Supporting information

Probing the reaction interface in Li-O₂ battery using electrochemical impedance spectroscopy: dual roles of Li₂O₂

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1 Electrochemical impedance models of Li-O₂ interfaces

(1) Exterior reaction case

The potential difference across the Li₂O₂ thin layer is given by,

\[ \phi_1 - \phi_3 = i_{et}\rho_{Li2O2}d_{Li2O2} \]  

(1)

with \( \rho_{Li2O2} \) being the resistivity of the Li₂O₂ thin layer. Luntz et al.¹ proposed that \( \rho_{Li2O2} \) can be described as,

\[ \rho_{Li2O2} = 4 \times 10^{-8} \sinh\left(\frac{6.5d_{Li2O2}}{1 \text{ nm}}\right) \Omega \text{m} \]  

(2)

In addition, there exists capacitive current across the Li2O2 thin layer,

\[ i_{dL}^{Li2O2} = C_{Li2O2} \frac{d(\phi_1 - \phi_3)}{dt} \]  

(3)

with the thin layer capacitance being,

\[ C_{Li2O2} = \frac{\varepsilon_{Li2O2}\varepsilon_0}{d_{Li2O2}} \]  

(4)

The total current density is given by,

\[ i_{tot} = i_{et} + i_{dL}^{Li2O2} \]  

(5)

At the Li₂O₂/electrolyte interface, the ORR current density is described using the Butler-Volmer equation,

\[ i_{ORR} = -i_0^O \exp\left(-\frac{\alpha_c F}{RT}(\phi_3 - \phi_2^{surf} - U_{ORR})\right) - \exp\left(\left(1 - \alpha_c\right)\frac{F}{RT}(\phi_3 - \phi_2^{surf} - U_{ORR})\right) \]  

(6)

Moreover, the double layer charging current density is written as,

\[ i_{dL} = C_{dL} \frac{d(\phi_3 - \phi_2^{surf})}{dt} \]  

(7)

with \( C_{dL} \) being the double layer capacitance of the Li₂O₂-electrolyte interface.

The total current density is,

\[ i_{tot} = i_{dL} + i_{ORR} \]  

(8)

In the bulk solution, oxygen diffusion is described by combining the continuity equation and the Fick’s law,

\[ \frac{\partial c_{O2}}{\partial t} = D_{O2} \frac{\partial^2 c_{O2}}{\partial x^2} \]  

(9)

with boundary conditions,
\[ D_0 \frac{\partial c_{O_2}}{\partial x} = \frac{i_{\text{ORR}}}{2F}, x = 0 \]  

and,

\[ c_{O_2} = c_{O_2}^{\text{bulk}}, x = l_e \]

with \( l_e \) being the characteristic scale of the bulk solution in the direction of oxygen diffusion.

The transport of lithium ions in the bulk solution is governed by,

\[ \frac{\partial c_{Li^+}}{\partial t} = \nabla \cdot (D_v \nabla c_{Li^+}) + \nabla \cdot \left((1 - t_+) \frac{J_e}{F}\right) \]

\[ J_e = -\sigma_e \nabla \phi_2 - (D_+^{\text{chem}} - D_-^{\text{chem}}) F \nabla c_{Li^+} \]

\[ \nabla \cdot J_e = 0 \]

with the boundary conditions,

\[ J_e = i_{\text{tot}}, x = 0 \]

and,

\[ c_{Li^+} = c_{Li^+}^{\text{bulk}}, \phi_2 = \phi_2^{\text{bulk}}, x = l_e \]

In the measurement of electrochemical impedance, the system is perturbed with a signal with a small amplitude. In this scenario, every system variable can be divided into a steady term, denoted with an over-bar, and a perturbed term, denoted with an over-tilde,

\[ x = \bar{x} + \tilde{x} \]

