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Field-Limited Migration of Li-Ions in Li-Ion Battery

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The migration of Li-ions in lithium-ion battery cannot be simply described by Fick's second law; the interactions among ionic migration, field, and stress need to be taken into account when analyzing the migration of Li-ions. Using the theory of thermal activation process, the flux for ionic migration under concurrent action of electric field and mechanical stress is found to be a nonlinear function of the gradient of electric potential and the gradient of stress. Electric field can either accelerate or retard the growth of the lithiation layer, depending on polarity of the field.

Si-based materials have attracted great interest for possible use as anode materials due to high specific capacity of Si (3580 mAh/g).[1] However, the specific volume change of Si during electrochemical cycling can reach to ~400%,[2] which can lead to catastrophic failure of lithium-ion battery (LIB). Low-dimensional Si-structures have been studied in rechargeable LIBs[3–7] to improve the cyclic performance and structural durability of Si-based anodes. The results from the studies[3–7] have demonstrated that low-dimensional Si-structures have the potential to offer high reversible capacity and long service life.

Ariel et al.[8] observed that the ability to store and deliver charge for electrochemical cells consisting of LiCoO$_2$(cathode)/SiO$_2$/Si(anode) was inversely proportional to current density. Zhou et al.[9] suggested that the driving force for Li-migration was the gradient of electric potential and the concentration gradient of Li ions. Recently, Liu et al.[10] noted that electric field accelerated the migration of the reaction front during the lithiation of Si nanowires. They pointed out that the quantitative information about the effects of electrical field on both Li diffusion and interface reaction was not available at the moment of their study.[10]

The theory of thermal activation process[11] has been applied to study diffusion in solids.[12] The purpose of this work is to analyze electromechanical effect on the lithium migration, using the theory of thermal activation process. We consider the lithium migration under concurrent action of electric field and mechanical stress as a thermal activation process and derive an expression for the flux of ions.

Physical Model

Consider a system, which consists of an electric anode, an alloy layer, and electrolyte, as shown in Fig. 1. The alloy layer is bounded by an anode-alloy interface and an alloy-electrolyte interface, as demonstrated by Liu et al.[10] for the lithiation of Si nanowires. Due to the large diffusivity of Li-ions, it is believed that the migration of Li-ions through the alloy layer and the reaction of Li-ions with the atoms of active materials to form Li-compound at the anode-alloy interface determine the growth of the alloy layer.

According to the theory of thermal activation process,[11] the probability of an ion moving from a stable state to another stable state is determined by the vibration frequency and the energetic fraction of ions which depends on the energy barrier, Q, between the two states. The net flux of ions in one dimension, j, can be expressed as

$$j = j_f - j_b = a n_f \nu_0 e^{-Q_f/kT} - a n_b \nu_0 e^{-Q_b/kT} \qquad [1]$$

where j_f is the forward flux, j_b is the backward flux, a is the distance between two stable states, ν_0 is the pre-factor, n is the concentration of ions, k is the Boltzmann constant, T is absolute temperature, and the subscripts of f and b represent the forward and backward, respectively.

The first-order Taylor series approximation of n gives

$$n \equiv n_f \approx n_b - a\frac{dn}{dx} \qquad [2]$$

For the migration of an ion of charge q in an electric field and a stress field from the site of $x_0 - a/2$ to the site of $x_0 + a/2$, the energy change to the first-order Taylor series approximation is $-qa(d\phi/dx) + \Omega a(d\sigma/dx)$ (<0). Thus, the energy barrier for the forward migration is

$$Q_f = Q|_{x=x_0-a/2} = Q_0 + q\phi + q\frac{a}{2}\frac{d\phi}{dx} + \sigma\Omega - \Omega\frac{a}{2}\frac{d\sigma}{dx} \qquad [3]$$

and the energy barrier for the backward migration is

$$Q_b = Q|_{x=x_0+a/2} = Q_0 + q\phi - q\frac{a}{2}\frac{d\phi}{dx} + \sigma\Omega + \Omega\frac{a}{2}\frac{d\sigma}{dx} \qquad [4]$$

