC-Li₂O₂ interface is given by the work function of GC, ∼5 eV. At the electrolyte-Li₂O₂ interface, $E_0 – E_F = 1.6 + eU_0 + e(\phi – \phi_{PZC})$, where the first term is the energy of Li/Li⁺ relative to vacuum zero, the second term is the energy of the redox couple relative to Li/Li⁺, and the third term accounts for any charging at the Li₂O₂-electrolyte interface, i.e., deviation of the interface from the potential of zero charge. Since Li₂O₂ is a wide bandgap insulator, it is likely that the conduction band (CB) is several eV above $E_F$. Upon application of a bias $eU_{bias}$ (shown in red) across the Li₂O₂ film, electrons only reach the electrochemical interface via transport through the previously grown peroxide layer. Thus, this electron transport is essentially equivalent to that observed in a biased metal-insulator-metal (MIM) junction. Note that Fig. 4 is drawn assuming some charging at the Li₂O₂-electrolyte interface.

In the following, we develop a first principles theoretical MIM model and show how charge transport through Li₂O₂ defines the critical thickness observed in the experiments. Note that in the absence of substantial charging at
the electrolyte-Li$_2$O$_2$ interface, the potential barrier is nearly symmetrical so that we use a symmetrical MIM model to describe the conductivity. We also note that when hole conductivity is dominant (as we show later to be the case for Li$_2$O$_2$), an equivalent picture for hole energies simply involves interchanging the conduction band by the valence band of Li$_2$O$_2$.

III. THEORY

Galvanostatic discharge in the Li$_2$O$_2$ battery depends on many interrelated factors, e.g., the thermodynamics and kinetics of the charge transfer processes, the surface composition, the transport of all species to the electrochemically active interface, and the nucleation and growth of the Li$_2$O$_2$ product. In this section, we develop a model for the charge transport through previously deposited Li$_2$O$_2$ films since this limits capacity during discharge. However, we will show later that this charge transport depends upon the surface species present during discharge and this, in turn, depends upon the thermodynamics and kinetics of the electrochemistry and the growth mechanism, so that we first briefly discuss these aspects of the discharge. Since the electrochemistry ultimately also depends on the charge transport, we develop a self-consistent model to couple the electrochemistry and the conductivity to explain the origin of the capacity fall-off observed in the Li$_2$O$_2$ batteries.

A. Growth mechanism of Li$_2$O$_2$

We assume that after an initial nucleation phase of Li$_2$O$_2$ on GC, that the electrochemistry is dominated by Li$_2$O$_2$ formation on Li$_2$O$_2$, that is, Li$_2$O$_2$ crystal growth. This assumption is certainly valid for deep discharges corresponding to death of the cell and there is ample experimental evidence for complete film formation on flat GC electrodes. In addition, the AFM measurements mentioned above clearly show that the GC surface is fully covered with the electrochemical deposit, both prior to and at sudden cell death. In fact, it is hard to rationalize the electrical passivation of the smooth GC cathode without the electrochemical deposit fully covering the electrochemically active GC surface. Since the AFM measurements suggest some variations in the thickness of the electrochemical deposit, the actual nucleation-growth of Li$_2$O$_2$ on itself must be somewhat complicated. However, for simplicity in the charge transport calculation we simply assume a layer by layer growth process, i.e., that we are dealing with a fixed $d$ corresponding to a number of layers rather than some average $d$ for a range of thicknesses. It is generally assumed that crystal growth occurs principally at kink and step sites since these allow the most stabilization of adspecies. We take this mechanism to be dominant in the growth during discharge. In particular, the thermodynamics for Li$_2$O$_2$ electrochemistry on Li$_2$O$_2$ steps has been discussed previously so that we use this mechanism to investigate charge transport during electrochemistry. This mechanism is given in terms of the following steps of charge transfer:

$\begin{align*}
(1) & \text{Li} \rightleftharpoons \text{Li}^+ + e^- \quad \text{(anode)}, \\
(2) & \text{Li}^+ + e^- + \text{O}_2^* \rightleftharpoons \text{Li}_2\text{O}_2^* \quad \text{(cathode)}, \\
(3) & \text{Li}^+ + e^- + \text{Li}_2\text{O}_2^* \rightleftharpoons \text{Li}_2\text{O}_2^2 \quad \text{(cathode)},
\end{align*}$

where the * refers to surface adsorbed species on the step sites.

