A Simple Model for Interpreting the Reaction–Diffusion Characteristics of Li-Air Batteries

R. E. Jones,* F. S. Gittleson,* J. A. Templeton, and D. K. Ward
Sandia National Laboratories, Livermore, California 94551, USA

With the goal of creating a model of a Li-air battery that is consistent with voltammetry data, we develop a full battery model capable of giving insight into details of cell operation otherwise inaccessible to common experimental techniques. With this model, we investigate the dependence of the current on: the diffusion characteristics of the electrolyte, the solubility of the ambient oxygen, the structure of the cathode, and aspects of the primary surface reaction. We explore modifications to a basic reaction-diffusion model of a full cell that bring better agreement with experimental data, including gas-electrolyte surface limited diffusion and a partially active cathode. We discuss how the basic form of the model and the simulated reaction and concentration profiles affect cell dynamics.

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Non-aqueous Li-air/Li2O2 batteries have the highest theoretical energy density of any existing battery technology,1–3 yet the practical application of these systems is hampered by electrolyte-related phenomena including material degradation and mass transport limited behavior. Ideally, electrolytes for Li-air batteries should exhibit high ionic conductivity, resistance to decomposition, high oxygen solubility and fast oxygen diffusion rates. While many groups have focused on the degradation aspects and a few groups have investigated oxygen mass transport as a function of electrolyte chemistry,4–6 fewer have deeply explored the impact of oxygen diffusion on cell performance (see Ref. 9 for a recent review of Li-air models). Here we use a computational approach with experimental validation to model a full Li-air battery under transport-limited conditions and extract the influence of reaction-diffusion parameters.

In designing Li-air battery systems voltammetry experiments play an important role in providing estimates of the reaction-diffusion properties which influence power density, energy density and cell lifetime. Voltammetry, a category of electroanalytic methods in which potential is varied linearly with time, has become a standard experimental tool to discern thermodynamics, kinetics and transport related to electrochemical processes. Randles and Sevcik derived a widely used tool to discern thermodynamics, kinetics and transport related to electrochemical processes. Randles and Sevcik derived a widely-used equation, these semi-empirical correlations are inappropriate for applications on devices with complex (i.e. porous) electrode geometries, as in Li-air batteries.

Modeling electrochemical processes under practical device conditions, such as in a coin cell, provides insight into phenomena not easily accessible by experimentation. Generally speaking, a number of physical mechanisms are important in a complete battery model such as the basic interplay of a chemical reaction driven by a thermodynamic potential and the diffusion of reactants and products. Given the complexity of battery operation, many researchers tend to focus on only a few aspects. Most attempts to model the discharge process in Li-air cells simulate the growth of Li2O2 thin films in electrode pores - a phenomenon that can severely limit the oxygen diffusivity over time.17–22 These models frequently predict pore clogging at the gas-electrolyte interface such that much of the interior electrode area becomes inactive. Some work has focused on discharge capacity limits caused by electronically insulating Li2O223,24 and other work has addressed the impact of oxygen and ion diffusivity as a function of porosity of electrode structure25,26 and electrolyte properties.4 One recent full battery model20 integrates many of these aspects and introduces an improvement to account for both surface film and solution-based reduction mechanisms in low and high donor number electrolytes,27 respectively. Despite the insight provided by these prior computational efforts, experimental validation has been limited.

To improve the process of electrolyte selection and prediction of device performance, we construct a Li-air battery model that reduces the complexity of competing factors to a simple reaction-diffusion equation.

We are motivated to develop a simple model that can: (a) represent voltammetry data and reduce it to estimates of diffusion with a complexity comparable to the semi-analytic Nicholson-Shain model, and (b), with validation, be used to predict cell response during cell discharge. The goal is to provide a direct, model-based estimate of the diffusion coefficient of oxygen in a coin-cell, like Ref. 28, as opposed to a specially designed measurement cell, such as a rotating disk electrode,29 or through an assumed viscosity–diffusion correlation.3 As our primary simplifying assumption, we neglect electrode passivation since this effect is considered negligible over the short timescales of voltammetry experiments when using fresh cells with pristine electrodes. Specifically, we assume that the cell response is diffusion-limited in these rapid experimental timescales and high rates of voltage cycling. This assumption is supported by the fact that high donor number electrolytes, such as DMSO, have been shown to promote longer lifetimes of O2 such that the passivating species, Li2O2, is not formed immediately, and not from a solely surface-based pathway.27 Other assumptions are discussed in the next section, in which we develop the model. The method section provides details of the experimental and computational methods we employed. In the results section, we explore the impact of assuming that the oxygen concentration at the air-cathode boundary is a constant given by solubility and external pressure, as in Refs. 18,19,24. In particular, we examine the concentration profiles and correspondence with the experimental data, and investigate both the effects of limited diffusion at the air-electrolyte interface and a partially active cathode. Lastly, in the discussion section we discuss the implications of the results, including on the design of porous cathodes.

