

High Energy, Long Cycle Life Lithium-ion Batteries for EV Applications

Donghai Wang¹
Arumugam Manthiram²

¹The Pennsylvania State University

²University of Texas at Austin

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Project ID: ES212

Overview

Timeline

- Project Start – Oct. 01 2013
- Project End – Sep. 30 2016
- Overall % Complete: **85%**
 - FY 2016 % Complete: 60%

Barriers

- Energy/power density
- Cycle and calendar life
- Battery component compatibility
- Abuse Tolerance

Budget

Total project funding: \$2,425 K

- DOE share: \$1,940K
- Contractor share: \$485K

FY 2014: \$1,243K
FY 2015-2016: \$1,182K

Partners

- EC Power (subcontract)
- Argonne National Lab
(Zhengcheng Zhang, collaboration)
- Lawrence Berkley National Lab
(Gao Liu and Vincent Battaglia, collaboration)

Relevance

Develop a **lithium-ion battery system** with high energy density, high power density, good cycle life, and safe operation for EV applications.

Project scope

Design and Fabrication of a lithium-ion cell:

- Layered Oxide Cathode – high energy/power, stable
- Advanced Silicon Alloy-carbon Anode – high energy/power, stable
- Functional Binder – improve cyclability
- Electrolyte – stabilize electrodes and improve safety

Performance targets

2.5 Ah cells

330 Wh/kg (770 Wh/L)

1600 W/L

Cycle life 500+ cycles

Excellent safety characteristics

Project Milestones

- **Nickel-rich layered oxide cathodes**

- Realization of Ni-rich $\text{LiNi}_{0.7}\text{Mn}_{0.15}\text{Co}_{0.15}\text{O}_2$ with high tap density ($\sim 2.4 \text{ g cm}^{-3}$) in 1 kg batch with controlled particle size (up to $20 \mu\text{m}$) and narrow size distribution. (complete)
- TOF-SIMS analysis reveals a multilayered SEI, active mass dissolution products, and a rock-salt phase formation. (complete)
- Surface conditioning with Mn-rich surface or other inert coatings offers a significant improvement in full-cell cyclability for large number of cycles (up to 1,600 cycles). (complete)

- **Si alloy-carbon composite anodes**

- Design and optimization of crosslinked binders with good electrode quality and battery performance. (complete)
- Optimization and scale-up of PSU Si anode material with 150g per batch. (complete)
- Scale-up electrode manufacture with 4.3 mAh/cm^2 capacity and above 99.5 % coulombic efficiency. (complete)

- **Electrolyte**

- Improve cell safety by enhancing voltage window and electrolyte electrochemical stability. (complete)
- Develop novel fluorinated electrolytes and additives to stabilize the anode SEI, prevent electrolyte reaction at the cathode surface. (complete)

- **Full Cells**

- TOF-SIMS analysis of a full cell after 3,000 cycles reveals that the active mass dissolution severely affects graphite surface with SEI damage and Li plating. (complete)
- Full cell performance verification with PSU Si-graphite anodes paired with NCM 523 cathodes. (complete)
- Prelithiation increases the 1st cycle efficiency to 80% in the full cells. (complete)
- Optimization of the anodes, cathodes, electrolyte and prelithiation for full cells. (in progress)
- Pouch cell fabrication, evaluation and delivery. (in progress)

Approach / Strategy

- **Nickel-rich layered oxide cathodes**

- A co-precipitation method with a continuously stirred tank reactor (CSTR) to obtain Ni-rich layered oxides with controlled composition and surface structure.
- Advanced characterization techniques (e.g., TOF-SIMS, XPS, and HAADF-STEM) with half and full cells to understand the degradation mechanisms.
- Four surface modification methods to realize a robust cathode-electrolyte interface and realize long-term cyclability with full cell.

- **Si-alloy carbon composite anodes**

- Design micro-sized Si anode materials with carbon coating to enable both good electrochemical performance and high tap density.
- Construct conductive network at the electrode level to achieve high areal capacity.

- **Functional binders**

- Prepare cross-linked binders to form interpenetrated conductive network to accommodate volume change of Si and improve integrity of Si electrodes.

- **Electrolytes**

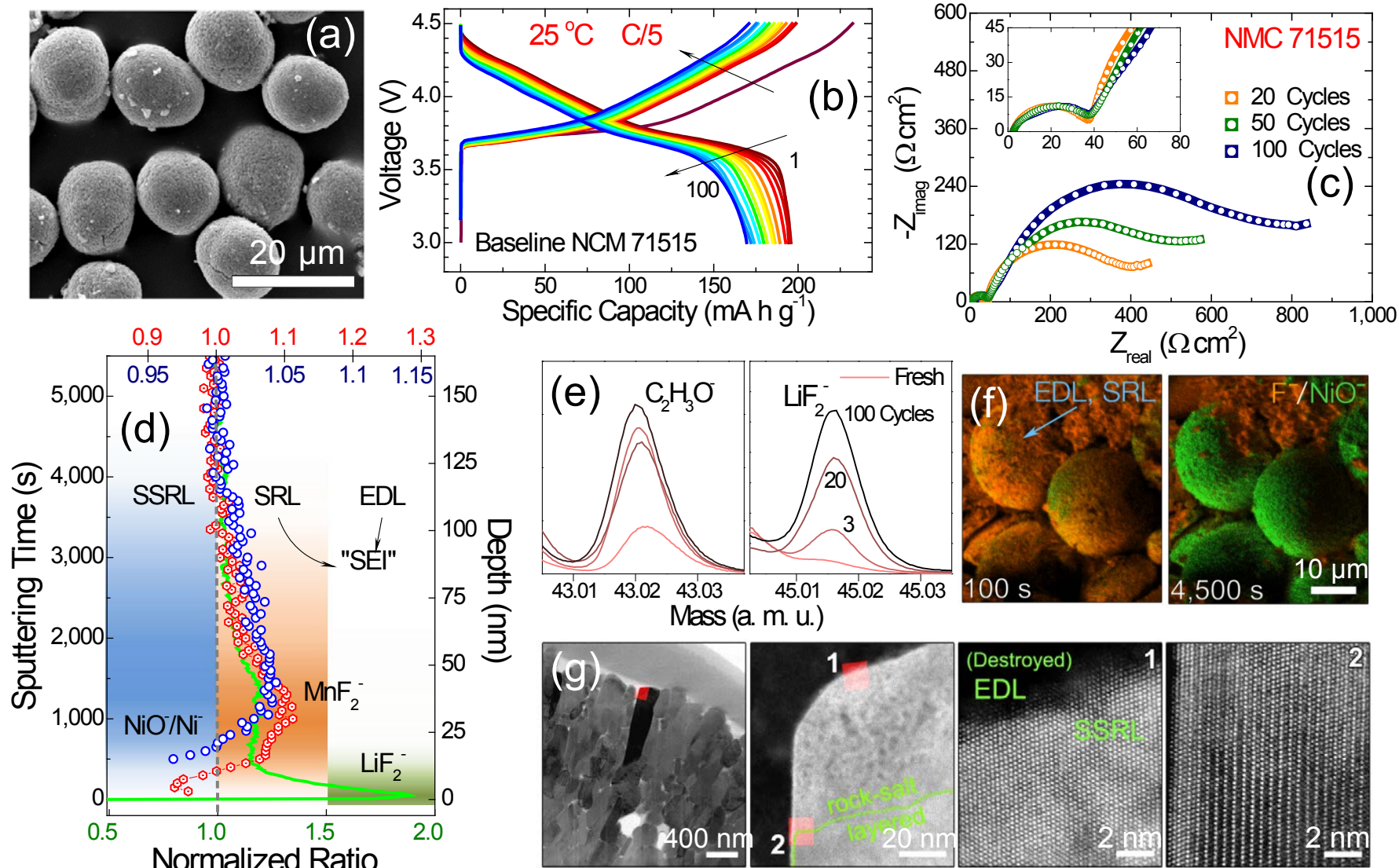
- Design fluorinated compounds as electrolyte solvents with intrinsic oxidation stability, non-flammability and capability of solid electrolyte interphase formation on the anode.