B. Thermodynamics at steps

Since the most stable Li$_2$O$_2$ surface, reconstructed Li$_2$O$_2$(1100) (previously labeled 100 in Ref. 7), contains two formula units of Li$_2$O$_2$ in a unit cell, reaction steps (1)–(3) above need to run twice before the initial and final states of the surface are the same. Figure 5 shows the calculated free energy diagram at four different potentials $U$ for reactants, products, and the intermediates in the reaction. The potential dependence is given by $-\alpha eU$, where $\alpha$ is the number of Li$^+$ + e$^-$ for each step. The standard potential is $U_0 = 2.71$ V and is closer to the experimental one of 2.96 V than that reported earlier due to a better description of the Li bulk energy (using the RPBE functional used in the rest of the calculations). The theoretical overpotential ($\eta$) is defined as the potential at which all steps are thermodynamically downhill relative to $U_0$, i.e., for discharge $\eta_{\text{dis}} = 2.71$ V – 2.26 V = 0.45 V and for charge $\eta_{\text{chg}} = 3.32$ V – 2.71 V = 0.61 V. We have found, quite generally, that this theoretical overpotential describes quite well the onset potential at which ion transfer surface electrochemical reactions have an appreciable rate. This implies that activation barriers in the individual steps in the kinetic mechanism are not determining the overpotentials. At the equilibrium potential, a mixed phase of LiO$_2^*$, its dimer 2LiO$_2^*$, and Li$_2$O$_2$ coexist at the surface. The potential limiting step during discharge ($\eta_{\text{dis}}$) is the addition of Li$^+$ to a LiO$_2^*$, while the generation of O$_2^*$ + Li$^+$ + e$^-$ from 2LiO$_2^*$ is potential limiting in charge ($\eta_{\text{chg}}$).

C. Kinetic model

Since the surface concentration of species changes with applied potential, we use a simple kinetic model to calculate the potential-dependent coverage of different species along the steps during discharge and charge. The rates of each of the electrochemical steps in Fig. 5 are represented by simple Butler-Volmer expressions with rate constants given by $k_i = k_0^i \max[\exp(-\alpha(eU - \Delta G)/k_BT)]$, with $k_0^i$ the pre-exponential and the exponential term describing the potential dependent energy terms. The max notation guarantees that when $\Delta G \gg eU$ that $k_i = k_0^i$. In this model, we set $\alpha = 1$ so that only thermodynamic limitations are included in the kinetics. There are undoubtedly additional kinetic barriers associated with the de-solvation of Li$^+$ in each of the steps, but this is included in the pre-factors $k_0^i$ since these are likely to be nearly the same for each of the steps, and hence, principally affect the absolute magnitudes of the rates rather than the a potential dependence in the relative kinetics between
D. Charge transport

Because charge transport through the electrochemical deposit during cell discharge resembles that of a MIM, we utilize a theoretical MIM configuration consisting of AuLi2O2Au layers to investigate the charge transport through Li2O2 films. Since metal electrodes are chosen to mimic both the electrolyte and the GC cathode, the calculations probes the pure charge transport of the Li2O2 films. Nevertheless, the work function of Au is quite similar to that of GC. Using Au in place of the electrochemical discharge reaction is equivalent to using a perfectly reversible redox couple in the electrochemistry. Therefore, the current calculated through the MIM structure depends only on the conductivity of the peroxide film.

