Modeling of an aprotic Li-O₂ battery incorporating multiple-step reactions

Y.X. Ren, T.S. Zhao *, P. Tan, Z.H. Wei, X.L. Zhou

Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

ABSTRACT

This paper reports on a one-dimensional lithium-oxygen (Li-O₂) battery model incorporating the competitive uptake of discharge intermediate between the electrode surface and the aprotic electrolyte. Unlike previous models, in which a single-step reaction is assumed for aprotic Li-O₂ batteries (2Li⁺ + 2e⁻ + O₂ → Li₂O₂), the present model more realistically depicts the electrochemical process in a battery system by taking account of multiple-step reactions, including the surface reduction reactions of absorbed oxygen (Li⁺ + O₂ + e⁻ → LiO₂⁻) and adsorbed superoxide (LiO₂⁻ + Li⁺ + e⁻ → Li₂O₂) along with the dissolution of superoxide into electrolyte. Transient and spatial analyses are performed to identify the limiting steps for the battery's performance, including oxygen transport and final discharge product precipitation. The effects of the kinetics of oxygen reduction reaction and superoxide dissolution are also investigated. In addition, the impact of cathode microstructures on the battery’s performance is studied. It is found that the electrolyte’s ability to dissolve the discharge intermediate (LiO₂) is critically important to improve the discharge capacity.

© 2016 Elsevier Ltd. All rights reserved.

* Corresponding author.
E-mail address: metzhao@ust.hk (T.S. Zhao).

http://dx.doi.org/10.1016/j.apenergy.2016.11.108
0306-2619/© 2016 Elsevier Ltd. All rights reserved.
1. Introduction

The advance in Li-ion batteries has transformed portable electronics in the past decades and is performing a remarkable role in the electrification of transport nowadays. On its journey towards more scaled-up application, the classical solid-state Li-ion battery is facing the bottleneck of low-energy-density storage [1,2]. Beyond the horizon of Li-ion batteries, the perspective for aprotic lithium-oxygen/air batteries (Fig. 1a) as a candidate for high-energy-density power source has been recognized. Predominantly, the aprotic Li-O2 cathode discharge electrochemistry is the Li+ involved two-electron reduction of oxygen to form lithium peroxide (Li2O2) at the cathode, with metallic lithium oxidation occurring at the anode:

Anode: \[ \text{Li} - \text{e}^{-} \rightarrow \text{Li}^{+} \]  \hspace{1cm} (1)

Cathode: \[ 2\text{Li}^{+} + \text{O}_2 + 2\text{e}^{-} \rightarrow \text{Li}_2\text{O}_2 \]  \hspace{1cm} (2)

where lithium, as the lightest metal, possesses a high specific capacity of 3860 mAh/g; and oxygen can be supplied from ambient air almost infinitely. Hence, the theoretical energy density of aprotic Li-O2 batteries is several times higher than that of existing Li-ion and flow batteries [3–7]. Though successful operations of Li-O2 batteries have been achieved recently, the underlying challenges for pursuing a practical aprotic Li-O2 battery have also emerged [8–11]. One is the exploration of stable electrolyte/electrode materials [12–18]. The other concerns for the insulating/insoluble lithium peroxide (Li2O2) as the discharge product [19–22]. Considering the complexity of coupled reaction and transport phenomena during Li2O2 formation, experimental study in tandem with mathematical modeling has been intensively exploited to accelerate research in this area [19].

Previous reports indicate that, the primary step in Li2O2 formation proceeds by oxygen diffusing and binding to active sites on the cathode surface, then reacting with Li+ ion in a concerted electrochemical reaction to form adsorbed LiO2 as:

\[ \text{Li}^{+} + \text{O}_2^{2-} + \text{e}^{-} \rightarrow \text{LiO}_2^{\text{ad}} \]  \hspace{1cm} (3)

where the superscript \( ^{\text{ad}} \) expresses adsorbed species [16]. Following the formation of adsorbed LiO2 (ad-LiO2), there emerge two diverse modes to form Li2O2, as shown in Fig. 1b [8,16,23,24]. Currently it is believed that surface-bound LiO2 can be dissolved in the electrolyte as:

\[ \text{LiO}_2^{\text{ad}} \rightarrow \text{LiO}_2 \]  \hspace{1cm} (4)

In general, the surface mechanism is promoted in electrolytes with low Gutmann donor or acceptor numbers (measures of Lewis basicity and acidity), whereas electrolytes with high donor or acceptor numbers enable a solution mechanism [24,25]. For the surface mechanism, the solvation as described above is weaker and the equilibrium shifts to the left. The adsorbed LiO2 on the cathode surface is electrochemically reduced to form Li2O2 precipitate:

\[ \text{LiO}_2^{\text{ad}} + \text{Li}^{+} + \text{e}^{-} \rightarrow \text{Li}_2\text{O}_2 \]  \hspace{1cm} (5)

With regard to the solution mechanism, LiO2, which has dissolved into the electrolyte, will be precipitated as Li2O2 through the chemical disproportion process:

\[ 2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2 \]  \hspace{1cm} (6)

Li2O2 precipitate formed via surface mechanism exhibits a thinner conformal layer resulting in fast surface passivation [26]. In contrast, solution mechanism promotes larger precipitated particles, leading to higher a capacity [25]. Though Li2O2 undergoes distinct formation processes, rapid drop of cell potentials can be observed for both modes at the last stage of discharge. Indeed, when the precipitation layer of Li2O2 grows, the air breathing cathode undergoes the active surface shrinkage, oxygen transport pathway blockage, and electron transport limitation, all of which can result in the drop of the discharge potential [21,27–29].