Consequently, the above controlling equations and boundary conditions can be rephrased in terms of the perturbed term as follows,

\[ \tilde{\phi}_1 - \tilde{\phi}_3 = \tilde{i}_{\text{et}} \rho_{Li2O2} d_{Li2O2} \]

\[ \tilde{i}_{d_{Li2O2}} = j \omega C_{Li2O2} (\tilde{\phi}_1 - \tilde{\phi}_3) \]

\[ \tilde{i}_{\text{tot}} = \tilde{i}_{\text{et}} + \tilde{i}_{d_{Li2O2}} \]

\[ \tilde{i}_{\text{ORR}} = \frac{F}{RT} \tilde{i}_{\text{ORR}}^{\varphi} \left( \phi_3 - \phi_2^{\text{surf}} - \tilde{U}_{\text{ORR}} \right) \]

\[ \tilde{i}_{dt} = j \omega C_{dt} (\tilde{\phi}_3 - \tilde{\phi}_2^{\text{surf}}) \]

\[ \tilde{i}_{\text{tot}} = \tilde{i}_{dt} + \tilde{i}_{\text{ORR}} \]

\[ j \omega \tilde{c}_{O_2} = D_0 \frac{\partial^2 \tilde{c}_{O_2}}{\partial x^2} \]
\[
D_{O_2} \frac{\partial \tilde{c}_{O_2}}{\partial x} = \frac{i_{\text{ORR}}}{2F}, x = 0
\]  
(23)

\[
\tilde{c}_{O_2} = 0, x = l_e
\]  
(24)

\[
j \omega \tilde{c}_{li^+} = D_e \frac{\partial^2 \tilde{c}_{li^+}}{\partial x^2}
\]  
(25)

\[
\nabla \cdot (-\sigma_e \nabla \tilde{\phi}_2 - (D_{+}^{\text{chem}} - D_{-}^{\text{chem}}) F \nabla \tilde{c}_{li^+}) = 0
\]

\[
-\sigma_e \nabla \tilde{\phi}_2 - (D_{+}^{\text{chem}} - D_{-}^{\text{chem}}) F \nabla \tilde{c}_{li^+} = i_{\text{tot}}, x = 0
\]  
(26)

\[
\tilde{c}_{li^+} = 0, \tilde{\phi}_2 = 0, x = l_e
\]  
(27)

The open circuit voltage of the ORR is determined by the Nernst equation,

\[
U_{\text{ORR}} = E_{\text{ORR}}^0 + \frac{RT}{F} \ln \left( \frac{c_{\text{surf}}^{\text{Li}+} c_{O_2}^{\text{surf}}}{c_{li^+}^{\text{surf}} c_{O_2}^{\text{surf}}} \right)
\]  
(28)

As a result, perturbation analysis gives,

\[
\bar{U}_{\text{ORR}} = \frac{RT}{F} \left( \frac{c_{\text{surf}}^{\text{Li}+} c_{O_2}^{\text{surf}}}{c_{li^+}^{\text{surf}} c_{O_2}^{\text{surf}}} \right)
\]  
(29)

Then, Eq.(19) is rephrased as,

\[
i_{\text{ORR}} = \frac{F_i_{\text{ORR}}}{RT} (\phi_3 - \phi_2^{\text{surf}}) - i_{\text{ORR}}^{0} \left( \frac{c_{\text{surf}}^{\text{Li}+} c_{O_2}^{\text{surf}}}{c_{li^+}^{\text{surf}} c_{O_2}^{\text{surf}}} \right)
\]  
(30)

Let us solve for the oxygen diffusion first.
The general solution to Eq.(22) is expressed as,

\[
\tilde{c}_{O_2} = f_1 \sinh (\Omega_{O_2} x) + f_2 \cosh (\Omega_{O_2} x)
\]  
(31)

with

\[
\Omega_{O_2} = \sqrt{\frac{j \omega}{D_{O_2}}}
\]  
(32)

which is the reciprocal of the characteristic length of oxygen diffusion at frequency \( \omega \).

By applying the boundary conditions, we have

\[
\tilde{c}_{O_2} = \frac{i_{\text{ORR}}}{2FD_{O_2} \Omega_{O_2}} \sinh \left( \Omega_{O_2} (x - l_e) \right)
\]  
(33)

As a result,
Then, we solve for $\tilde{c}_\text{Li}^+$ in a similar manner.

$$
\tilde{c}_\text{Li}^+ = -\frac{i_{\text{tot}}}{F(D_+^{\text{chem}} - D_-^{\text{chem}})\Omega_e} \sinh\left(\Omega_e(x - l_e)\right) \cosh(\Omega_e l_e)
$$

with

$$
\Omega_e = \sqrt{\frac{j\omega}{D_e}}
$$

being the reciprocal of the characteristic length of Li$^+$ diffusion at frequency $\omega$.

