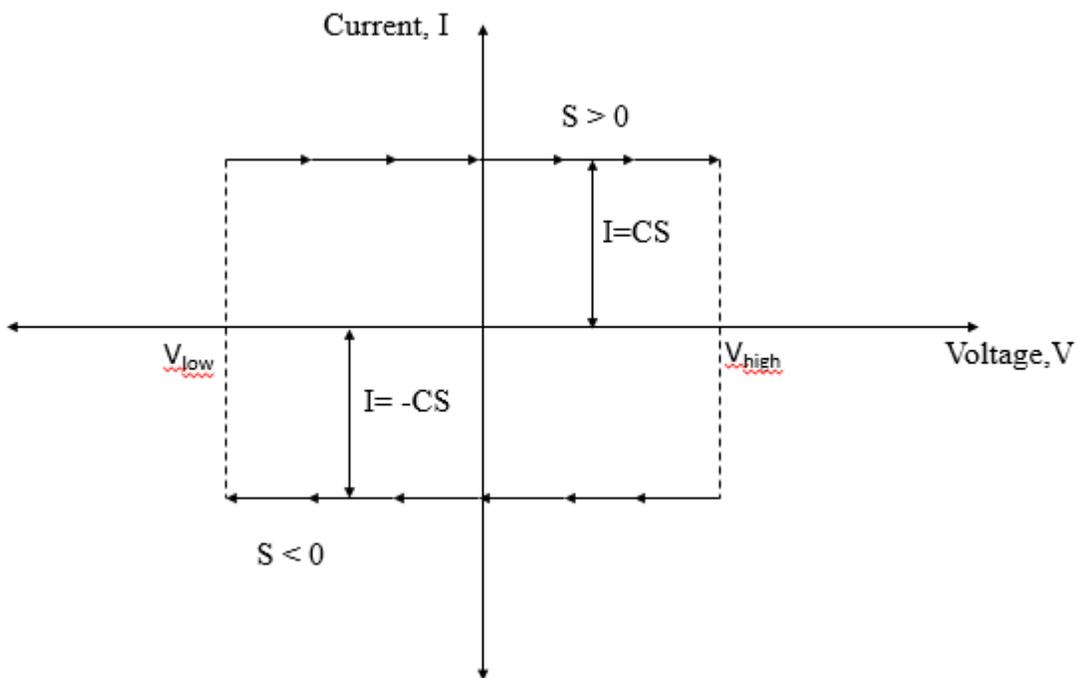**Linear Sweep Voltammetry**

Linear Sweep Voltammetry $\rightarrow$ $V(t) = \pm St$ where $S$ is the scan rate (change in voltage per time).

Definition of Current: $I = \dfrac{dQ}{dt}$ where $Q$ is charge

Definition of an ideal Capacitor: $Q = CV$ where $C = C(V)$ is the capacitance which can be a function of voltage but not time

Substitution: $I = \dfrac{d(CV)}{dt} = C\dfrac{dV}{dt} = \pm CS$

The following plot is obtained when performing cyclic voltammetry if $C$ is a constant with respect to voltage, there is no resistance, and the scan has voltage bounds of $V_{low}$ and $V_{high}$:



If linear sweep voltammetry is performed at multiple scan rates on a system of constant capacitance, the magnitude of the current will increase with scan rate.

Ideal Solution/Lattice Gas Model for Lithium Ion Intercalation

$Li^{+} + e^{-} \rightarrow Li_{(sol)}$

$O + e^{-} \rightarrow R$
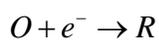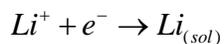
Let $x = \dfrac{C_{Li^+}}{C_{max,\ Li^+}}$

It may help to think of the lithium ion intercalation as a binary mixture of empty spaces that could contain lithium ions and spaces that contain lithium ions.

Definition of activity: $a_R \approx \dfrac{C_{Li^+}}{C_{max,\ Li^+} - C_{Li^+}} = \dfrac{\dfrac{C_{Li^+}}{C_{max,\ Li^+}}}{1 - \dfrac{C_{Li^+}}{C_{max,\ Li^+}}} = \dfrac{x}{1-x}$

Assuming $a_O = a_e = 1$.

