Mechanistic diagnosis and prognosis on Li-ion battery degradation

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Objectives and motivations

To diagnose and predict battery behavior is challenging, mainly because degradation is path-dependent.
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To diagnose and predict battery behavior is challenging, mainly because degradation is path-dependent.

Laboratory testing cannot replicate the complexity of real usage.

Need proper tools to understand, diagnose and predict cell behavior under any conditions or variations in history (sequence of events)

Synthesize the battery degradation from different modes and sequences
Laboratory testing
Degradation mechanisms

From literature:

Diagnostics: Tracking and quantifying the contributions of the 3 categories through life of the cell

- Thermodynamics
  - Change in active material
  - Change in lithium inventory

- Kinetics
  - Changes in ohmic and faradic resistance

Extremely difficult to have a model to accommodate all phenomena in a simple simulation process

**BUT can we only quantify their effects on the cell?**

J. Groot, State of Health Estimation of Li-ion batteries cycle life test methods
Laboratory testing
Quantifying each category

Experimentally: possible by coupling 2 techniques:

Incremental capacity curves evolution

2C aging at RT

How can we replicate that with a model?

Change in ohmic and faradic resistances

Change in active material

Change in lithium inventory

Rest cell voltages evolution

Dubarry et al. J. Power Sources 196 (2011) 10336
Dubarry et al. J. Power Sources, 196(7), (2011) 3420
Dubarry et al. J. Power Sources 194 (2009) 551
Modeling and simulation
Model framework considerations

Electrochemical models
“Balance of plant”

\[
\frac{d\theta}{dt} - A_{\text{mech}} \int \left( \frac{\epsilon}{\epsilon_{\text{cell}}} \right) \exp \left( \frac{(1-\sigma)\chi F}{RT} (\Phi_{i} - \Phi_{e} - U) \right) \nonumber
\]

Use mechanistic descriptions with system topology for analysis

Equivalent circuit models (Electrical)

Universal, flexible, simple; mechanistic for diagnosis
Difficult for path dependence

Empirical models

Need a large amount of training data to derive fitting parameters and algorithms

Emulate path dependence?

Emulate the effects of the 3 categories

Use conservation principles to solve kinetic and mass transport equations

Computation intensive; very challenging with path dependence; difficult for diagnosis

Different flavors with “forward looking” approach

Predict model
Mechanistic emulator concept
Thermodynamic aspects 1 – Amount of active material involved

Start from the schematic view of a Li-ion cell:

By adjusting loading ratio (scaling) and position of PE and NE (translation), we can simulate the effect of any LAMs.

- Change in active material
- Change in lithium inventory
- Changes in ohmic and faradic resistance

Dubarry, Truchot and Liaw, *J. Power Sources*, 219 (2012) 204-216
Mechanistic emulator concept
Thermodynamic aspects 2 – Amount of Li inventory involved

Start from the schematic of a Li-ion cell:

By adjusting position of PE and NE (translation), we can also simulate LLIs.

Change in active material
Change in lithium inventory
Changes in ohmic and faradic resistance

Dubarry, Truchot and Liaw, *J. Power Sources*, 219 (2012) 204-216
Mechanistic emulator concept
Kinetic aspects – Ohmic and Faradic resistance changes

Change in active material
Change in lithium inventory
Changes in ohmic and faradic resistance

Dubarry, Truchot and Liaw, *J. Power Sources*, 219 (2012) 204-216
ECM Modeling and Simulation
Allows accurate V vs. Q simulations

ECM truthfully reflects thermodynamics & kinetics

Dubarry and Liaw, *J. Power Sources* 174 (2007) 856
Mechanistic emulator concept
Kinetic aspects – Ohmic and Faradic resistance changes

Half cell with ECMs:
Emulate change in kinetics

Change in active material
Change in lithium inventory
Changes in ohmic and faradic resistance

Dubarry, Truchot and Liaw, *J. Power Sources*, 219 (2012) 204-216
Mechanistic emulator concept
Thermodynamic aspects 3 – Structural changes

Core shell: ECMs in series

Mixture: ECMs in parallel

Example of the hydration of LiFePO$_4$

30% LiFePO$_4$•H$_2$O

Example of a composite positive electrode

Multi-cell ECMs:
Emulate thermodynamic changes by introducing new electro-active phases.