In line with the experimental investigations, developing sophisticated mathematical models to mimic Li-O2 battery’s discharge process is imperative to investigate species transport, discharge product dissolution/precipitation as well as the effects of key properties of electrode/electrolyte on the battery performance. Most
existing models focus on the transport phenomena coupled with electrochemical reactions in the cathode electrode [23,30–37]. Towards a rational description of the discharge product precipitation process, using a continuum transport model, Xue et al. introduced the concept of electron tunneling to realistically depict the electron transport limitation of Li₂O₂ and studied the impact of cathode microstructure. Considering the anisotropic arrangement of electrode, with a multiscale model, Bao et al. presented the discharge product precipitation in a three-dimensional reconstructed electrode [38]. To study the inherent process of precipitation, Horstmann et al. developed a nanoscale continuum model while Lau and Archer studied the nucleation and growth process of Li₂O₂ [39,40]. Besides the discharge product precipitation, species transport in the air breathing cathode has also received research efforts. Models based on the partially-wetted cathode and active cathode have been proposed respectively, to overcome the barrier of oxygen transport [41–43]. As mentioned, the multiple-step reactions that occur in Li-O₂ batteries directly impact on the formation of Li₂O₂ as well as species transport. However, sporadic Li-O₂ battery models consider the correlation of multiple-step reactions in modeling the battery's performance, in sharp contrast with the experimental efforts [8,31,44,45].

To address this concern, a discharge model that employs the interfacial oxygen reduction reaction and phase transfer kinetics, is developed. Unlike previous models, in which a single-step reaction is assumed for Li-O₂ aprotic Li-O₂ batteries, the present model specifically depicts the formation and dissolution of discharge intermediate (LiO₂) based on the updated experimental knowledge [24,44]. The surface reduction reactions of adsorbed oxygen and adsorbed superoxide are both considered. With this model, (a) transient and spatial analyses have been performed to reveal the reaction and transport phenomena for the battery’s performance; (b) the effects of LiO₂ dissolution on the reaction kinetics and species transport were discussed; (c) considering the electrode’s microstructure, the effect of LiO₂ dissolution on the discharge product precipitation was also provided. Overall, by incorporating multiple-step reactions that occur in Li-O₂ battery, the proposed model is expected to realistically predict the battery’s discharge process.

2. Theoretical

As shown in Fig. 1a, an aprotic Li-O₂ battery is usually composed of a Li foil anode, a glassy fiber separator, and a porous cathode. Both the separator and cathode are usually saturated in an aprotic organic solvent with lithium salt additives. Herein, the model takes account of the simultaneous surface reduction reactions of adsorbed oxygen and reduced oxygen species and their dissolution into electrolyte. Specific interactions of electrode/electrolyte will affect the discharge performance by varying the fractions of specific reaction mechanisms. To consider the precipitation of final discharge product and its physical impacts, the microstructure of the electrode is described by the pore size distribution, while the electronic conductivity of film-like Li₂O₂ deposit layer is given on the basis of electron tunneling. As with any theoretical model, the one proposed here is expected to work within a set of conditions, thereby the following general assumptions are made:

1. The existences of parasitic reactions and the decomposition of electrolyte/electrode are neglected.
2. The precipitation layer demonstrates a film-like morphology at a rather high specific current density as in this case. Li₂O₂ on the surface will act as an active substrate for continued adsorption of oxygen [46,47].
3. The mass transfer of soluble O₂ is by diffusion only and the O₂ concentration is saturated at the cathode/current collector interface.

Moreover, the species and electron transports will be exploited in a one-dimensional domain. To describe the impact of cathode microstructure, the insoluble precipitations are assumed to fill into a series of spherical pores with a given pore size distribution, which will be described by a coupled one-dimensional domain.

2.1. Reaction kinetics

A surface reaction model based on the fractions of surface occupied by species and free active sites is exploited. The following
kinetic equations describe the volumetric current sources of ORR ($j_a$) in Eq. (3) and the electrochemical reduction of adsorbed LiO$_2$ to adsorbed Li$_2$O$_2$ ($j_b$) as described in Eq. (5) at a quasi-steady state:

$$j_a = 2A_{\text{eff}}F \sinh(\alpha_2nF/RT)$$

$$j_b = 2A_{\text{eff}}F \sinh(\alpha_1nF/RT)$$

where the exchange current density is $I_a = k_bF\theta_{\text{LiO}_2} \left( \frac{C_{\text{LiO}_2}}{C_{\text{ref LiO}_2}} \right)$ and $I_b = k_bF\theta_{\text{LiO}_2} \left( \frac{C_{\text{LiO}_2}}{C_{\text{ref LiO}_2}} \right)$; $\alpha$ represents the transfer number; and $A_{\text{eff}}$ is the active specific surface area (m$^{-1}$), which will be specifically discussed in Section 2.2. $\theta$ represents the surface fraction occupied by adsorbed oxygen, while $\theta_{\text{LiO}_2}$ represents the surface fraction occupied by adsorbed LiO$_2$. It is assumed that $\eta_a \approx \eta_b = \eta$ and transfer number a equals 0.5 for two reactions [48]. On the other hand, due to the oxygen-involved surface adsorption as described in Eq. (3), we have

