Rate-dependent morphology of Li_2O_2 growth in Li-O_2 batteries: Supporting Information

Birger Horstmann,[*,†,‡,¶,§] Betar Gallant,[†] Robert Mitchell,[†] Wolfgang G. Bessler,[‖] Yang Shao-Horn,[†] and Martin Z. Bazant[*,†]

Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA, German Aerospace Center, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany, Helmholtz Institute Ulm, Albert-Einstein-Allee 11, 89069 Ulm, Germany, University of Stuttgart, Pfaffenwaldring 6, 70550 Stuttgart, Germany, and Offenburg University of Applied Sciences, Badstraße 24, 77652 Offenburg, Germany

E-mail: birger.horstmann@dlr.de; bazant@mit.edu

1. Numerical details

We numerically integrate the DAE system of Eq. 13 and Eq. 14 in MATLAB employing the DAE-solver *ode15s*. It is an implicit, variable order solver. Periodic boundary conditions are used. Spatial derivatives are calculated with first order central differencing. The spacing of grid points is given by the distance between molecules $d_\perp$. Simulations were performed in systems of length $L = 500$ nm (Figs. 4,5,6a) and $L = 1000$ nm (Fig. 6b).

---

[*]To whom correspondence should be addressed
[†]Massachusetts Institute of Technology
[‡]German Aerospace Center
[¶]Helmholtz Institute Ulm
[§]Stuttgart University
[‖]Offenburg University of Applied Sciences

2. Oxygen reduction reaction

Here, we explain that the global Butler-Volmer rate in Eq. 4 is based on an elementary kinetics description of the rate of the oxygen reduction reaction. For first charge transfer step of the oxygen reduction reaction (ORR) rate limiting, we predict the symmetry factor $\alpha = \frac{1}{4}$. This is in good agreement with the symmetry factor $\alpha = 0.2$ for the ORR measured on glassy carbon. We take into account the activity of dissolved oxygen a_{O_2} and the reaction intermediate a_{LiO_2}. Thus, we demonstrate the dependence of the rate of the ORR on the oxygen concentration here. In the main article, however, we work with constant oxygen pressure and assume $a_{O_2} = 1$. For easy notation, we continue to assume constant activities for lithium ions and electrons, $a_{Li^+} = a_{e^-} = 1$.

The ORR reaction involves two single-electron transfer steps with lithium dioxide as the intermediate species

$$Li^+ + e^- + O_2 \quad \longrightarrow \quad LiO_2 \tag{S1}$$

$$Li^+ + e^- + LiO_2 \quad \longrightarrow \quad Li_2O_2. \tag{S2}$$
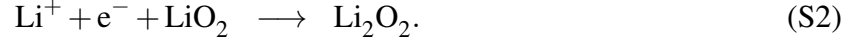
If the first charge transfer step is rate limiting, the second one is in equilibrium. The latter allows us to write

$$k_B T \ln a = -\Delta\Phi + k_B T \ln a_{Li_2O} \tag{S3}$$

or

$$a_{Li_2O} = a e^{-\frac{e\Delta\Phi}{k_B T}}. \tag{S4}$$

The rate limiting charge transfer should determine the overall rate [Bazant, M. Accounts of Chemical Research 2013, 46, 1144],

$$I^1 = A \cdot I_0^1 \left[e^{-\alpha^1 e\eta^1/k_B T} - e^{(1-\alpha^1)e\eta^1/k_B T} \right], \tag{S5}$$

where the superscript 1 denotes the first charge transfer step.

In the following, we will show that the global Butler-Volmer rate (see Eq. 4) used in the article is identical to twice the elementary reaction rate (see Eq. S5), i.e., $I = 2I^1$, if we set

$$\alpha = 0.5\alpha^1. \tag{S6}$$

In our case, we describe the ORR symmetric elementary charge transfers, i.e., $\alpha^1 = \frac{1}{2}$, via a global reaction rate with $\alpha = \frac{1}{4}$. We restate the equilibrium potential (see Eq. 3) taking into account a varying oxygen activity a_{O_2}

$$\Delta\Phi_{eq} = -\frac{k_B T}{2e} \ln\left(\frac{a}{a_{O_2}}\right) \tag{S7}$$

and give the equilibrium potential $\Delta\Phi_{eq}^1$ of the first charge transfer

$$\Delta\Phi_{eq}^1 = -\frac{k_B T}{e} \ln\left(\frac{a_{O_2}}{a_{Li_2O}}\right) - \Delta\Phi$$