*Electrochemical Society Member.
*E-mail: rjones@sandia.gov

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Theory

In our model development, our first assumption is that the primary reaction
\[ O_2 + e^- \rightarrow O_2^- \]  
behaves essentially irreversibly due to consumption of the product \( O_2^- \) by a subsequent reaction (or other mechanism that removes \( O_2^- \) from proximity of the cathode surface).\(^{30}\) This assumption is based on the choice of a highly polar model electrolyte (DMSO). Hence we employ only the forward part of the Butler-Volmer equation (cf. Ref. 31, Eq 3.5.32) to model the reaction density:
\[ r = -\sigma c \kappa \exp \left( \frac{a e \psi}{k_B T} \right) \]  
where \( \sigma \) is the (reactant accessible) surface area density of the cathode, \( k \) is the kinetic rate associated with the reaction, \( e \) is the elemental charge, \( \psi = \phi - \phi_0 \) is the local potential relative to the reference voltage \( \phi_0 \), \( k_B \) is Boltzmann’s constant, and \( T \) is the temperature. Note that a negative sign is used in Eq. 2 since the species of interest, \( O_2^- \), is being consumed. Since we are assuming an irreversible reaction, it is important to note that \( \psi \) is not an over-potential with which \( \phi_0 \) would be defined by no net reaction \( r = 0 \). Also, note the surface area density \( \sigma = S/V \), where \( S \) is the total surface area of the cathode and \( V \) is its apparent volume, takes a surface reaction coefficient \( k \) to a volumetric coefficient \( \sigma k \).

We also assume that, given the aspect ratio of our coin cells, the diffusive transport within the cell is essentially one-dimensional. (We use \( x \) for the coordinate in the transport direction with origin \( x = 0 \) at the separator-cathode boundary and \( x = L \) at the cathode-air boundary, refer to Fig. 1.) Furthermore, we assume that, given the high dissolved salt concentrations we employed (0.5 M LiBF\(_4\)/DMSO relative to 0.0003 M \( O_2 \), refer to Table I and Experimental procedure section), Li\(^+\) is available in abundance so that only \( O_2^- \) transport is of interest and that cross-species diffusion coefficients are negligible. Since \( O_2 \) is charge neutral, we omit an electrostatic model; and, since the cathode is conducting we assume \( \varphi(x,t) \) is uniform (and independent of \( x \)) in the cathode. Hence, we only introduce a reaction-diffusion equation:
\[ \varepsilon \dot{c} = \frac{1}{\tau} D \kappa c + r \]  
\[ \text{governing transport where } D \text{ is the bulk diffusion coefficient, } \varepsilon \text{ is the porosity giving a concentration } \bar{c} \text{ based on the apparent volume (vs. the true concentration } c \text{ referenced to the volume of fluid), and } \tau \text{ is the tortuosity giving an effective diffusion length for the diffusive flux } J = -(D/\tau) \bar{c}, \text{ by rescaling } x. \text{ Note that these porosity and tortuosity corrections to the basic reaction-diffusion equation applied separately to the separator and cathode, and are from Refs. 32,33. Non-dimensionalizing Eq. 3:} \]
\[ \hat{c} = \left( \frac{D}{\tau L^2} \right) \bar{c} + (\sigma k) \exp \left( \frac{a e \psi}{k_B T} \right) \bar{c} \]  
with \( \bar{c} = c/c_{eq} \), where \( c_{eq} \) is the equilibrium concentration of \( O_2 \), and \( L \) being the length of the cathode in the transport direction, gives the similarity parameters formed from the inverse time-scales: diffusion \( \hat{D} = D/(\tau L^2) \); reaction \( \hat{k} = \sigma k \); and the external potential \( (a e \psi)/(k_B T) \), where \( \psi \) is the voltage scan rate which is constant in the voltammetry conditions we consider. Note, since the porosity and tortuosity of the separator and cathode are distinct, we use the cathode values for the similarity parameters. In particular, the reaction-diffusion ratio
\[ \frac{\hat{k}}{\hat{D}} = \frac{\sigma k \tau L^2}{D} \]  
can be recognized as a version of the Damköhler number and is the only intrinsic time-scale ratio. The exponential of the applied potential modifies the reaction timescale, however, so that an effective Damköhler number is
\[ \text{Da}(\psi) = \frac{\sigma k \tau L^2}{D} \exp \left( \frac{a e \psi}{k_B T} \right) \]  
In fact, the exponential effect of the external potential is the only non-linearity in Eq. 4. In the following, we will use the non-dimensionalized potential \( \hat{\psi} = \frac{e \psi}{k_B T} \).