$$\theta_{\text{LiO}_2} = k_{\text{LiO}_2} \left[ \frac{C_{\text{LiO}_2}}{C_{\text{ref LiO}_2}} \right]$$

which establishes the relationship between the surface fraction occupied by adsorbed oxygen and free active sites. LiO$_2$ dissolution rate ($r_s$) can be defined as described in Eq. (4). Quasi-steady-state assumption here is employed and the concentration of adsorbed LiO$_2$ is assumed to be consistent within a calculation time step. Therefore, we can obtain:

$$r_s = r_a - r_b = \frac{j_a - j_b}{A_{\text{eff}}F}$$

Moreover, $r_s$ (mol/m$^2$s) is assumed to be proportional with the surface coverage fraction

$$r_s = k_s\theta_{\text{LiO}_2}$$

where $k_s$ is a rate constant of LiO$_2$ dissolution. Furthermore, discharge current sources follow the conservation equation $j = j_a + j_b$, and a dimensionless number $\gamma$ is defined as $\gamma = k_s/k_b$. The surface coverage fractions of ad-oxygen, ad-LiO$_2$, and active site follow the conservation equation $\theta_a + \theta_{\text{LiO}_2} + \theta = 1$ as shown in Fig. 1b. According to the kinetic constants given for reactions, within a time step, there will emerge a specific surface coverage situation, in which reaction rates are in equilibrium and can be assumed as representative. Ultimately, a relationship between local current source and overpotential can be developed:

$$j = 2A_{\text{eff}}Fk_s\theta_{\text{LiO}_2}(\gamma + 1) \left[ \frac{C_{\text{LiO}_2}}{C_{\text{ref LiO}_2}} \right] \sinh(\alpha nF/RT)$$

where $\theta_{\text{LiO}_2}$ and $\gamma$ can be obtained as:

$$\theta_{\text{LiO}_2} = \frac{1}{\gamma \left[ 1 + \left( \frac{C_{\text{LiO}_2}}{C_{\text{ref LiO}_2}} \right) \right] + 1}$$

$$\gamma = \frac{1}{2} \sinh(\alpha nF/RT) \left[ \frac{C_{\text{LiO}_2}}{C_{\text{ref LiO}_2}} \right]$$

Therefore, the reaction kinetic is independent of species’ surface coverage fractions and determined by species concentration along with four rate constants $k_s$, $k_b$, $k_a$, and $k_{\text{LiO}_2}$, which can be estimated by fitting the reported discharge profile [23]. Far above the exchange current as in this case, the overall rate becomes independent of the chemical potential of adsorbed LiO$_2$ [49]. Therefore, the cathode activation overpotential, $\eta$, can be defined as:

$$\eta = \phi_{\text{elode}} - \phi_{\text{elute}} - 2.86$$

where $\phi_{\text{elode}}$ is the electrode potential, $\phi_{\text{elute}}$ is the electrolyte potential and the equilibrium potential of the cathode reaction

$$(\text{Eq. (2)})$$
is experimentally determined as 2.86 V vs Li/Li$^+$ at room temperature [50].

2.2. Cathode structure

In this section, we depict the cathode microstructure evolution induced by the discharge product precipitation. For the porous electrodes with the anisotropic arrangement (e.g. carbon fiber paper), the lateral distribution of species along the electrode surface needs to be considered [51-54]. In the present work, we assume an isotropic electrode property for the nanoporous carbon electrode fabricated from carbon powders, which is commonly used in Li-O$_2$ battery research, and incorporate the pore size distribution to realistically model the electrode microstructure evolution.

To mimic the microstructure evolution, saturation level $s$ is firstly defined and can be expressed as: $s = \frac{V_{\text{LiO}_2}}{V_{\text{ref LiO}_2}}$, in which $V_{\text{LiO}_2}$ is a measure of choked pore volume compared with the initial volume $V_0$ in a local element. In our study, at the given element $x_i$ for instance, the local saturation level $s$ can be obtained as the integration of current density over time as:

$$s(x_i, t) = \int_0^t \frac{\omega_{\text{LiO}_2}}{\rho_{\text{LiO}_2}} \left[ \frac{j_a}{F} + r_s \right] dt$$

where $\omega_{\text{LiO}_2}$ is the molar weight of lithium peroxide and $\rho_{\text{LiO}_2}$ is the density of lithium peroxide. $r_s$ is defined for the chemical disproportion’s impact on saturation, which will be discussed in Section 3.2. Further, the local porosity can be updated as:

$$\varepsilon = (1 - s)\varepsilon_c$$

During discharge, the average film thickness within a local element evolves as the integration of local current density over time as:

$$\delta_{sV} = \frac{\lambda_{\text{LiO}_2}}{A_{\text{eff}}F \rho_{\text{LiO}_2}} \int_0^t \frac{j_a}{F} dt$$

where $\lambda$ represents the probability of electron tunneling, which is involved in the calculation of effective surface area $A_{\text{eff}}$ (Eq. (19)). It can be reasonably assumed that the kinetic rate constants ($k_a$, $k_b$, $k_s$, $k_{\text{LiO}_2}$) are independent of the pore size, implying that the pores with various sizes can have identical film growth rates. Subsequently, we employ the local average film thickness $\delta_{sV}$ in calculating the effective specific surface area [55]:

$$A_{\text{eff}} = \frac{1 - \text{erf}(\delta_{sV} - 7)}{2} \int_0^r \frac{3(r - \delta_{sV})^2}{r^3} \varepsilon_c \text{PSD}(r) dr$$

