TAILORING INTEGRATED LAYERED AND SPINEL ELECTRODE STRUCTURES FOR HIGH CAPACITY LITHIUM-ION CELLS

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Project ID # BAT049

Overview

Timeline

- Start date: FY16
- End date: FY18
- Percent complete: 75%

Budget

- Total project funding: 100% DOE
- FY17 Funding:
  - Composite Electrodes: $500K
  - Spinel Components: $500K

Barriers

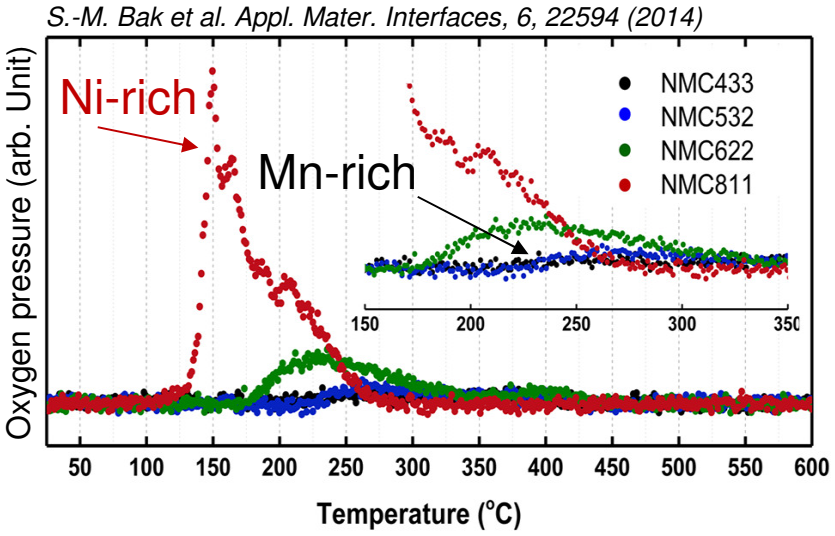
- Low energy density
- Cost
- Abuse tolerance limitations

Partners

- Lead PI: Michael Thackeray, Co-PI: Jason Croy
- Collaborators:
  - CSE, Argonne: Eungje Lee, Arturo Gutierrez, Meinan He, Roy Benedek, John Zhang
  - APS, Argonne: Mali Balasubramanian (XAS), Yang Ren (XRD)
  - CNM, Argonne: Jie Wang (TEM)
  - Northwestern University, NUANCE: Vinayak Dravid, Jinsong Wu (TEM)
  - ORNL: Harry Meyer, Rose Ruther (XPS)
  - Industry: Argonne licensees and collaborators

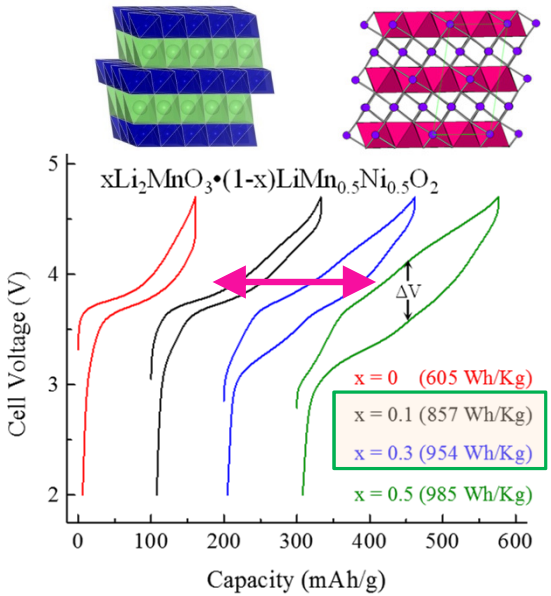
Relevance

Safety



High manganese linked to thermal stability

Energy



>900 Wh/kg possible with Li/Mn-rich materials

Cost (supply/demand)

A shift of just 10% of the global car fleet to EVs would create demand for 400,000 tonnes of nickel, in a 2 million tonne market. Glencore sees nickel shortage as EV demand burgeons

– Ivan Glasenberg, Glencore CEO

Safety, Cost, Energy, Supply and Demand could be critical issues for Ni/Co chemistries
– Mn-rich alternatives may provide competitive, necessary, future options

Milestones

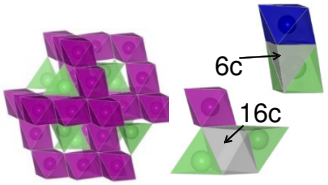
- Explore the energy content, and stabilization thereof, of moderate Li_2MnO_3-content (25%<x<50%) $y[xLi_2MnO_3 \bullet (1-x)LiMO_2] \bullet (1-y)LiM_2O_4$ (M=Mn, Ni,Co), layered-layered and layered-layered-spinel electrodes; target capacity ≥220 mAh/g. **Complete/ongoing.**

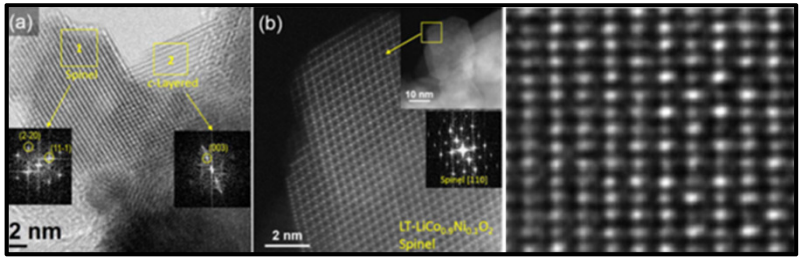
- Identify surface-treatment strategies that enable layered-layered-spinel electrodes to maintain high capacities (≥220 mAh/g) and high rate performance (~200 mAh/g at 1C). **Achieved/ongoing.**

- Demonstrate oxide energy densities ≥750 Wh/kg_{oxide} in full-cell testing of surface-modified, layered-layered-spinel electrodes. **Achieved.**

Approach

- Exploit the concept and optimize the performance of ***structurally-integrated*** "composite" electrode structures with a prime focus on "layered-layered-spinel" (LLS) materials.