By integrating over the reacting cathode, we obtain the total current
\[ I = FA \int_0^L r \, dx = \frac{(\sigma k) F V c_{eq}}{L} \int_0^1 \hat{c} \, dx \exp \left( \frac{a e \hat{\psi}}{k_B T} \right) \]  
where \( A \) is the cross-sectional area of the cathode, and Faraday’s constant \( F \) is a conversion factor from moles of electrons to Coulombs. Note that this equation, like the Nicholson-Shain relation, implies...
that the peak current will scale linearly with the concentration of dissolved oxygen $c_\infty$. Clearly, the evolution of $c(x, t)$ and hence $\tilde{c}(t)$ will scale linearly with $c_\infty$. It is also evident that $I(t)$ depends on a constant $I_0$ (which scales with $Q_0 = F \nu c_\infty$ the initial capacity of the cathode), the average (normalized) concentration in the cathode $\bar{c}(t)$, and an exponential of the applied potential $\Phi(t)$. Lastly, given the initial condition $c(x, 0) = c_\infty$ (hence $\bar{c}(x, 0) = 1$), the initial current $I(0) = I_0 \Phi(0) = I_0 \exp(\alpha \Phi(0))$ is greater than zero.

In models commonly used to extract diffusion coefficients, such as Nicholson-Shain,$^{15,16}$ the peak over a voltage sweep is used to determine the diffusion coefficient $D$. Since $\Phi(t)$ is monotonically and exponentially increasing for a linear voltage sweep, the average concentration $\bar{c}(t)$ must decrease faster than $\Phi(t)$ for a diffusion limited peak in $I(t)$ to appear. In fact, $I_0 \Phi(t)$ gives an upper bound to the current at any point in the sweep. For the proposed model, the current $I(t)$ in Eq. 7 has a maximum where

$$ I = I_0 \left( \int_0^1 \dot{c} \, dx \, \exp(\alpha \tilde{\phi}) + \int_0^1 \dot{\tilde{c}} \, dx \, \alpha \tilde{\phi} \exp(\alpha \tilde{\phi}) \right) $$

$$ = I_0 \left( \int_0^1 \tilde{D} \tilde{c}^0 + \tilde{k} \tilde{\phi} \tilde{c} \, dx \, \Phi + \alpha \tilde{\phi} \tilde{c} \right) \Phi = 0 $$

given that $\tilde{\phi}$ is a constant for a linear voltage sweep. Hence, the influx of $O_2$ into the cathode at maximum current $I$ is

$$ -\tilde{D} \tilde{c}^0 \tilde{c}(t_{\text{max}}) = (\alpha \tilde{k}) \Phi(t_{\text{max}}) + \alpha \tilde{\phi} \tilde{c}(t_{\text{max}}) $$

which includes the influx

$$ J_{\text{in}} = \pm \frac{AD}{\tau} c_{\text{in}} = \frac{ADc_\infty}{L} \tilde{c} = -Q_0 \tilde{D} \tilde{c} $$

from the separator, at $\tilde{\phi} = 0$ with a $+$, and air, at $\tilde{\phi} = 1$ with a $-$, sides of the cathode. Note that influx from the separator can be significant for relatively large separators and fast scan rates and qualitatively this boundary acts similar to the Robin boundary introduced in Eq. 13.

To obtain the evolution of the average concentration in the cathode $\tilde{c}(t)$, we need the boundary conditions: (a) zero flux of (molecular) oxygen at the Li anode

$$ J = -ADc_{\text{in}} = 0 \quad \text{at} \quad x = 0 $$

(b) continuity of the (true) concentration $c$ at the separator-cathode interface

$$ \|c\| = c(0^+, t) - c(0^-, t) = 0 \quad \text{at} \quad x = 0 $$

Table I. Known and unknown parameters: For reference $V = AL = 41.5 \text{ mm}^2$ and $\sigma = S / V = 200 \text{ mm}^{-1}$. Pore radius in the separator, 1.6 $\mu$m, and cathode, 0.421 $\mu$m, are large relative to the size at which molecular transport is important. The total amount of reactants initially present in the cathode $Q_0 = F \nu c_\infty = 1.3 \text{ mC}$.