- **Prelithiation**

- Apply prelithiation at pouch cells using solid Li metal particles to improve cycling efficiencies

Technical Accomplishments

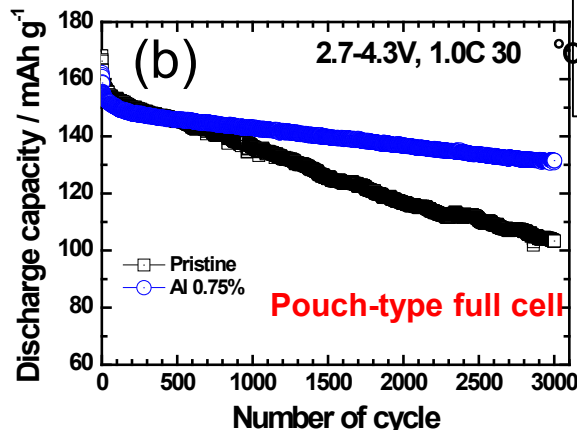
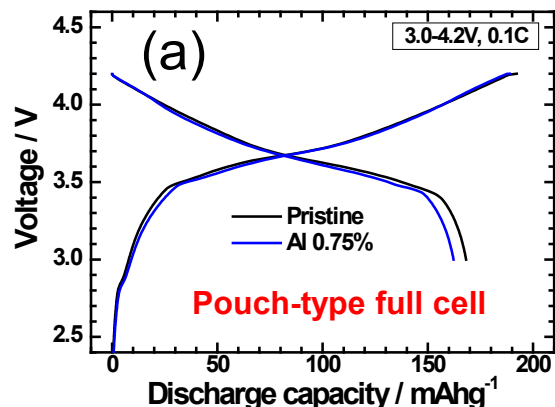
I. Degradation of Ni-rich $\text{LiNi}_{0.7}\text{Mn}_{0.15}\text{Co}_{0.15}\text{O}_2$



EDL: electrolyte decomposition layer; **SRL:** surface reaction layer; **SSRL:** surface structural reorganization layer

Technical Accomplishments

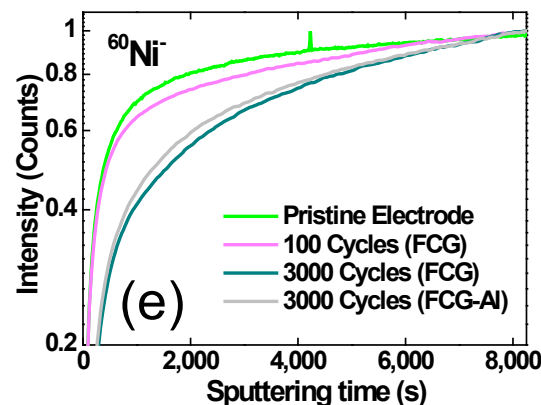
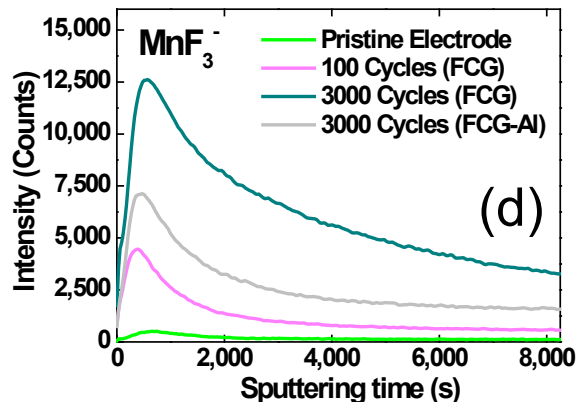
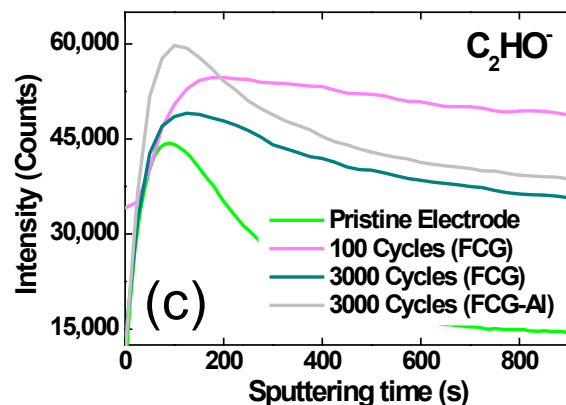
II. ToF-SIMS of cycled Ni-rich cathode (3000 cycles)



Cycled electrodes from Prof. Yang-Kook Sun, Hanyang Univ.

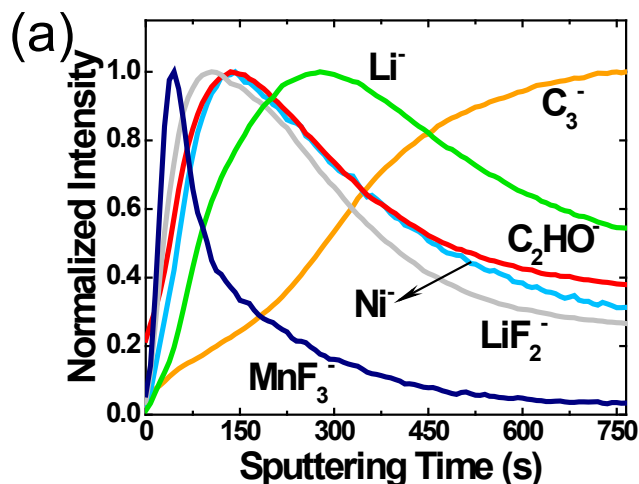
- The organic surface deposits do not show substantial buildup as cycling proceeds (30 °C), while the corrosion products continuously accumulate

Sample	0.1C, 1 st Discharge Specific Capacity	1 st Efficiency	1C, 1 st Discharge Capacity	1C Cycle Retention
FCG	168.1 mAh/g	87.5 %	19.31 mAh	65.1% (3000 th)
FCG-Al doped	162.2 mAh/g	85.9 %	17.31 mAh	83.2% (3000 th)