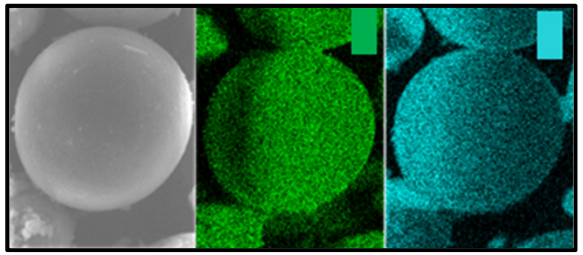
Compatibility of cubic-close-packed planes

Complex, integrated, layered-layered-spinel structures

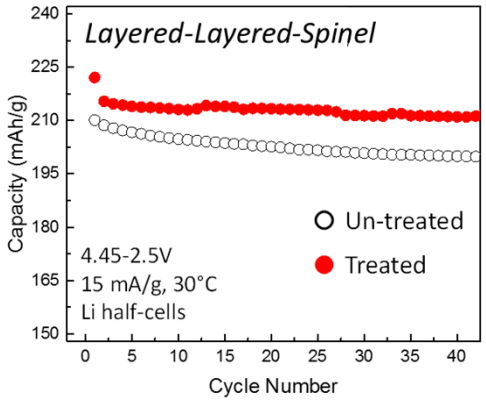
Enable:

1. High first-cycle efficiencies
2. Enhanced rate performance
3. Relative stability

- Design effective strategies to ***mitigate surface degradation*** of integrated structures to improve and maintain their stability and rate capability when charged to high potentials (4.5-4.6 V).



Novel surface treatments for LLS

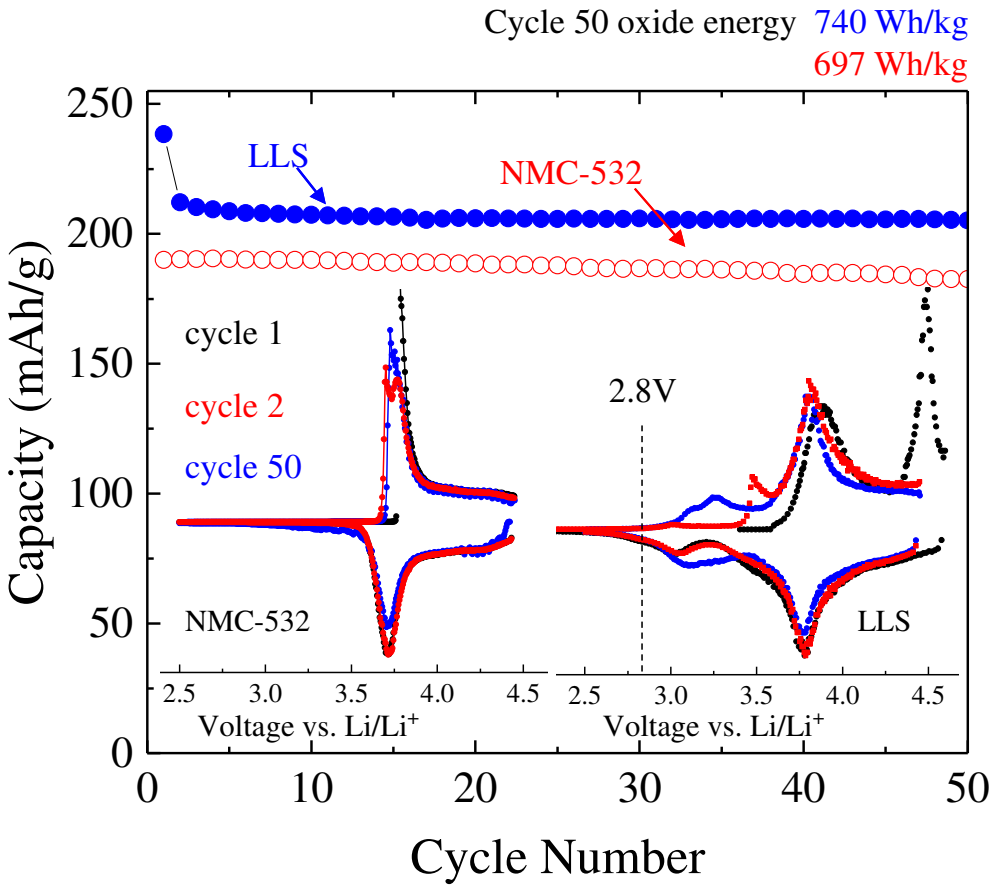


Unique surface modifications of layered-layered-spinel particles

Enable:

1. High capacity retention
2. Low impedance rise
3. Improved rate performance

Development of Mn-Rich Layered-Layered-Spinel

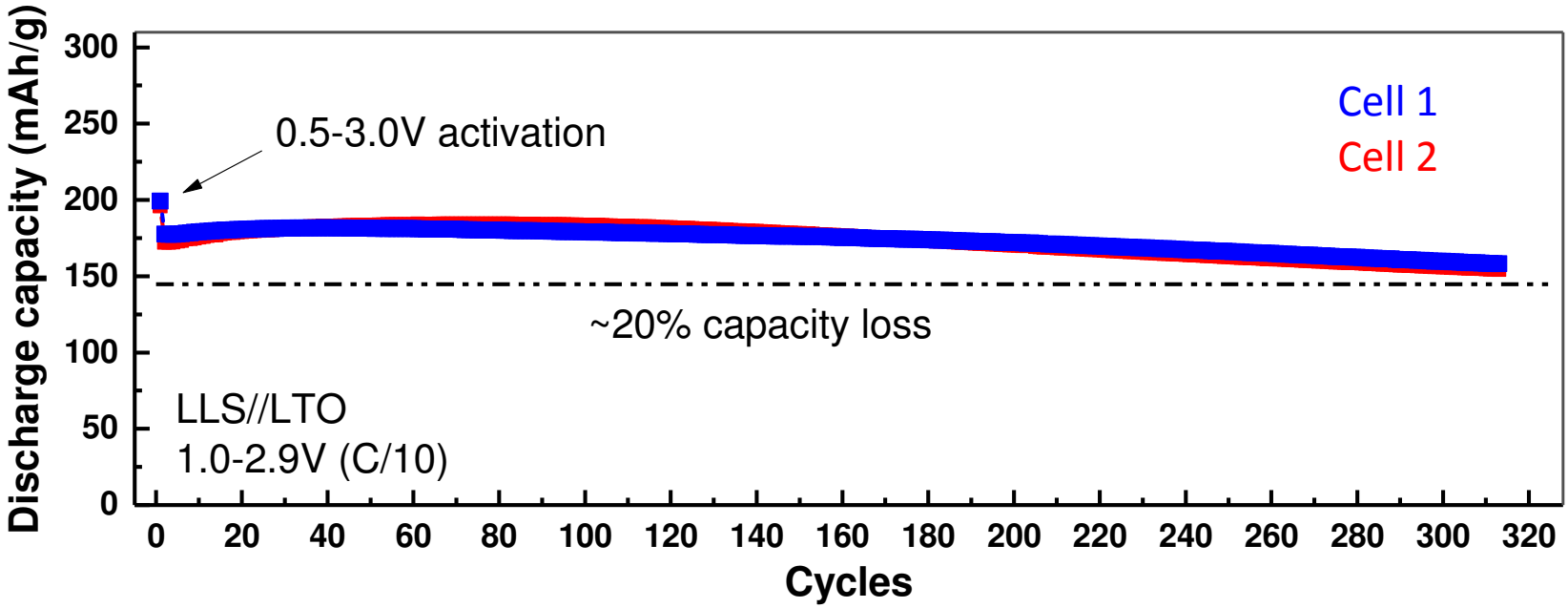


ANL-developed, Mn-rich LLS composition

- *First-cycle efficiencies of **~95%***
- *Oxide energies of **~750 Wh/kg** at <4.5V$_{Li/Li+}$*
- *>200 mAh/g of stable capacity between ~2.8-4.45V$_{Li/Li+}$*
- *Outperforms Ni-rich, NMC-532 in both capacity and energy under tested protocols (half-cells, 30°C, ~C/15)*

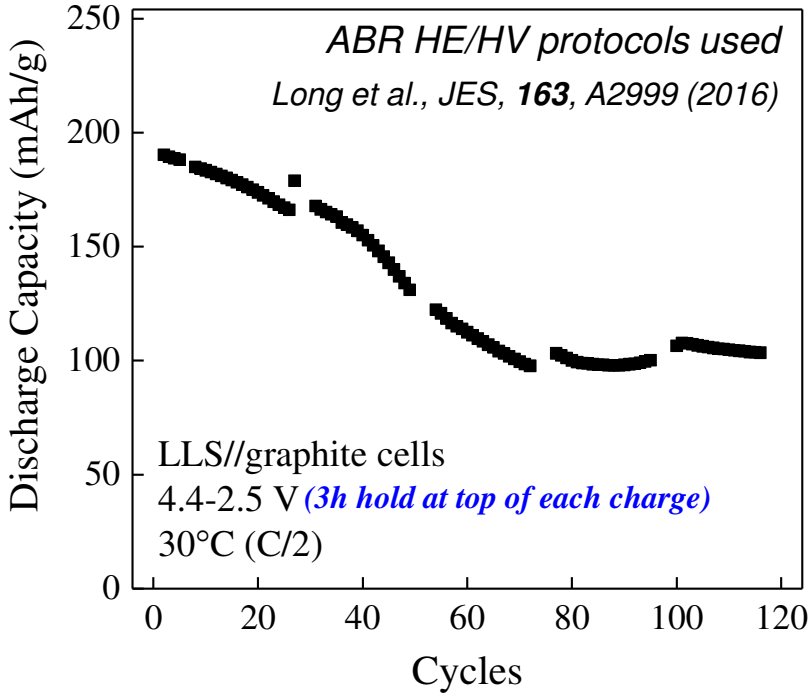
- Small-scale testing against NMC-532 cathodes shows that the LLS materials are promising options
- Baseline material developed establishes platform to build on with high oxide-specific energy, high efficiency, and stability competitive with Ni-rich, layered, NMC-532

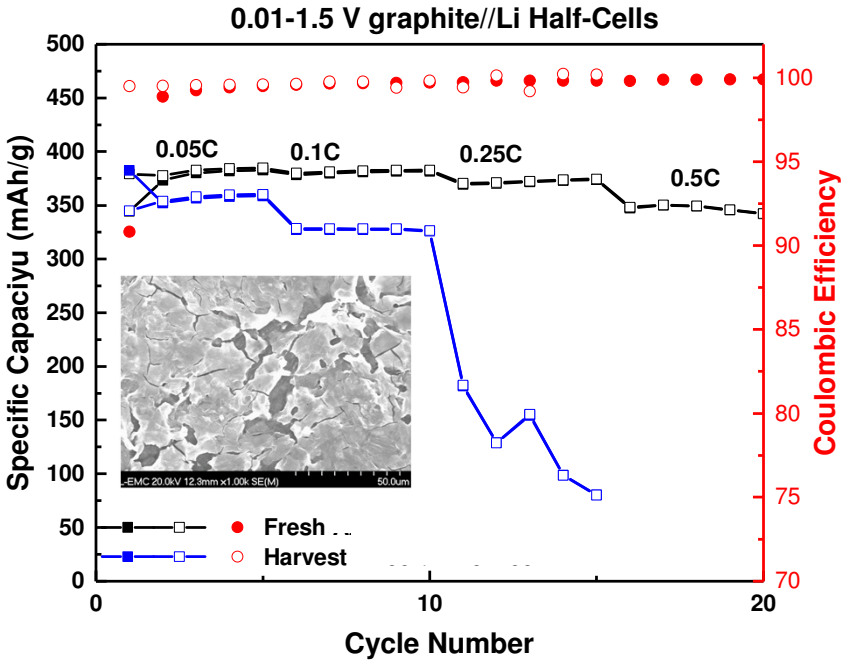
Development of Mn-Rich Layered-Layered-Spinel