| Symbol | Description | Value | Source |
|--------|-------------|-------|--------|
| $L$    | cathode thickness | 0.235 mm | El-Kharouf, 2012$^{25}$ |
| $L_s$  | separator thickness | 0.260 mm | Whatman GF/A spec sheet |
| $A$    | cathode cross-sectional area | 1.76 cm$^2$ | |
| $S$    | cathode effective surface area | 83 cm$^2$ | capacitance measurement |
| $\epsilon$ | cathode porosity | 0.365 | El-Kharouf, 2012$^{25}$ |
| $\epsilon_s$ | separator porosity | 0.9 | El-Kharouf, 2012$^{25}$ |
| $\tau$ | cathode tortuosity | 2.92 | |
| $\tau_s$ | separator tortuosity | $\approx 1.0$ | |
| $c_\infty$ | equilibrium O$_2$ concentration | 0.33 mM | IUPAC-NIST Solubility Data Series |
| $q_0$ | open circuit voltage | 3.04 V | |
| $T$    | temperature | 295 K | |
| $\alpha$ | charge transfer coefficient | $\geq 0.5$ | quasi-irreversible reaction |
| $k$    | surface reaction coefficient | 0.001–1.0 mm/s | see Table II |
| $D$    | bulk diffusion coefficient | 0.001–0.01 mm$^2$/s | see Table II |
| $s$    | surface diffusion coefficient | 0.01–0.1 mm/s | estimated: $s = D_L \ell < 0.1 \text{ mm}$ |

Experimental procedure—The Li-air coin cells we employed were assembled primarily from off-the-shelf components. A carbonaceous gas diffusion layer with microporous layer (Sigracet 25BC), see Table I for dimensions and other properties, was used as the oxygen electrode in Li-air coin cell experiments. The effective surface area

$$ \tilde{c} = -k \Phi(t) \tilde{c} $$

and the solution

$$ \tilde{c}(t) = \exp \left( -\frac{k}{\alpha \tilde{\phi}} \exp(\alpha \tilde{\phi} t) \right) $$

for constant $\tilde{\phi}$. In this case the current

$$ I(t) = I_0 \exp(\alpha \tilde{\phi} t - \frac{k}{\alpha \tilde{\phi}} \exp(\alpha \tilde{\phi} t)) $$

peaks at $t_{\text{max}} = 1/n \log \frac{c_\infty}{c_\infty - c}$. Clearly, for the copped system, the model predicts that max current is proportional to scan rate $\tilde{\phi}$.

Method

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of the electrode, see Table I, was determined by measurement of the double layer capacitance using a symmetric cell with a 1 M LiTFSI/1-methyl-1-butyl pyrrolinium bis(trifluoromethanesulfonyl)imide electrolyte (as opposed to a Bruggeman-like correlation based on geometry of overlapping spheres used to connect to porosity and tortuosity). The Li-air electrolyte consisted of dimethyl sulfoxide (DMSO, anhydrous, Sigma Aldrich) with various concentrations of lithium tetrafluoroborate (LiBF₄, 99.99% battery grade, Sigma Aldrich). The separator was Whatman GF/A glass fiber paper. Lithium metal counter electrodes were purchased from MTI Corp. Stainless steel CR2032 coin cell cases with perforated tops, wave springs and stainless steel shims were purchased from MTI Corp.

Cells were assembled by stacking a Li metal anode (on top of a wave spring and shim), a glass fiber separator (impregnated with 60 μL of electrolyte) and a carbon electrode (with the microporous layer oriented toward the separator). A flattened Ni foam (MTI Corp.) spacer was placed between the oxygen electrode and coin cell case to increase the air headspace and improve conductivity across the carbon electrode. After crimping, cells were allowed to equilibrate in dry air (< 6 ppm H₂O, Matheson) at open circuit potential for 6 hrs before cycling.

Oxygen reduction in coin cells were evaluated by cyclic voltammetry (CV) with a 0.5 M LiBF₄/DMSO electrolyte at various scan rates {0.5, 0.1, 0.2, 0.5, 1.0} mVs using a BioLogic MPG-2 battery tester. The observed reduction reaction with a DMSO electrolyte is assumed to be the one electron process, refer to Eq. 1.

