ARTICLE TYPE

Advanced model framework for solid electrolyte intercalation batteries

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A Supporting Information

A.1 Functional derivative of $G[c_2]$

The Gibbs energy G is implicitly time- and space-dependent, *i.e.* $G[c_2(\vec{r}_2, t)]$. Therefore, we have to use a functional derivative instead of a classical partial derivative to compute the derivative of $G[c_2(\vec{r}_2, t)]$ with respect to $c_2(\vec{r}_2, t)$.

The functional derivative $\frac{\delta F[\rho(r)]}{\delta \rho(r)}$ is defined such that for all test functions $\psi(r)$

$$< \frac{\delta F[\rho(r)]}{\delta \rho(r)}, \psi(r) >= \frac{d}{d\varepsilon} F[\rho(r) + \varepsilon \psi(r)] \bigg|_{\varepsilon=0}.$$
 (1)

For the Gibbs energy formulation (equation (8) of the paper)

$$G[c_2(\vec{r_2})] = \int_{V_2} \mu_{\rm F} \cdot c_2 + RTc_2 \ln c_2 + \mu_{\rm E} \cdot (1 - c_2) + RT \cdot (1 - c_2) \ln(1 - c_2) + \alpha \cdot c_2(1 - c_2) + \nu_2 F(c_2 - c_{\rm A}) \cdot \Phi dV$$
(2)

the derivative with respect to the ion concentration is

$$<\frac{\delta G[c_{2}(\vec{r}_{2})]}{\delta c_{2}(\vec{r}_{2})}, \psi(\vec{r}_{2}) > = \frac{d}{d\varepsilon} \int_{V_{2}} \mu_{\rm F} \cdot (c_{2} + \varepsilon\psi) + RT(c_{2} + \varepsilon\psi) \ln(c_{2} + \varepsilon\psi) + \mu_{\rm E} \cdot (1 - (c_{2} + \varepsilon\psi)) + RT \cdot (1 - (c_{2} + \varepsilon\psi)) \ln(1 - (c_{2} + \varepsilon\psi)) + \alpha \cdot (c_{2} + \varepsilon\psi)(1 - (c_{2} + \varepsilon\psi)) + \nu_{2}F((c_{2} + \varepsilon\psi) - c_{\rm A}) \cdot \Phi dV \Big|_{\varepsilon=0}$$

$$(3)$$

$$= \int_{V_2} \mu_{\rm F} \cdot \psi + \psi RT \ln(c_2 + \varepsilon \psi) + RT(c_2 + \varepsilon \psi) \frac{\psi}{(c_2 + \varepsilon \psi)} - \mu_{\rm E} \cdot \psi - \psi RT \cdot \ln(1 - (c_2 + \varepsilon \psi))$$
⁽⁴⁾

$$-RT \cdot (1 - (c_2 + \varepsilon\psi)) \frac{\psi}{(1 - (c_2 + \varepsilon\psi))} + \alpha \cdot \psi(1 - 2(c_2 + \varepsilon\psi)) + \nu_2 F\psi \cdot \Phi dV \Big|_{\varepsilon=0}$$

$$= \int_{V_2} \mu_{\rm F} \cdot \psi + \psi RT \ln c_2 - \mu_{\rm E} \cdot \psi - \psi RT \cdot \ln(1 - c_2) + \alpha \cdot \psi(1 - 2c_2) + \nu_2 F \psi \cdot \Phi dV$$
(5)

$$= \int_{V_2} \left(\mu_{\rm F} + RT \ln c_2 - \mu_{\rm E} - RT \cdot \ln(1 - c_2) + \alpha \cdot (1 - 2c_2) + \nu_2 F \cdot \Phi \right) \cdot \psi \, dV \tag{6}$$

$$= < \underbrace{\mu_{\rm F} + RT \ln c_2 - \mu_{\rm E} - RT \cdot \ln(1 - c_2) + \alpha \cdot (1 - 2c_2) + \nu_2 F \cdot \Phi}_{=\frac{\delta G[c_2(\vec{r}_2)]}{\delta c_2(\vec{r}_2)}}, \psi(\vec{r}_2) >$$
(7)

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Thus the chemical potential is

$$\Rightarrow \mu_2 = \mu_{\rm F} + RT \ln c_2 - \mu_{\rm E} - RT \cdot \ln(1 - c_2) + \alpha \cdot (1 - 2c_2) + \nu_2 F \cdot \Phi, \tag{8}$$

which is used in equation (10) of the paper to derive the flux for ions in a solid electrolyte.

