Supporting information for:

Impact of Li_2O_2 Particle Size on Li-O_2 Battery Charge Process: Insights from a Multi-Scale Modeling Perspective

by

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Table S1: Parameters values implemented in the model

Parameters	Values	Units	Sources
Physical constants			
Gas constant	8.31	$J.K^{-1}.mol^{-1}$	*universal value*
Faraday constant	96485	$C.mol^{-1}$	*universal value*
Boltzmann constant	1.38×10^{-23}	$m^2.kg.s^{-2}.K^{-1}$	*universal value*
Planck constant	6.62×10^{-34}	$m^2.kg.s^{-1}$	*universal value*
Bruggeman coefficient	1.5	/	*universal value*
Cell parameters			
Cathode thickness	4.86×10^{-5}	m	*Ref 1*
Electrode (carbon) specific surface area	7.68×10^{9}	$m^2.m^{-3}$	*adapted from Ref 1*
Carbon volume fraction in the cathode	1.65×10^{-1}	/	*adapted from Ref 1*
Pristine cathode porosity	0.791	/	*adapted from Ref 1*
Separator porosity	0.5	/	*Assumed*
Li^+ initial concentration	1×10^{3}	$mol.m^{-3}$	*Ref 1*
O_2 initial concentration	4.43	$mol.m^{-3}$	*Ref 2*
$LiO_{2(ip)}$ initial concentration	1	$mol.m^{-3}$	*Assumed*
$LiO_{2(s)}$, Li_2O_2 molar volume	1.98×10^{-5}	$m^3.mol^{-1}$	*Ref 3*
Initial volume fraction of $Li_2O_{2(f)}$	0.122	/	*Assumed*
Initial thin-film $Li_2O_{2(f)}$ particles radius (r_f)	7×10^{-9}	m	*Ref 4*
Initial large $Li_2O_{2(p)}$ particles radius (r_p)	75×10^{-9}	m	*adapted from Ref 5*
$LiO_{2(s)}$ monolayer thickness	3×10^{-10}	m	*Assumed*
Li^+ diffusion coefficient	1×10^{-9}	$m^2.s^{-1}$	*Ref 1*
O_2 diffusion coefficient	1.67×10^{-9}	$m^2.s^{-1}$	*Ref 2*
$LiO_{2(ip)}$ diffusion coefficient	1.3×10^{-9}	$m^2.s^{-1}$	*Assumed*
Absolute temperature	298	K	*Defined*
Electrochemical parameters			
Charging rate	1	$A.m^{-2}_{geometric}$	*Ref 1*
Equilibrium potential reaction 1	3.4	V	*Ref 3*
Equilibrium potential reaction 2	2.96	V	*Ref 6*
Equilibrium potential reaction 3	3.1	V	*Ref 2*
Equilibrium potential reaction 5	0	V	*Assumed*
Charge transfer coefficients (α) in reaction 1	0.4	/	*fitted*

Charge transfer coefficients (α) in reaction 2	0.3	/	*fitted*
Charge transfer coefficients (α) in reaction 3	0.5	/	*fitted*
Charge transfer coefficients (α) in reaction 5	0.5	/	*assumed*
Surface tension ($\sigma_{LiO_{2(s)}}$)	10	$J.m^{-2}$	*assumed*
Kinetic parameters			
O_2 mass transfer coefficient	1×10^{-4}	/	*Fitted*
Forward kinetic rate constant reaction 1	1×10^{-11}	$mol.s^{-1}.m^{-2}$	*Fitted*
Forward kinetic rate constant reaction 2	1×10^{-10}	$mol.s^{-1}.m^{-2}$	*Fitted*
Forward kinetic rate constant reaction 3	1×10^{-8}	$mol.s^{-1}.m^{-2}$	*Fitted*
Backward kinetic rate constant reaction 1	1×10^{-3}	$mol.s^{-1}.m^{-2}$	*Calculated*
Backward kinetic rate constant reaction 2	1×10^{-3}	$mol.s^{-1}.m^{-2}$	*Calculated*
Backward kinetic rate constant reaction 3	2.26×10^{-6}	$mol.s^{-1}.m^{-2}$	*Calculated*
Numerical parameters			
Cathode number of bins	10	/	*Defined*
Separator number of bins	5	/	*Defined*

Reference

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Numerical method description

a) Numerical description of the system

To solve numerically the governing equations, spatial and temporal discretizations are needed. The separator and the cathode are represented in one-dimension, and they are divided into several equal sized control volumes or bins. P and Q are the number of bins in the separator and cathode respectively. In the meantime, a sufficiently small time step for discretization leading to a reasonable computational time is required.

