Introduction to the Materials Science of

Rechargeable Batteries

Week 5: Battery Architectures and Design Guidelines
Lecture 5.2: The Reaction Zone Model

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$\text{Li}_x\text{C}_6 | \text{Li}_y\text{Mn}_2\text{O}_4 \quad T=25^\circ\text{C}$

$1 \text{ C} = 2.08 \text{ mA/cm}^2$

Cell potential (V) vs. Normalized capacity

- 0.2 C
- 1 C
- 3 C
- 2 C
- 4 C
- 5 C
- 7 C
Newman’s Reaction Zone Model

reacted unreacted

(micrograph, courtesy of Quinn Horn)
Equivalent Circuit
Moving Boundary Concept

separator

\[ h_s \]

\[ x_r \] (reaction zone)

\[ h_c \]

unreacted

reacted
The Reaction Zone and Utilized Charge

Concept of reaction zone applied to battery discharge

\[ x_r (1 - \epsilon) q = i t \]

\[ \Rightarrow x_r = \frac{it}{(1 - \epsilon)q} \]

\[ t = 0s \]

\[ t = t_d \]
The Voltage of the Battery

reacted unreacted

\[
\phi = U - i \left( \frac{L_s}{\kappa_s} + \frac{x_r}{\kappa} \right)
\]

\[
\Rightarrow \phi = U - i \frac{L_s}{\kappa_s} - \frac{i^2 t \kappa_s \varepsilon^{3/2}}{\kappa_s \varepsilon^{3/2} (1 - \varepsilon) q}
\]
Results for “Ideal” LiMn$_2$O$_4$

\[ \Rightarrow \phi = U_0 - i \frac{L_s}{\kappa_s} - \frac{i^2 t}{\kappa_s \varepsilon^{3/2} (1 - \varepsilon) q} \]
How does it compare to the experiment?
Three Optimization Restrictions

• Short circuit limit  \[ i_{\text{max}} = \frac{U\kappa_s}{h_s} \]

• Cut-off voltage  \[ \phi \geq \phi_o \]

• Maximal Capacity  \[ h_c(1 - \varepsilon)q = it_d \]

Battery stops running if ANY of these constraints are satisfied
Complete Charge Utilization Limit

\[ x_r = \frac{it}{(1 - \epsilon)q} \Rightarrow h_c = \frac{it_d}{q(1 - \epsilon)} \]

\[ E = \left( U - \frac{h_s}{\kappa_s} i \right) it_d - \frac{i^3 t_d^2}{2 \kappa_s \epsilon^{3/2} (1 - \epsilon) q} \]

- (linear) separator
- (quadratic) ohmic loss
- (cubic) polarization
- (reaction) loss

\[ = (1 - \epsilon) q h_c \left( U - \frac{h_s}{\kappa_s} i - \frac{i h_c}{2 \kappa_s \epsilon^{3/2}} \right) \]
Optimal Thickness and Porosity

\[ E[W \, hr/m^2] \]

\[ h_c[m] \]

\[ \varepsilon = 0.4 \]

\[ \varepsilon = 0.5 \]

\[ \varepsilon = 0.6 \]

\[ \varepsilon = 0.7 \]

\[ \varepsilon = 0.8 \]

\[ \varepsilon = 0.9 \]
Optimal values

Optimal thickness

$$h_c^* = \varepsilon^{3/2} \left( \frac{\kappa_s U - h_s i}{i} \right)$$

Optimal porosity

$$\varepsilon^* = \frac{3}{5} = 0.6$$
Cut-Off Voltage Limit

Battery is active if and only if \( \phi \geq \phi_0 \)

\[
\Rightarrow \quad t_d = \frac{q(1 - \varepsilon)\varepsilon^{3/2}(U\kappa_s - \phi_0\kappa_s - h_s i)}{i^2}
\]

(discharge time)

\[
\Rightarrow \quad E = q(1 - \varepsilon)\varepsilon^{3/2} \frac{((U - \phi_0)\kappa_s - h_s i)((U + \phi_0)\kappa_s - h_s i)}{2i\kappa_s}
\]

useful energy
Optimal Thickness and Porosity

\[ E[\text{W hr/m}^2] \]

\[ h_s \text{[m]} \]

\( \varepsilon = 0.4, 0.5 \)
\( \varepsilon = 0.7 \)
\( \varepsilon = 0.8 \)
\( \varepsilon = 0.9 \)

\( h_s^{\text{min}} \)
\( h_s^{*} \)
Revised Optimal Values

“Optimal” separator thickness

\[ h_s^* = \frac{\kappa_s (U - \phi_\circ)}{i} \quad h_s^{\text{min}} = \frac{\kappa_s U}{i} \]

(more like limits)

THE Optimal porosity

\[ \varepsilon^* = \frac{3}{5} = 0.6 \]

Assume \( x_r \leq h_c \)
Summary of Assumptions

- For ohmically limited system ONLY
- Material potential is state of charge independent
- Porosity is time-independent
- Diffusion does NOT matter in this system