Consequently,

$$
e_{\text{Li}^+}^{\text{surf}} = \frac{i_{\text{tot}}}{F(D_+^{\text{chem}} - D_-^{\text{chem}})\Omega_e} \tan\left(\Omega_e l_e\right)
$$

The potential distribution is given by,

$$
\tilde{\phi}_2 = -\frac{i_{\text{tot}}}{\sigma_e} \left( -1 \frac{\sinh(\Omega_e(x - l_e))}{\cosh(\Omega_e l_e)} + x - l_e \right)
$$

As a result,

$$
e_{\text{surf}}^{\text{Li}^+} = \frac{i_{\text{tot}}}{\sigma_e} \left( -\frac{\tan(\Omega_e l_e)}{\Omega_e} + l_e \right)
$$

Inserting Eqs.(34),(37) into Eq.(30) leads to,

$$
i_{\text{ORR}} = \frac{FI_{\text{ORR}}}{RT} \left( \tilde{\phi}_3 - \tilde{\phi}_2^{\text{surf}} \right)
- i_{\text{ORR}}^0 \left( \frac{1}{2FD_0\tilde{c}_O_2^{\text{surf}}} \frac{\tan(\Omega_2 l_e)}{\Omega_2} i_{\text{ORR}} \right)
- \left( \frac{1}{F(D_+^{\text{chem}} - D_-^{\text{chem}})\tilde{c}_\text{Li}^+^{\text{surf}}} \frac{\tan(\Omega_e l_e)}{\Omega_e} i_{\text{tot}} \right)
$$

That is,
\[ i_{\text{ORR}} \left( 1 + \frac{i_{\text{ORR}}^0}{2FD_{O_2}c_{O_2}^{\text{surf}}} \frac{\tanh(\Omega_{O_2}l_{O_2})}{\Omega_{O_2}} \right) = \frac{i_{\text{ORR}}^0}{F(D_{+}^{\text{chem}} - D_{-}^{\text{chem}})c_{Li^+}^{\text{surf}}} \frac{\tanh(\Omega_e l_{Li^+})}{\Omega_e} (i_{\text{ORR}}) + j\omega C_{dl}(\phi_3 - \phi_2^{\text{surf}}) + \frac{F_i_{\text{ORR}}^0}{RT} (\phi_3 - \phi_2^{\text{surf}}) \]

As a result, we obtain,

\[ i_{\text{ORR}} = \frac{j\omega C_{dl} i_{\text{ORR}}^0}{F(D_{+}^{\text{chem}} - D_{-}^{\text{chem}})c_{Li^+}^{\text{surf}}} \frac{\tanh(\Omega_e l_{Li^+})}{\Omega_e} + \frac{F_i_{\text{ORR}}^0}{RT} \frac{\phi_3}{\Omega_e} \]

\[ - \phi_2^{\text{surf}} \]

Returning to the current conservation law, we know,

\[ i_{\text{tot}} = i_{\text{ORR}} + j\omega C_{dl}(\phi_3 - \phi_2^{\text{surf}}) \]

Substituting Eq. (42) into Eq. (43) gives,

\[ i_{\text{tot}} = \left( \frac{j\omega C_{dl} i_{\text{ORR}}^0}{F(D_{+}^{\text{chem}} - D_{-}^{\text{chem}})c_{Li^+}^{\text{surf}}} \frac{\tanh(\Omega_e l_{Li^+})}{\Omega_e} + \frac{F_i_{\text{ORR}}^0}{RT} \frac{\phi_3}{\Omega_e} \right) \]

\[ + \frac{i_{\text{ORR}}^0}{2FD_{O_2}c_{O_2}^{\text{surf}}} \frac{\tanh(\Omega_{O_2}l_{O_2})}{\Omega_{O_2}} \frac{F_i_{\text{ORR}}^0}{RT} \frac{\phi_3}{\Omega_e} \]

\[ - \phi_2^{\text{surf}} \]