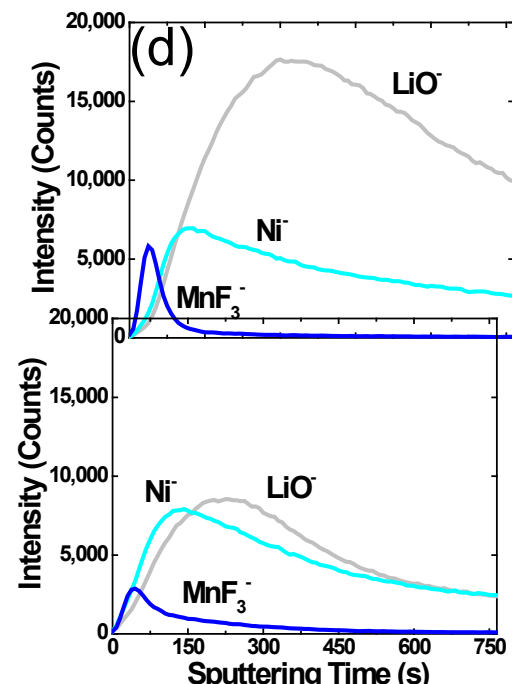
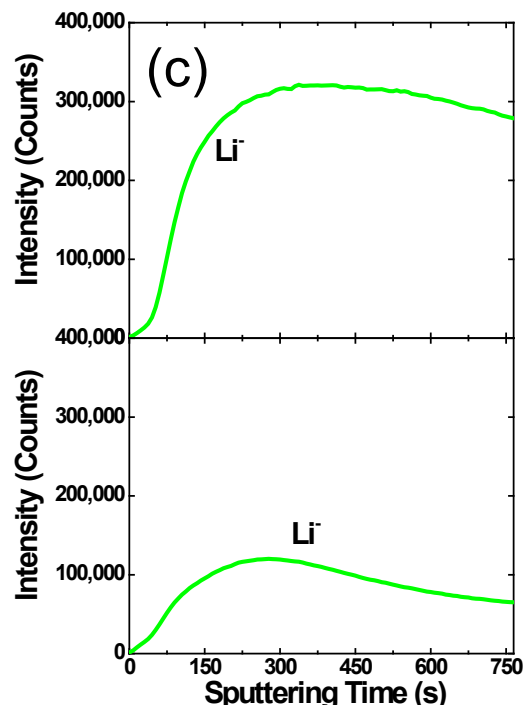
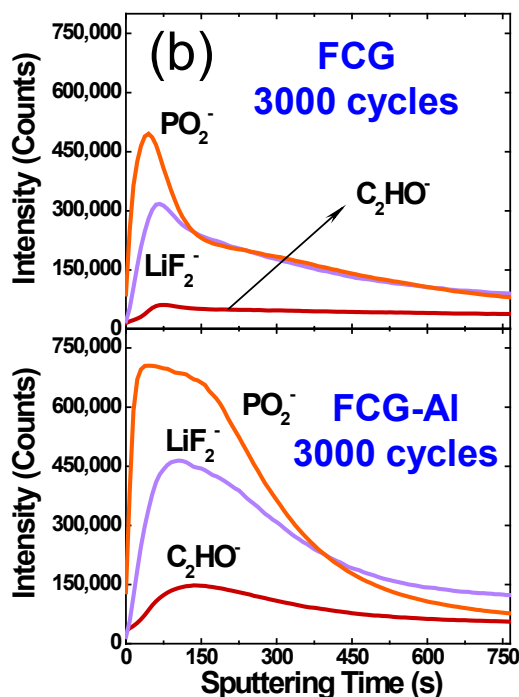
Technical Accomplishments

III. ToF-SIMS of cycled graphite anode (3000 cycles)



Cycled electrodes from Prof.
Yang-Kook Sun, Hanyang Univ.

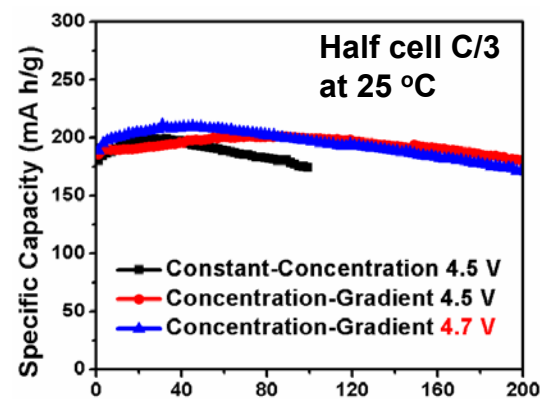
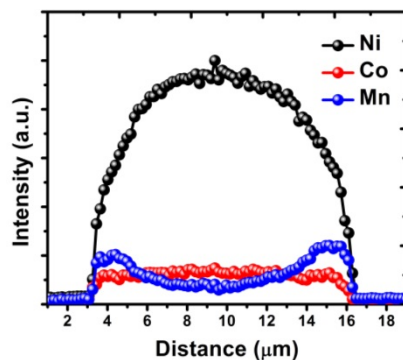
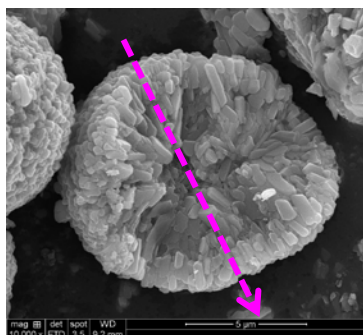
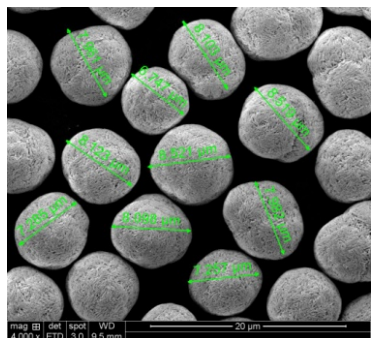
- Cycled graphite also exhibits multilayer feature
- Al-doping reduces the amount of dissolution products from the cathode on the graphite surface, SEI damage, and Li plating



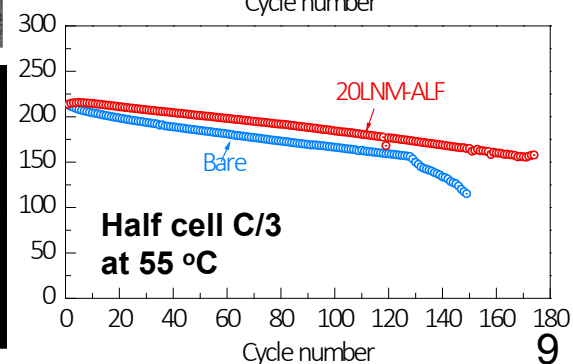
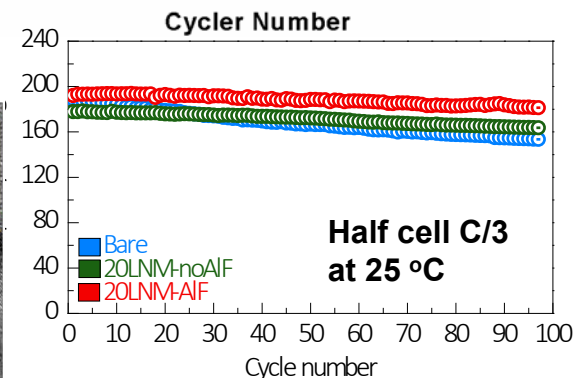
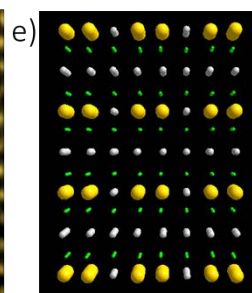
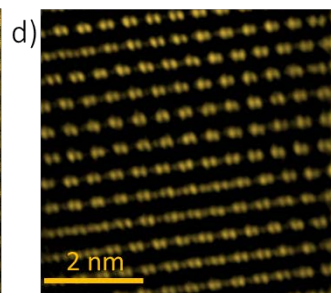
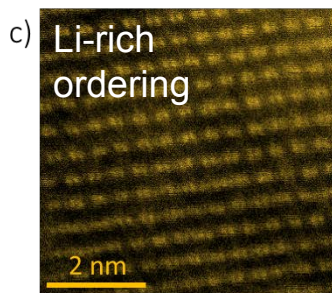
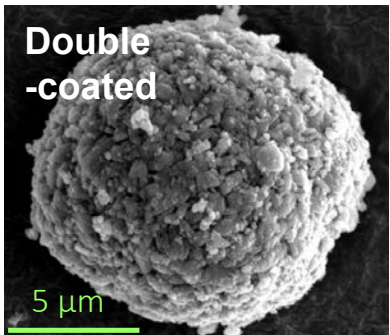
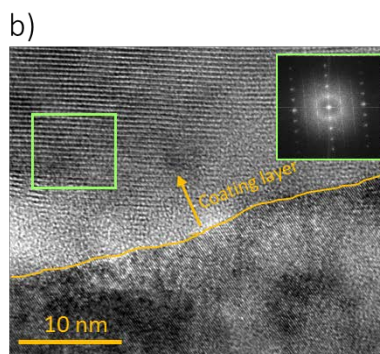
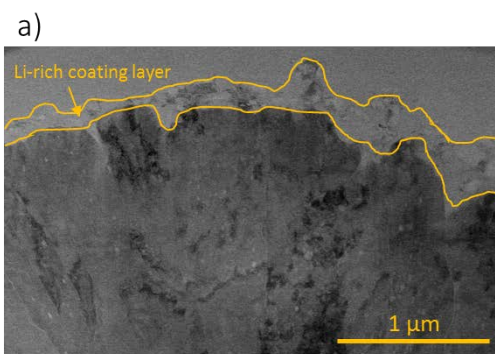
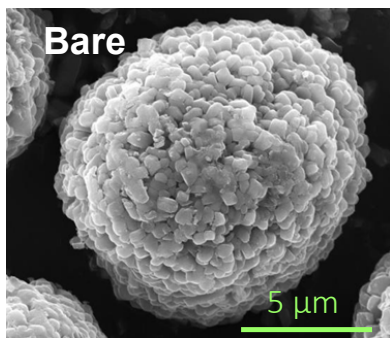
Technical Accomplishments