In the above equations, the decrease of effective specific surface area is attributed to the lowering of probability that electron can transport to the interface and the physical shrinkage of pore size. Despite electron tunneling, another mechanism for charge transport through Li$_2$O$_2$ is the hopping of hole polarons. Both mechanisms might coexist, while at a practical current density as in our case, electron tunneling is suggested to be a predominant factor [22]. Based on the electron tunneling approximation, when the film reaches a certain thickness (10 nm in this case), the film growth terminates [21]. Assuming consistent pore number distribution, the physical shrinkage of specific surface area can be derived from the pore size distribution PSD($r$), where PSD($r$) is the volume percentage of all pores with radius not exceeding $r$ [55].
2.3. Species and charge transport

Corresponding to the reactions that occur within the cathode, mass transport is critical to the discharge performance. Based on the macroscopic approach of the porous electrode, conservation equations of species transport is expressed as:

$$\frac{\partial C_i}{\partial t} = -\nabla N_i + S_i$$ (20)

where subscript $i$ represents $\text{Li}^+$, $\text{O}_2$ or $\text{LiO}_2$ in electrolyte respectively. $C_i$ is the bulk concentration of species $i$ in the electrolyte. $N_i$ is molar flux of species $i$ in the electrolyte, and $S_i$ is the reaction source term of species $i$. According to the Bruggeman correlation, $D_{i,\text{eff}} = \varepsilon_i^{1.5} D_i$. The molar flux and source term of species $i$ can be defined as shown in Table 1.

The distribution of $\text{LiO}_2$ across the cathode is considered as by diffusion only, assuming that $\text{LiO}_2$ can stably exist before $\text{LiO}_2$'s chemical disproportion occurs. The diffusivity of $\text{LiO}_2$ is herein assumed as identical with the diffusivity of soluble oxygen. Within the cathode region, from the separator side to the air inlet (attached with the current collector), the ionic current is gradually transformed into electronic current. For the charge conservation, the sum of the volumetric charge generation rate of ionic electrolyte and solid phase is zero and their absolute values can be determined by the local current source $j$ obtained from kinetic equations in Section 2.1 and the active specific surface area $A_{\text{eff}}$ in Section 2.2:

$$\nabla i_{\text{elode}} = -\nabla i_{\text{lyte}} = A_{\text{eff}}j$$ (21)

Moreover, the electronic potential $\psi_{\text{elode}}$ and electrolyte potential $\psi_{\text{lyte}}$ can be correlated with the current densities by:

$$\dot{i}_{\text{lyte}} = -\kappa_{\text{eff}} \nabla \psi_{\text{lyte}} - \frac{2RT \kappa_{\text{eff}}}{F} (1 - \tau_i) \left(1 + \frac{\partial \ln f}{\partial \ln C_i} \right) \ln C_{\text{Li}^+}$$ (22)

$$\dot{i}_{\text{elode}} = -\sigma_{\text{eff}} \nabla \psi_{\text{elode}}$$ (23)

where $\kappa_{\text{eff}} = \varepsilon_i^{1.5} \kappa_1$, $\sigma_{\text{eff}} = (1 - \varepsilon_i)^{1.5} \sigma$, also following the Bruggeman correlation.

2.4. Boundary conditions

The computational domain includes the anode/separator interface, the separator ($l_{\text{app}} = 30 \mu m$) and the cathode. An electric ground condition is employed at the anode/separator interface (I). At this interface, lithium metal is electro-oxidized to compensate the consumption of lithium-ion and electric migration in the binary electrolyte, which can be expressed as:

$$-\frac{\partial C_{\text{Li}^+}}{\partial x} = (1 + \tau_i) \frac{j_{\text{app}}}{F}$$ (24)

At the cathode/separator interface (II), concentration gradient of oxygen $\nabla C_{\text{O}_2} = 0$, concentration gradient of dissolved lithium superoxide $\nabla C_{\text{LiO}_2} = 0$, $i_{\text{elode}} = 0$ mA/cm$^2$, $i_{\text{lyte}} = i_{\text{app}}$.

Within the cathode region, the ionic current is gradually transformed into electronic current. At the cathode/current collector interface (III), $C_{\text{O}_2} = C_{\text{O}_2, \text{ref}} = 1.86$ mol/m$^3$, which is determined by the oxygen solubility in the aprotic dimethyl sulfoxide electrolyte, and $i_{\text{elode}} = i_{\text{app}}$.

2.5. Numerical details

The conservation equations and the boundary conditions described above are discretized using a finite element method. Each element in the separator and cathode region has a length of 1 $\mu m$, which is microscopically large, enabling the description of microstructure. Also, an extra dimension is coupled with the one-dimensional reaction/transport domain to describe the pore size distribution.

Before discharge, molar concentrations of $\text{Li}^+$ and $\text{O}_2$ are assumed as uniformly distributed to guarantee convergence at the initial time step. In each time step, the cell voltage is calculated as a difference of the electric potentials at boundary I and III and compared with a cut-off voltage of 2.0 V and for each time step a residual value under $10^{-4}$ was reached. Detailed simulation flowchart can be found in Fig. 2. Kinetic constants and diffusion coefficients are estimated from dimethyl sulfoxide based electrolyte and the categorized computational parameters can be found in Table 2.