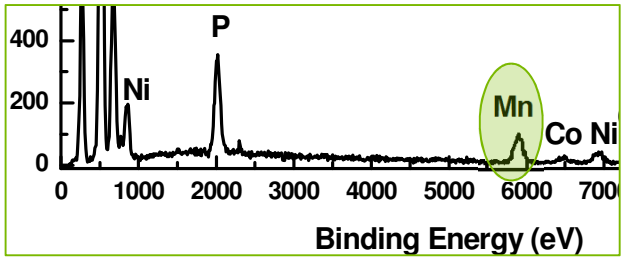


- Using LTO as the anode greatly mitigates deleterious side reaction that can cause capacity fade in graphite-based cells or impedance rise in Li-metal cells where LTO is also of practical interest
- Testing of layered-layered-spinel baseline in "full-cell" LLS//LTO configurations verifies stability of cathode to lithium extraction/insertion where the LLS is the source of Li
- ~350 cycles (~180 mAh/g, 4.45$V_{Li/Li+}$) achieved in LLS//LTO coin-cells before ~20% loss

Identification of Critical Surface Issues





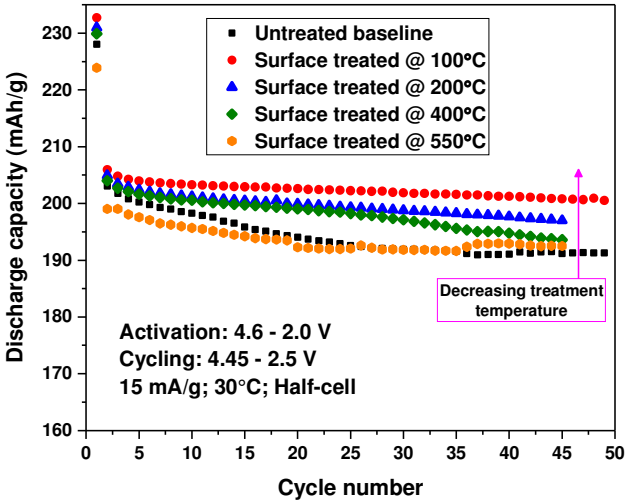


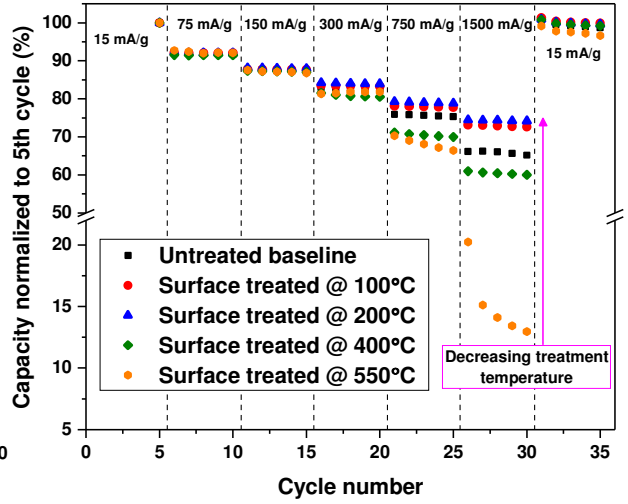
- Cycling with graphite anodes reveals large capacity fade under harsh cycling protocols
- SEM characterization shows damaged graphite with high Mn content and poor rate capability, ***top right*** (cathode rate was virtually unaffected – *not shown*)
- Occurs even with some surface treatments that improve LLS//Li-metal cells → tailored surfaces are needed to mitigate Mn dissolution – major factor in LLS//Gr degradation

Stabilization of Surfaces: Chemical Modification

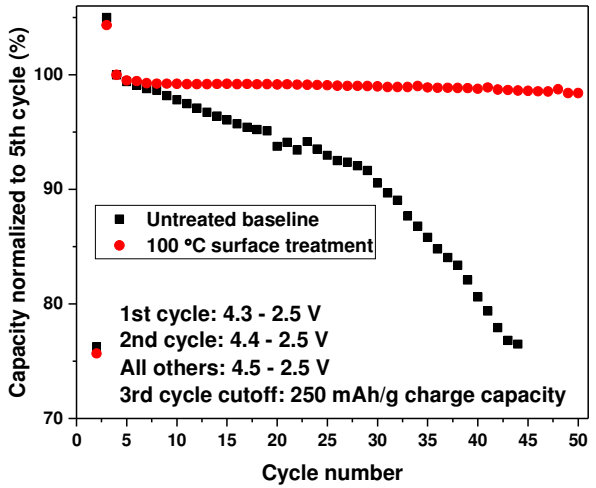
Technical Accomplishments

Capacity retention and Rate performance

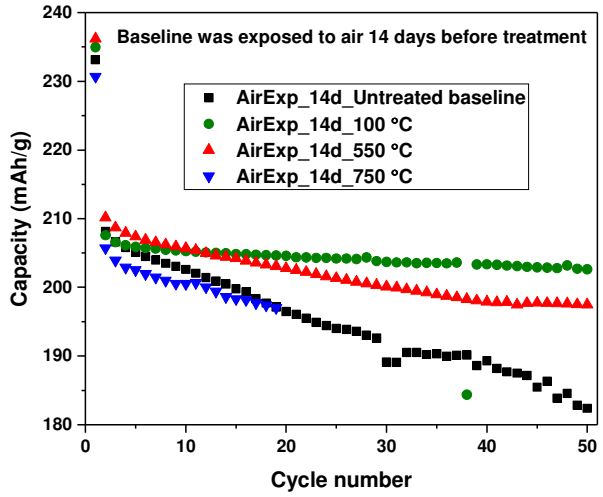




Harsh cycling conditions



Poor storage conditions



For LLS, Li/Mn-rich surfaces, lower processing temperatures:

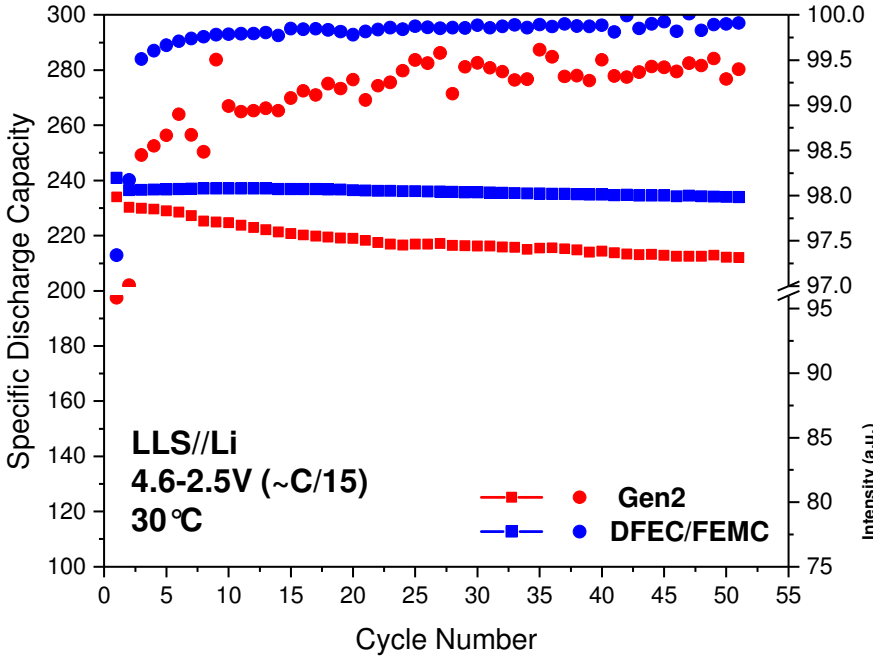
- Improve capacity retention
- Improve rate performance at high rates
- Perform better even under harsher cycling conditions
- Are effective even when storage conditions are poor
- Examples given are Al-based treatments but…
- Phosphates, oxides, and fluorides also processed *(ongoing)*

Solution stoichiometry & post-annealing must be tailored to cathode composition – all treatments are not equal on all compositions, or in graphite cells, but stabilized high-rate surfaces are possible

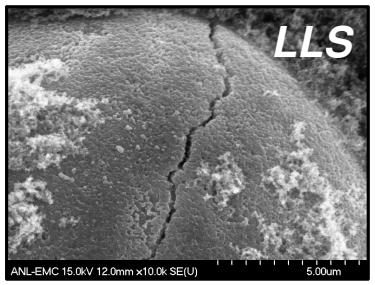
Stabilization of Surfaces: Electrolytes

Technical Accomplishments

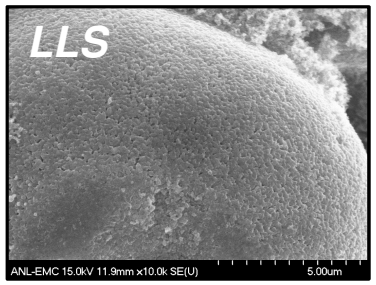
High-voltage cycling of LLS in F-electrolyte