All transport calculations are performed within density functional theory as implemented in the GPAW package using the Atomic Simulation Environment. The GPAW package is a real space grid algorithm based on the projector augmented wave function method with a frozen core approximation. The finite bias transport calculations are performed using a non-equilibrium Green’s function (NEGF) method as implemented within GPAW. Following the standard notation used in the electron transport literature, we refer to the Li2O2 slab and four layers of Au on each side as the central region (C) and bulk metallic Au as left (L) and right (R) leads. The left (L) and right (R) leads are kept at different chemical potentials \( \mu \) to simulate an applied bias voltage of \( U_{bias} = (\mu_L - \mu_R)/e \) across the central region. As a consequence of electronic screening, the potential inside the electrodes converges rapidly to the bulk value and sets the boundary conditions for the electrostatic potential inside C. Rather than obtaining the wave functions from the eigenvalue equation, the transmission is solved by using the NEGF of the central region and more details about this method can be found elsewhere. The electron transport calculations are performed using a localized LCAO basis set, i.e., linear combination of atomic orbitals, as implemented in GPAW.

Because the electrolyte facing surface concentrations of the LiO2* and Li2O2 species vary with \( U \) during discharge, we investigate electronic transport through Li2O2 films for the two limiting cases given in Fig. 7, i.e., with Li2O2 at both the surfaces and for LiO2* at one of the surfaces. Reconstructed Au(110) was chosen for the MIM electrode surface as it has the closest registry with the Li2O2 structure and charge transport through the interface depends slightly on this. The energy of the structure of the Li2O2 used to match the Au(110) surface is within 0.02 eV/formula unit of the bulk structure and corresponded to ~5% mismatch in lattice constants. The interfaces were then structurally relaxed using a 4 layer Au.
slab and 5 layers of Li$_2$O$_2$/Li$_2$O$_2$+LiO$_2$ in the direction normal to the interface. This structural relaxation was minimal. In any event, the exact structure of the interface only weakly affected the magnitude of the conductivity. The distances from the relaxed slab was used to construct a bulk system of alternating layers of Au (5 layers) and Li$_2$O$_2$ (5 layers). The central monolayer of Au and Li$_2$O$_2$ were fixed and the remaining atoms were relaxed. Subsequent structures for thicker layers were built up by adding layers of Li$_2$O$_2$ to the center using its bulk geometry when this had been matched to the lattice of Au and relaxed in the transport direction. Sensitivity to the choice of the electrode material was checked by using Pt(110) as the electrode interface for the pure Li$_2$O$_2$ films. The transport results were qualitatively similar to that for Au(110) electrodes and the Li$_2$O$_2$ film since they depend principally on the electronic properties of the Li$_2$O$_2$ (and the tails of the metal s,p wave functions that is similar for the two metals). It is likely that there would be larger differences in the transport calculations for the two metals in the Li$_2$O$_2$-LiO$_2$ structures due to the higher reactivity of Pt(110).

The geometric relaxation and energies of the stable interface structures were calculated with GPAW in its normal real space mode with a grid spacing of \( h = 0.18 \), which is sufficient for high energy accuracy. These relaxed structures were then used for the electron transport calculations using an LCAO basis set. While the energetics obtained from a limited LCAO basis set is not very accurate, it is suitable for the transport calculations. For the transport calculations, the central region describing the metal-(Li$_2$O$_2$/Li$_2$O$_2$+LiO$_2$)-metal interfaces contains 4 layers of metal on either side and varying layers of Li$_2$O$_2$/Li$_2$O$_2$+LiO$_2$ between the metal. We have verified that this is sufficient to achieve convergence of the current and potential drop across the interfaces. The electrode regions, i.e., Au(110), were calculated with normal density functional theory (DFT) with periodic boundary conditions. We used a (6,2,1) k-point sampling for the NEGF self-consistent loop and a (12,4,1) k-point grid for evaluating the current. The PBE functional is used for exchange-correlation, and a LCAO basis set corresponding to single-zeta plus polarization is adopted for all atomic species. We have verified that the transport results are converged with respect to the size of the minimal LCAO basis set by comparing some transport calculations to those using a double-zeta plus polarization basis. In the finite bias calculations, a positive bias is defined as passing current from the left to the right, i.e., passing current from the metal to Li$_2$O$_2$, corresponding to battery discharge and negative bias corresponds to battery charge.