IV. Strategies to enhance cyclability-I

1. Concentration gradient with Ni-rich core and Mn-rich surface: $\text{LiNi}_{0.75}\text{Co}_{0.10}\text{Mn}_{0.15}\text{O}_2$



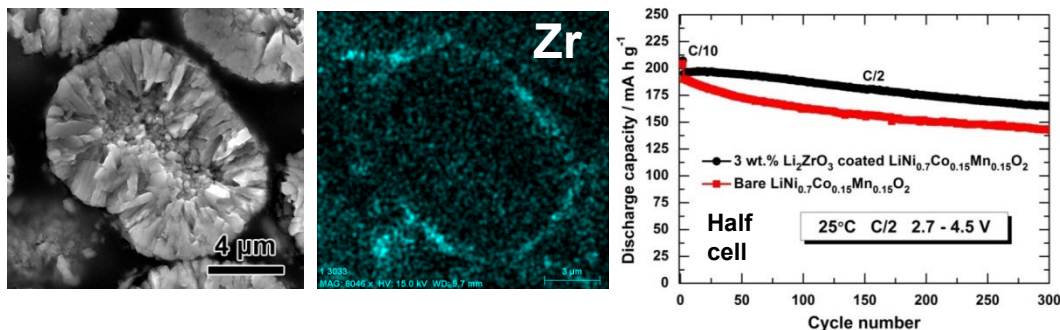
2. Double-coated $\text{AlF}_3@\text{Li}_2\text{MnO}_3@\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$



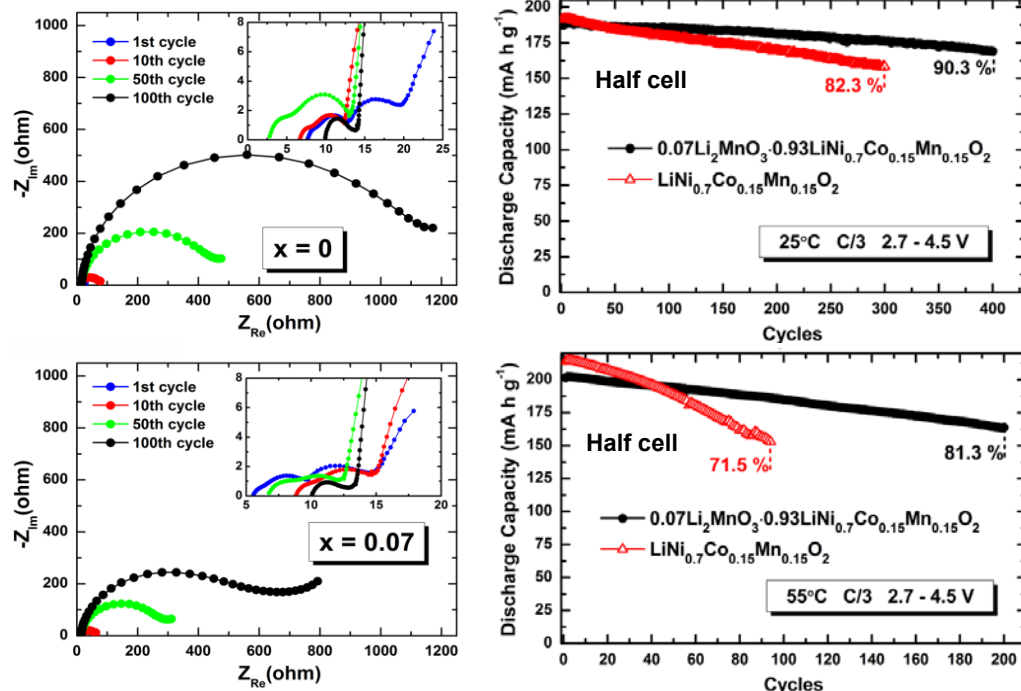
Technical Accomplishments

IV. Strategies to enhance cyclability-II

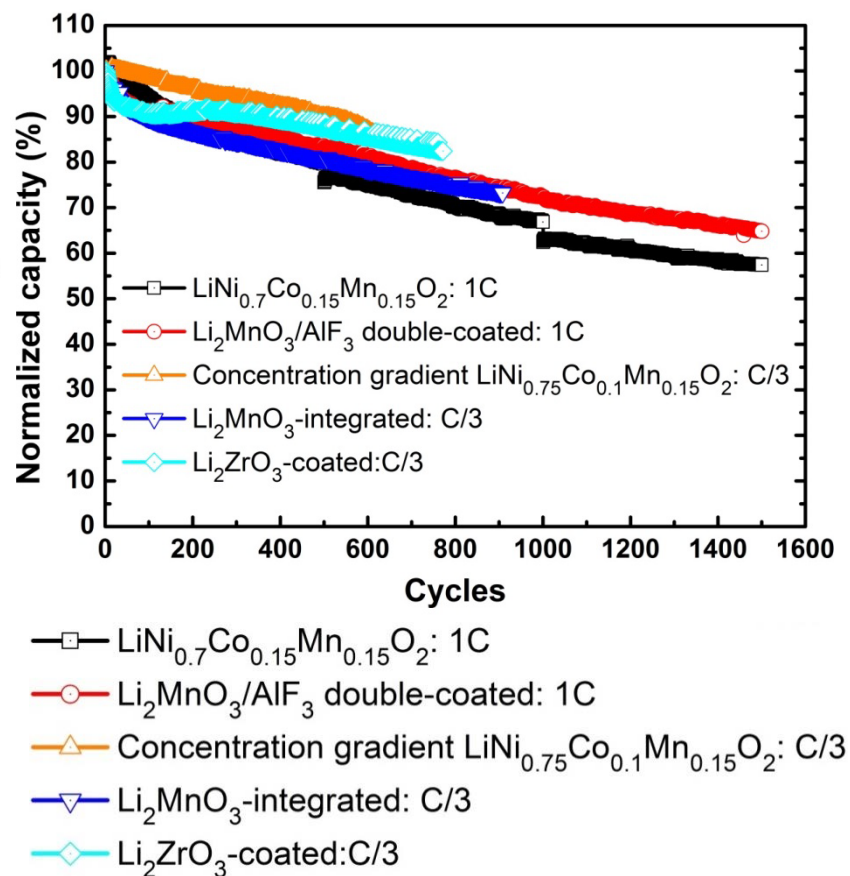
3. Li_2ZrO_3 -coated $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$



