Modeling of lithium–oxygen batteries with the discharge product treated as a discontinuous deposit layer

C.Y. Jung, T.S. Zhao*, L. An

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

HIGHLIGHTS

- A theoretical model for non-aqueous Li-O2 batteries was developed.
- The model eliminates the assumption of the formation of a continuous solid deposit.
- Effect of the current density on the morphology of the discharge product is studied.
- The model enables an accurate prediction of the battery performance.

ABSTRACT

In this paper, a one-dimensional mathematical model for a non-aqueous lithium–oxygen battery is developed. Unlike previous models, in which all the depositions of the discharge product, lithium peroxide (Li2O2), onto carbon surfaces are treated as continuous solid films, the present work models the formation of Li2O2 as a discontinuous deposit layer. Moreover, the effect of discharge current density on the morphology of the Li2O2 deposit is considered. These treatments enable a more realistic simulation of the effect of the discharge product formation on carbon surfaces. The numerical discharging results are found to be in very good agreement with the experimental data at different current densities including 0.05, 0.1 and 0.2 mA cm⁻². The present model is subsequently used to investigate the effect of the design parameters of the cathode (including the electrode thickness, the effective surface area and the cathode utilization) on the discharge performance.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Non-aqueous electrolyte lithium (Li)–oxygen (O2) batteries have garnered increasing attention since they were first reported by Abraham and Jiang, primarily due to its high energy density [1]. The specific capacity of a non-aqueous Li–O2 battery can reach to approximately 1000 mAh g⁻¹ electrode, which is 3 times higher than that of state-of-the-art conventional Li-ion batteries (300 mAh g⁻¹ electrode) [2,3]. As research and development of the Li–O2 battery are still at early stages, investigations have focused on exploring the discharge behavior at the fundamental level.

During discharge, Li metal is oxidized to form Li ions (Li⁺) and electrons, which migrate to the cathode, respectively, through the electrolyte and through the external circuit and react with O2 to form Li2O2. In this oxygen reduction reaction (ORR), lithium superoxide (LiO2) might be generated as an intermediate species in a range of discharging voltages, which will eventually turn into Li2O2 [4–6]. Peng et al. reported the first evidence of LiO2 by combining cyclic voltammetry (CV) and in-situ surface-enhanced Raman spectroscopy of the 0.1 M lithium perchlorate in acetonitrile saturated with O2 [4]. Subsequently, Allen et al. and Yang et al. found the traces of LiO2 followed by the generation of Li2O2 using low-temperature Raman spectroscopy and X-ray diffraction with different non-aqueous electrolytes, e.g., dimethoxyethane (DME) and triethylene glycol dimethyl ether [5,6]. Li2O2 is an electrical insulator and O2 permeation through non-aqueous electrolytes is approximately three times slower than in an aqueous electrolyte [7,8]. As a result, the specific capacity drastically decreases with an increase in the discharge current density [9,10].

A number of mathematical models have been developed in order to gain a better understanding of the discharge behavior in a Li–O2 battery. Sandhu et al. developed a diffusion-limited model for a Li–O2 battery with an organic electrolyte flooded with O2 [11]. However, in their model, the effect of the Li2O2 deposit layer on the performance was neglected, which plays an important role in...
determining the overall discharging curve. Subsequently, Albertus et al. investigated the effect of the lithium carbonate (Li2CO3) deposit layer [12]. They succeeded in predicting the discharging performance, which is mainly dominated by the growth of an electrically-passive deposit layer. Similarly, Sahapatsombut et al. developed a sub-model to investigate the effect of the Li2O2 deposit layer [13,14].

In many of the previous models, a key assumption is that the carbon surface is covered by a continuous solid film of Li2O2, where electrons are conducted to the external surface and trigger an ORR [12–16]. Based on both theoretical and experimental approaches, a solid film of the Li2O2 deposit on carbon surfaces is acceptable when discharge current density is sufficiently high [7,12]. However, at low discharge current densities, the ORR is more preferable in the discontinuous deposit layer before carbon surfaces are completely covered with the Li2O2. Some evidence, e.g., SEM and optical images, indicate that the carbon surface is not completely covered with Li2O2 at typical operating conditions [17–19]. Thus, previous models have difficulties in predicting the performance with varying discharge current densities.