The oxygen reduction reaction was similarly studied on a 5 mm diameter glassy carbon (GC) electrode (Pine Instruments) for comparison, using a Pt counter electrode and LiLi⁺ reference. Stationary electrode voltammograms were analyzed using the Tafel equation to determine the charge transfer coefficient, 𝛼 = 0.65. Diffusion coefficients of O₂ were determined using a rotating ring disk electrode (RRDE) by observing the transit time from a GC disk to an Au ring (6.5 mm inside and 7.5 mm outside diameter) at various rotation rates {100, 150, 200} rpm. For this set of experiments, the disk electrode was stepped from 2.9 V to 2.5 V while the ring was held at a constant 2.5 V. Transit time was calculated according to the equation:

\[ τ_i = K \left( \frac{V}{D} \right)^{1/3} \omega^{-1} \]  

Where \( τ_i \) is the transit time, \( K \) is a geometric constant, \( V \) is the kinematic viscosity, \( D \) is the diffusion coefficient, and \( ω \) is the rotation rate.

**Numerical solution.**—To obtain a numerical solution to compare with experimental CV data, we discretized the non-dimensional governing Equation 4 in space with the standard Galerkin finite element method using a non-uniform grid to resolve the high concentration gradients at the boundaries. Since the exponential rise of the external potential leads to a stiff system of differential equations in time, we use a solver capable of switching between time-integration methods appropriate for stiff and non-stiff behaviors. We benchmarked the code against the analytical solutions including Eq. 16 and the standard diffusion solution for \( k = 0 \):

\[ c(x, t) = c_∞ \left( 1 + \exp \left( \frac{Dπ²}{4L²} t \right) \cos \left( \frac{π x}{2L} \right) \right) \]

which gives \( c(t) = 1 - \frac{c_∞}{2} \exp \left( -\frac{Dπ²}{4L²} t \right) \). In addition, we did convergence studies for both the spatial and temporal discretizations and used time-steps sufficiently small to maintain accuracy.

**Model calibration.**—With reference to Table I, we take the equilibrium concentration \( c_∞ \) and the various geometric parameters as given data. The remaining parameters: \( a, k, D \) and \( s \), are used to fit the experimental data. A few observations are germane to the calibration. First, the response of the model scales linearly with \( c_∞ \). Hence, errors in this data, e.g. due to variations in the ambient pressure, leads directly to errors in \( c(t) \) and \( I(t) \). Second, the reaction coefficient \( k \) and the surface to volume ratio \( σ \) are paired in all the relevant equations; and, so they cannot be determined independently from the CV data and, given an independent estimate of \( σ \), errors in \( k \) will lead to additional errors in \( k \) determined by calibration to the CV data. Furthermore, \( k \) and the reference potential \( φ₀ \) are confounded in that changes in one have the same effect on \( I(t) \) as changes in the other, i.e. shifting the predicted potential by \( φ₀ \) for a given \( k \) is the same as employing a different reaction coefficient \( k_0 = k \exp \left( -\frac{a c_∞}{kT} \right) \) so that: \((a c_∞)k \exp \left( -\frac{a c_∞}{kT} \right) = (a c_∞)k \exp \left( \frac{a c_∞}{kT} \right) \). In fact an order of magnitude change in \( k \) is on par with a shift of \( φ₀ = 0.12 \) V (for \( a = 1/2 \) and \( T = 300 \) K).

We base the calibration on the usual least-squares error norm

\[ \min_{Δφ, k, D, S} \left[ ∑_i \left| I_i - I(φ(t_i) + Δφ, k, D, S) \right|^2 w_i \right] \]

with experimental current samples \( I_i \), sample times \( t_i \), error weights \( w_i \), and data model

\[ I(t) = I(φ(t) + Δφ, k, D, S) \]  

Here, \( ε \) is error in the current \( I \) and \( Δφ \) is treated as error in the potential \( φ \). Given that there are errors in both the input and output data, we split the optimization into inner and outer loops to solve the orthogonal distance regression problem. First, we estimate \( \phi(t) \) from the initial rise of the CV curve and, given an estimate of \( k \), we solve for \( φ₀ = \frac{a c_∞}{kT} \ln \frac{t_0}{t} \) so that the initial current is below a threshold \( I_0 = 0.001 \) mA. Then the outer minimization, over \( D \) and \( s \), is handled by a standard Gauss-Newton optimizer and the inner minimization is accomplished by simply shifting the current \( I(t) \), given by the outer optimization, by the average error in \( φ \). This procedure is motivated by minimizing the potential error \( ∑_i |I(φ) - I(φ₀)|^2 \) which leads to \( ∑_i (φ(t_i) - φ₀) = 0 \) and hence \( φ₀ = 0 \) assuming the inverse of \( I = I(φ(t)) \) is monotonic (i.e. we only use the rise phase of the CV). The feasible ranges for \( D \) and \( k \) are suggested by independent measurements given in Table II.

