Introduction to the Materials Science of

Rechargeable Batteries

Week 4: Reversible and Irreversible Interfacial Reactions
Lecture 4.1: The Butler-Volmer Relation

By R. Edwin Garcia
Associate Professor of Materials Engineering
Purdue University
The Electrode-Electrolyte Interface

\[ a = 0.4 \text{ nm} \]
\[ \lambda = 0.96 \text{ nm} \]
The Electrode-Electrolyte Interface

\[ \nabla^2 \phi = \frac{z e c^*}{\varepsilon_r \varepsilon_o} \sinh \left( \frac{z e \phi}{k_b T} \right) + \frac{\rho_o(x, y, z)}{\varepsilon_r \varepsilon_o} \quad \text{(non-linear equation)} \]

\[ \nabla^2 \phi = \frac{z^2 e^2 c^*}{\varepsilon_r \varepsilon_o k_b T} \phi + \frac{\rho_o(x, y, z)}{\varepsilon_r \varepsilon_o} \quad \text{(linearized equation)} \]

\[ \kappa^2 = \frac{z^2 e^2 c^*}{\varepsilon_r \varepsilon_o k_b T} \quad \text{(Debye constant)} \]
The Charge at the Interface

$C_j$ ($10^5 \text{ mol/m}^3$) vs. $x$ (nm)

$t = 200 \text{ ns}$

$\phi$ (V)

$\rho$ ($10^{10} \text{ C/m}^3$)

$\xi$

$\rho$

$\phi$

$C_j$ ($\text{mol/m}^3$)

$2 \text{ Å}$

Elements of Reaction Theory

reacted charge:

\[ J_T = J_F - J_B \]

\[ J_T = zF c_s k_F - zF (c_T - c) k_B \]

backwards/forward reaction rates

\[ k_F = k_F^0 \exp \left( -\frac{\Delta G_f}{RT} \right) \]

\[ k_B = k_B^0 \exp \left( -\frac{\Delta G_b}{RT} \right) \]

The effective overpotential:

\[ \eta_T = \eta + \frac{RT}{zF} \ln \left( \frac{c_T - c}{c_s} \right) \]
Elements of Reaction Theory: Continued...

\[ Li \Leftrightarrow Li^+ + e^- \]

Detailing the rate at which Li intercalates

\[ LiM \Leftrightarrow e^- + Li^+ + M \]

The simplest interfacial kinetics

\[
\vec{J} \cdot \hat{n} = i_\circ \left( \exp\left( \frac{\alpha_a F z \eta}{RT} \right) - \exp\left( - \frac{\alpha_c F z \eta}{RT} \right) \right)
\]

\[
i_\circ = F k_r (c_T - c_s)^{\alpha_a} c_s^{\alpha_c}
\]
Tafel Kinetics

Butler-Volmer Kinetics:

\[ \vec{J} \cdot \hat{n} = i_0 \left( \exp \left( \frac{\alpha_a F z \eta}{RT} \right) - \exp \left( - \frac{\alpha_c F z \eta}{RT} \right) \right) \]

\[ i_0 = F k_r (c_T - c_s)^{\alpha_a} c_s^{\alpha_c} \]

if \( \alpha_a = \alpha_c = 1/2 \) and \( \frac{F z \eta}{RT} \ll 1 \)

\[ \vec{J} \cdot \hat{n} = i_0 \frac{F z \eta}{RT} \]
Tafel Kinetics

\[ \frac{\vec{J} \cdot \hat{n}}{i_0} \]

\[ \frac{F \, \eta}{RT} \]

BV

T
Effect on Power Density

\[ \frac{I}{k_r F A} \]

\[ Q(t) = A(\eta, T)c^{1/2}(1 - c)^{1/2} \]

initial instantaneous power

end of battery life
Battery Design: Power vs Energy

\[
\frac{c(t)}{c_T} = \frac{1}{2} \left( 1 - \left(1 - c(t) \right)^{1/2} \right)
\]

\[
Q(t) = \frac{\partial c}{\partial t} = A(\eta, T)c^{1/2}(1 - c)^{1/2}
\]

initial instantaneous power

end of battery life
The Charge Rate in a Porous Electrode

\[ A \dot{Q} = j_{bv} A \]
\[ = j_{bv} \frac{A}{V} V \]
\[ = j_{bv} aA \]
\[ = j_{bv} a h_c A \]

\[ \Rightarrow \dot{Q} = j_{bv} a h_c \]

\((\text{mA/cm}^2)\)
The Charge Capacity Rate

For a reaction-limited electrode (including porosity):

\[
\dot{Q}_c = \frac{\partial Q_c}{\partial t} = j_{bv}a_ch_c
\]

\[
= \frac{3F\kappa_c^a}{r_p^c}c_s^{\alpha_c} (c_T - c)^{\alpha_c} \sinh\left(\frac{zF\eta}{RT}\right)(1 - \epsilon_T^c)h_c
\]

- Instantaneous current is state of charge-dependent
- Like before, the thicker the electrode, the more charge you get
- Now, the smaller the particle size, the greater the instantaneous current
- This description does not account for porosity (ohmic) losses
The Charge Capacity Ratio, Again

Charge rate of a porous electrode:

\[
\dot{Q}_c = \frac{3Fz k_r^c}{r_p^c} c_s^{\alpha_a} (c_T - c)^{\alpha_c} \sinh\left(\frac{zF\eta}{RT}\right)(1 - \epsilon_T^c) h_c
\]

The capacity ratio, time-dependent:

\[
R_c = \frac{Q_c}{Q_a} \Rightarrow Q_c = R_c Q_a \Rightarrow \dot{Q}_c = R_c \dot{Q}_a \Rightarrow R_c = \frac{\dot{Q}_c}{\dot{Q}_a}
\]

\[
\Rightarrow R_c = \frac{k_r^c (1 - \epsilon_T^c) h_c r_a (c_T^c - c^c)^{\alpha_c}}{k_r^a (1 - \epsilon_T^a) h_a r_c (c_T^a - c^a)^{\alpha_c}}
\]

continued...
The Charge Capacity Ratio, Continued

For a kinetically limited system:

\[
R_c = \frac{k_r^c (1 - \epsilon_T^c) h_c r_a (c_T^c - c^c)^{\alpha_c}}{k_r^a (1 - \epsilon_T^a) h_a r_c (c_T^a - c^a)^{\alpha_c}}
\]

If you assume that \( c_T^a \geq c_T^c \):

\[
c^c = c_T^c x
\]
\[
c^a = c_T^c (1 - x)
\]

\[
\Rightarrow R_c = R_c^\circ \left( \frac{1 - x}{y + x} \right)^{\alpha_c}
\]
\[
y = \frac{c_T^a - c_T^c}{c_T^c}
\]
\[
R_c^\circ = \frac{k_r^c (1 - \epsilon_T^c) h_c r_a}{k_r^a (1 - \epsilon_T^a) h_a r_c}
\]
Capacity Ratio Charge State Dependence

\[
\sqrt{\frac{1-x}{y+x}}
\]

\[y = 1/3\]

\[y = 0\]

\[c^a_T = c^c_T\]

\[y = 1\]

\[c^a_T = 2c^c_T\]