4. Li_2MnO_3 -integrated $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$



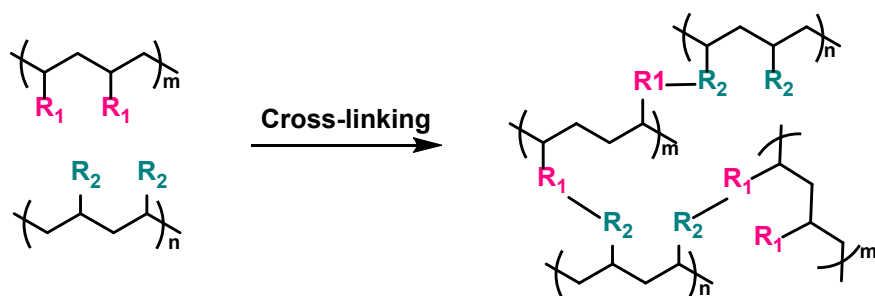
Long-term full-cell cyclability



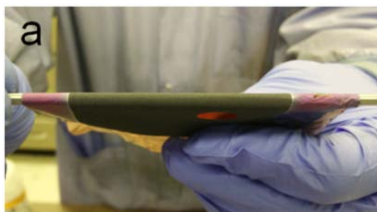
Good long-term cyclability has been achieved with surface-controlled Ni-rich cathodes in pouch-type full cells

Technical Accomplishments

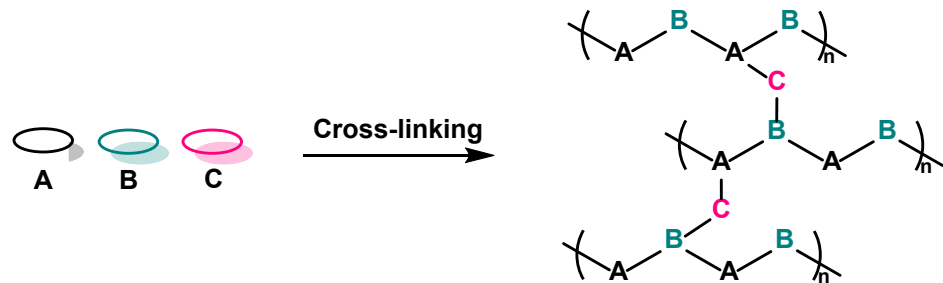
V. Cross-linked binders enabling fabrication of high quality Si anodes with good performance



PSU Si with binder I



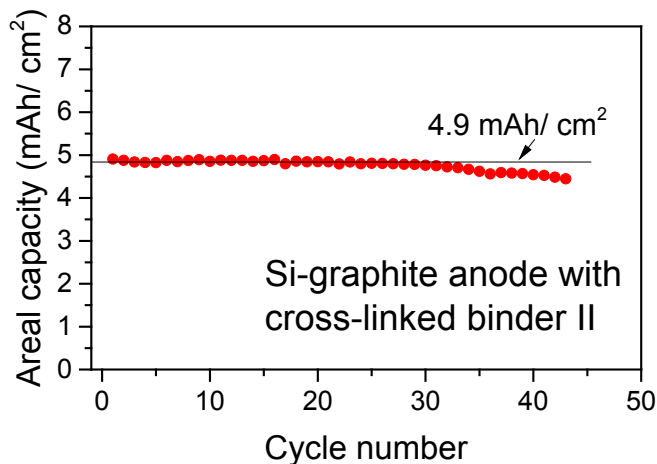
Mass loading limit: 4 mg/cm^2



PSU Si with binder II



Target: 5.8 mg/cm^2



Electrode information: Si-Graphite anode

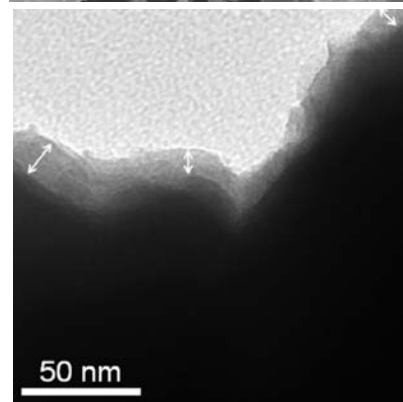
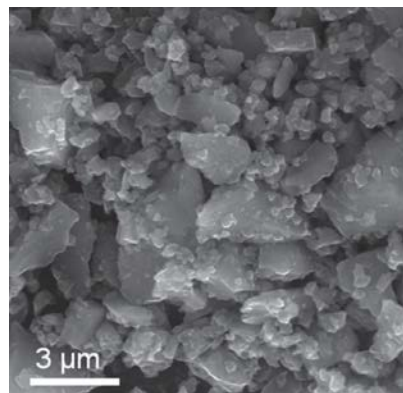
Electrode capacity
excluding current collector: 850 mAh/g