**Results**

The experimental voltammetry data is shown in Fig. 2. From the (upper) log current plot, it is evident that the Tafel region, where the forward reaction dominates, is \( ψ > 0.2 \) V. Also, given the location of the peaks in the (lower) current plot, it is clear that the reference for the potential is somewhat arbitrary. The black trend line in the log plot (upper) with slope 0.65 mA/V generally reflects the trend in the current at all scan rates \( φ \).

The general phenomenology of the current response of the model to a linear ramp of voltage is shown in Fig. 3a. Apparently, for the given model the primary influence on the peak current is the exponent \( α = 0.65 \) and the scan rate \( φ \). Increasing the reaction coefficient \( k \) or reference potential \( φ₀ \) shifts the current-potential curve right. The bulk diffusion coefficient \( D \) primarily affects the minimum after the peak and the surface diffusion coefficient \( s \) primarily affects the slope of the current post-minimum. Given the model form \( I(t) = I(φ(t)) \) (refer to Eq. 7) a peak in the current \( I \) appears when the average concentration in the cathode \( ć \) decreases faster than the exponential of the potential \( φ = \exp(αψ) \) increases. Comparing the model and the experimental current evolution in Fig. 2, the pre-Tafel region is not modeled well; however, the peak height is relatively independent of \( ć \). As Fig. 3b shows, initially, as the potential ramps, the concentration is relatively constant, then rapidly decreases effectively to zero in the neighborhood of the peak and subsequent trough in the current. For this example, the influx \( J \) from the air side grows to be a significant contributor to the current \( I \) and hence the total consumption of reactants \( Q \) exceeds that which is present in the cell prior to the voltage sweep. Also, the average concentration is relatively constant...
Table II. (a) Reaction coefficient $k$ and (b) bulk diffusion coefficient $D$, including our independently measured values for $D$ using a rotating ring disk electrode (RRDE). Given our estimate of $k = 200$ mm$^{-2}$, see Table I, the likely range of $0.1–100.0$ l/s. For reference our measured value of viscosity of the DMSO electrolyte is 2.07 mPa-s.

| Reaction Coefficient $k$ [mm/s] | Electrolyte               | Source                      |
|---------------------------------|---------------------------|-----------------------------|
| 0.0021                          | 0.1 M LiBF$_4$/DMSO       | Laoire, 2010$^5$            |
| 0.010                           | 0.1 M TEAClO$_4$/DMSO     | Sawyer & Roberts, 1966$^{46}$|
| 0.30                            | 0.1 M TBAClO$_4$/DMSO     | Wendt, 1995$^{47}$          |
| 0.90                            | 0.1 M TBAClO$_4$/DMSO     | Ortiz, 2003$^{48}$          |

| Diffusion Coefficient $D$ [mm$^2$/s] | Electrolyte               | Source                      |
|-------------------------------------|---------------------------|-----------------------------|
| 0.00167                             | 0.1 M LiBF$_4$/DMSO       | Laoire, 2010$^5$            |
| 0.00323                             | 0.1 M TEAClO$_4$/DMSO     | Sawyer & Roberts, 1966$^{46}$|
| 0.00749                             | 0.5 M TBAClO$_4$/DMSO     | Collins, 2000$^{49}$        |
| 0.00305                             | 0.1 M TEAClO$_4$/DMSO     | Sawyer & Roberts, 1966$^{46}$|
| 0.00146                             | 0.5 M LiBF$_4$/DMSO       | This work                   |

Figure 2. Coin cell cyclic voltammetry data. The black trend line in the (upper) log plot has slope 0.65 mA/V and is offset from the data for clarity.

for $\phi < 0.3$ V so the current tracks the increase in $\Phi(t)$ until the diffusion limited peak is encountered at $\phi > 0.3$. As the potential is returned to $\phi = 0$ the concentration in the cathode grows slowly, fed from the environment and separator. In all subsequent results, we only simulate the ramp up in potential for efficiency. From Table I, the likely range of $k = \sigma k$ is $0.1–100.0$ l/s, and likewise $\tilde{D} = D/1.2^2$ $0.01–10.00$ l/s.