3. Results and discussion

3.1. Model validation

To validate the reliability of our model, we exploit the experimental conditions, including geometric parameters, specific surface area ($1.98 \times 10^7$ m$^{-1}$) and kinetic rates in dimethyl sulfoxide, to simulate the discharge curve as shown in Fig. 3, which agrees well with the experimental result [23]. For a demonstrative

---

Table 1: Molar flux and reaction source term of species $i$.

<table>
<thead>
<tr>
<th>Species in electrolyte</th>
<th>Molar flux of species $i$</th>
<th>Reaction source term of species $i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Li}^+$</td>
<td>$N_{\text{Li}^+} = -D_{\text{Li}^+} \nabla C_{\text{Li}^+} + \frac{l_{\text{app}}}{F} S_{\text{Li}^+} = \frac{l_{\text{app}}}{F}$</td>
<td></td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>$N_{\text{O}<em>2} = -D</em>{\text{O}<em>2} \nabla C</em>{\text{O}_2}$</td>
<td>$S_{\text{O}_2} = -\frac{F}{RT}$</td>
</tr>
<tr>
<td>$\text{LiO}_2$</td>
<td>$N_{\text{LiO}<em>2} = -D</em>{\text{LiO}<em>2} \nabla C</em>{\text{LiO}_2}$</td>
<td>$S_{\text{LiO}<em>2} = \frac{l</em>{\text{app}}}{F} - r_d$</td>
</tr>
</tbody>
</table>
the complete utilization of the air breathing cathode. In Fig. 4 a,
the first place to ensure that the oxygen transport can guarantee
anode, except in Section 3.4 where we discuss the effects of pore
distribution [55].

Fig. 3. Comparison between the predicted discharge curve with the experimental
result [23], the method to calculate the specific capacity can be found in literature
[55].

Table 2
Computational parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic conductivity</td>
<td>( \kappa )</td>
<td>0.211 S/m</td>
<td>[56]</td>
</tr>
<tr>
<td>Electric conductivity</td>
<td>( \sigma )</td>
<td>100 S/m</td>
<td>[57]</td>
</tr>
<tr>
<td>Diffusion coefficient of ( \text{Li}^+ )</td>
<td>( D_{\text{Li}} )</td>
<td>( 8.0 \times 10^{-11} ) m²/s</td>
<td>[56]</td>
</tr>
<tr>
<td>Diffusion coefficient of ( \text{O}_2 )</td>
<td>( D_{\text{O}_2} )</td>
<td>( 3.7 \times 10^{-9} ) m²/s</td>
<td>[23]</td>
</tr>
<tr>
<td>Transference number of ( \text{Li}^+ )</td>
<td>( \alpha_{\text{Li}} )</td>
<td>0.43</td>
<td>[57]</td>
</tr>
<tr>
<td>Derivative of natural logarithm of ( \text{Li} ) activity to ( \text{Li}^+ ) concentration</td>
<td>( \frac{\partial \text{ln} \alpha_{\text{Li}}}{\partial \text{ln} \alpha_{\text{Li}^+}} )</td>
<td>-1.09</td>
<td>[57]</td>
</tr>
<tr>
<td>Porosity of the separator</td>
<td>( \varepsilon_{\text{sep}} )</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>Porosity of the cathode</td>
<td>( \varepsilon_{\text{c}} )</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>Solubility limit of oxygen</td>
<td>( C_{\text{O}_2, \text{ref}} )</td>
<td>1.86 mol/m³</td>
<td>[23]</td>
</tr>
<tr>
<td>Reference concentration of ( \text{Li}^+ ) ion</td>
<td>( C_{\text{Li}^+, \text{ref}} )</td>
<td>1000 mol/m³</td>
<td></td>
</tr>
<tr>
<td>( \text{Li}_2\text{O}_2 ) mass density</td>
<td>( \rho_{\text{Li}_2\text{O}_2} )</td>
<td>2140 kg/m³</td>
<td>[55]</td>
</tr>
<tr>
<td>Molar weight of ( \text{Li}_2\text{O}_2 )</td>
<td>( \omega_{\text{Li}_2\text{O}_2} )</td>
<td>0.046 kg/mol</td>
<td>[55]</td>
</tr>
</tbody>
</table>

3.2. Species transport in the cathode

In this section, we investigate the effect of cathode thickness in
the first place to ensure that the oxygen transport can guarantee
the complete utilization of the air breathing cathode. In Fig. 4a,
we showed the predicted discharging curves with various cathode
thicknesses (750, 250 and 100 μm) at 1 mA/cm². Indeed, the insuf-
cient supply of oxygen is a realistic issue facing air breathing cathodes [58].
For the cathode with a large thickness of 750 μm, merely 20–30% of capacity can be utilized as shown in Fig. 4b,
which is congruent with its discharge curve compared with the
cathode with a thickness of 100 μm. In general, a decrease in the
cathode thickness can considerably improve the cathode utiliza-
tion by obtaining more uniform distribution of \( \text{Li}_2\text{O}_2 \). In Fig. 4c,
the capacity declines considerably with the increase of the dis-
charge current (from 0.5 to 4 mA/cm²), as the supplied oxygen cannot
ensure the complete cathode utilization at a higher discharge rate. It is worthwhile noting that the discharge capacity at 0.5 mA/cm² is slightly higher than that at 1 mA/cm², as a portion of capacity can be provided by the dissolved \( \text{LiO}_2 \). In addition, the overvoltage at the voltage plateau increases with the logarithm of the
discharge current, indicating that the discharge plateau can
be also limited by the kinetics of electrochemical reactions occur-
ring within the cathode. To further probe into the activation loss of
\( \text{Li}_2\text{O}_2 \) battery, we discuss the effects of the species transport as well as
reaction kinetics in the latter part.