From the Nernst Equation the following relationship can be obtained:

$$\text{Interfacial Voltage at Cathode} = \Delta\phi_{eq} = \Delta\phi^\theta - \frac{kT}{e}\ln\left(\frac{a_R}{a_O a_e}\right) = \Delta\phi^\theta - \frac{kT}{e}\ln\left(\frac{x}{1-x}\right)$$

Solving for x,

$$\Delta\phi_{eq} = \Delta\phi^\theta - \frac{2kT}{e}\tanh^{-1}(2x-1) \qquad \rightarrow \qquad x = \frac{1}{2}\tanh\left(\frac{(\Delta\phi^\theta - \Delta\phi_{eq})e}{2kT}\right) + \frac{1}{2}$$

Note: The definition of $\tanh^{-1}(y) = \dfrac{1}{2}\ln\left(\dfrac{1+y}{1-y}\right)$. If we define a new variable $y = 2x-1 \rightarrow x = \dfrac{y+1}{2}$ it
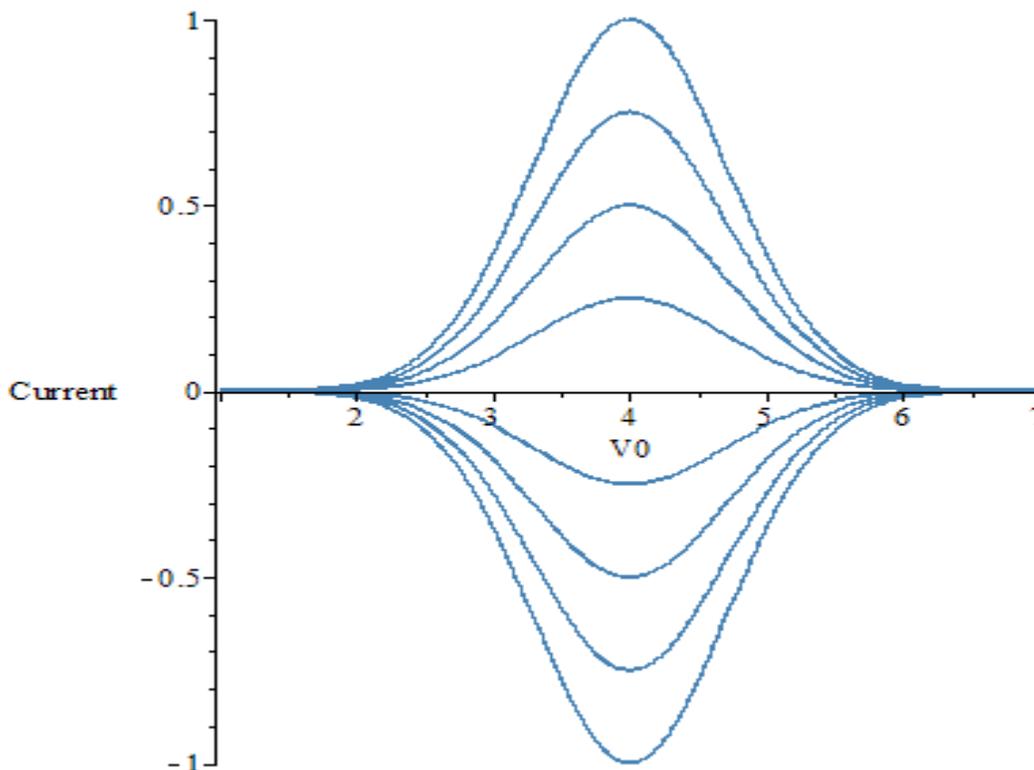
becomes easier to see how $\ln\left(\dfrac{x}{1-x}\right) = 2\tanh^{-1}(2x-1)$.