Finally, the interfacial impedance is given by,
To account for the frequency dispersion phenomena, we generalize Eq. (45) as,

$$Z_{\text{int}}^e = \frac{\ddot{\Phi}_1}{\ddot{t}_{\text{tot}}} = \frac{\ddot{\Phi}_1 - \ddot{\Phi}_2 + \ddot{\Phi}_3 - \ddot{\Phi}_2^{\text{surf}} + \ddot{\Phi}_2^{\text{surf}}}{\ddot{t}_{\text{tot}}}$$

$$= \left( \frac{1}{\rho_{\text{Li}_2O_2} d_{\text{Li}_2O_2}} + \frac{j \omega \varepsilon_{\text{Li}_2O_2} e_0}{d_{\text{Li}_2O_2}} \right)^{-1} + \frac{l_{\text{Li}^+}}{\sigma_e} \left( 1 - \frac{\tanh(\Omega e_{\text{Li}^+})}{\Omega e_{\text{Li}^+}} \right)$$

$$+ \left( \frac{j \omega C_{\text{dt}}}{2 F D_{\text{O}_2} e_0^{\text{surf}}} + \frac{i_0^{\text{O}_2} \tanh(\Omega_{\text{O}_2} l_{\text{O}_2})}{\Omega_{\text{O}_2} l_{\text{O}_2}} \right)^{-1} \frac{F_1^{\text{O}_2}}{RT} + \frac{j \omega C_{\text{dt}}}{2 F D_{\text{O}_2} e_0^{\text{surf}}} + \frac{i_0^{\text{O}_2} \tanh(\Omega e_{\text{Li}^+})}{\Omega e_{\text{Li}^+}}$$

$$+ \left( \frac{1}{\rho_{\text{Li}_2O_2} d_{\text{Li}_2O_2}} \right)^{-1} + \frac{l_{\text{Li}^+}}{\sigma_e} \left( 1 - \frac{\tanh(\Omega e_{\text{Li}^+})}{\Omega e_{\text{Li}^+}} \right)$$

$$+ \frac{i_0^{\text{Li}^+}}{\sigma} \left( 1 - \frac{\tanh(\Omega e_{\text{Li}^+})}{\Omega e_{\text{Li}^+}} \right)$$

By introducing two variables,

$$\lambda_{\text{O}_2} = \frac{i_0^{\text{O}_2} \tanh(\Omega_{\text{O}_2} l_{\text{O}_2})}{\Omega_{\text{O}_2} l_{\text{O}_2}}, \lambda_{\text{Li}^+} = \frac{i_0^{\text{Li}^+} \tanh(\Omega e_{\text{Li}^+})}{\Omega e_{\text{Li}^+}}$$

That reflects the effects of oxygen and Li$^+$ transport on the ORR, we get the following simplified expression,

$$Z_{\text{int}}^e = \left( \frac{1}{\rho_{\text{Li}_2O_2} d_{\text{Li}_2O_2}} + \frac{j \omega \varepsilon_{\text{Li}_2O_2} e_0}{d_{\text{Li}_2O_2}} \right)^{-1} + \left( \frac{\frac{F_1^{\text{O}_2}}{RT}}{1 + \lambda_{\text{O}_2} + \lambda_{\text{Li}^+}} \right)^{-1}$$

To account for the frequency dispersion phenomena, we generalize Eq.(48) as,
\[ Z_{\text{ex}} \mid_{\text{int}} = \left( \frac{1}{\rho_{\text{Li}_2\text{O}_2} d_{\text{Li}_2\text{O}_2}} + \left( j \omega \right)^{n_i} e_{\text{Li}_2\text{O}_2} e_0 \right)^{-1} \]

\[ + \left( \frac{F_i^{0\text{RR}}}{RT} + \left( j \omega \right)^{n_i} C_{\text{dl}} (1 - \lambda_{\text{Li}^+}) \right)^{-1} \]

\[ + \frac{l_{\text{Li}^+}}{\sigma_{\text{e}}} \left( 1 - \tanh \left( \Omega_e l_{\text{Li}^+} \right) \right) \]

with \( 0 < n_{i=1,2} \leq 1 \).