In this work, the effect of the discontinuous Li2O2 deposit layer on the discharge performance is investigated. The effect of discharge current density on the morphology of the Li2O2 deposit on carbon surfaces is explored by introducing an empirical relation. At different discharge current densities, more realistic predictions on the performance are achieved in comparison with experimental data. Furthermore, the proposed model enables an accurate prediction of the optimal thickness of the cathode by evaluating the opposing influences of the deposit layer on the effective surface area and the cathode utilization. With different discharge current densities and cathode thicknesses, the distribution of the Li2O2 volume fraction is examined as an indicator of the cathode utilization level.

2. Mathematical model

As illustrated in Fig. 1, a non-aqueous Li−O2 battery is composed of a Li foil anode, a microporous separator and a carbon cathode in an aprotic organic solvent saturated with lithium salt, in which the geometric dimensions are given in Table 1.

![Fig. 1. A schematic illustration of a Li−O2 battery during discharge. The model domain is marked by red solid-dot lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

During discharge, Li metal is oxidized to form Li ions and electrons, i.e.:

$$\text{Li} \rightarrow \text{Li}^+ + e^- \quad (1)$$

which are transported, respectively, through the electrolyte and through the external circuit to the cathode and react with oxygen to form LiO2:

$$\text{Li}^+ + \text{O}_2 + e^- \rightarrow \text{LiO}_2 \quad (2)$$

As Li2O2 is chemically unstable, it is widely accepted that Li2O2 is generated either by the electrochemical reduction [20]:

$$\text{Li}_2\text{O}_2 + \text{Li}^+ + e^- \rightarrow \text{Li}_2\text{O}_2 \quad (3)$$

or by the chemical disproportionation [21,22]:

$$2\text{Li}_2\text{O}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2 \quad (4)$$

The different paths for the formation of Li2O2, described above, equally involve two equivalent moles of electrons. As the discharge depth increases, the Li2O2 deposit on carbon surfaces may decrease the effective surface area and hinder the transport of Li+ and O2. Thus, in this work, the Li2O2 deposit on carbon surfaces is assumed to be a porous layer to investigate the effect of discharge current density. For simplicity, the following assumptions are made:

1. The non-aqueous electrolyte, i.e., 1 M LiPF6 in a 1:2 mixture of propylene carbonate (PC) and DME is regarded as a binary solution.
2. The Butler−Volmer equation is used to describe the ORR kinetics in which the anodic and cathodic terms depend on molar concentrations of the Li2O2, O2 and Li+ on the carbon surface.
3. To study the discharging behavior, only the formation of Li2O2 is considered, although Li2CO3 may form at the carbon/Li2O2 interface [23].
4. The Li-foil anode is treated as a thin layer.
5. The physical domain is assumed to be isothermal at a current density of less than 0.2 mA cm$^{-2}$ [24].

2.1. Species transport

According to the reaction mechanism of the ORR, the transport of Li+ and solvated O2 is critical to the discharge performance. Based on the macroscopic approach of the porous electrode, the conservation equation of species $i$ can be written as:

$$\frac{\partial(zC_i)}{\partial t} = -\nabla \cdot N_i + S_i \quad (5)$$

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Geometric and operating parameters [9].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters/symbols</td>
<td>Value</td>
</tr>
<tr>
<td>Thickness of the separator/t$_{sep}$</td>
<td>$5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Thickness of the cathode/t$_{c}$</td>
<td>$7.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Electrode area/A</td>
<td>5</td>
</tr>
<tr>
<td>Porosity of the separator/ε$_{sep}$</td>
<td>0.39</td>
</tr>
<tr>
<td>Initial porosity of the cathode/ε$_{c}$</td>
<td>0.73</td>
</tr>
<tr>
<td>Initial specific surface area of the cathode/α$_0$</td>
<td>$3.75 \times 10^6$</td>
</tr>
<tr>
<td>Molar concentration of the lithium ion/C$_{Li^+}$</td>
<td>1000</td>
</tr>
<tr>
<td>Mass loading of the carbon/M</td>
<td>0.2211</td>
</tr>
<tr>
<td>Radius of the carbon black/r$_a$</td>
<td>$2.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Operating temperature/T</td>
<td>298</td>
</tr>
<tr>
<td>Operating pressure/P</td>
<td>1</td>
</tr>
</tbody>
</table>
where the $C_i$ is the bulk concentration of species $i$ in the electrolyte, $\varepsilon$ is the volume fraction of void space that is filled with liquid electrolyte and $S_i$ is the source/sink term of species $i$. The $N_i$ is molar flux of species $i$ in the electrolyte. By neglecting convective transport in a liquid electrolyte, the molar flux of species $i$ can be defined as:

$$N_{Li^{+}} = -D_{Li^{+}} \text{eff} \nabla C_{Li^{+}} + \frac{i_{i,\text{Li^{+}}} t_s}{F}$$ (6)  

$$N_{O_2} = -D_{O_2} \text{eff} \nabla C_{O_2}$$ (7)

where the $D_{Li^{+}} \text{eff}$ and $D_{O_2} \text{eff}$ are the effective diffusivity of $Li^{+}$ and $O_2$, respectively, and can be expressed by the Bruggeman correlation as [25]:

$$D_{Li^{+}} \text{eff} = e^b D_{Li^{+}}$$ (8)  

$$D_{O_2} \text{eff} = e^b D_{O_2}$$ (9)

where the Bruggeman factor, $b$, of 1.5 is widely accepted without further examination for the $Li^{+}$ transport in the non-aqueous electrolytes [11–16]. The $t_s$ and $F$ represent transference number of $Li^{+}$ and $O_2$, respectively. Because the 1 M LiPF$_6$ in 1:2 (v:v) PC:DME mixture solvent is used, the $t_s$ can be estimated as 0.43 if the electrolyte is regarded as a binary solution [10]. Based on the $^7$Li NMR and electrochemical impedance measurements, the diffusion coefficient of $Li^{+}$ is defined as a function of $Li^{+}$ molar concentration [26–28]:

$$D_{Li^{+}} = \frac{kRT}{2zF^2 Li^{+}}$$ (10)

where the ionic conductivity, $\kappa$, can be expressed as:

$$\kappa = 0.314 + 1.744 \cdot \left(1 - e^{-0.00135C_{Li^{+}}^{\frac{1}{3}}}ight)$$ (11)

2.2. Charge transport and electrochemical kinetics

The ionic current density, $i_e$, can be defined as a function of the gradient of ionic potential and transference number as [13,29]:

$$i_e = -\kappa \varepsilon \nabla \phi_e - \frac{2RT \kappa}{F} \left(1 - t_s\right) \left(1 + \frac{\partial \ln f}{\partial \ln C_{Li^{+}}}\right) \nabla \ln C_{Li^{+}}$$ (12)

where the effective ionic conductivity, $\kappa_{\text{eff}}$, is estimated by the Bruggeman correlation [25]:

$$\kappa_{\text{eff}} = e^b \kappa$$ (13)

The electric current density, $i_s$, is solely dominated by electron conduction through the carbon matrix of the cathode, which is expressed as:

$$i_s = -\sigma_{\text{eff}} \nabla \phi_s$$ (14)

$$\sigma_{\text{eff}} = (1 - \varepsilon)^b \sigma$$ (15)

Although the intrinsic electric conductivity of the carbon black (CB) is approximately 400 S m$^{-1}$, the solid matrix of the cathode is typically formed with 10–20 wt.% of PTFE, PVDF or $Li^{+}$-Nafion binder, which causes a decrease in conductivity to as low as 100 S m$^{-1}$ [10].