$$\ln\left(\frac{x}{1-x}\right) \rightarrow \ln\left(\frac{\dfrac{y+1}{2}}{1-\dfrac{y+1}{2}}\right) = \ln\left(\frac{1+y}{1-y}\right) = 2*\left[\frac{1}{2}\ln\left(\frac{1+y}{1-y}\right)\right] = 2\tanh^{-1}(y) = 2\tanh^{-1}(2x-1)$$

Charge Equation: $Q = \left(\text{charge of Li}^+\right)*\left(\text{amount of Li}^+\right) = eC_{Li^+} = eC_{max,\ Li^+}x$

From Pseudocapacitance: $C_F = -\dfrac{dQ}{dV} = eC_{max,\ Li^+}\dfrac{dx}{dV} = \dfrac{e^2 C_{max,\ Li^+}}{2kT}\operatorname{sech}^2\left(\dfrac{(\Delta\phi^\theta - \Delta\phi_{eq})e}{2kT}\right)$

$$\operatorname{sech}(z) = \frac{1}{\cosh(z)} = \frac{2}{e^z + e^{-z}}$$

2

The figure above is the result of only faradaic pseudocapacitance assuming there is a finite amount of reactant and therefore a finite reaction capacity. Peak occurs at equilibrium potential, $V_0$. Also, size increases linearly with increasing scan rate.

For an infinite reservoir, it would have an infinite capacity and would go to infinity as voltage goes to infinity.
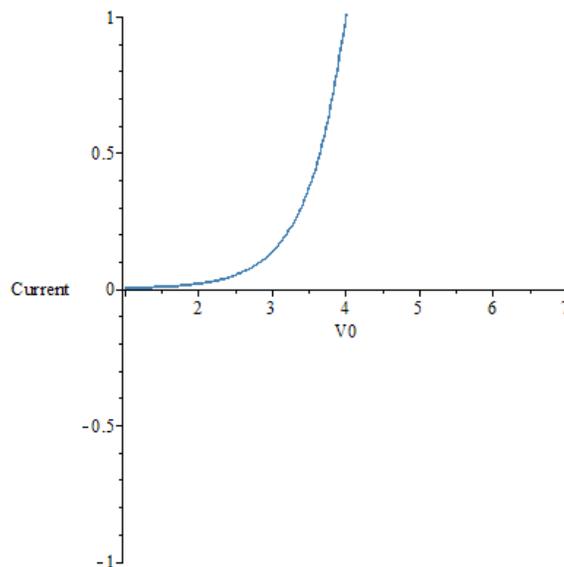
Generally, when doing cyclic voltammetry every peak corresponds to a reaction taking place in the system. The system in Figure 4 is indicative of three reactions in a given system. The reactions take place at approximately -1, 1, and 4 volts.
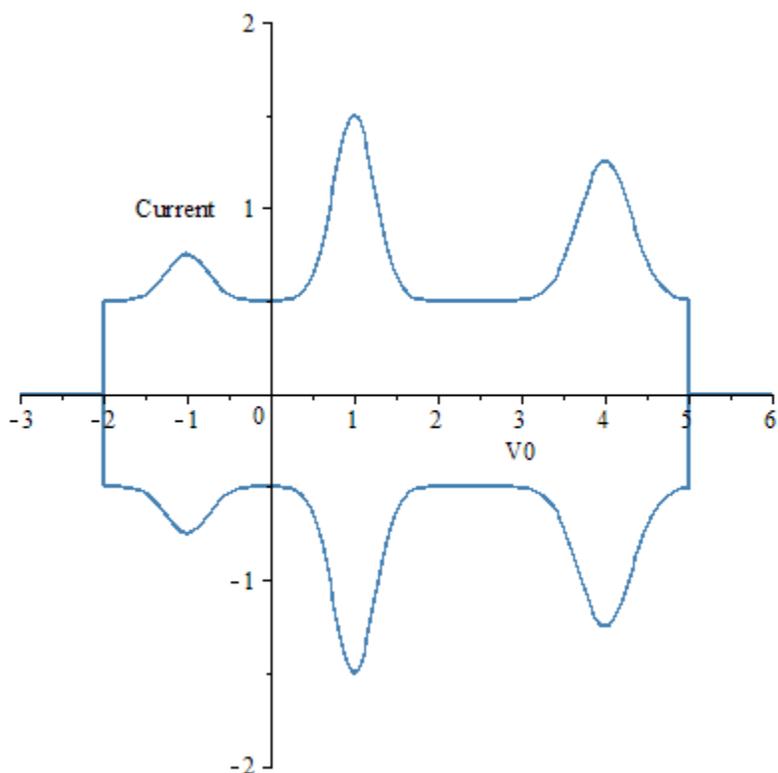