Figure 8(a) shows the projected density of states for the O \( p_x, p_y \), and \( p_z \) orbitals of Li$_2$O$_2$ at \( U = 0 \) when sandwiched between the Au(110) electrodes. The \( p_x, p_y \) orbitals are the dominant contributions to the valence band and \( p_z \) orbital is the dominant contribution to the conduction band of Li$_2$O$_2$.\(^{20} \) Note that in this calculation the location of these bands relative to the Fermi energy \( E_F \) is well defined because of the Au(110) electrodes. The bandgap of Li$_2$O$_2$ is poorly described in DFT and GW calculations show that this is almost exclusively due to an artificial lowering of the conduction band by \( \sim 3 \) eV in DFT.\(^{8,20} \) At both levels of description, the Fermi level is close to the valence band and electrical conductivity is therefore dominated by holes rather than electrons. Since the valence band is well described by DFT, we
use that level of description in the calculation of conductivity.
The O $p_x$, $p_y$, and $p_z$ orbitals for the LiO$_2$ layer of the Li$_2$O$_2$-
LiO$_2$ structure are shown in Fig. 8(b). It can be seen that the
Fermi level is pinned by the O 2$p_y$ orbital of the vacancy layer
of LiO$_2$.

Figure 9 shows the calculated current-bias response curve
for the Li$_2$O$_2$ and Li$_2$O$_2$-LiO$_2$ structures of varying thickness
(number of layers of Li$_2$O$_2$). In Fig. 9, the current for a fixed
thickness exhibits the roughly linear + exponential depend-
ence with bias characteristic of MIM structures. The cur-
rent in Fig. 9(a) is symmetric with the sign of bias due to the
symmetric nature of the interfaces. On the other hand, Li$_2$O$_2$-
LiO$_2$ structures in Fig. 9(b) have a slight asymmetry due to
the asymmetry of the interfaces.

Figure 10 shows the current at different fixed bias (+0.1
and ±0.6 V) as a function of the film thickness $d$, defined
as the distance between the innermost Au layers in the two
electrodes for the given number of Li$_2$O$_2$ layers in the cen-
tral region. A bias of +0.1 V is characteristic of the onset of
the exponential decrease in cell voltage, while a bias of +0.6
V is characteristic of complete cell death. The current decays
exponentially with $d$ for a fixed bias, with a steeper decay for
the lower bias potentials. At fixed bias and $d$, the current is
always higher when LiO$_2$ is present at the interface. This is
completely as anticipated from the projected density of states
(PDOS) since LiO$_2$ $p_y$ states are pinned at EF, and we thus get
better conductivity when the surface species is LiO$_2^*$. Thi
s is the major reason that it is important to know the actual sur-
face composition during discharge in order to compare with
experiment.

IV. THEORY—EXPERIMENT COMPARISON

In this section, we use a simple model combining
the electrochemistry and transport limitations to construct
a theoretical capacity plot to compare with that observed

FIG. 9. Calculated current-bias curves for the two different calculation se-
tups as a function of number of layers between the electrodes of (a) pure
Li$_2$O$_2$ and (b) Li$_2$O$_2$ + 1 layer LiO$_2$ at the interface.