For the charge conservation, the sum of the volumetric charge-generation rate of the electrolyte and solid phase is zero, which can be expressed as:

$$\nabla \cdot \mathbf{i}_e + \nabla \cdot \mathbf{i}_s = 0$$ (16)

where the transfer current density at electrolyte/electrode interface can be calculated by:

$$\nabla \cdot \mathbf{i}_e = -\nabla \cdot \mathbf{j}_e = a_0(1 - \theta) j$$ (17)

with the specific surface area, $a$, being defined as the area of the carbon surface per unit volume of the cathode.

At the cathode, the Butler–Volmer equation is applied to model the kinetics of ORR [13]:

$$j_c = nF \left(k_a C_{Li_{2}O_2,s} \exp\left(\frac{(1 - \alpha)nF}{RT} \eta_c\right) - k_c C_{Li_{2}O_2,s}^2 C_{O_2,s} \exp\left(-\frac{\alpha nF}{RT} \eta_c\right)\right)$$ (18)

where $F$, $k$, $n$ and $\alpha$ represent the Faraday constant, reaction kinetic constant, number of electrons involved and transfer number, respectively. The cathode overpotential, $\eta_c$, can be defined as:

$$\eta_c = \phi_i - \phi_e - \Phi_{\text{ORR}} - \Delta \phi_{\text{Li_2O_2}}$$ (19)

where $\Delta \phi_{\text{ORR}}$ and $\Delta \phi_{\text{Li_2O_2}}$ are the standard potential of ORR and voltage loss across the $Li_2O_2$ deposit layer.

2.3. Transport through the discontinuous $Li_2O_2$ deposit layer

As the discharge depth increases, $Li_2O_2$ deposits more onto carbon surfaces, causing a reduction in the effective surface area and hindering the $Li^{+}$ and $O_2$ supply. Therefore, the surface coverage of $Li_2O_2$ deposit onto carbon surfaces, $\theta$, i.e., a fraction of the adsorption sites occupied by $Li_2O_2$, plays a key role in determining the overall discharge performance. The $Li_2O_2$ coverage can be calculated by the following empirical equation [13]:

$$\theta = \beta \left(\frac{\epsilon_{Li_{2}O_2}}{\epsilon_{V_0}}\right)^{\gamma}$$ (20)

where the geometric factors, $\beta$ and $\gamma$, represent the effects of the substrate and deposit morphology, respectively. Specifically, $\beta$ explains the influence of partial pressure of the adsorption species, $Li_2O_2$, which is mainly due to the geometrical shape of the substrate [30]. However, if the substrate, namely, CB, is regarded as a complete sphere, $\beta$ is assumed to be 1, which gives [13]:

$$\theta = \left(\frac{\epsilon_{Li_{2}O_2}}{\epsilon_{V_0}}\right)^{\gamma}$$ (21)

Note that for a given $\beta$, Eq. (21) can be used to study the effect of $\gamma$ on the surface coverage of $Li_2O_2$.

Fig. 2 shows the illustration of the formation of the $Li_2O_2$ deposits at low and high discharge current densities. As the discharge current density decreases, a decrease in the $Li_2O_2$ partial pressure leads to fewer nucleation sites, which results in the formation of the island-like deposits on carbon surfaces. Hence, at very low discharge current densities, $\gamma$ has a high value approaching 10 based on the formation of the ideal island-like deposits. Adversely, at very high discharge current densities, $\gamma$ has a low value approaching 0 based on the formation of the ideal plate-like deposits occupying a large number of nucleation sites [31]. Therefore,
\( g \) is defined as inversely proportional to discharge current density, which can be expressed as:

\[
\gamma = \frac{c}{i_{\text{m,app}}}
\]  

(22)

The mass-specific current density, \( i_{\text{m,app}} \), is:

\[
i_{\text{m,app}} = \frac{i_{\text{app}}}{M \cdot c}
\]  