$$= 2\Delta\Phi_{eq} - \Delta\Phi \tag{S8}$$

making use of Eq. S4 and Eq. S7 [Bazant, M. Accounts of Chemical Research 2013, 46, 1144]. This allows us to write the overpotential of the first charge transfer step in the simple form

$$\eta^1 = \Delta\Phi - \Delta\Phi_{eq}^1 = 2\eta. \tag{S9}$$

Furthermore, the global exchange current (see Eq. 6) [Bazant, M. Accounts of Chemical Research 2013, 46, 1144]

$$I_0 = \frac{2ek_0 a^\alpha a_{O_2}^{1-\alpha}}{\gamma_\ddagger} \tag{S10}$$

and the one of the first charge transfer step are related by

$$I_0^1 = \frac{ek_0^1 a_{Li_2O}^{\alpha^1} a_{O_2}^{1-\alpha^1}}{\gamma_{\ddagger}}$$

$$= \frac{ek_0 a^{\alpha} a_{O_2}^{1-\alpha}}{\gamma_{\ddagger}} \frac{a^{\alpha}}{a_{O_2}^{\alpha}} e^{2\alpha e \Delta\Phi/k_B T}$$

$$I_0^1 = \frac{1}{2} I_0 e^{\alpha 2 e\eta/k_B T}. \tag{S11}$$

Finally, we insert the overpotential η^1 (see Eq. S9) and the exchange current I_0^1 (see Eq. S11) into the Butler-Volmer rate of the first charge transfer step (see Eq. S5)

$$I^1 = A \cdot I_0^1 \left[e^{-\alpha^1 e\eta^1/k_B T} - e^{(1-\alpha^1)e\eta^1/k_B T} \right]$$

$$= \frac{1}{2} A \cdot I_0 \cdot e^{\alpha 2 e\eta/k_B T} \left[e^{-4\alpha e\eta/k_B T} - e^{(2-4\alpha)e\eta/k_B T} \right]$$

$$= A \cdot I_0 \left[e^{-\alpha 2 e\eta/k_B T} - e^{(1-\alpha)2 e\eta/k_B T} \right]$$

$$I^1 = \frac{1}{2} I, \tag{S12}$$

to yield half of the global Butler-Volmer rate stated in Eq. 4.

Let us finally rewrite the global Butler-Volmer rate in order to make clear its dependence on oxygen activity

$$I = A \frac{2ek_0}{\gamma_{\ddagger}} \left[a_{O_2} e^{-\alpha 2 e\Delta\Phi/k_B T} - a_{O_2} e^{(1-\alpha)2 e\Delta\Phi/k_B T} \right]. \tag{S13}$$

Thus, the pressure of O_2 drives the forward rate and the activity of Li_2O_2 drives the backward rate.

To summarize, we demonstrated that the global Butler-Volmer rate stated in Eq. 4 is an accurate describtion of the ORR. Its derivation takes into account reaction intermediates as well as the oxygen pressure. The latter is encoded in the overpotential η^1 (see Eq. S9) and the exchange current I_0^1 (see Eq. S11). Because transport of molecular oxygen O_2 is fast in the standard electrolytes for $Li-O_2$ batteries and oxygen partial pressure is kept constant during experiments, we do not expect a significant impact of oxygen activity on the electrodeposition of Li_2O_2.

3. Stability analysis

In this section, we provide additional mathematical details on the stability analysis. First, we derive the exponential growth rate for linear instability in Eq. 17. We decompose total surface height $\tilde{h} = \tilde{h}_0 + \delta\tilde{h}_{\tilde{k}}$ into height of the uniform film $\tilde{h}_0$ and of fluctuations $\delta\tilde{h}_{\tilde{k}}$ of wavenumber $\tilde{k}$. Their second derivative is $\frac{\partial^2 \delta\tilde{h}}{\partial\tilde{x}^2} = -\tilde{k}^2 \delta\tilde{h}$. $\delta A = 0$ vanishes because A depends on h through the square of $\frac{\partial h}{\partial x}$ only. In order to determine $\delta(\Delta\tilde{\Phi})_{\tilde{k}}$, we study the effect of fluctuations in surface height on the mean discharge current in Eq. 14