Here, Q_0 is the energy barrier with $\phi = 0$ and $\sigma = 0$, ϕ is electric potential, σ is stress, and Ω is the ionic volume. Substituting Eqs. 2–4 into Eq. 1 yields

$$j = 2an\nu_0 e^{-(Q_0+q\phi+\sigma\Omega)/kT} \sinh\frac{a}{2kT}\left(\Omega\frac{d\sigma}{dx} - q\frac{d\phi}{dx}\right)$$
$$- a^2\nu_0\frac{dn}{dx}e^{-(Q_0+q\phi-q\frac{a}{2}\frac{d\phi}{dx}+\sigma\Omega+\Omega\frac{a}{2}\frac{d\sigma}{dx})/kT} \qquad [5]$$

The net flux is a nonlinear function of the electric field intensity and the stress gradient. Equation 5 reveals the dependence of the effective diffusivity of ions on stress and electric field. Both the electric field and the stress field can alter the apparent activation energy of the ion migration in LIBs. The result also suggests that the stress gradient and the field play an important role in the alloy formation during electrochemical cycling. Note that Shenoy et al.[13] and Yang[14] had discussed the effect of the solute concentration on Young's modulus. Due to the effect of stress on the diffusion of ions and the effect of the solute concentration on mechanical properties, there exists the coupling between stress and diffusion.

For high electric field, $|d\phi/dx| \gg 0$, the contribution of the backward migration to the flux is negligible, and the ion migration is driven by electric field. In general, $q \sim e = 1.6 \times 10^{-19}$ C, $\Omega \sim 15.6$ Å^3 for Li ions, and $a = 3.49$ Å for Li. One has
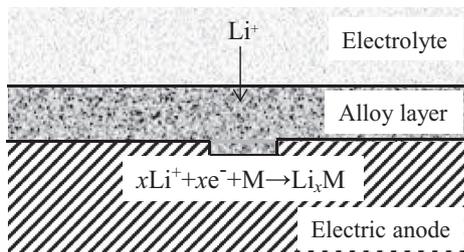
$$\sinh\frac{a}{2kT}\left(\Omega\frac{d\sigma}{dx} - q\frac{d\phi}{dx}\right) \approx \frac{a}{2kT}\left(\Omega\frac{d\sigma}{dx} - q\frac{d\phi}{dx}\right) \qquad [6]$$

which has less than 5% in difference for $|d\sigma/dx| < 421$ MPa/nm and $|d\phi/dx| < 41$ V/μm at 298 K with $a|qd\phi/dx - \Omega d\sigma/dx|/2kT$ $\leq a(|qd\phi/dx| + \Omega|d\sigma/dx|)/2kT < 0.557$. Using $Q_0 = 0.70$ eV for Li diffusion in a-silicon,[15] one has

$$e^{-(Q_0+q\phi-q\frac{a}{2}\frac{d\phi}{dx}+\sigma\Omega+\Omega\frac{a}{2}\frac{d\sigma}{dx})/kT} \approx e^{-Q_0/kT} \qquad [7]$$

which has less than 5% in difference for $|d\sigma/dx| < 421$ MPa/nm, $|d\phi/dx| < 41$ V/μm, $|\phi| < 0.36$ V, and $|\sigma| < 3.66 \times 10^9$ GPa with

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Figure 1. Schematic of the lithiation process with the reaction front moving into electric anode.