When \( \frac{i_{\text{RR}}^{0}}{i_{\text{Li}^+}^{0}} \ll 1 \) or \( \Omega_{e} l_{\text{Li}^+} \gg 1,\Omega_{o} l_{\text{O}_2} \gg 1 \), which are usually satisfied in experiments, Eq.(49) is further reduced to,

\[ Z_{\text{ex}} \mid_{\text{int}} = \left( \frac{1}{\rho_{\text{Li}_2\text{O}_2} d_{\text{Li}_2\text{O}_2}} + \left( j \omega \right)^{n_i} e_{\text{Li}_2\text{O}_2} e_0 \right)^{-1} + \left( \frac{F_i^{0\text{RR}}}{RT} + \left( j \omega \right)^{n_i} C_{\text{dl}} \right)^{-1} \]

(50)

(2) Interior reaction case

Different from the exterior reaction case, the interior reaction case involves transport of oxygen and lithium-ions across the porous \( \text{Li}_2\text{O}_2 \) thin film. We denote the porosity of the \( \text{Li}_2\text{O}_2 \) thin film as \( \zeta_{\text{Li}_2\text{O}_2} \). The effective oxygen diffusion coefficient is written as,

\[ D_{O_2}^{\text{eff}} = D_{O_2} \zeta_{\text{Li}_2\text{O}_2}^{n} \]

(51)

where the exponential factor \( n \) is usually in the range of \( (1.5, 4) \).

Similarly, the effective lithium-ion diffusion coefficient and conductivity are written as,

\[ D_{e}^{\text{eff}} = D_{e} \zeta_{\text{Li}_2\text{O}_2}^{n} \]

(52)

\[ \sigma_{e}^{\text{eff}} = \sigma_{e} \zeta_{\text{Li}_2\text{O}_2}^{n} \]

(53)

respectively.

It is important to note that the resistance corresponding to the electron transport through the \( \text{Li}_2\text{O}_2 \) thin layer is neglected in the interior reaction case.

According to the electrical circuit analogy in Figure 1(b) in the main text, the interfacial impedance of the interior reaction case is expressed as,

\[ Z_{\text{in}} \mid_{\text{int}} = \left( \frac{F_i^{0\text{RR}}}{RT} + \left( j \omega \right)^{n_i} C_{\text{dl}} (1 - \lambda_{\text{Li}^+}) \right)^{-1} + Z_{d}^{\text{Li}_2\text{O}_2} + Z_{d}^{e} \]

(54)

where \( \lambda_{\text{Li}_2\text{O}_2} \) and \( \lambda_{\text{Li}^+}^{\text{Li}_2\text{O}_2} \) are corresponding to the \( \text{Li}_2\text{O}_2 \) thin layer with effective transport properties, \( Z_{d}^{\text{Li}_2\text{O}_2} \) is the impedance of lithium-ion transport through the \( \text{Li}_2\text{O}_2 \) thin layer,

\[ Z_{d}^{\text{Li}_2\text{O}_2} = \frac{d_{\text{Li}_2\text{O}_2}}{\sigma_{e}^{\text{eff}}} \left( 1 - \frac{\tanh \left( n_{\text{eff}} d_{\text{Li}_2\text{O}_2} \right)}{n_{\text{eff}} d_{\text{Li}_2\text{O}_2}} \right) \]

and \( Z_{d}^{e} \) is the impedance of lithium-ion transport
through the bulk electrolyte phase, \( Z_d^e = \frac{t_{Li^+}}{\sigma_e} \left( 1 - \frac{\tanh(\Omega_e t_{Li^+})}{\Omega_e t_{Li^+}} \right) \).

Eq.(54) accounts for \( Li^+ \) transport through the bulk solution and the \( Li_2O_2 \) thin layer, and oxygen diffusion through the \( Li_2O_2 \) thin layer. However, the effect of oxygen diffusion through the bulk solution is neglected, which is shown to be of minor significance in the exterior reaction case.