FIG. 10. Conductance plot at two fixed biases as a function of the distance between the electrodes as defined by the number of layers. Solid points are for
Li$_2$O$_2$ while open points are for Li$_2$O$_2$ with LiO$_2$ at the surface of one electrode.
The current density can be written as the electrochemical reaction rate (or current $j$) subject to the conditional constraint that the rate of charge transport through the Li$_2$O$_2$ film $j_t$ is sufficient to drive the required electrochemical current. This can be written as

$$j = j_0 \exp(-\Delta G(\eta) - \Delta G(\eta = 0)/R_q T)[j_t(\theta, U_{bias}) \geq j],$$

where $j_0$ represents the exchange current density, $\eta$ is the overpotential, $\Delta G(\eta) - \Delta G(\eta = 0)$ is the free energy shift of the rate limiting step at $U - U_0$, and $j_t$ is the rate or current for charge transport from one Au(110) interface through the film to the other interface which depends on both the bias $U_{bias}$ and the population of the surface species $\theta$. $U_{bias}$ is the potential across the film. The surface species $\theta$ for $j_t$ is taken as the appropriate linear combination of $j_t$ through pure Li$_2$O$_2$ and Li$_2$O$_2$-LiO$_2$ as defined by $U - U_{bias}$. In terms of an equivalent electrical circuit for galvanostatic discharge at dc (where capacitances can be ignored), this rate expression can be rewritten as current at an applied potential $U$ through two resistances that are in series and additive; one representing the film resistance $R_{film}$ (which depends on bias and surface composition) and the charge transfer resistance for the electrochemical reaction $R_{CT}$ which depends upon kinetic overpotential. At a fixed length $d$, the following equation represents the overall resistance:

$$R_{tot}(U, \theta) = R_{film}(U_{bias}, \theta) + R_{CT}(\eta) \quad \text{with} \quad U = U_0 - U_{bias} - \eta,$$

$R_{film}$ depends on the population of the different species $\theta$, which is itself an implicit function of $U - U_{bias}$. $U_{bias}$ is determined by the bias needed to give the required electrochemical current across the film. This is dependent on the thickness of the film grown and the population of the surface species. As a result, the problem needs to be solved in a self-consistent way, where a guess for the state of the surface species is obtained by using the thermodynamic overpotential obtained for the growth process. Using that guess for the population of different species, the film resistance is calculated. Using the potential at the electrolyte interface, we once again solve for the surface species and continue until convergence is obtained. This is repeated as $d$ increases. The calculation of the film resistance for larger lengths is done using an exponential fit to the calculated data at fixed bias, as shown in Fig. 10.

Figure 11 shows the calculated capacity plot for galvanostatic discharge at a current density of $j = 1 \mu A/cm^2$ and $\eta = 0.45 V$. For $d < 5$ nm, there are no electrical conductivity limitations so that the galvanostatic discharge potential is determined solely by the kinetic overpotential for charge transfer, $\eta$. For $d > 5$ nm, conductivity limitations dominate and the cell voltage drops off exponentially with $d$. The exponential drop in $U$ at $d \sim 5$ nm is the fundamental origin of the phenomenon described as a critical thickness for supporting electrochemistry that is observed in the experiments.

In this model of a perfect crystalline Li$_2$O$_2$ lattice and without considering phonons, there is no mechanism for resistivity in the film. Electrical conductivity occurs solely through tunneling of holes through the barrier defined by the valence band and $E_F$. In reality, Fig. 3 indicates that there is resistivity in the film prior to reaching the critical thickness because of the gradual drop in $U$ in Fig. 3(a) or in $j_0$ in Fig. 3(b). This is likely due to defects produced in the film during growth. Therefore, we also consider a case where a phenomenological resistance that is proportional to $d$ is added to the equivalent circuit to account for defect scattering. This gives the following expression for $R_{tot}$:

$$R_{tot}(U, \theta) = R_{film}(U_{bias}, \theta) + R_{CT}(\eta) + \beta d \quad \text{with} \quad U = U_0 - U_{bias} - \eta - j\beta d,$$

where $\beta$ is chosen to give a voltage drop of $\sim 0.1 V/nm$ as observed in the experiments. In this case, the voltage drop across the interface increases as the film grows and this results in a shift of the most stable surface species from LiO$_2^*$ to Li$_2$O$_2^*$. 