b) Mass transport

Transport across the positive electrode of electroactive species solubilized in the electrolyte (Li^+, O_2 and $LiO_{2(ip)}$) is solved using Fick law

$$J_i = -D_{eff} \frac{\partial c_i}{\partial x}$$

[S1]

where D_{eff} is the effective diffusion coefficient and c_i is the concentration of a specie i in the electrolyte. In the porous media, D_{eff} is correlated with the porosity by

$$D_{eff} = D_0 \varepsilon^\beta \qquad \text{[S2]}$$

where ε is the porosity of positive electrode or separator, β is the Bruggeman coefficient and D_0 is the bulk diffusion coefficient. Thus the following equation is derived from the mass balance equation for species i

$$\frac{\partial n_i}{\partial t} = -V \, \nabla J_i + \gamma_i V \qquad \text{[S3]}$$

where V is the electrode volume, n_i is the quantity of the species in moles, γ_i is the source term, standing for the rate of consumption or generation rate of species from chemical or/and electrochemical reaction j,

$$\gamma_i = \sum_j s_{ij} v_j \qquad \text{[S4]}$$

where s_{ij} is the stoichiometric coefficient of the concerned species in reaction j; v_j is the reaction rate for reaction j. For the electrochemical reactions, v_j is obtained with

$$v_j = \frac{A_j i_j^{far}}{V n_e F}$$

[S5]

n_i in equation [S3] is related to the concentration c through

$$n_i = c V_{electrolyte} = c \varepsilon V$$

[S6]

Combining Eq. S1 and S3, the mass balance equation of specie i, can be rewritten as

$$\frac{\partial z_i}{\partial t} = \frac{\partial}{\partial x}\left(\varepsilon^\beta D_0 \frac{\partial c_i}{\partial x}\right) + \gamma_i$$

[S7]

$$z = \varepsilon c \qquad \text{[S8]}$$

where a new variable z is introduced as apparent concentration. The above partial differential equation is solved by using the finite volume method.

At the gas/electrolyte interphase, we adopt as boundary condition the flux of the releasing O_2 in a similar way as in our previously reported models on water electrolyzers [L. F. L. Oliveira *et al.*, Phys. Chem. Chem. Phys., **14** (2012), 10215; L. F. L Oliveira *et al.*, Electrochim. Acta, **110** (2003), 363]

$$\vartheta_{O_2} = K\left(c_{O_2} - H_p P_{O_2}\right) \text{ at } x = P + Q \qquad \text{[S9]}$$

where K is the interface mass transfer coefficient, H_p is the Henry constant and P_{O_2} is the partial pressure of O_2 in gas phase. The fluxes of the other species are zero at this interface.

The boundary condition at the separator/cathode interface ($x = L_{sep}$) assumes continuity of the fluxes of all the species, i.e. we have

$$\vartheta_{i,sep} = \vartheta_{i,cat} \text{ at } x = P \qquad \text{[S10]}$$

As for the anode/separator interface ($x = 0$), only the flux of $Li_{(l)}^+$ is considered to be non-zero, given by

$$\vartheta_{Li^+} = -\frac{i_5^{Far}}{F} \quad \text{at} \quad x = 0 \qquad \text{[S11]}$$

where i_5^{Far} is the current density of the $Li_{(l)}^+$ reduction reaction at the anode (Eq. S5). According to the adopted convention, the sign of the current flux in Eq. S11 is negative, since the flux of electron enters the anode during reduction.

c) Porosity and particle size evolution

During the recharge process, the continuous oxidation of Li_2O_2 leads to the evolution of their particle sizes as well as the electrode porosity. Together with the molar volume (ω) of Li_2O_2 and LiO_2, the volume change of particles in the ith bin can be obtained from

$$\frac{\partial V_{p,i}}{\partial t} = \frac{\omega_{Li_2O_2}}{N_{p,i}V_i}\frac{\partial n_{Li_2O_2(p),i}}{\partial t} + \frac{\omega_{LiO_2(s)}}{N_{p,i}V_i}\frac{\partial n_{LiO_2(s),i}}{\partial t} \qquad \text{[S12]}$$

$$\frac{\partial V_{f,i}}{\partial t} = \frac{\omega_{Li_2O_2}}{N_{f,i}V_i}\frac{\partial n_{Li_2O_2(f),i}}{\partial t} \qquad \text{[S13]}$$

where the consumption rate ($\frac{\partial n}{\partial t}$) is calculated from Eq. S3 by neglecting the diffusive term since the solid species are immobile and V_i is the volume of the ith bin. Therefore, the porosity change in the ith bin can be calculated from

$$\frac{\partial \varepsilon_i}{\partial t} = -(N_{p,i}\frac{\partial V_{p,i}}{\partial t} + N_{f,i}\frac{\partial V_{f,i}}{\partial t})$$

[S14]

Chart S1: Model flow chart