(23)

where \( i_{\text{app}} \) and \( M \) represent the applied current density and mass loading of carbon per unit volume of the cathode, respectively. The empirical constant, \( c \), is mainly affected by materials used for the catalyst and the electrolyte. Due to the lack of the microscopic observations, the empirical constant, \( c \), was obtained to be 1.75 mA g\(^{-1}\) by fitting the experimental discharge data. Therefore, the effect of discharge current density on the geometric factor is investigated by fixing the materials used in the cathode. Here, the \( \text{Li}_2\text{O}_2 \) deposits on carbon surfaces are considered to be uniformly distributed, where the transport through the deposit layer is described as.

For the transport of \( \text{Li}^+ \) and \( \text{O}_2 \) molecules through the deposit layer, the diffusion flux can be estimated by Fick’s law\,[13], where the species molar concentration at the carbon surface can be derived as:

\[
C_{i,\text{int}} = C_i + \frac{t_{\text{Li}_2\text{O}_2} F}{D_{i,\text{Li}_2\text{O}_2} \cdot n F}
\]  

(24)

The thickness of the deposit layer, \( t_{\text{Li}_2\text{O}_2} \), and effective diffusion coefficient of species \( i \), \( D_{i,\text{Li}_2\text{O}_2} \), can be estimated by:

\[
t_{\text{Li}_2\text{O}_2} = \left( \frac{t_{\text{DL}}}{1 - \varepsilon} + 1 \right) r_{\text{cb}}
\]  

(25)

\[
D_{i,\text{Li}_2\text{O}_2} = (1 - \theta)^b D_i
\]  

(26)

The volume fraction of the \( \text{Li}_2\text{O}_2 \) deposit layer, \( \varepsilon_{\text{DL}} \), can be defined as:

\[
\varepsilon_{\text{DL}} = \frac{\varepsilon_{\text{Li}_2\text{O}_2}}{\theta}
\]  

(27)

In addition, the voltage loss through the \( \text{Li}_2\text{O}_2 \) deposit layer can be obtained by\,[32]:

\[
\Delta \phi_{\text{Li}_2\text{O}_2} = \int_c r_{\text{Li}_2\text{O}_2} F \kappa_{\text{eff}} \, dt
\]  

(28)

2.4. Initial and boundary conditions

The initial \( \text{O}_2 \) concentration is calculated based on the \( \text{O}_2 \) solubility in the 1 M \( \text{LiPF}_6/\text{PC-DMEM} \) electrolyte under 1 atm and 25 °C, respectively\,[9]. Specifically, molar concentrations of \( \text{Li}^+ \) and \( \text{O}_2 \) are assumed as uniformly distributed before discharge. In addition, the steady-state solutions of the ionic and electric currents based on the initial \( \text{Li}^+ \) and \( \text{O}_2 \) concentrations were used as the initial profiles to ensure the convergence at the first time step. All the design and operating parameters are given in Table 1, which are identical to experimental conditions reported elsewhere\,[9].

For the numerical analysis of galvanostatic discharging process, the following boundary conditions are used in calculations. At the boundary I (anode/separator interface),

\[
\frac{\partial C_{\text{Li}^+}}{\partial x} = (1 + t_i) \frac{i_{\text{app}}}{F}
\]  

(29)

\[ C_{\text{O}_2} = 0 \text{ mol m}^{-3} \]  

(30)

At the boundary II (separator/cathode interface),

\[
\frac{\partial \phi_i}{\partial x} = 0
\]  

(31)

At the boundary III (cathode/current collector interface),

\[
\frac{\partial C_{\text{Li}^+}}{\partial x} = \frac{\partial C_{\text{O}_2}}{\partial x} = 0
\]  

(32)
C\textsubscript{O}_2 = 3.26 \text{ mol m}^{-3} \quad (32)

\begin{equation}
\frac{\partial \phi_x}{\partial x} = k_{\text{app}} \quad (33)
\end{equation}

\begin{equation}
\frac{\partial \phi_x}{\partial x} = 0 \quad (34)
\end{equation}

