Selected US CERC-CVC Research on Improving Battery Safety and Reliability

美国CERC-CVC提高电池安全性和可靠性的研究

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Top four emitters in 2011 covered 62% of global emissions
China (28%), United States (16%), EU27 (11%), India (7%)
Seven Joint Clean Energy Initiatives (2009)

- Electric Vehicles Initiative
- Energy Efficiency Action Plan
- Renewable Energy Partnership
- 21st Century Coal
- Shale Gas Resource Initiative
- Energy Cooperation Program
- U.S.-China Clean Energy Research Center

**Clean Vehicles**

- Building Energy
- Clean Coal
Industrial Partners

U.S.
- Ford
- Delphi
- Denso
- Eaton
- Toyota
- Honda
- pjm
- TE Connectivity
- Aramco Services Company

China
- SAIC
- Geely
- JAC
- CAERI
- CANTARC
- KeyPower
- ECTEK
- Lishen
- Potevio
- JJE
1. Advanced Batteries and Energy Conversion
2. Advanced Biofuels, Clean Combustion and APU
3. Vehicle Electrification
4. Lightweight Structures
5. Vehicle-Grid Integration
• **Degradation**: Combine modeling and advanced characterization to understand degradation mechanisms in Li-ion batteries.

• **Modeling, Controls, and Implementation**: To extend battery life, develop battery management systems with on-board balancing technologies. Review protocols for battery testing & safety. Explore pathways for reuse & recycling of batteries.

• **New Chemistries**: Advance Li-air and Li-sulfur chemistries towards commercial viability by revealing limiting phenomena and developing materials/architectures that overcome these obstacles.
Projects and Personnel

Degradation
- Babu (OSU)
- Bhushan (OSU)
- Conlisk (OSU)
- Cao & Canova (OSU)
- Daniel (ORNL)
- Leung (Sandia)
- Amine (ANL)
- Qiu (THU)

Modeling & Controls
- Bernstein & Stein (UM)
- Lu (THU)

Protocols, Recycling
- Bloom, Gaines, Sullivan (ANL)
- Hua (THU)

New Chemistries
- Siegel (UM)
- Van der Ven (UM)
- Shao-Horn (MIT)
- Ceder (MIT)
- Wu (BIT)
- Kang (THU)
- Qui (THU)
- He (THU)
• NDP Measurement Techniques for Improved Electrochemical Performance and Aging Models of Li-ion Batteries (Canavo, Cao, Nagpure)

• Data-Based Techniques for Battery-Health Prediction (Stein, Bernstein, Ersal)

• Battery State of Health Estimation Based on Incremental Capacity Analysis (Sun and Peng)
Neutron Depth Profiling:

**Operating Principles**

- Sample is bombarded with a low energy neutrons (energy ~ 0.025 eV);
- Difference between the residual energy of the particle emerging from the surface and energy of the particle at its origin is measured;
- Relate to the depth of the reacting lithium atom and Li concentration.

**Advantages:**

- Li cross-section for NDP is 940 barn (1 barn = 10^{-24} cm^2), one of the largest among the light elements.
- Direct quantitative measurement of lithium concentration possible.
- Depth resolution of 100 nm possible.
- Non-destructive sample preparation necessary.
- Technique is well known and largely applied for *ex-situ* characterization of Li-ion cells.
First Year Milestones:

Benchmarking of OSU-NDP

<table>
<thead>
<tr>
<th>Cells</th>
<th>C-rate</th>
<th>SOC</th>
<th>Temperature (°C)</th>
<th>Ah Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td>unaged</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>C2-1-1</td>
<td>2</td>
<td>0-10%</td>
<td>55</td>
<td>5830</td>
</tr>
<tr>
<td>C4-1-1</td>
<td>4</td>
<td>0-10%</td>
<td>55</td>
<td>5540</td>
</tr>
<tr>
<td>C7-3-1</td>
<td>~7</td>
<td>68% ±7%</td>
<td>45</td>
<td>3441</td>
</tr>
</tbody>
</table>

The NDP facility at OSU was benchmarked by conducting measurements of the Li concentration in electrodes harvested from aged cells.

The same samples were previously tested at the NDP facility at the National Institute of Standards (NIST).

OSU-NDP facility has low thermal neutron flux \((8.5 \times 10^6 \text{ n/cm}^2 \text{ s})\) as compared to NIST facility \((1.2 \times 10^9 \text{ n/cm}^2 \text{ s})\), but has an improved acquisition system with solid state energy detectors.
First Year Milestones: Benchmarking of OSU-NDP

The profiles match in terms of shape, concentration, and depth values. Difference in the profiles close to the surface (first few nanometers) is caused by error in aligning the zero depth with the first channel in the detector.