The slower the scan rate, the more equilibrated the system becomes at each point in time. Therefore, the peaks will more closely line up at each $V^0$ the slower the scan is performed. Increasing the scan rate leads to more transient behavior observed in the reaction and in the transport.
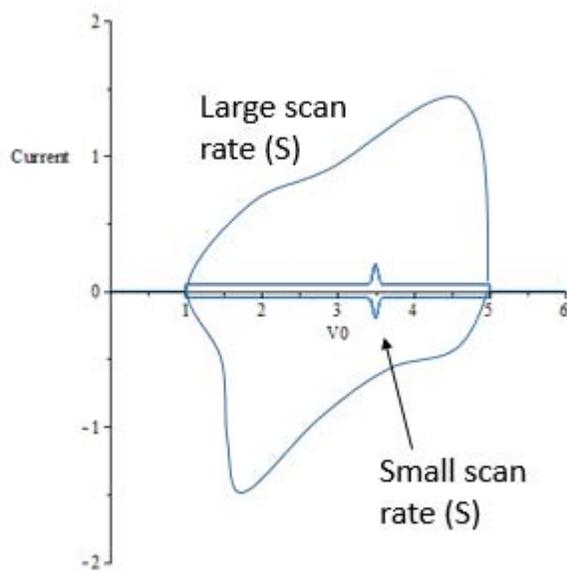
To reiterate, if the points in the CV are generated near equilibrium $(S \rightarrow 0)$ it will create a symmetric peak shift that linearly decreases in size with scan rate. At low scan rates this behavior is indicative of a capacitor because minimal resistance is present while the system is at equilibrium. If the scan rate is large, resistance comes into play and asymmetries begin to occur.

$$C_F = \frac{e^2 C_{max,\ Li^+}}{2kT} \operatorname{sech}^2\left(\frac{\left(\Delta\phi^\theta - \Delta\phi_{eq}\right)e}{2kT}\right)$$

$$\lim_{\left(\Delta\phi^\theta - \Delta\phi_{eq}\right)\to 0} C_F \approx \frac{e^2 C_{max,\ Li^+}}{2kT} \exp\left(\frac{\left(\Delta\phi^\theta - \Delta\phi_{eq}\right)e}{2kT}\right)$$

If CV was performed at 0 Kelvin, there would not be any width to the peak. The width is related to prefactor in the exponential, $\frac{e}{2kT}$. At room temperature $\frac{kT}{e} \approx 26mV$.

**Regular Solution Model**

$$\Delta S_M = k * \ln(\Omega) \text{ where } \Omega = \text{ number of configurations } = \frac{N_s!}{\displaystyle\prod_{i=0}^{N} n_i!}$$

$$\Delta H_M \neq 0$$

$$G = H - TS$$

$$s = \frac{S}{N_s} \text{ and } h = \frac{H}{N_s} \text{ and } g = \frac{G}{N_s}$$

Using Stirling's Approximation, the intensive entropy can be calculated.

$$s = \frac{k \ln\left(\dfrac{\left(N_{Li^+} + N_{Hole}\right)!}{N_{Li^+}! * N_{Hole}!}\right)}{N_{Li^+} + N_{Hole}} \rightarrow -k\left(x\ln(x) + (1-x)\ln(1-x)\right) \quad \text{where } x = \frac{N_{Li^+}}{N_{Li^+} + N_{Hole}}$$

The assumed form of the enthalpy of mixing is shown below.