(3) Model parameters

Tabel S1. Model parameters for model simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity of ( Li_2O_2 ) film, ( \rho_{Li_2O_2} )</td>
<td>( 4 \times 10^8 \sinh(6.5d_{Li_2O_2}/1\text{ nm}) \text{ } \Omega\text{m} )</td>
<td>1</td>
</tr>
<tr>
<td>Dielectric constant of ( Li_2O_2 ) film, ( \epsilon_{Li_2O_2} )</td>
<td>19</td>
<td>2</td>
</tr>
<tr>
<td>Double layer capacitance of ( Li_2O_2)-electrolyte interface, ( C_{dl} )</td>
<td>( 10-50 \text{ } \mu\text{F} \text{ cm}^{-2} )</td>
<td>3</td>
</tr>
<tr>
<td>Thickness of ( Li_2O_2 ) film, ( d_{Li_2O_2} )</td>
<td>0-10 nm</td>
<td>Variable</td>
</tr>
<tr>
<td>Ionic conductivity of electrolyte, ( \sigma_e )</td>
<td>( 1 \times 10^{-2} \text{ } \text{Sm}^{-1} )</td>
<td>4</td>
</tr>
<tr>
<td>Diffusivity of ( Li^+ ) in electrolyte, ( D_e )</td>
<td>( 1 \times 10^{-6} \text{ } \text{cm}^2\text{s}^{-1} )</td>
<td>5</td>
</tr>
<tr>
<td>Oxygen diffusivity in electrolyte, ( D_{O_2} )</td>
<td>( 1.24 \times 10^{-5} \text{ } \text{cm}^2\text{s}^{-1} )</td>
<td>6</td>
</tr>
<tr>
<td>Exchange current density of ORR, ( i_{ORR}^0 )</td>
<td>( 0.1-1.5 \text{ } \text{nA} \cdot \text{cm}^{-2} )</td>
<td>7</td>
</tr>
<tr>
<td>Characteristic length of bulk electrolyte, ( l_e )</td>
<td>1 mm</td>
<td>Assumed</td>
</tr>
<tr>
<td>Saturated oxygen concentration, ( c_{O_2}^{sat} )</td>
<td>0.135 mM</td>
<td>6</td>
</tr>
<tr>
<td>Li-ion concentration in bulk electrolyte, ( c_{Li^+}^{bulk} )</td>
<td>1 M</td>
<td>Experimental value</td>
</tr>
<tr>
<td>Porosity of ( Li_2O_2 ) film, ( \zeta_{Li_2O_2} )</td>
<td>0.01</td>
<td>Assumed</td>
</tr>
<tr>
<td>Bruggeman factor, ( n )</td>
<td>1.5</td>
<td>Common value</td>
</tr>
</tbody>
</table>

(4) Estimates of coefficients

Figure S 1. Magnitude of coefficients in Eq.(49) based on the parameters given in Table S1.

(5) Impedance of species transport in the \( Li_2O_2 \) layer
2 Experimental details and data analysis

A multiple-neck air-tight glass cell with inlet and outlet valves was used as the cell fixture. The working electrode is made of a planar Au disc with a diameter of 1 mm or a planar glass carbon disc with a diameter of 2 mm. Two Pt electrodes serve as the counter electrode and the reference electrode, respectively.

The electrolyte solvent, DMSO (Sigma-Aldrich, 99.9%), was distilled under vacuum over NaNH2 (Sigma-Aldrich, 98%) and then dried for at least 3 days over freshly activated 4 Å molecular sieve resulting in a final water content of < 10 ppm, as determined by a Mettler-Toledo Karl Fischer titration apparatus. The electrolyte salt, LiClO4 (Sigma-Aldrich, 99.99%), was dried by heating under vacuum at 160°C for 24 h.

The oxygen concentration was saturated. The temperature was controlled using a thermostatic waterbath. Electrochemical impedance spectroscopy was recorded using a VMP3 electrochemical workstation (Biologic).

At the pristine state, EIS measurement was conducted at several temperatures in the range between 30°C and 75°C. The frequency range was \(10^5 – 10^{-2}\) Hz. The amplitude of the stimulus was 20 mV.