The response and fit for the model with bulk diffusion $D$ and surface concentration $c(L, t) = c_{\infty}$ equal to the equilibrium value $c_{\infty}$ (the limit $s \to \infty$) is shown in Fig. 4. Fig. 4a shows the peak current has low sensitivity to the diffusion coefficient $D$ and the reaction coefficient $k$ and that no peaks occur for diffusion coefficients $D$ higher than $\approx 10^{-4}$ mm$^2$/s for the reaction coefficients we explored. Fig. 4b compares the simulation, $\log D = -4.1$ and $\log \tilde{k} = -2$, with the largest peak current to the experimental CV data for $\phi = 1.0$ mV/s. Clearly the simulated peak current is more than an order of magnitude lower than the experimental value. As mentioned, the potential at which the peak occurs is of less importance due to the arbitrary reference potential. Given the model form $I(t) = I_0 c(t) \Phi(t)$, a peak in the current $I$ only appears when the average concentration in the cathode $\bar{c}$ decreases faster than the rate of increase of the exponential of the potential $\Phi$, as Fig. 4c shows. Fig. 4d shows that the concentration profile evolves as expected from diffusion coupled with regional depletion due to reaction, and is fixed at the equilibrium value $c_{\infty}$ at the air-cathode boundary. The evolution of the reaction profile is more complex. It is evident from Fig. 4d as the potential function $\Phi$ grows large the fixed concentration boundary condition leads to spike at the boundary as the remainder of the cathode depletes of reactant. Initially, the reaction profile is fairly uniform like the concentration profile but as the concentration of O$_2$ becomes localized at the boundaries of the cathode and the driving potential is increasing exponentially, the reaction profile becomes nearly singular at both boundaries. This effect...
explains why high $D$ simulations do not display current peaks: the concentration in the cathode never depletes sufficiently.

The response and fit for the model with a limited surface flux boundary condition is shown in Fig. 5. Peak current $I_{\text{peak}}$ as a function of bulk diffusion coefficient $D$ and surface diffusion coefficient $s$ is shown in Fig. 5a. High values of $s$ lead to surface diffusion being the limiting process as evidenced by the relative insensitivity the $I_{\text{peak}}(D)$ curves to increases in $D$. Fig. 5b supports this finding. Here we see the remnants of a first peak in current $I$ that is more evident for higher surface diffusion solutions, i.e. approaching the fixed boundary concentration limit $s \to \infty$, and a second higher peak that appears only for low values of $s$. This behavior is consistent with phenomenology described in Fig. 3, i.e. sufficiently high $D$ fills in the first trough in the current and a maximum current results only when the surface diffusion becomes the limiting process. Fig. 5c shows for this version of the model with the parameters that lead to the highest current, log $k = -4$, $D = 0.00126$ mm$^2$/s, $s = 0.1$ mm/s, the influx of oxygen $J$ nearly matches the production of current $I$ over the full range of the voltage sweep. Also, the evolution of the concentration $C$ in the cathode displays on the first portion of the sigmoidal shape of that in Fig. 4c. Lastly, both the concentration and reaction profiles shown in Fig. 5d are much less severe than in Fig. 4d as the concentration at the air-cathode boundary relaxes to zero like that at the separator-cathode boundary.

To check if the model is consistent with the CV data across all the scan rates we ran the model at $\dot{\phi} \in \{0.05, 0.10, 0.50, 1.00\}$ mV/s. Since the parameters that effect the highest peak currents are at the limit at which no diffusion limited peaks occur in the parameter space, it is not surprising that these values did not lead to diffusion peaks at all the rates $<1.00$ mV/s. So we explored the parameters that lead to lower peak currents. The results of the scaling of the peak current with the scan rate are shown in Fig. 6. It is evident that the model scaling at high scan rates for both the fixed concentration and limited surface diffusion boundary conditions does not match the CV data which follows a $I_{\text{peak}} \sim \sqrt{\phi}$ trend. Given (a) our understanding that peaks only occur when the concentration is allowed to relax to zero where reaction is occurring, and (b) the reasoning that the model should reduce to a square root of scan rate scaling found in Nicholson-Shain when the reacting portion of the cathode approaches a surface (as opposed to a volume), we explored the model response to allowing reaction on only a fraction of the cathode. This modification of the model is also motivated by an apparent change in composition/structure shown in the upper left panel of Fig. 1 which possibly leads to functional changes in the electrochemistry of the cathode. Physically, this modified model emulates a partially filled and/or partially coated cathode. From Fig. 6, it is clear that as the reaction on the air side of the cathode is progressively inactivated the current-scan rate trend becomes $I_{\text{peak}} \sim \Phi$. 
Figure 5. Limited flux boundary condition at the air-cathode surface. (a) Peak current as a function of diffusion coefficient $D$, and reaction coefficient $\tilde{k}$. (b) Comparison of the simulated and experimental evolution of current $I$ with potential $\Phi$ at scan rate $\dot{\Phi} = 1.0$ mV/s. (c) Components affecting the current $I$: $J$ influx from the air boundary, the potential function $\Phi = \exp(\tilde{\Phi})$, and the total concentration in the cathode $C = \overline{V}c$, as well as charge transferred $Q$ (all plotted on a log scale). (d) Profiles of the reaction field $r$ and concentration of O$_2$ $c$ as a function of time.