FIG. 11. A theoretical capacity plot of the cell voltage as a function of the length of the Li$_2$O$_2$ interlayer spacing (with the appropriate species surface concentrations $\theta$ determined by the electrochemistry at the given potential surface potential $U-\eta$ for a discharge current density $j = 1 \mu A/cm^2$. At this discharge condition, $\theta$(LiO$_2^*$) $\approx 0.9$ and $\theta$(Li$_2$O$_2^*$) $\approx 0.1$. 

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as the film grows. This leads to some effect in the fall-off length as Li$_2$O$_2$ is less conducting compared to LiO$_2$ surface species (see Fig. 10). The results obtained from this model are in good agreement with the experiments. This highlights the strong coupling that the electrochemistry and conductivity play in determining the discharge characteristics of the Li-air battery.

V. SUMMARY AND CONCLUSIONS

In this paper, we use both electrochemical experiments and first principles theory to probe and understand the origin of the phenomenon of sudden death in Li-O$_2$ cells which limit their capacity to far less than the theoretical maximum. We show that the sudden death is related to a critical thickness of Li$_2$O$_2$ deposit, above which charge transport to the Li$_2$O$_2$-electrolyte interface is insufficient to support the electrochemistry.

The experiments use a reversible outer sphere redox couple (ferrocene/ferrocenium or Fe/Fc$^+$) to probe charge transport through films of Li$_2$O$_2$ electrochemically grown on a smooth glassy carbon electrode by Li$_2$O discharge. Both cyclic voltammetry and electrochemical impedance spectroscopy of the redox couple as a function of discharge capacity (or film thickness) show that even this reversible redox reaction shows a sudden death at film thickness nearly identical to that of the Li-O$_2$ cells. Since the Fc/Fc$^+$ redox only depends upon charge transport to the Li$_2$O$_2$-electrolyte interface, we conclude that these charge transport limitations are also responsible for the sudden death in the Li-O$_2$ cells.

A first principles MIM model using Au(110) electrodes is developed to probe electrical conductivity through Li$_2$O$_2$ films of varying thicknesses. Bias dependent charge transport is calculated using the non-equilibrium Green’s function method as implemented in GPAW. Since the electrical conductivity depends on the species present at the Li$_2$O$_2$-electrolyte interface (LiO$_2$, 2LiO$_2$, and Li$_2$O$_2$) as well as the potential bias across the film, and the species present at the interface depends on the potential and charge transport to the interface, a self-consistent model is developed to treat the charge transport and electrochemistry simultaneously. The calculations show that charge transport is dominated by tunneling of holes and this gives a natural explanation for a critical thickness to support electrochemistry. When the film thickness is less than the critical thickness, the tunneling current is sufficient to support the electrochemistry. However, when the film thickness is greater than the critical thickness, the output potential dies exponentially as the bias required to support the electrochemical current increases exponentially. The critical thickness calculated from the MIM model is in very good agreement with that observed experimentally in actual cells and the redox couple experiments.

Charge transport calculations for the (reconstructed) Li$_2$O$_2$(0001) surface using Au(111) electrodes showed a very similar exponential decrease in conductivity with $d$ and with magnitudes similar to that reported here. Therefore, the phenomenon of sudden death in cell discharge at a Li$_2$O$_2$ film thickness of 5–10 nm is anticipated to be independent of the growth direction. A detailed comparison of charge transport in the two directions will be reported later.

We believe that the conductivity limitations discussed here are a significant challenge for developing practical Li-air batteries. Engineering higher charge transport through doping or some other strategy will undoubtedly be necessary if one is ever to realize the promise of a high specific energy Li-air battery.

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