As shown in Fig. 5a and b, we show the \( \text{Li}^+ \) ion and soluble oxy-
gen concentration distribution along the cathode. Due to the abun-
dancy of \( \text{Li}^+ \) ion, from the separator side to air inlet, the decrease of \( \text{Li}^+ \) ion concentration is maintained within 10%. In contrast, from
air inlet to separator side, soluble \( \text{O}_2 \) decreases significantly, as
the \( \text{O}_2 \) solubility and its diffusivity are inherently small. As can be seen in
Fig. 5c, the absolute value of local current source at air inlet is higher than that at separator side until the depth of dis-
charge (DoD) reaches 32%, indicating a higher film growth rate during this period. When DoD increase from 32% to 80%, the local
current source reaches a peak value, which subsequently moves
from the air inlet to the separator side. Corresponding to the local
current source distribution, this message is further confirmed in
Fig. 5d, where it is found that the film thickness at air inlet grows
faster, leading to a faster shrinkage of effective specific surface area. Thus, the most electrochemically active sites will migrate
towards the separator side, as shown in Fig. 5c. In brief, dependent
on the cathode thickness, the sluggish oxygen transport is a valid
limiting step resulting in non-uniform distributions of local current
density and discharge product. When extending similar analysis to
a thicker cathode, it is reasonable to infer that the region near the
separator side suffers from insufficient oxygen supply and the preci-
pitated \( \text{Li}_2\text{O}_2 \) film terminates growth before reaching the limit of
\( \text{Li}_2\text{O}_2 \)’s electronic conductivity.

3.3. Effects of kinetic rate constants

Following the species transport, in this section, effects of kinetic
rate constants \( (k_1, k_2, k_3, k_{\text{ad}}, k_{\text{d}}) \) are considered with ORR rate and
\( \text{Li}_2\text{O}_2 \) dissolution rate being specifically discussed. Here, we firstly show the logarithm of local current source (log(\( j \))-cell potential (\( \varphi \)) relationship at a steady state without the variation of species.

Usually, for sufficiently large deviations from equilibrium, a lin-
ear correlation between the potential and logarithm of current can be
observed for noncatalytic, simple, and single step reduction/oxi-
dation [46]. Shown in Fig. 6a, increase of the rate constant of ORR (\( k_1 \)) promotes the current density at lower overvoltages. As can be estimated, Fig. 6d the rate constant of \( \text{O}_2 \)-involved surface adsorp-
tion reaction (\( k_{\text{ad}} \)) has a similar effect as \( k_1 \) to enhance current den-
sity at lower overpotentials. In contrast, shown in Fig. 6b, increased electrochemical reduction of \( \text{Li}_2\text{O}_2 \) (\( k_3 \)) makes log(\( j \))-\( \varphi \) curve more approach a linear relationship, as the dissolution will be sup-
pressed in this case and the overall reaction is approaching a single
step reaction as 2\( \text{Li}^+ + \text{O}_2 + 2\text{e}^- \rightarrow \text{Li}_2\text{O}_2 \).

Moreover, as shown in Fig. 6c, the promotion of \( \text{Li}_2\text{O}_2 \) dissolution (\( k_3 \)) visibly deviates the log(\( j \))-\( \varphi \) curve from the linear one. With the increase of \( k_3 \) from 10⁻⁸ to 10⁻⁴ mol/m²s, more electronic current will be provided by the formation of \( \text{Li}_2\text{O}_2 \) as 2\( \text{Li}^+ + \text{O}_2 + 2\text{e}^- \rightarrow \text{Li}_2\text{O}_2 \). At a given overpotential, the local current source \( j \) is also increased as \( \text{Li}_2\text{O}_2 \) dissolution allows more free sites for oxygen adsorption [30].

In addition to the kinetic analysis, we incorporate the effects of kinetics in the battery modeling, including ORR and \( \text{Li}_2\text{O}_2 \) dissolu-
tion. In the \( \text{Li}_2\text{O}_2 \) battery research, the kinetic rate constant of
ORR (\( k_1 \)) is of interest to study the electrode surface's catalytic
activity, while the kinetic rate constant for \( \text{Li}_2\text{O}_2 \) dissolution (\( k_3 \))
represents the intensity of solution mechanism in a specific elec-
trolyte. We note that the intensity of solution mechanism should
be determined by the ratio of \( k_3/k_1 \) [30]. Nevertheless, as the me-
chanism of electrochemical reduction (\( k_3 \)) is still unclear, at present
we discuss the effect of \( k_1 \).
When the solution mechanism is promoted, specifically in our case, the rate constant of LiO$_2$ dissolution ($k_s$) increases, the site occupied by ad-LiO$_2$ ($h_{LiO2}$) will be released correspondingly. Therefore, as shown in Fig. 7a, the surface sites for oxygen reduction reaction ($h_{O2}$) can be increased, lowering the activation overpotential for ORR. In addition, higher $k_s$ leads to the decrease of $j_{b0}$, and
thus reduces the surface growth of discharge product (Li2O2) as can be estimated from Eqs. (13) and (14), boosting the discharge capacity. Such simulated results agree with several recent experimental findings. For instance, Choi et al. found that the strong adsorption of lithium superoxide on the catalyst surface can retard ORR; Johnson et al. found that the capacity and voltage plateau of cells are visibly increased with the increase of the electrolyte’s donor number, both of which adequately confirmed the rationality of our modeling [24,59].

