Overview of the Life of Li-Ion Batteries

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Overview

- The Importance of Battery Life
- Life Models
  - Loss of Cyclable Lithium
    - Li Loss through SEI Growth
  - Site Loss Model
  - Impedance Growth
- Conclusions
Battery Life – Determined by the decrease in power/capacity that occurs over time.

Calendar Life – loss on standing

Cycle Life – loss during charge/discharge cycles

Graphs showing capacity retention and voltage over storage period and cycles.
Goal: 10-15 Year Battery Life

Net Energy Removed (at C/1 discharge rate)
Possible Types of Fading Curves in Cycle Life Testing

- Want to account for impedance growth and capacity loss due to calendar time and cycling
- Current state of the art relies upon extrapolation of experimental results
- Simple functional forms are preferred
Key Aspects of Lithium-Ion Cells

1) Insertion compounds that provide sites for lithium

2) Amount of cyclable lithium
Approach

- Model loss of cyclable lithium and/or sites using simple differential equations that can be readily solved
  - Life simulation is possible in reasonable time (minutes to hours)
  - Arbitrary test conditions (rates, depth of discharge, etc.)

- Models available in Battery Design Studio® for user-friendly interface
SEI allows transport of lithium but inhibits electron transfer. Formation of SEI results in loss of cyclable lithium.

Rate of SEI formation

\[ \frac{dL}{dt} = k_0 e^{-fL} \]

Graphite

\[ L \]

\[ \text{SEI} \]
Electron Tunneling Model

Equil Fade-9-1
Equil Fade-9-3
Equil Fade-9-5
Equil Fade-9-6

\[
\frac{dL}{dt} = k_0 e^{-fL}
\]

A: \(k_0=1\times10^{-2}, f=8675\)
B: \(k_0=1\times10^{-4}, f=6211\)
C: \(k_0=1\times10^{-6}, f=3737\)
D: \(k_0=1\times10^{-7}, f=2502\)
Tunneling model does not predict an effect of voltage on capacity fade.
Vinylene carbonate

\[
\text{O} \quad + \quad 2e^- \quad + \quad 2\text{Li}^+ \quad \rightarrow \quad \text{Li}_2\text{CO}_3 \quad + \quad -(\text{C}=\text{C}-0)-
\]

Schematic of SEI at Graphite

Crystalline solid ion conductor

Polymeric film

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Acid Generation at Positive

\[ LiMO_2 \rightarrow MO_2 + Li^+ + e^- \]

\[ i_{Li^+} = Fk_p \exp \left[ \frac{F(\phi_1 - \phi_2 - \phi_{eq} - i\rho_f L_p)}{RT} \right] \]

\[ ROH \rightarrow RO + H^+ + e^- \]

\[ i_{H^+} = Fk_{H^+} \exp \left[ \frac{F(\phi_1 - \phi_2 - \phi_{eq,H^+} - i\rho_f L_p)}{RT} \right] \]

Net Reaction

\[ Li^+ + MO_2 + ROH \rightarrow H^+ + LiMO_2 + RO \]
Acid attack of SEI

\[ \text{CH}_3\text{CH}_2\text{OLi} + \text{H}^+ \rightarrow \text{ROH} + \text{Li}^+ \]

\[ \text{Li}_2\text{CO}_3 + \text{H}^+ \rightarrow \text{LiHCO}_3 + \text{Li}^+ \]
Electron Tunneling with Acid Generation Model

Simulated Calendar Life Test

Acid generation model predicts lower voltages significantly reduce fade rate.
Electron Tunneling with Acid Generation Model

Simulated Cycle Life Test

- 4.2 Volts
- 4.0 Volts

Acid generation model predicts lower voltages significantly increase cycle life.

EquilFade-9-6-1
Particle Expansion/Contraction Damages SEI

\[ R_{\text{break}} = k I N_{\text{sei}} \left( \frac{I}{Q} \right)^p |x - x_o| \]

- \(x_o\) is value at stoichiometry at last time current changed sign.

Equation predicts capacity loss increases with charge/discharge current and magnitude of SOC swing.
Simulated Cycle Life
Acid Generation Models

- No acid generation
- Acid generation
- Acid generation + SEI destruction due to SOC swings
Possible Mechanisms for Site Loss

- Electrical isolation of particles due to
  - Expansion of positive, recovery from compression or cycling
  - Break-up of agglomerates
  - Resistive film formation on surface

- Change in surface chemistry
  - Phase change to insulating or material with low Li diffusivity
  - Composition change, perhaps due to acidic impurities
Site Loss Model

\[
\frac{dQ_{site}}{dt} = -\frac{k_{site}}{Q_{site}^{p_{site}}}
\]

Expect site loss to accelerate as lose sites, since remaining sites are exercised more vigorously and have fewer neighbors to contact.
Site Loss + SEI Growth Models

\[
\frac{dQ_{\text{sei}}}{dt} = \frac{k_{\text{sei}}}{Q_{\text{sei}}}
\]

\[
\frac{dQ_{\text{site}}}{dt} = -\frac{k_{\text{site}}}{Q^{p_{\text{site}}}_{\text{site}}}
\]
Site Loss + SEI Growth Models

Impedance Growth

\[ R_{\text{cell}} = R_0 + r_{\text{sei}} N_{\text{sei}} + \frac{r_{\text{site}}}{Q_{\text{site}}} \]
Summary

- Defining feature of lithium-ion cells are the lithium sites and the amount of lithium available for cycling, which are determined by electrode loadings, irreversible capacity loss on formation, and equilibrium curves.

- The most common shapes for capacity fade curves can be rationalized by simple models for lithium and site loss.
Constant Ah Throughput

- Cell passes fixed amount of Ah ($Ah_{life}$) before reaching end of life

Mathematically:

$$N_{cycles} = \frac{Ah_{life}}{Ah_{cell} \cdot DOD}$$

Basis:
Cell Cap., Ah = 1.0
Ah-life = 10,000