Lastly, we explored how changing the size of the cathode relative to the size of the cell affects the peak current ($L_c + L_s = 1$ mm, log $D = -6$, log $\tilde{k} = -4$). Fig. 7 shows that the peak current is directly proportional to cathode width. This scaling is due to the fact that the concentration profiles in the cathode are essentially uniform except near the separator and air boundaries. It also implies the separator has little influence on power performance.

Discussion

In searching for the simplest model that represents the experimental voltammetry data of a Li-air battery, we constructed a one-dimensional reaction-diffusion model that assumed forward Butler-Volmer reaction kinetics throughout a homogenized porous cathode and made basic assumptions about how the oxygen in the ambient air entered the cell. In particular, we explored the effects of limited diffusion at the air-cathode boundary and also a partially activated cathode. The first modification of the commonly used model\textsuperscript{18,19} where the oxygen concentration at the open boundary is fixed at the equilibrium concentration, increases the correspondence of peak current with experimental measurements but did not lead to the experimental scaling of peak current with scan rate. The model does display the experimental trend if a significant portion of the cathode on the air side is made inert. It is unlikely that this correspondence is due to partial flooding of...
There are certain aspects of the model behavior that are likely to be predictive even with modifications to the surface dissolution and reaction aspects. The phenomenological dependence of the current on the bulk and surface diffusion coefficients are relevant to metal-air batteries in general. The primary quantitative result of the model is that, given Eq. 7, a higher partial pressure of ambient oxygen would increase $c_{\infty}$ and hence scale the current output proportionally. However, it is unclear if this proportionality would hold if the transport of $Li^+$ was the rate limiting aspect; in this case, we would need to add the diffusion of $Li^+$, amend the reaction model to be sensitive to the $Li^+$ concentration, and possibly add cross-species diffusion effects. Second, the model form $I = I_0 e^\Phi$ explains how peaks in the current under voltammetry conditions occur as a direct competition between the decreasing average concentration, $\bar{c}$ and the rapidly increasing exponential of applied voltage $\Phi$. Third, this work shows that CV, with the scan rates we studied, leads to very concentrated reactions at the boundaries of the cathode. Given this is likely to be characteristic of the cell under high power demands, a design using hierarchical pores, grading of porosity and/or non-uniform application of catalyst, will exhibit more optimal performance but may not fully alleviate this issue.

Certainly more work is required, ranging from fundamental investigations of the air/cathode interface and cathode structure to optimizing the cell design through structure and chemistry. In summary, the contributions of this work are: (a) the derivation of a simple algebraic relationship between cell current, exponential of the overpotential and the average concentration of reactant in the cathode; (b) the demonstration that spatial singularities develop the concentration and reaction profiles which limit cell performance; (c) the finding that a perfect cell should have a peak current-scan rate scaling different than $I \sim \sqrt{\bar{c}}$ and yet a practical cell follows this trend; (d) the experimental trend $I \sim \sqrt{\bar{c}}$ is likely due to the singular reactions at the air boundary being prevented, as opposed to limited surface diffusion of the ambient oxygen; and (e) the discrepancy between predicted and measured current-scan rate trends can be used as a diagnostic for the functionality of porous cathodes in practical cells. This work has relevance to practical Li-air and other metal-air systems where interfaces are imperfect and it is difficult to experimentally determine the impact of reaction-diffusion characteristics. To our knowledge this is the only work to (a) use voltammetry as a tool to understand diffusion, as opposed to degradation, in these systems; and (b) directly evaluate the impact of diffusion limitations due to the porous electrode structure and its interfaces.

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Figure 7. Effect of changing the cathode width $L_c$ on the peak current. The overall cell width $L = L_c + L_s$ is fixed at 1 mm. The inset shows the evolution of concentration in the cathode for various cathode widths.