Moreover, we note that more soluble O2 will be consumed as shown in Fig. 7b with an increase in the proportion of solution mechanism, suggesting that ORR provides more electronic current than the electrochemical reduction reaction. A lower utilization ratio of O2 will then emerge as a notable issue facing those batteries dominated by the solution mechanism.

As discussed above, promoted LiO2 dissolution can mitigate the surface passivation while improves the ORR kinetics. More specifically, the shrinkage of porosity during discharge is investigated considering the separated surface and solution-phase growths of Li2O2. The effect of chemical disproportion rate (rd), which has an effect on the saturation level of electrode, is considered, where it assumes the chemical disproportion rate is proportional with LiO2 concentration in electrolyte and it does not participate in the ongoing process of film growth. Shown in Fig. 8a, at krd = 10^-6 mol/m^2 s, which is of relatively low LiO2 dissolution rate as analyzed above, the porosity-film thickness curves almost overlap. If krd is further increased to 10^-5 mol/m^2 s, a larger variation can be observed, implying the chemical disproportion rate at this stage has a real impact, as more LiO2 has dissolved into the electrolyte. Shown in Fig. 8b, the porosity at the last stage of discharge decreases to 0.38 from 0.73 if rd = 0.1CLiO2, while for the cell dominated by surface growth only, this value is 0.46. Therefore, the solution-phase growth of Li2O2 enables the cathode to accommodate more discharge product and prolong the capacity corresponding to the discharge profiles in Fig. 7a. Revealing mechanisms to explain the solution-phase growth of Li2O2 along with sensitivity analysis of the mathematical tools are also ongoing in the lab.
To finish this section, the synergetic effect of ORR rate ($k_s$) and Li$_2$O$_2$ dissolution rate ($k_d$) is studied. Shown in Fig. 9, when Li$_2$O$_2$ dissolution is relatively sluggish, an increase in ORR rate can more effectively increase the voltage plateau. It implies that both the promotion of surface and solution mechanisms can boost the discharge voltage plateau, however, in an electrolyte system with a high solvation power, an electrode surface with high catalytic activity might not fully demonstrate its superiority, as the improvements in $\theta_d$ and $k_s$ exist spontaneously. Moreover, high ORR catalytic activity usually implicates an enhanced adsorption for soluble O$_2$ along with reduced oxygen species (LiO$_2$), which should not be desirable for Li$_2$O$_2$ dissolution [59,60].

On the basis of above analysis, we note that Li$_2$O$_2$ can be dissolved into the electrolyte and participate in chemical disproportionation, leading to apparent performance enhancement in the form of higher discharge potential and discharge capacity. Therefore, in addition to the effects of electrode surface’s electrocatalytic activity, the electrolyte’s solvation power should be taken into account in the performance evaluation. As the model offers a comprehensive interpretation of experimental results including the discharge curves and linear scan voltammetry (I-V relationship), in the real battery design, the model can perform a role for investigating the roles of oxygen reduction reaction and discharge intermediate (LiO$_2$) dissolution on the battery’s performance.

### 3.4. Effects of the cathode structure

In addition to the reaction kinetics, the specific surface area of cathode microstructure is imperative for the description of discharge overpotential. Here, we arrive at the discussion of the effect of cathode microstructure. Specifically for the nanoporous carbon electrode fabricated from carbon powders, which is commonly exploited in Li$_2$O$_2$ battery research, we assume an isotropic electrode fabricated from carbon powders, which is commonly exploited in Li$_2$O$_2$ battery research, we assume an isotropic electrode property and incorporate the pore size distribution to realistically mimic the electrode microstructure evolution. Although small pores benefit high surface area for lowering the overpotential, reducing the pore size results in faster specific surface area shrinkage and electrode surface passivation [61]. A critical tradeoff is thus found to exist in designing the air cathode structure for the Li$_2$O$_2$ battery. As discussed in the last section, enhanced solution mechanism performs a role in prolonging the discharge capacity by promoting the solution-phased growth of discharge product, which inevitably affects the cathode microstructure evolution. Therefore, at different Li$_2$O$_2$ dissolution rates the effect of the cathode structure on the battery performance will be specially discussed. Herein, assuming that cathode materials have identical microstructure, the chemical disproportion rate ($r_s$) is studied. Shown in Fig. 9, when Li$_2$O$_2$ dissolution rates exist spontaneously. Moreover, high ORR catalytic activity usually implicates an enhanced adsorption for soluble O$_2$ along with reduced oxygen species (LiO$_2$), which should not be desirable for Li$_2$O$_2$ dissolution [59,60].