$$
\begin{aligned}
0 &= \delta\tilde{\bar{I}} = \frac{1}{L}\int_0^L \delta\tilde{I}\mathrm{d}x \\
&= -\delta(\Delta\tilde{\Phi})_{\tilde{k}}\left[\alpha e^{-\alpha\Delta\tilde{\Phi}_0} + (1-\alpha)a(\tilde{h}_0)e^{(1-\alpha)\Delta\tilde{\Phi}_0}\right] - \frac{(1-\alpha)a(\tilde{h}_0)e^{(1-\alpha)\Delta\tilde{\Phi}_0}}{L}\int_0^L \delta\tilde{\mu}_{\tilde{k}}\mathrm{d}x,
\end{aligned}
\tag{S14}
$$

where $\Delta\tilde{\Phi}_0$ is the voltage step required for uniform growth, which solves $\tilde{I}(\tilde{h}_0, \tilde{\eta}_0) = \tilde{\bar{I}}$. The integral

$$
\int_0^L \delta\tilde{\mu}_{\tilde{k}}\mathrm{d}x = \left[\frac{\partial\tilde{\mu}}{\partial\tilde{h}} - \tilde{k}^2 \frac{\partial\tilde{\mu}}{\partial\frac{\partial^2\tilde{h}}{\partial\tilde{x}^2}}\right]\int_0^L \delta\tilde{h}_{\tilde{k}}\mathrm{d}x = 0
\tag{S15}
$$

vanishes for all $\tilde{k} > 0$. Therefore, according to Eq. S14, $\delta(\Delta\tilde{\Phi})_{\tilde{k}} = 0$ vanishes, too. We can now calculate the dynamics of the fluctuations $\delta\tilde{h}_{\tilde{k}}$ from Eq. 13

$$
\frac{\partial\delta\tilde{h}_{\tilde{k}}}{\partial\tilde{t}} = -\delta\tilde{h}_{\tilde{k}}a(\tilde{h}_0)e^{(1-\alpha)\Delta\tilde{\Phi}_0}\left[\frac{\partial\tilde{\mu}_{\mathrm{hom}}}{\partial\tilde{h}} - \tilde{k}^2 \frac{\partial\tilde{\mu}}{\partial\frac{\partial^2\tilde{h}}{\partial\tilde{x}^2}}\right].
\tag{S16}
$$

We want to substitute $\tilde{\bar{I}}$ and $\tilde{\eta}_0$ for $a(\tilde{h}_0)$ and $\Delta\tilde{\Phi}_0$. To this aim, we write for the homogeneous base state

$$
\begin{aligned}
\tilde{\bar{I}} &= e^{-\alpha\Delta\tilde{\Phi}_0} - a(\tilde{h}_0)e^{(1-\alpha)\Delta\tilde{\Phi}_0} \\
&= a(\tilde{h}_0)e^{(1-\alpha)\Delta\tilde{\Phi}_0}\left[e^{-\Delta\tilde{\Phi}_0 - \tilde{E}_0 - \tilde{\mu}(\tilde{h}_0)} - 1\right] \\
\tilde{\bar{I}} &= a(\tilde{h}_0)e^{(1-\alpha)\Delta\tilde{\Phi}_0}\left[e^{-\tilde{\eta}_0} - 1\right]
\end{aligned}
\tag{S17}
$$

and rewrite Eq. S16

$$\frac{\partial \delta \tilde{h}_{\tilde{k}}}{\partial \tilde{t}} = \frac{-\tilde{\bar{I}} \delta \tilde{h}_{\tilde{k}}}{\exp(-\tilde{\eta}_0) - 1} \left[\frac{\partial \tilde{\mu}_{\text{hom}}}{\partial \tilde{h}} - \tilde{k}^2 \frac{\partial \tilde{\mu}}{\partial \frac{\partial^2 \tilde{h}}{\partial \tilde{x}^2}} \right]. \tag{S18}$$

The exponential growth rate in Eq. 17 is

$$\tilde{s}(\tilde{k}; \tilde{\bar{I}}) = \frac{\frac{\partial \delta \tilde{h}_{\tilde{k}}}{\partial \tilde{t}}}{\delta \tilde{h}_{\tilde{k}}}. \tag{S19}$$

The marginal stability curve in Fig. 4 is determined by solving $\tilde{s} = \tilde{\bar{I}}$ for $\exp(-\tilde{\eta}_0)$ and substituting into Eq. 4.

In Fig. 4, we determine surface roughness $\Delta[h]$ as normalized standard deviation of $h(x)$ according to

$$\Delta[h] = \sqrt{\frac{1}{L} \int_0^L \frac{\left(h(x) - \bar{h}\right)^2}{\bar{h}^2} \mathrm{d}x} \tag{S20}$$

with the mean height

$$\bar{h} = \frac{1}{L} \int_0^L h(x) \mathrm{d}x. \tag{S21}$$