Experimental and Theoretical Characterization of Electrode Materials that Undergo Large Volume Changes and Application to the Lithium-Silicon System

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Interfacial boundary conditions. Differentiating the right-hand side of Eq. 15 with respect to time produces

$$\frac{\partial}{\partial t} \int_0^{L(t)} c(t, z) dz = -\frac{i(t)}{F}$$

for all times t . The left side of Eq. 15 depends on both time t and $L(t)$. Differentiating the integral can be done by means of the chain rule and the fundamental theorem of calculus:

$$\frac{\partial}{\partial t} \int_0^{L(t)} c(t, z) dz = \frac{dL}{dt} c(t, L(t)) + \int_0^{L(t)} \frac{\partial}{\partial t} c(t, z) dz$$

Using Eq. 10 in the second term on the right along with the boundary condition 13, we obtain a boundary condition to be applied at the electrode-electrolyte interface $z = L(t)$:

$$\begin{aligned} \frac{dL}{dt} c(t, L(t)) - \int_0^{L(t)} \frac{\partial N}{\partial z} dz &= \frac{dL}{dt} c(t, L(t)) - (N(L(t)) - N(0)) \\ &= \frac{dL}{dt} c(t, L(t)) - N(L(t)) = -\frac{i(t)}{F} \quad \text{or} \quad xc_T \frac{dL}{dt} - N = -\frac{i}{F} \end{aligned}$$

A similar treatment of Eq. 16 can be applied to produce

$$(1-x)c_T \frac{dL}{dt} - N_H = \frac{i}{F}$$

Thus, at the surface, we have the two independent equations. When the two equations are summed,

$$c_T \frac{dL}{dt} - (N + N_H) = 0$$

Upon re-arrangement of the above two equations and subtraction to eliminate dL/dt , we obtain

$$(1-x)N - xN_H = \frac{i}{F}$$

Dynamic equilibrium. We investigate the slow-scan, equilibrium condition in this Appendix, characterized by $V = U$ for all times during the potential scan. Current is related to the flow of charge Q :

$$i = \frac{1}{A} \frac{\partial Q}{\partial t} \quad \text{or} \quad i = \frac{1}{A} \frac{\partial Q}{\partial x} \frac{\partial x}{\partial U} \frac{\partial U}{\partial t} = \frac{1}{A} \frac{\partial Q}{\partial x} \frac{\partial x}{\partial U} v$$

where A is the electrode geometric area and v is the potential scan rate. The linear-sweep voltammetry experiments begin with no Li in Si, $x = 0$. Under equilibrium conditions, the charge Q in the electrode is related to x by

$$Q = AL_0(c_{Si,x=0})x\xi F = AL_0c_{T,0}xF \quad \text{and} \quad \frac{\partial Q}{\partial x} = AL_0(c_{Si,x=0})\xi F = AL_0c_{T,0}F$$

Combining these two equations, we find

$$i = L_0(c_{Si,x=0})\xi F v \frac{\partial x}{\partial U} = L_0 \left(\frac{\rho_{Si,x=0}}{MW_{Si}} \right) \xi F v \frac{\partial x}{\partial U} = L_0c_{T,0}F v \frac{\partial x}{\partial U}$$

$$\tilde{i} = \frac{L_0}{D_0c_{T,0}} \frac{1}{F} i = \frac{L_0}{D_0c_{T,0}} \frac{1}{F} L_0c_{T,0}F v \frac{\partial x}{\partial U} = v \frac{L_0^2}{D_0} \frac{\partial x}{\partial U}$$

A similar procedure can be used to represent dynamic equilibrium under de-lithiation.