On the basis of above analysis, we note that Li$_2$O$_2$ can be dissolved into the electrolyte and participate in chemical disproportionation, leading to apparent performance enhancement in the form of higher discharge potential and discharge capacity. Therefore, in addition to the effects of electrode surface’s electrocatalytic activity, the electrolyte’s solvation power should be taken into account in the performance evaluation. As the model offers a comprehensive interpretation of experimental results including the discharge curves and linear scan voltammetry (I-V relationship), in the real battery design, the model can perform a role for investigating the roles of oxygen reduction reaction and discharge intermediate (LiO$_2$) dissolution on the battery’s performance.

3.4. Effects of the cathode structure

In addition to the reaction kinetics, the specific surface area of cathode microstructure is imperative for the description of discharge overpotential. Here, we arrive at the discussion of the effect of cathode microstructure. Specifically for the nanoporous carbon electrode fabricated from carbon powders, which is commonly exploited in Li$_2$O$_2$ battery research, we assume an isotropic electrode property and incorporate the pore size distribution to realistically mimic the electrode microstructure evolution. Although small pores benefit high surface area for lowering the overpotential, reducing the pore size results in faster specific surface area shrinkage and electrode surface passivation [61]. A critical tradeoff is thus found to exist in designing the air cathode structure for the Li$_2$O$_2$ battery. As discussed in the last section, enhanced solution mechanism performs a role in prolonging the discharge capacity by promoting the solution-phased growth of discharge product, which inevitably affects the cathode microstructure evolution. Therefore, at different Li$_2$O$_2$ dissolution rates the effect of the cathode structure on the battery performance will be specially discussed. Herein, assuming that cathode materials have identical specific void volume (porosity assumed as 0.73 in our study), pore size distribution (PSD) with single peak is investigated. Shown in Fig. 10a, the pore size distribution of the nanoporous electrodes can be mathematically described by a bimodal log-normal distribution function reported in previous literature [55].

Shown in Fig. 10b, at a lower Li$_2$O$_2$ dissolution rate, when the porous cathode is dominated by smaller pores, the battery has a slightly higher discharge voltage plateau due to its larger specific surface area. However, the effective specific surface area shrinks faster and encumbers the increase of the specific capacity. As can be seen in Fig. 10d, for the simulated cathode with smaller pores (mainly below 10 nm), the decrease of surface area does not reach the region of electron tunneling as depicted in Eq. (19), which will induce the rapid drop other than a gradual decrease. Indeed, under this situation, the decrease of available surface area is attributed to the physical shrinkage or pore chocking. Thereby, when the simulated system enables faster Li$_2$O$_2$ dissolution, Li$_2$O$_2$ precipitation will emerge more slowly. Correspondingly, the rapid shrinkage of surface area will be improved.

Shown in Fig. 10c, with $k_s$ increasing from $10^{-6}$ to $10^{-5}$ mol/m$^2$ s, the simulated cathode with smaller pores demonstrates both larger discharge capacity and voltage plateau, even Li$_2$O$_2$ precipitation surface is still available for subsequent reactions. Therefore, it can be reasoned that in an electrolyte system where the solution mechanism is promoted, a high-surface area air cathode should be more desirable. Also, it can be reasoned that closer electrode/Li$_2$O$_2$ contact will be enabled by small pores, resulting in more efficient
Li$_2$O$_2$ decomposition for the charge process [20]. It is worthwhile noting that there is a critical trade-off between specific surface area and tolerance of pore choking, and the solution mechanism performs an essential role in mitigating the pore choking issue. In brief, promoting solution mechanism is highly noted as it benefits the increase of voltage plateau and capacity. Developing aprotic electrolytes that can intensively stabilize the LiO$_2$ has attracted research efforts, which is supposed to be a predominant focus for boosting the performance of Li-O$_2$ batteries [16,62].

Overall, under the rational simplifications, the model shows its feasibility for use in real battery engineering as it captures main features of the Li-O$_2$ battery’s discharge process, such as sluggish oxygen transport, discharge product precipitation in non-uniform microstructure and the discharge intermediate dissolution. With these features, this model might be used to screen excellent combinations of electrodes and electrolytes by efficiently predicting the practical discharge capacities. Moreover, the model can be also exploited for use in modeling the Li-S battery, which also undergoes the dissolution and precipitation processes during discharge [63–66].

4. Conclusions

In summary, a transient one-dimensional model for aprotic lithium-oxygen incorporating the effects of electrode and electrolyte on kinetics is developed considering the multiple-step reactions. In this paper, we discuss the results following the line of species transport, kinetics and electrode structure. To conclude, we have presented that (a) species and current distributions are significantly affected by the oxygen transport limitation and Li$_2$O$_2$ precipitation; (b) promoting discharge intermediate (LiO$_2$) dissolution can decrease the activation overpotential by releasing adsorption sites for ORR and prolong the discharge capacity, though the oxygen utilization can be also lowered; (c) passivation of the high-surface-area air cathode can be efficiently mitigated by dissolving more LiO$_2$ in the electrolyte. Overall, via the numerical method, we reveal the critical role of considering LiO$_2$ dissolution in monitoring the battery’s performance. It can be reasoned that identifying suitable combinations of electrolytes and air cathodes to circumvent capacity limitations will be a critical enabling factor for a practical Li-O$_2$ battery.

Acknowledgment

The work described in this paper was fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. 16213414).

References


Haro M, Vicente N, Garcia-Belmonte G. Oxygen reduction reaction promotes Li desorption from cathode surface in Li–O₂ batteries. Adv Mater Interfaces 2015;2.