### 3. Results and discussion

The model equations for Li\textsuperscript{+}, O\textsubscript{2}, and ionic and electric currents, along with the physico-chemical properties listed in Table 2, are numerically solved using a commercial software, Fluent. The C-based code is developed using the User Defined Function (UDF)\[33] to impose the effect of the discontinuous Li\textsubscript{2}O\textsubscript{2} deposit layer. All the simulations were performed with 40 iterations per 50-s time step to meet the convergence criteria of a residual value of 10\textsuperscript{-3}. In each time step, the cell voltage is calculated as a difference of the electric potentials at boundary I and III and compared with an experimental cut-off voltage of 2.0 V \[9\].

#### 3.1. Model validation

As observed in Fig. 3, the discharging curves predicted by the proposed model, i.e., porous deposit-layer model, are compared with the previous solid deposit-layer model. In the previous model, the voltage loss through a solid-deposit layer is defined as a function of the Li\textsubscript{2}O\textsubscript{2} volume fraction, which is calculated as \[13\]:

\begin{equation}
\Delta \phi_{\text{Li}_2O_2} = \int_{0}^{x} R_\text{film} \Delta \phi_x \text{Li}_2O_2 \quad (35)
\end{equation}

Simulation results are further compared with experimental data at 0.1 mA cm\textsuperscript{-2} and 1.0 mA cm\textsuperscript{-2}, representing low and high discharge current densities, respectively \[9\].

From experimental data, a significant difference between discharge behaviors at low and high current densities can be observed. At 0.1 mA cm\textsuperscript{-2}, the cell voltage generally remained constant, followed by a gradual decrease to the cut-off voltage. However, at 1.0 mA cm\textsuperscript{-2}, the cell voltage linearly decreased until the discharge was abruptly terminated. Hence, the formation of the island-like deposit layer at low current densities may allow maintenance of the voltage plateau until carbon surfaces are saturated with Li\textsubscript{2}O\textsubscript{2}.

For the solid deposit-layer model, the cell voltage linearly decreased with an increase in the discharge depth at 0.1 mA cm\textsuperscript{-2}. Since the solid deposit-layer model is based on the formation of the continuous Li\textsubscript{2}O\textsubscript{2} film with a homogeneous thickness, a linear voltage loss through the Li\textsubscript{2}O\textsubscript{2} deposit layer is obtained with an increase in the discharge depth. However, for the porous deposit-layer model, the cell voltage was nearly constant until the discharge depth reached approximately 600 mAh g\textsuperscript{-1}, followed by a gradual decrease. At 1.0 mA cm\textsuperscript{-2}, the numerical predictions from the solid deposit-layer model and the porous deposit-layer model were similar to each other, indicating that the morphology of the deposit layer may become close to the continuous solid film due to a significant increase in the Li\textsubscript{2}O\textsubscript{2} coverage. Therefore, the porous deposit-layer model provides a more accurate prediction on the discharge behavior, especially at sufficiently low current densities. It should be noted that state-of-the-art non-carbon cathode barely achieved a discharge current density of 1.0 mA cm\textsuperscript{-2} \[34\], while most carbon-based cathodes were operated at discharge current densities below 0.4 mA cm\textsuperscript{-2} \[9,18,21\].

#### 3.2. Effect of discharge current density

Discharge current density is one of the key parameters which can influence the formation of the Li\textsubscript{2}O\textsubscript{2} deposit layer. Fig. 4 shows the predicted discharging curves at different current densities of 0.05, 0.1 and 0.2 mA cm\textsuperscript{-2}. The predicted curves are in excellent agreement with the experimental data obtained by Read \[9\]. Moreover, the proposed model enables the prediction of a decreasing rate of the cell voltage with an increase in the discharge current density. Fig. 5 shows the surface coverage of Li\textsubscript{2}O\textsubscript{2} deposits onto carbon surfaces at different discharge current densities. Here, the Li\textsubscript{2}O\textsubscript{2} coverage drastically increased with an increase in the...
discharge current density, which indicates that an increasing number of nucleation sites induced a transition of the Li$_2$O$_2$ morphology from the island-like shape to the plate-like shape.