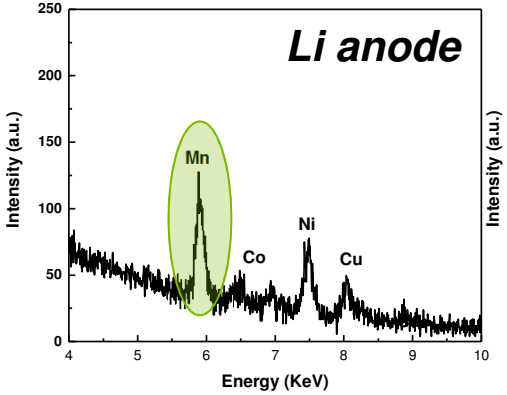


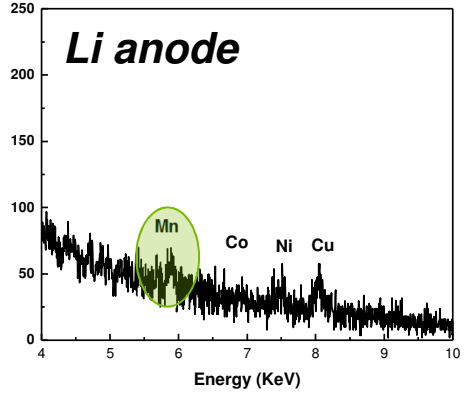
50 cycles in EC:EMC



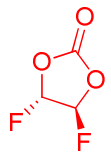
50 cycles in DFEC:FEMC





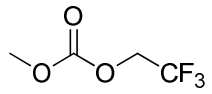


DFEC



(4*S*,5*S*)-4,5-difluoro-1,3-dioxolan-2-one

FEMC

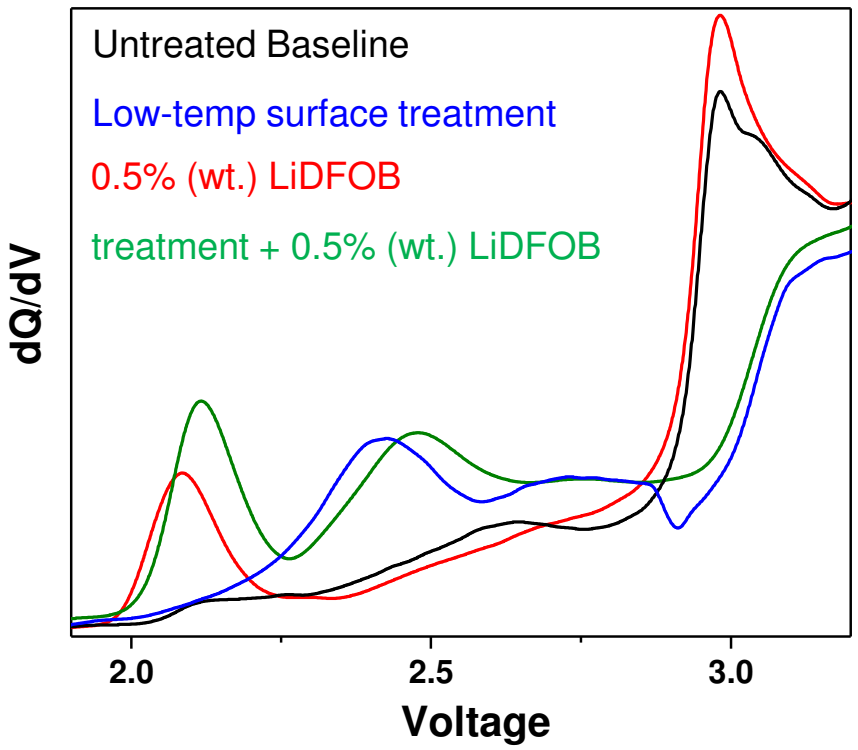


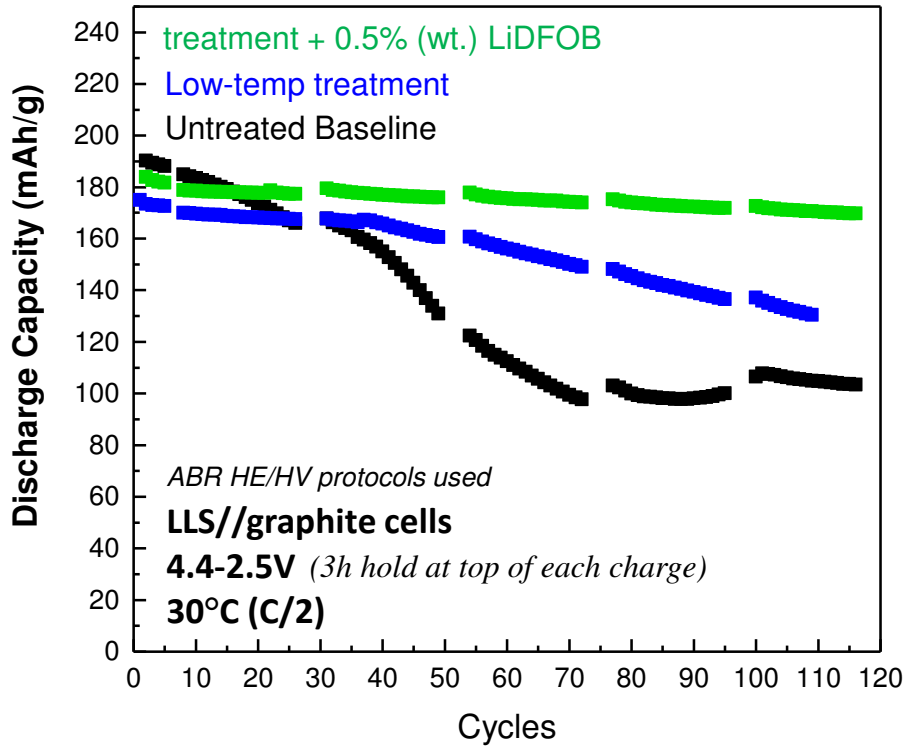
methyl (2,2,2-trifluoroethyl) carbonate

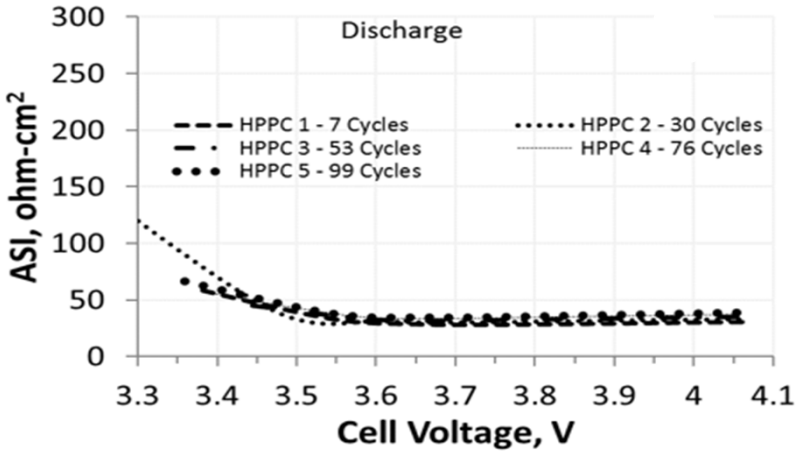
Stable cathode surface with little detectable metal dissolution for fluorinated formulation

- Fluorinated electrolytes show promise in stabilizing Mn-rich cathode surfaces – positive benefits observed for Li-metal anodes as well ***(See also BAT335)***
- Layered-layered-spinel baseline achieves stable capacity of ~240 mAh/g at 4.6V$_{Li/Li+}$