Mass loading: 5.8 mg/cm^2

Binder: PSU binder II

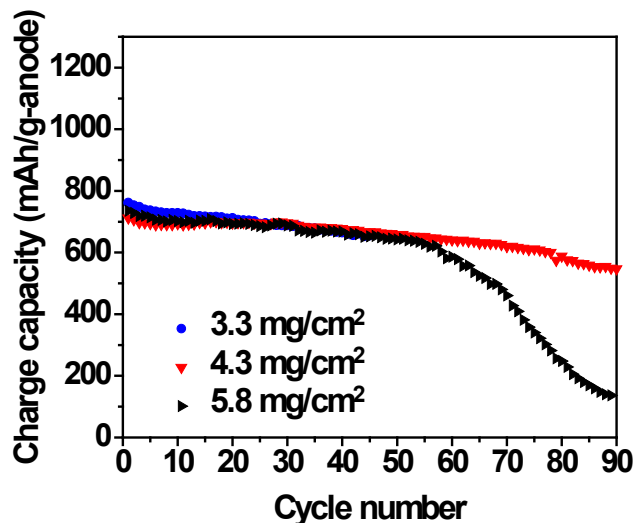
Technical Accomplishments

VI. PSU Si material scale up and electrode optimization

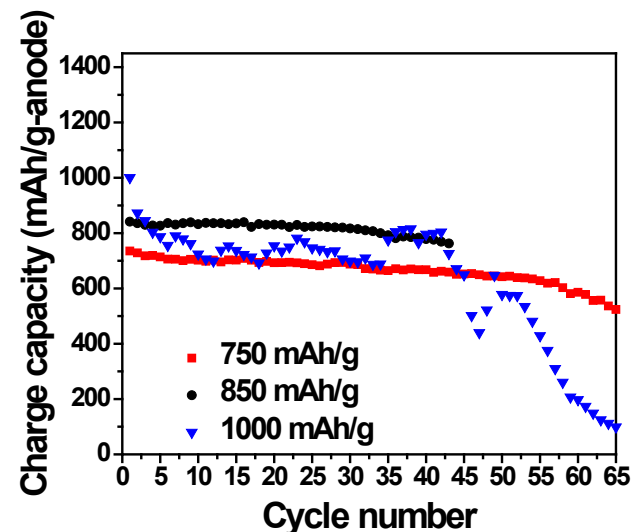


100 g/batch

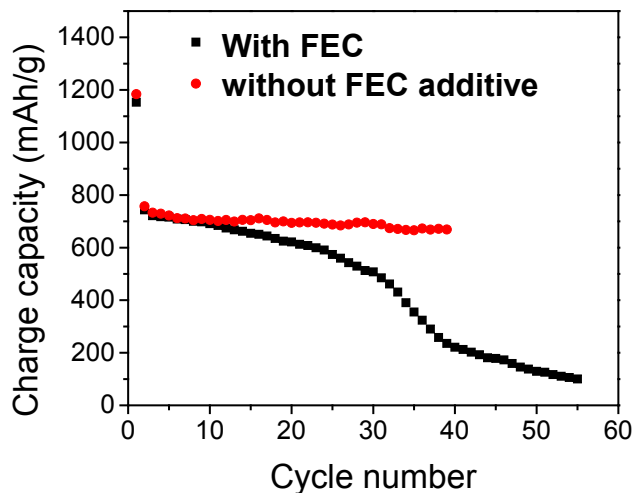
PSU Si-graphite anodes (750 mAh/g)



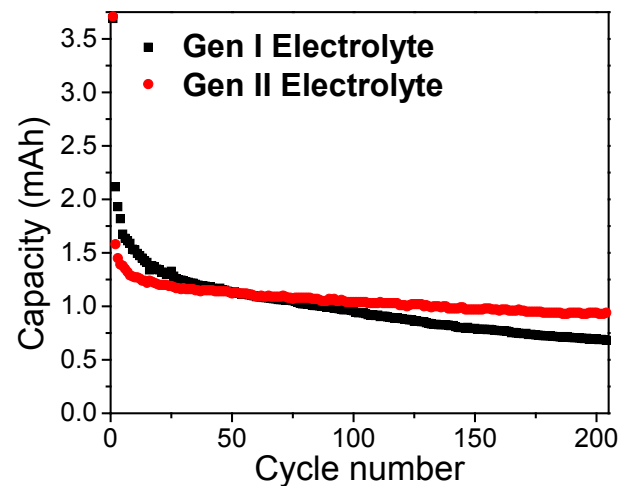
PSU Si-graphite anodes (5.8 mg/cm²)



PSU Si-graphite anodes
(750 mAh/g, 4.3 mg/cm²)



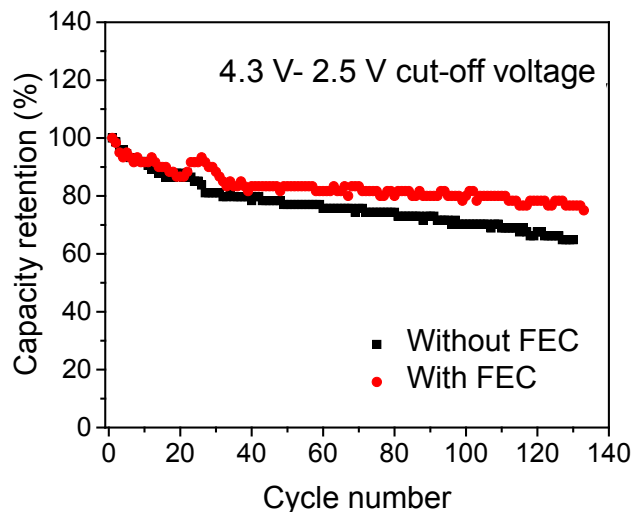
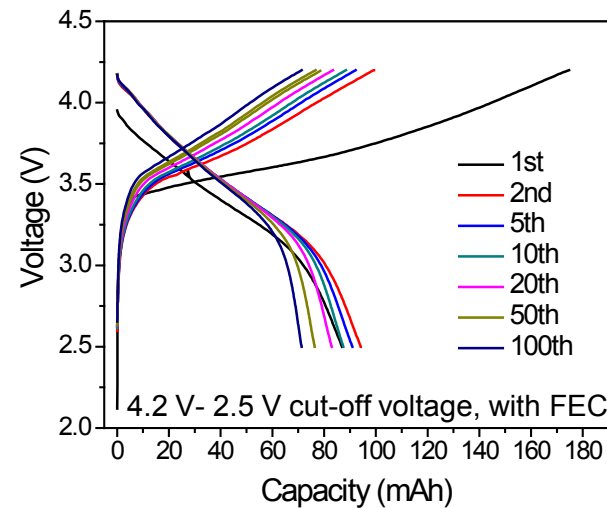
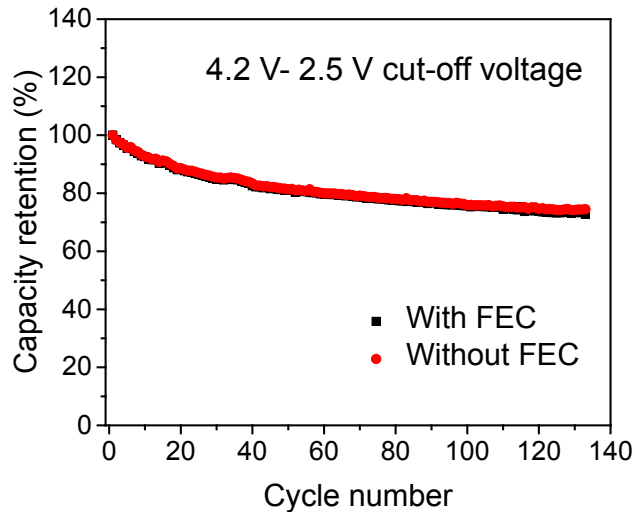
PSU Si-graphite anodes with NCM523
(coin cells, 750 mAh/g, 4.3 mg/cm²)



Technical Accomplishments

VII. Performance verification and optimization in pouch-type full cells

- NCM523 cathode – PSU Si-graphite anode with a specific capacity of 750 mAh/g



Cell information:

Voltage: 4.2 / 4.3 V – 2.5 V

Current: 100 mA/g

Size: 4.4 * 5.6 cm

N/P ratio: 1.2

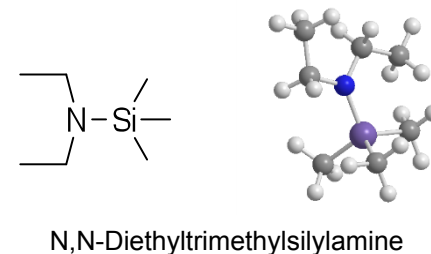
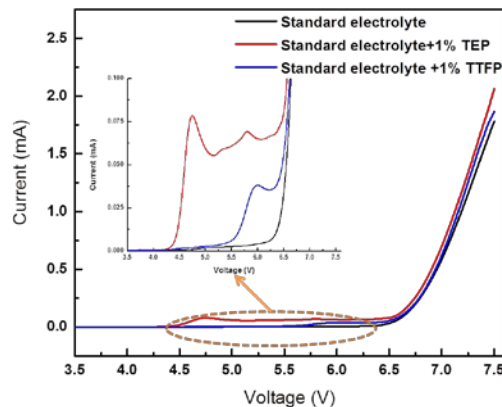
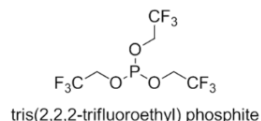
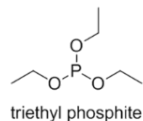
Remaining issues:

Low 1st cycle efficiency of 58%

Optimization of N/P ratio

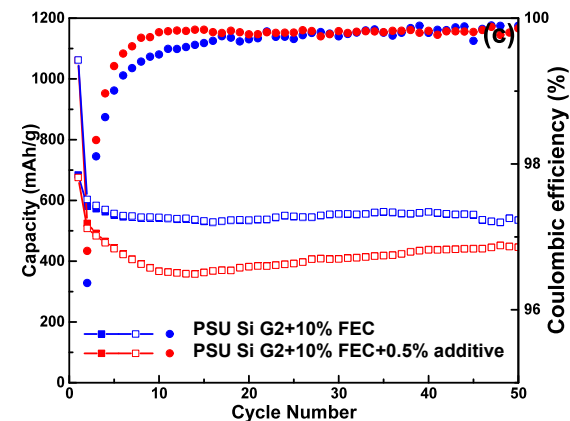
Technical Accomplishments

VIII. Electrolyte additive development



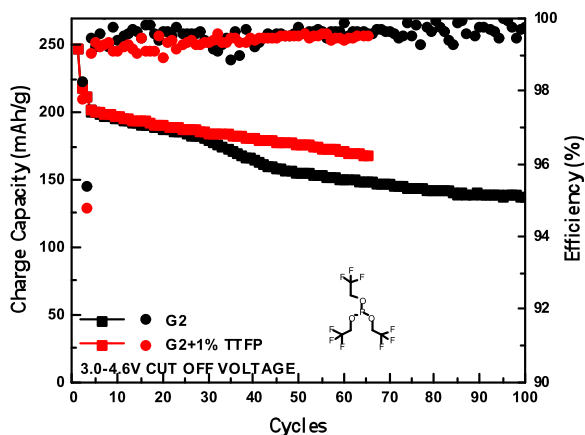
Structural formulas for TEP and TTFP additives.

Oxidation decomposition of TEP and TTFP additives.

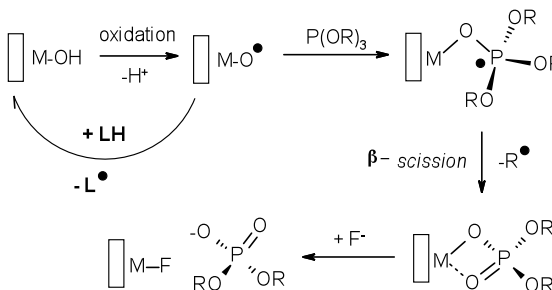


Capacity retention of ANL electrolyte additive on PSU Si/C anode.

- 1.0 M LiPF₆ EC/EMC 3/7 +10% FEC+0.5% Additive
- Si-C/Li half cell
- specific capacity is based on total electrode weight

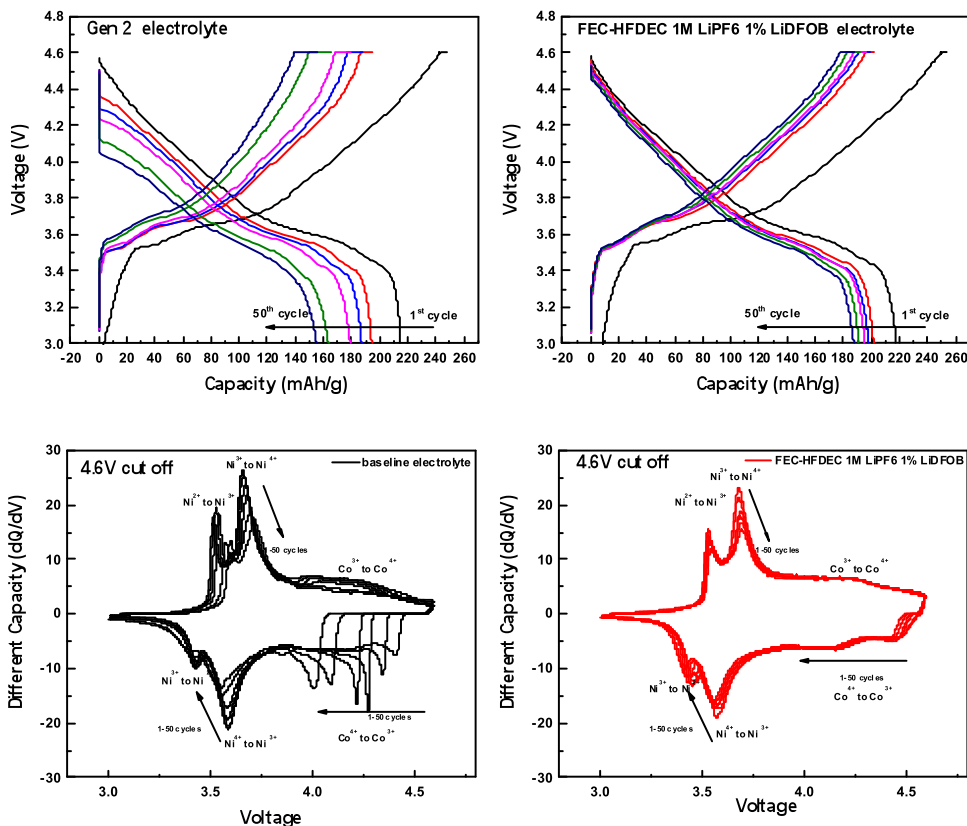


TTFP additive impact on capacity retention of NCM/Li cell. Proposed electrocatalytic cycle of TTFP.

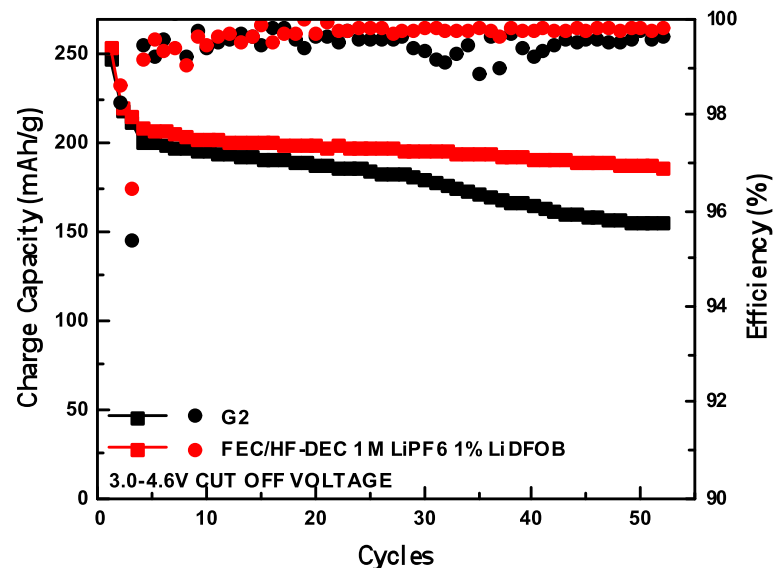


Technical Accomplishments

IX. Fluorinated electrolyte development with expanded voltage window and improved performance



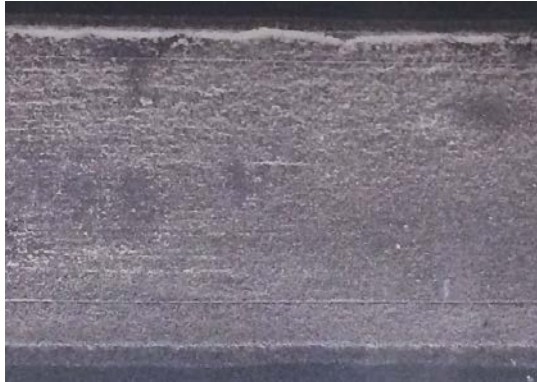
Charge and discharge voltage profiles and dQ/dV data of the optimized FEC/HF-DEC/LiPF₆ electrolyte in a NCM523/graphite full cells.