Change in active material

Change in lithium inventory

Changes in ohmic and faradic resistance

Dubarry, Truchot and Liaw, J.Power Sources, 219 (2012) 204-216
Degradation Modes emulation
Summarizing the approach

Unique mechanistic inference technique
ECMs for half cells + full-cell module
Backward looking approach: choose the degradation & look for effects on cell performance characteristics
Use experimental half-cell data: easy to incorporate new chemistry

Emulates the effects of most of the well-established degradation mechanisms

Chemistry, rate, extent of rxn

Change in active material
Change in lithium inventory
Changes in ohmic and faradic resistance

Benefits? Validation? Ease of use?

Dubarry, Truchot and Liaw, J.Power Sources, 219 (2012) 204-216
Mechanistic diagnosis and prognosis
Unique capabilities and benefits

Dubarry, Truchot and Liaw, *J. Power Sources*, 219 (2012) 204-216
Mechanistic diagnosis and prognosis

Validation

Model validated on several chemistries

Graphite // LFP  Graphite // NMC  Graphite // LMO

Graphite // \{NMC+LMO\}

- Experiment
  - 12% capacity loss

- Simulations
  - 11% LLI : 12% capacity loss

LTO//NMC

- 11% LLI + 5% LAM\textsubscript{NMC}
  - 12% capacity loss

Voltage response and capacity variations (stage I and stage II) replicated

Additional validation in progress via collaborations
Mechanistic diagnosis and prognosis

Path dependence emulation

If the effect of a path is known, it can be emulated: Prognosis and path dependence emulation

Effect of path: from any sources of information (e.g., laboratory testing, literature, physical modeling,...)

Complement other modeling approaches
Reduce complexity: Could be the link between battery material research and BMS

Computation is not intensive. Easy to parameterize. Easy to use.
Mechanistic diagnosis and prognosis
Graphical user interface: the 'alawa toolbox

Simple, fast, powerful and accurate diagnosis and prognosis tool

Stand alone GUI available for license or collaboration
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Mahalo for your attention! Questions?

Full publication list available on
Synthesize Degradation Modes via a Diagnostic Model

Conclusions

Our approach:

ECMs for half cells + full-cell module

**Backward looking** approach: simulate the degradation & look for effects on cell performance characteristics

\[ V_{\text{cell}} = V_{\text{PE}} - V_{\text{NE}} \]

- Use experimental half-cell data: easy to set up and change chemistry
- Degradations described by ECM parameters and electrodes position to each other
- Could be the missing link between electrochemical models and BMS

Dubarry, Truchot and Liaw, *J. Power Sources*, 219 (2012) 204-216
Mechanistic Li-ion battery degradation diagnosis and prognosis

Graphical user interface: the ‘alawa toolbox

Display the results

Flexibility

Preset plots or any variable

3D maps available for large datasets
Mechanistic diagnosis and prognosis
Graphical user interface: the ‘alawa toolbox

‘alawa is Hawaiian for diagnose
Mechanistic diagnosis and prognosis

Graphical user interface: the ‘alawa toolbox

Choose chemistry from popup menu

From imported half cell data

Choose cell design parameters

Loading ratio $\frac{Q_{NE}}{Q_{PE}}$, SEI offset and ohmic resistance
Mechanistic diagnosis and prognosis
Graphical user interface: the ‘alawa toolbox

Emulate the degradation
Manual change of loading and offset
Degradation mode equations

Computation time
0.3 s for 6 cycles / 50s for 150 cycles

Display simulation results
Flexible: preset plots or any variable
3D maps for large datasets