$$h = h_0(x)(1-x) = h_0\left(x - x^2\right) \text{ where } h_0 \text{ is the pair interaction energy}$$
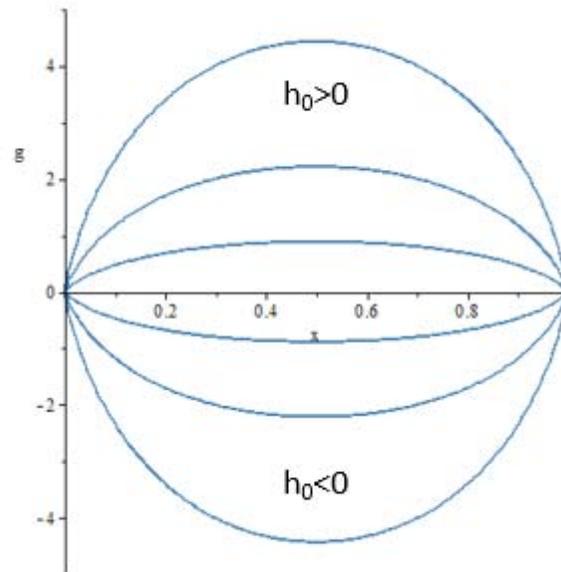
$h_0 > 0$: Attractive forces between particles $\rightarrow$ each pair lowers the energy $\rightarrow -h_0 x^2$

Can also be thought of as a repulsive force between a hole/vacancy and a particle on a lattice.

Combining these two expressions yields the intensive Gibbs energy of mixing.

$$g = h_0\left(x - x^2\right) + Tk\left(x\ln(x) + (1-x)\ln(1-x)\right) + \mu_0 x$$

A plot of g is shown below.

At high temperatures, the enthalpy term becomes negligible compared to the entropy term. Physically speaking, interactions between particles become meaningless compared to their arrangement.

This figure below was derived at a different temperature. It shows that the Gibbs energy can be minimized by separating into two stable phases, one that is lithium ion rich, and another that is lithium ion deficient.
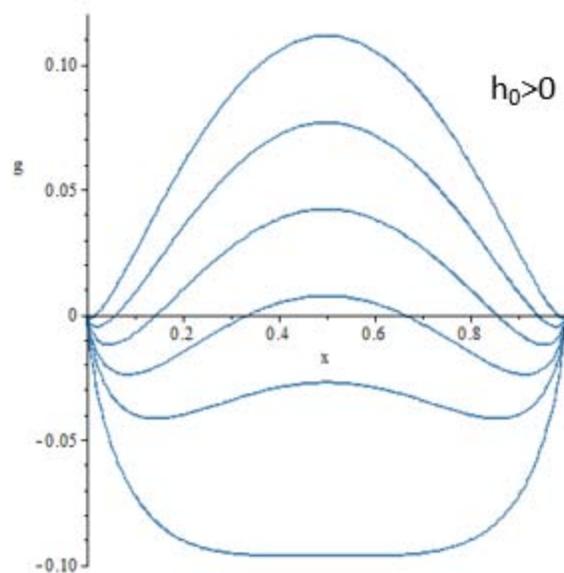


The derivative of g with respect to x yields the diffusional chemical potential.

$$\mu = \frac{dg}{dx} = kT \ln\left(\frac{x}{1-x}\right) + h_0\left(1-2x\right) + \mu_0$$

The second term on the right hand side in the above equation is the interaction energy.

$$kT \ln\left(\frac{x}{1-x}\right) = kT \ln(x) - kT \ln(1-x)$$

The first term on the right hand side of the equation above is the particle entropy. The second term is the hole/vacancy entropy.

Finally, I can write down an expression for the open circuit voltage as a function of mean filling fraction using this final relationship.

$$V_O = V^0 - \frac{\mu(x)}{e}$$

$$\boxed{V_O = V^0 + \frac{h_0}{e}(2x-1) + \frac{Tk}{e}\left(\ln(1-x) - \ln(x)\right)}$$

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