Stabilization of Surfaces: Combined Approach







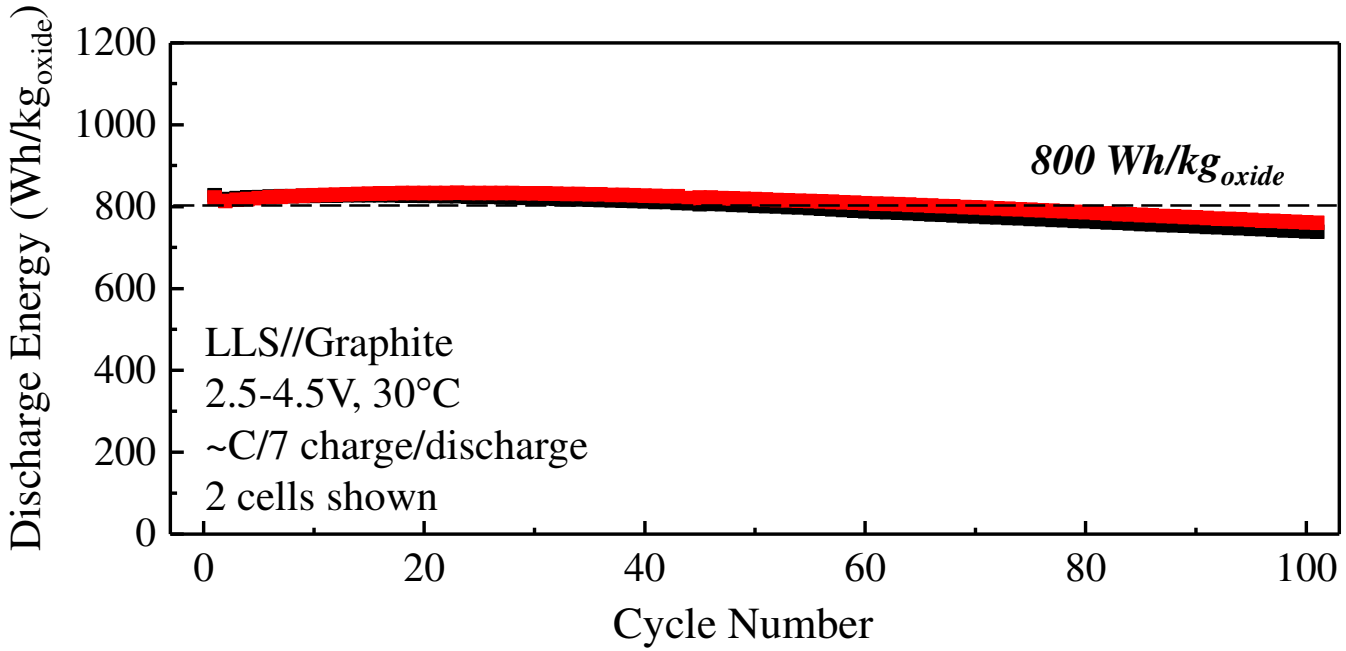
- Certain surface treatments have a unique interaction with LiDFOB additive
- Surface treatments allow very low levels of additive to be effective
- Unique combination allows ***very stable*** cycling and ***~zero impedance rise in LLS//Gr cells***

Stabilization of Surfaces: High-Energy Cells

Technical Accomplishments

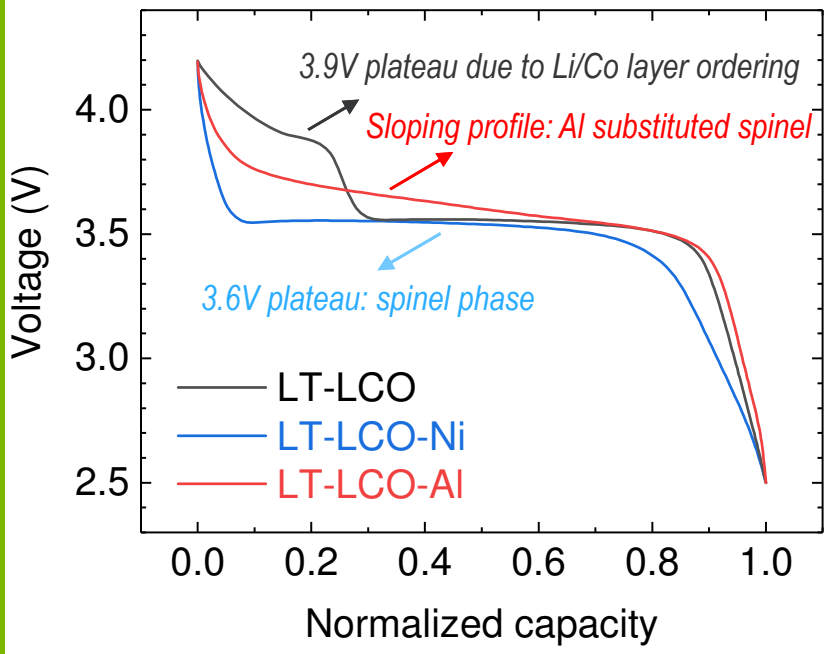
(See also BAT335)

Three-component, LLS cathode performance in "full-cell" configuration

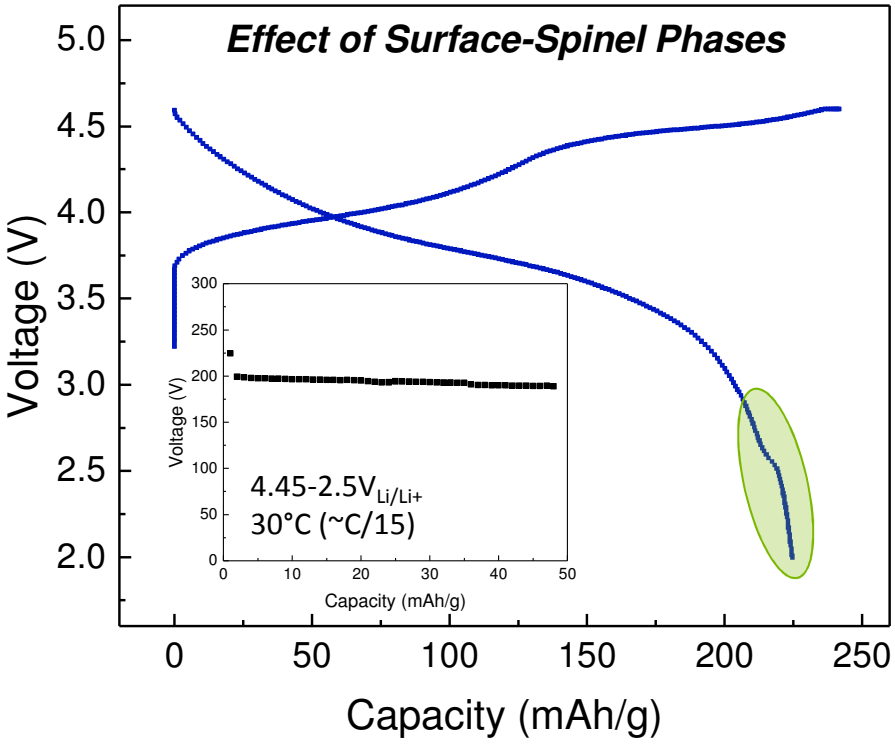


- Very robust graphite SEIs can be enabled by fluorinated electrolyte formulations
- Mitigation of anode side reactions due to metal dissolution enables high-energy retention in LLS//graphite cells
- **~800 Wh/kg$_{oxide}$** demonstrated for ~100 cycles to 4.5V *(Collab with CSE electrolyte group, J. Zhang)*
- Improvement in the performance of Mn-rich, LLS electrodes continues with promise