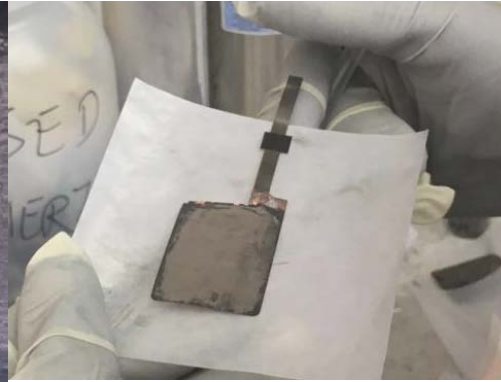
Comparison of capacity retention of the NCM523/graphite cells in G2 electrolyte and fluorinated electrolyte cycled between 3.0-4.6 V.

Technical Accomplishments

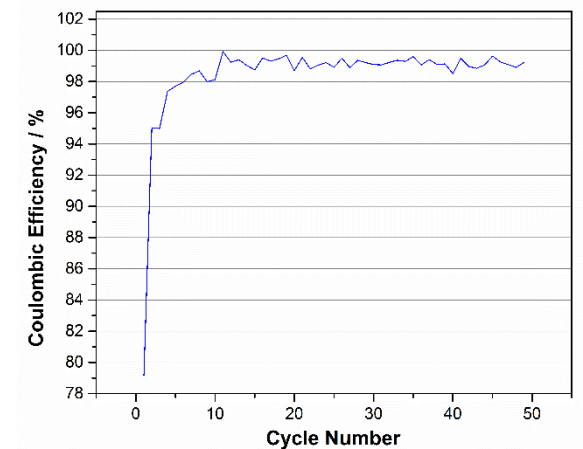
X. Prelithiation



12cm x 20cm SLMP coated
graphite electrode



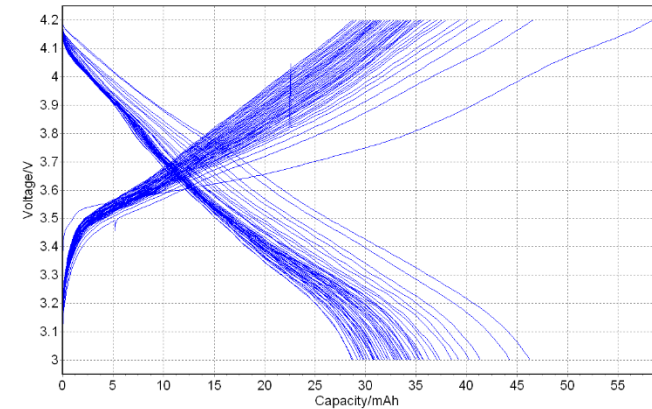
SLMP coated Si based
electrode 3cm x4cm



Coulombic efficiency of prelithiated full cell

	Cell#	Loading (mg/cm ²)	Test Procedure	Theoretical Capacity (mAh/g)	Current (mA)	Electrolyte
Cathode	NMC	36.759	0.05C 2 cycles then 0.1C	150	2.569 for 0.05C & 5.138 for 0.1C	1M LiPF ₆ , EC/DEC 30%FEC
Anode	PSU Si	10.619	0.05C 2 cycles then 0.1C	1000	2.569 for 0.05C & 5.138 for 0.1C	1M LiPF ₆ , EC/DEC 30%FEC

Electrodes configuration



Capacity-voltage curve of prelithiated full cell

Response to Reviewer Comments

Comment: “With 500 mAh/g and 3 mAh/cm² the capacity or loading are not outstanding, it is recommended to address the potential of the Si-C approach towards higher capacities and the interaction with cycle life.”

Response: We have focused on development of anode with 750 mAh/g and 4.2 mAh/cm² and demonstrates its cycling performance in pouch-type full cells.

Comment: “The reviewer questioned that the high degradation of the cathode material down to 100 mAh/g at C/3 discharge rate after 500 cycles is critical, ...and it is recommended to look in detail on the effect causing this degradation. ”

Response: We have used advanced characterization techniques (e.g., TOF-SIMS, XPS and HAADF-STEM) to understand the degradation mechanism.

Comment: “The reviewer recommended prioritizing which action items give the highest output in a short time, and the highest benefit to approach the target on cell level.”

Response: We have focused on evaluation and optimization at full cell level for each cell component (e.g., the cathode, anode, binder and electrolyte) and process (e.g., prelithiation) aiming to approach the technical target at pouch cells.

Collaboration

- Working with EC Power on design, development and testing of pouch cells.
- Working with Argonne National Laboratory on concurrent electrolyte additive development and testing for both cathodes and anodes.
- Working with Lawrence Berkeley National Laboratory on prelithiation of Si anodes and pouch cell testing.
- Independent testing of pouch cells is being conducted by Idaho National Lab.

Remaining Challenges and Barriers

- The cyclability of Ni-rich cathodes needs to be improved while keeping the capacity above 200 mAh/g
- Elevated temperature (e.g., 55 °C) cycle performance needs to be improved
- Safety concerns regarding thermal runaway needs to be overcome
- Further surface optimization coupled with advanced characterization methodologies could help overcome the remaining problems in cathodes
- Key challenges in anode are to improve the 1st cycle efficiency, cycling efficiency and cycling stability of PSU Si-graphite anodes at high mass loading in full cells.
- Compatibility between electrolytes containing various additives and both cathodes and PSU Si anodes needs to be further investigated to improve cycling stability of electrodes and full cells.

Proposed Future Work

- Understand the role of carbon additives during the formation and evolution of cathode interphases, which is crucially related to the cell performance
- Develop further understanding of the composition-structure-performance relationship to mitigate the thermal runaway issue
- Further increase specific capacity of Si anode while maintaining good cycling efficiency and stability in high mass-loading anodes in full cells
- Using prelithiation techniques to solve the low 1st cycle efficiency issue and improve cycling stability
- The final surface-stabilized Ni-rich cathodes will be coupled with optimized PSU Si anode and electrolytes in full cells to enhance the energy density while maintaining the cycle life

Summary

- Ni-rich layered oxide cathodes with optimized particle size and surface structure along with high tap density ($\sim 2.4 \text{ g cm}^{-3}$) have been produced in large quantity (1 kg per batch).
- A comprehensive understanding of the surface degradation of the cathode and graphite anode during cell cycling has been developed by employing in-depth TOF-SIMS analysis.
- Good cyclability up to 1,600 cycles with pouch-type full cells has been demonstrated with surface-controlled Ni-rich layered oxide cathodes.
- Crosslinked binders enable good electrode quality at high mass loading and cell performance for Si-based anodes.
- PSU Si anode materials scale up and optimizations of the specific capacity, mass loading, electrolyte and additive in the full cells.
- Full cell performance verification of PSU Si-graphite anodes in pouch cells.
- Development of FEC-HF DEC electrolyte and other electrolyte additives to improve stability of cathode and anode, and cycling performance of full cells.
- Prelithiation of PSU Si-graphite electrodes has increased the 1st cycle efficiency to 80% in pouch-type full cells.