Afterwards, the cell was discharged at 500 \(\mu\)A cm\(^{-2}\) (for the GC electrode) and 1000 \(\mu\)A cm\(^{-2}\) (for the Au electrode) to \(-1.5\) V (vs the open-circuit voltage). After galvanostatic discharge, the cell was relaxed for 10 min. Afterwards, EIS data were recorded. It is noted that after the cell is re-discharged to the sudden death after temperature change, so as to compensate the dissolution of Li\(_2\)O\(_2\) during the EIS measurement and temperature adjustment.

EIS data was fitted using the developed physical models in Matlab. The code is available by contacting Jun Huang at jhuangelectrochem@qq.com.

3 Discharge profiles
Figure S 3. Discharge of a glass carbon electrode in 0.1 M LiClO\textsubscript{4} in DMSO to sudden death at 500 \, \textmu{A} \cdot \text{cm}^{-2}. The 1\textsuperscript{st} curve corresponds to the first discharge at 30\textdegree C. After a rest period of 10 min, EIS measurement was conducted. Afterwards, the temperature was adjusted to 40\textdegree C. To compensate the dissolution of Li\textsubscript{2}O\textsubscript{2} during the EIS measurement, the cell was discharged for the 2\textsuperscript{nd} time at 40\textdegree C. This procedure was repeated at other temperatures.

4 Open circuit voltage during relaxation

Figure S 4. Relaxation of an Au electrode in 0.1 M LiClO\textsubscript{4} in DMSO after discharge to sudden death at 1000 \, \textmu{A} \cdot \text{cm}^{-2}. The potential is with respect to the Pt reference electrode.

5 Parameters of the Li\textsubscript{2}O\textsubscript{2} layer
Figure S5. Parameters of the Li$_2$O$_2$ layer formed on a glass carbon electrode in 0.1 M LiClO$_4$ in DMSO. (a) shows the high-frequency part of Figure 3(b) in the main text. (b) shows the relation between ln($R_eT$) and $\frac{1}{T}$. (c) listed the extracted parameters. Note that the film thickness depends on $\delta$, the roughness factor, which is taken to be $\delta = 5$.

The film thickness can be estimated in several ways. Usually, the film thickness can be calculated from the charge corresponding to the formation of Li$_2$O$_2$, that is,

$$d_{Li2O2} = \frac{M_{Li2O2}Q}{2\chi_{Li2O2}E}$$

(55)

with $M_{Li2O2}$ being the molar mass of Li$_2$O$_2$, $Q$ the charge density (Cm$^{-2}$) corresponding to the formation of Li$_2$O$_2$, $\chi_{Li2O2}$ the density of Li$_2$O$_2$. However, this method expressed in Eq.(55) suffers from the ambiguities in $Q$ as it is well known that there are two reaction pathways, namely, the surface-mediated and the solution-mediated pathway, and hence the charge corresponding to the conformal Li$_2$O$_2$ film accounts for only a fraction of the total charge density.

Another approach, which is adopted in this study, is based on the film capacitance, $C_{Li2O2}$, which is given by,

$$d_{Li2O2} = \frac{\epsilon_{Li2O2}\epsilon_0}{C_{Li2O2}}$$

(56)

As listed in Table S1, we use $\epsilon_{Li2O2} = 19$ adopted from Kaiser et al.$^2$ $C_{Li2O2}$ is fitted from the EIS data. If the constant phase element (CPE) is involved, namely, $n_{i=1,2} < 1$ in Eq.(49), $C_{Li2O2}$ is converted from the CPE parameters according to the approach suggested by Hirschorn et al.$^8$ It is important to bear in mind that area-specific $C_{Li2O2}$, Fm$^{-2}$, needs the value of the real active surface area in the electrode, which is challenging to be determined accurately. In this work, we assume a surface roughness factor of $\delta = 5$, 

<table>
<thead>
<tr>
<th>Ionic conductivity at 30°C</th>
<th>Activation energy</th>
<th>Fill thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.1 \times 10^{-9} \text{ S cm}^{-1}$</td>
<td>41.6 kJ mol$^{-1}$</td>
<td>$\sim 20 \text{ nm}$</td>
</tr>
</tbody>
</table>
and we obtain a film thickness of ca. 20 nm at the sudden death.
Note and references