Stabilization of Surfaces: Structures



Comparison of voltage profiles for the pristine, Ni-, and Al-substituted LT-LCO cells



- Detailed studies of novel, spinel compositions revealed the ability of Ni and Al substitutions to stabilize low-temperature (~400°C) spinel phases to higher temperature synthesis (up to ~800°C) ***See BAT235***
- Stabilization to higher temperature allows deposition of Al/Ni-substituted spinel phases on the surfaces of layered-layered and layered-layered-spinel particles
- Lithiated, $Li_{1.2}Co_{1.85}Ni_{0.1}Al_{0.05}O_4$ spinel surfaces improved capacity retention of Li/Mn-rich particles when deposited at ~500°C - ***ongoing***

Response to Previous Year Reviewer Comments

General Comments

- The reviewer remarked that, as always, the PI does great hypothesis driven research. The approach is systematic and builds on the learnings as it progresses. There is a nice consideration of the balance of effects as deficiencies in the Li-rich material are addressed.

- The present project is well designed with new cathode structures, feasible as shown by the experimental data, and adequately integrated with the other DOE efforts on the high-capacity LL cathodes.

- The reviewer stated that excellent progress has been made in designing the LL cathodes with embedded spinel component.

Response

- We thank the reviewers for their time and encouraging comments concerning our manganese-rich cathode work and the progress being made.

Response to Previous Year Reviewer Comments

General Concerns

- …the materials in this series need to be charged to much higher voltages compared to lithium-cobalt oxide (LCO). The stability of material—including decomposition and reaction with electrolytes over hundreds cycles—is still in question.

Response

- Yes, LCO is operated at lower voltages but does not give the energy density, cost, or safety required of transportation technologies. Most “next-gen” cathode materials are studied because of their ability to deliver high capacities, generally at higher voltages than LCO, LFP, LMO... We agree that decomposition and reaction with the electrolytes is a critical issue. The follow-up studies for FY17 presented herein addresses those issues and have shown impressive progress as can be viewed in the data slides.

Response to Previous Year Reviewer Comments

General Concerns

- Examining the very first charge, i.e., the initial activation of very high capacity using X-ray absorption near edge structure (XANES) and differential electrochemical mass spectroscopy (DEMS) seems to be very important to understand the LL or LLS materials better. The reviewer asked what is basically so much oxidized beyond Ni, and said O2 evolution creating O2 deficiency with Mn (III). It is not clear just by looking at the formula.

Response

- The PIs of this project have considerable expertise examining the mechanisms involved with Li- and Mn-rich materials. It is now well established that oxygen participates in the electrochemistry of these samples with the evolution of oxygen, especially along the first charge cycle. The creation of Mn3+ is also an over simplification of the disordered, under-coordinated environments that form and the subsequent electrochemical processes involved and much has been published on these mechanisms in the past by the PIs. However, spectroscopy coupled with DEMS will indeed be very helpful and informative in going forward, especially with respect to the stabilization of the surfaces of these particles and we thank the reviewer for his/her comments.

Response to Previous Year Reviewer Comments

General Concerns

- The reviewer asked could the 6% of spinel component be expected to stabilize 94% of the LL structure for extended periods of operation (beyond hundreds of cycles and months of operation), and if there is any direct evidence for the elimination of the transition metal (TM) migration. There is evidence for the local domains of spinel and layered phases, but the reviewer asked would it be possible to verify if the spinel content (in the bulk) is close to the targeted 6%, and are the electrode loadings here are close to the practical values of 30 mg/cm2.

Response

- 6% spinel will not completely "stabilize" 94% of the bulk. However, in combination with the overall chosen Li and Mn content, the incorporated spinel allows for relative stability compared to pure layered-layered structures. In addition, the gain in efficiency (i.e., 1st cycle) and better rate performance due to the spinel, allow these compositions to achieve fairly high capacities in a lower voltage window, thereby, also adding to the stability of the material. It is very tough to verify the exact amount of incorporated spinel-type domains and we continually work on synthesis and characterization to that end. Hand-made electrodes at 30 mg/cm2 would likely have issues other than materials issues. However, we are now engaging with industry and electrodes are being tested.

Proposed Future Research

- The project will continue to focus on engineering of the bulk nanostructure in terms of spinel, spinel-type arrangements, and dopants. This approach is currently being applied to modify surfaces with promising results.
- The concepts of anion redox and how such processes are governed by local, atomic relationships will be pursued.
- In addition, further engagement with industry is ongoing to continually evaluate the practical nature of these and newly designed cathodes.
- ***Future work is subject to funding***

Summary

- Safety and cost are still major drivers in the lithium-ion industry and this project seeks to address the limitations therein
- Manganese-rich electrodes are being developed in order to realize competitive alternatives to Ni/Co-rich chemistries
- Three-component, Mn-rich, *"Layered-Layered-Spinel"* composite cathodes have been designed that show competitive oxide energies as compared with an industrial NMC-532
- Surface modifications have been developed that improve rate, retention, and impedance characteristics of these Mn-rich electrodes
- Combined approaches of new surface materials and electrolyte formulations have demonstrated ***~800 Wh/kg$_{oxide}$*** energy densities in full-cell configurations using graphite anodes
- Continued improvements in stability (i.e. energy retention) are expected based on these promising results

Remaining Challenges and Barriers

- Significant concerns with high-energy, NMC-based, lithium-ion batteries are cost and safety. Not only with respect to Co in terms of cost, but safety with respect to nickel-rich NMCs; which may also become cost prohibitive depending on increased demand. Mn-rich alternatives to Ni/Co-based NMCs provide promising options for safe, high-energy batteries. The concept of layered-layered-spinel materials has shown steady progress in terms of efficiency, rate, capacity, and surface stability. Critical challenges going forward will include:

    - Further improvements to structural stability
    - Advanced synthesis of engineered surface structures
    - Additional improvements in impedance
    - Testing and analysis of large cell formats