$|q\phi + \sigma\Omega|/Q_0 \leq (|q\phi| + |\sigma\Omega|)/Q_0 < 0.051$. Under these conditions, Eq. 5 is approximated as

$$j = \frac{a^2 n \nu_0}{kT} e^{-Q_0/kT}\left(\Omega\frac{d\sigma}{dx} - q\frac{d\phi}{dx}\right) - a^2\nu_0\frac{dn}{dx}e^{-Q_0/kT}$$

$$= \frac{nD}{kT}\left(\Omega\frac{d\sigma}{dx} - q\frac{d\phi}{dx}\right) - D\frac{dn}{dx} \qquad [8]$$

with D being the diffusivity of ions in the alloy layer. The net flux of the ion migration is a linear function of the concentration gradient, the potential gradient, and the stress gradient for small electric field and mechanical stress, and small gradient of stress. Note that Eq. 8 reduces to a form of Nernst-Planck's flux equation[16] for $\sigma = 0$ and to the stress-limited diffusion[17,18] for $\phi = 0$.

Growth of Alloy Layer

Consider the lithiation of a Si film in contact with an electrolyte. Assume uniform stress distribution in the lithiation layer, i.e. $d\sigma/dx = 0$, as used by Liu et al.[10] in studying the lithiation of Si nanowires. Equation 8 is reduced to

$$j = -\frac{nqD}{kT}\frac{d\phi}{dx} - D\frac{dn}{dx} = \frac{nqD}{kT}\frac{\Delta\phi}{X} - D\frac{dn}{dx} \qquad [9]$$

for a constant potential difference, $\Delta\phi$, across the lithiation layer. Here, X is the thickness of the lithation layer. The flux of lithium ions from the electrolyte into the surface of the lithiation layer, $j(x = 0)$, is

$$j(x = 0) = \alpha(n_{eq} - n_{in}) \qquad [10]$$

where α is a transport coefficient of lithium ions cross the interface between the electrolyte and the lithation layer, n_{eq} is the local equilibrium concentration in the electrolyte at the interface, and n_{in} is the local concentration in the lithiation layer at the interface. For a first order reaction at the interface between the Si and the lithiation layer, the flux is

$$j(x = X) = \beta n_0 \qquad [11]$$

Here, β is the reaction velocity, and n_0 is the local concentration in the lithiation layer at the interface. At the steady state, there is

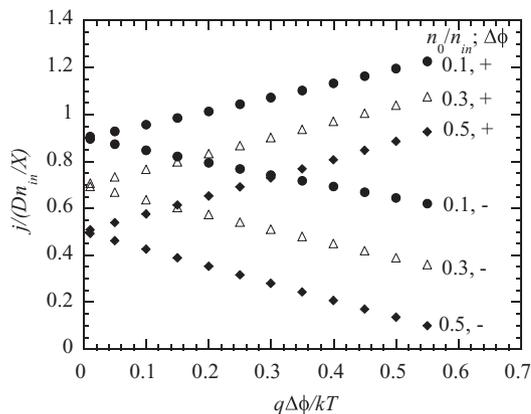$$\frac{D}{X}\cdot\frac{q\Delta\phi}{kT}n - D\frac{dn}{dx} = j_{in} = j_{out} \qquad [12]$$

Using the conditions, $n(x = 0) = n_{in}$ and $n(x = X) = n_0$, one obtains

$$n = n_{in} + \frac{n_{in} - n_0}{1 - e^{q\Delta\phi/kT}}(e^{qx\Delta\phi/kTX} - 1) \qquad [13]$$

which gives the flux as

$$j = \frac{Dn_{in}}{X}\cdot\frac{q\Delta\phi}{kT}\left(1 - \frac{1 - n_0/n_{in}}{1 - e^{q\Delta\phi/kT}}\right) \qquad [14]$$

Figure 2 shows the variation of the flux with the parameter $q\Delta\phi/kT$ for various ratios of n_0/n_{in}. Obviously, the electric field can either increase or decrease the flux of ions, depending on polarity of the

Figure 2. Variation of the flux of lithium ions in the lithiation layer with potential difference.

field. For the field direction the same as the concentration gradient, the field increases the flux of ions across the interface between the lithiation layer and electrolyte; while, for the field direction opposite to the concentration gradient, the field decreases the flux of ions. Such behavior is due to that the electric force on the ions can have either the same or opposite direction to the chemical force on the ions due to the concentration gradient.