A.2 Non-dimensional System of Equations

For the purpose of numerical simulations and model analysis it is convenient to introduce nondimensional variables. Further, we assume that our battery model is isotropic in y and z direction. This reduces the model to a 1-dimensional system and the diffusion tensor \mathbf{D}_i to a scalar D_i . The non-dimensional variables are

$$\varphi = \frac{F}{RT}\Phi, \ \tau = \frac{1}{t_{\rm S}} \cdot t \in [0, 1] \text{ and } \xi_i = \frac{x_i}{L_i} \in [0, 1],$$

with the overall simulation time $t_{\rm S}$. Unless noted otherwise, all calculations were performed with the following setting of parameters:

$$\begin{array}{ll} L_1 = 100 \, \mathrm{nm} & C_{\mathrm{I}} = 80 \, \mu \mathrm{F cm}^{-2} & T = 298 \, \mathrm{K} & \Delta G_{\mathrm{f},\mathrm{A}}^{\ddagger} = 1.15 \, \mathrm{eV} & \Delta G_{\mathrm{f},\mathrm{C}}^{\ddagger} = 1.15 \, \mathrm{eV} \\ L_2 = 100 \, \mathrm{nm} & \Phi_{\mathrm{A}} = 2 \, \mathrm{V} & \varepsilon_{\mathrm{E}} = 50 & \Delta G_{\mathrm{b},\mathrm{A}}^{\ddagger} = 3 \, \mathrm{eV} & \Delta G_{\mathrm{b},\mathrm{C}}^{\ddagger} = 3 \, \mathrm{eV} \\ L_3 = 100 \, \mathrm{nm} & \Phi_{\mathrm{C}} = -2 \, \mathrm{V} & \varepsilon_{\mathrm{I}} = 10 & \beta = 0.5 \end{array}$$

Note that we still use ∇ as derivative operator, which for the 1-D case is $\nabla = \frac{\partial}{\partial \xi_i}$. This leads to the non-dimensional system of equations:

Anode

$$\frac{L_1^2}{D_1 t_{\rm S}} \frac{\partial c_1(\xi_1, \tau)}{\partial \tau} = \nabla \cdot (\nabla c_1(\xi_1, \tau)) \tag{9}$$

Solid Electrolyte

$$\frac{L_2^2}{D_2 t_{\rm S}} \frac{\partial c_2(\xi_2, \tau)}{\partial \tau} = \nabla \cdot \left(\left(\frac{1}{1 - c_2} - \frac{2\alpha}{RT} c_2 \right) \nabla c_2 + c_2(\xi_2, \tau) \nabla \varphi(\xi_2, \tau) \right)$$
(10)

$$\nabla^2 \varphi(\xi_2, \tau) = \frac{L_2^2 F^2 \nu_2}{\varepsilon_0 \varepsilon_{\rm E} R T} (c_2(\xi_2, \tau) - c_{\rm A}) \tag{11}$$

Cathode

$$\frac{L_3^2}{D_3 t_{\rm S}} \frac{\partial c_3(\xi_3, \tau)}{\partial \tau} = \nabla \cdot (\nabla c_3(\xi_3, \tau)) \tag{12}$$

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A.3 Comparison between classical PNP and the newly derived Equations

A comparison of the spatial ion and potential distribution between the classical PNP System (equation (18) of the paper) and the more rigorous formulation presented in this work (equation (14) of the paper) is given in Figure 1.



Fig. 1 Comparison of the classical PNP system and the modified PNP system.

The simulation of the classical equations (Figure 1(a)) shows a mole fraction of cations greater than 1 near the electrode surface, which is caused by the vast amount of mobile ions. The classical equations describe ion hopping as randomly allowed Poisson processes, and blocked sites are not considered. Hence, the probability of a jump between adjacent sites is just proportional to the energy barrier between the two sites and the thermal oscillation. However, in the case of the electrode/electrolyte interface, in which an electrostatic potential forces ions to be collected or reduced near the surface, this simplification might not be valid anymore.

The jump probability is also dependent on the probability that an adjacent site is empty. Since solid electrolytes are rather concentrated solutions, the amount of mobile ions (n_2) with respect to the amount of sites $(\tilde{n}_2 + \tilde{m}_2 = \nu_2)$ is large compared to classical dilute liquid electrolyte systems. In this case, the probability of an empty site must be taken into account explicitly.¹

In the case of a Nernst–Planck flux, this effect is not incorporated, which leads to the overestimation of ion concentration near the surface.

The derived generalization of the PNP system accounts for the finite amount of vacancies, resulting in a realistic behaviour of the ion concentration in the space charge region.

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¹ B. Horrocks and R. Armstrong, J. Phys. Chem. B, 1999, 103, 11332–11338.