Even though there is significant difference in the count rate at NIST and at OSU due to the difference in the available neutron flux, the eight solid state detectors at OSU provide significant number of counts to establish accurate concentration profiles along the depth of the samples.

Analysis is currently being repeated for all samples tested at NIST.
Continued improvement of the facility will enable in-situ testing not in vacuum.

Full calibration against NIST test results.

Validate prototype cells by comparing against conventional half-cell;

Use experimental results to improve Li-ion electrochemical models.
RCSI is a technique for data-based modeling that can identify a dynamic subsystem whose inputs and outputs are not measured.

RCSI is based on RCAC (Retrospective Cost Based Adaptive Control) Technique.

The Subsystem Model: 

Ramadass et al. Health Model

- **Power Fade** through increased resistance
- **Capacity fade** through consumed Li-ions
- Driven by side reaction intercalation current

Side Reaction Intercalation Current $J_s$

$$J_s = -i_{0,s}a_n e^{-\left(\frac{\alpha F}{RT} \eta_s\right)}$$

Resistive Film $\delta_{film}$

$$\frac{\partial \delta_{film}}{\partial t} = -\frac{J_s M_p}{\alpha n \rho_f F}$$

$$R_{film} = R_{SEI} + \frac{\delta_{film}}{K_p}$$

Side Reaction Intercalation Current $J_s$

$$J_s = -i_{0,s} a_n e^{-\frac{\alpha_F}{RT} \eta_s}$$

RCSI Submodel Identification

- Identifies submodel and state
- Uses error signals to tune submodel
- Driven by side reaction intercalation current

Without an identification technique, we have no knowledge about the battery SoH. RCSI provides us with an estimate for how the battery SoH changes as measured by the film growth. The estimates are very close to the true values. True values are not available in practice, but the estimates are accurate during the constant current charging phase when film growth is most significant.

![Graph showing film resistance over time for different charging and discharging modes: CC discharge, CV discharge, CC charge, CV charge.](image-url)

The graph illustrates the evolution of film resistance over time for different modes of charging and discharging. The estimated values are depicted by solid lines, while the true values are shown by dashed lines. The graph helps in understanding the impact of different charging modes on film growth.
RCSI works well during the constant current charging phase, because this is the only phase where battery SoH is identifiable.
Spec for LiFePO4 cells (APR18650M1) manufactured by A123 Systems.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Capacity</td>
<td>1.1Ah</td>
</tr>
<tr>
<td>Nominal Voltage</td>
<td>3.3V</td>
</tr>
<tr>
<td>Constant Voltage</td>
<td>Charging Voltage 3.7V</td>
</tr>
<tr>
<td>Power</td>
<td>3000W/Kg, 5800W/L</td>
</tr>
</tbody>
</table>

– Transforms plateaus on V-Q curve into identifiable peaks on incremental capacity curve (dQ/dV)
– Reflects the staging phenomena in lithium intercalation process
– Amplified sensitivity

• Full charging/discharging V-Q curves not available in real-life operation
• ICA performed with partially charging data
  – Numerical derivative
  – Polynomial curve fitting (5th order)

Results by numerical derivative

Results by polynomial curve fitting

• Numerical Derivative
  – Applicable to data set at any capacity range
  – Computationally expensive
  – Resulting curves are noisy

• Polynomial Curve Fitting
  – Smooth and suitable for quantitative analysis
  – Efficient identification algorithm is readily available
  – Highly sensitive to the selection of data set

• A more robust and flexible method is needed

SVR Basics:
  – Phenomenological and data driven
  – Model derived through an optimization process
  – Non-parametric function estimation
  – Excellent approximation and generalization capabilities
  – Low sparsity and model complexity

\[
f(x_n) = \sum_{i=1}^{N} \beta_i k(x_i, x_n)
\]

\[
\text{minimize } \frac{1}{2} \|\beta\|_1 + w \sum_{n=1}^{N} \xi_n,
\]

subject to
\[
\begin{align*}
y_n - \sum_{i=1}^{N} \beta_i k(x_i, x_n) & \leq \varepsilon + \xi_n \\
\sum_{i=1}^{N} \beta_i k(x_i, x_n) - y_n & \leq \varepsilon + \xi_n \\
\xi_n & \geq 0
\end{align*}
\]
• Apply the SVR algorithm iteratively as battery ages
• Robust in effective aging signature extraction

• The SVR model built upon the data from one single cell is able to predict the capacity fading of 7 other cells with less than 1% error.

Correlation identified from cell #7

Used for capacity fading prediction of other cells
• CERC-CVC is a US-China collaborative team with capabilities to address a broad range of battery-related R&D:
  – Near term: Safety, implementation, degradation, system modeling, controls
  – Future: New chemistries

• Responsive to industrial inputs and needs
3rd CERC-CVC annual meeting on August 19-20 2013 in Beijing!