Substituting Eq. 13 in Eq. 12 and using the conditions of (10) and (11), one obtains

$$n_0 = \frac{\alpha n_{eq}}{\alpha + \beta + \frac{\alpha\beta}{D}X - \alpha\left(1 + \frac{\beta X}{2D}\right)\cdot\frac{q\Delta\phi}{kT}} \qquad [15]$$

for $|q\Delta\phi| \ll kT$. Equation 15 gives the growth of the lithiation layer as

$$\frac{dX}{dt} = j\tilde{\Omega} = \frac{\alpha\beta\tilde{\Omega}n_{eq}}{\alpha + \beta + \frac{\alpha\beta}{D}X - \alpha\left(1 + \frac{\beta X}{2D}\right)\cdot\frac{q\Delta\phi}{kT}} \qquad [16]$$

with $\tilde{\Omega}$ being the volume of the reaction product formed per unit of lithium ions transported. Integrating Eq. 16 yields

$$\left(\frac{1}{\beta}\left(1 - \frac{q\Delta\phi}{kT}\right) + \frac{1}{\alpha}\right)DX + \frac{1}{2}\left(1 - \frac{q\Delta\phi}{2kT}\right)X^2 = n_{eq}D\tilde{\Omega}t \quad [17]$$

The growth of the lithiation layer follows a parabolic law, with the coefficients being dependent on the potential difference applied to the layer. Using $\alpha \approx \beta \approx 1.63 \times 10^{-10}$ ms^{-1} [19] and $D = 1.1 \times 10^{-13}$ cm^{2}s^{-1} for Li diffusion in a-silicon,[20] the temporal growth of the lithiation layer is depicted in Fig. 3 for three values of $q\Delta\phi/kT$.
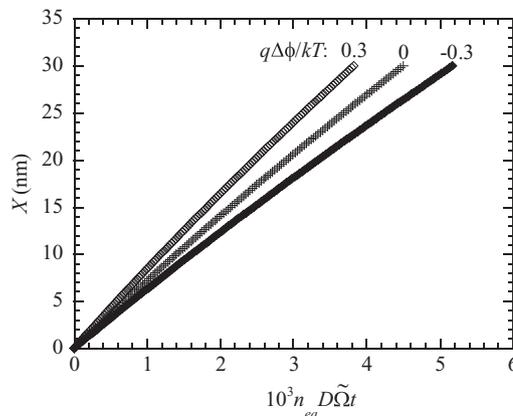
Figure 3. Temporal growth of the lithiation layer for three values of the potential difference.

The thickness of the lithiation layer increases with increasing the lithiation time, as expected, and is dependent on polarity of the field. The electric field can either accelerate or retard the growth of the lithiation layer. When the field direction is the same as the concentration gradient, the electric field accelerates the growth of the lithiation layer, qualitatively in accord with the observation of Liu et al.[10] Generally, electric field can cause the distribution of ions in the lithiation layer. One needs to solve the Poisson equation to obtain the field effect on the distribution and diffusion of Li ions in the lithiation layer.

Conclusions

Using the theory of thermal activation process, an analytical relation among the net flux for ionic migration, the stress gradient, the potential gradient, and the concentration gradient is derived. The net flux is a nonlinear function of the stress gradient and the potential gradient. For small electric field and mechanical stress, the net flux becomes a linear function of the stress gradient and the potential gradient, the same as those from irreversible thermodynamics. Using the linear relationship for small electric field and uniform stress, the growth of the lithiation layer subjected to a concentration gradient and a constant potential difference between the interface of the lithiation layer/electrolyte and that of the lithiation layer/anode is analyzed. The temporal growth of the lithiation layer follows a parabolic law. The applied electric field can either accelerate or retard the growth of the lithiation layer, depending on polarity of the field.

Acknowledgment

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