To further investigate the effect of discharge current density on the specific capacity, the cathode utilization is evaluated by exploring the volume fraction of Li$_2$O$_2$ at different discharge current densities of 0.05, 0.1 and 0.2 mA cm$^{-2}$. As observed in Fig. 6, the volume fraction of Li$_2$O$_2$ is less homogeneously distributed with increasing the discharge current density at a fixed discharge depth of 40 mAh. Specifically, Li$_2$O$_2$ deposits accumulate near the cathode current collector where the O$_2$ molar concentration is high. At 0.2 mA cm$^{-2}$, the volume fraction of Li$_2$O$_2$ reaches approximately 0.23 at boundary III, which is 23 times higher than that at boundary II due to low O$_2$ transport [35]. As a result, the cell is terminated at lower discharge depth as the discharge current density increases.

### 3.3. Effect of cathode thickness

The cathode thickness plays an important role in determining the effect of Li$_2$O$_2$ deposits on the effective surface area and the cathode utilization, eventually dominating the discharging performance. Mass loading of carbon is decreased with decreasing the cathode thickness, leading to an increase in the discharge current density per unit mass of carbon. Therefore, the surface coverage of Li$_2$O$_2$ deposits onto carbon surfaces can be varied with different cathode thicknesses. Moreover, a degree of the cathode utilization can be significantly affected by the O$_2$ transport resistance, which is proportional to the cathode thickness.

Fig. 7 shows the predicted discharging curves with different cathode thicknesses of 750, 250, 100 and 50 µm at 0.1 mA cm$^{-2}$. Mostly, the specific capacity increases with a decrease in the cathode thickness, although the cell voltage consistently decreased due to a reduction in the effective surface area. Therefore, a decrease in the cathode thickness is strongly related to a trade-off between the mass transport of O$_2$ and the effective surface area.

Here, an optimal cathode thickness is presumed to exist in between 50 µm and 100 µm due to the opposing influences of the Li$_2$O$_2$ deposit layer on the effective surface area and the cathode utilization. As observed in Fig. 8, the Li$_2$O$_2$ coverage increased with reducing the cathode thickness due to an increase in the discharge current density per unit mass of carbon. This suggests that a decreasing rate of the total effective surface area may be even higher than the cathode thickness, which leads to a significant...
cathode utilization. Consequently, it can be concluded that taking into account the formation of the discontinuous deposit layer, with varying morphologies of Li$_2$O$_2$, enables more accurate predictions to be made on the discharge performance with different design parameters of the cathode.

Acknowledgments

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. 622712).

References

D: diffusion coefficient, m² s⁻¹

F: Faraday constant, C mol⁻¹

i: current density, A m⁻²

j: transfer current density, A m⁻²

M: mass loading of carbon, g m⁻³

N: molar flux, mol m⁻² s⁻¹

p: geometric factor

R: gas constant, J mol⁻¹ K⁻¹

R_film: electric resistivity across the solid deposit layer, Ω m²

r: radius, m

Σ: source/sink term, mol m⁻³ s⁻¹ or A m⁻³

T: temperature, K

t: thickness, m

t⁺: transference number of Li⁺

z: charge number of Li⁺

Greek letters

α: transfer number

β: geometric factor of the substrate

c: volume fraction

γ: geometric factor of the deposit

δ: overpotential, V

θ: Li₂O₂ surface coverage

e: ionic conductivity, S m⁻¹

σ: electronic conductivity, S m⁻¹

Φ: potential, V

Subscripts

app: applied

c: cathode

cb: carbon black
e: electrolyte phase
eff: effective
i: species
int: interface
Li₂O₂: lithium peroxide
Li⁺: lithium ion
m: mass specific
O₂: oxygen

s: solid phase

sep: separator

θ: initial