

Enabling High-Energy/Voltage Lithium-Ion Cells for Transportation Applications: Part 2 Materials

Project ID: ES253

*Principal Investigator: Anthony K. Burrell
Chemical Sciences and Engineering Division
Argonne National Laboratory*

*Annual Merit Review
DOE Vehicle Technologies Program
Arlington, VA
8-12 June, 2015*

This presentation does not contain any
proprietary, confidential, or otherwise restricted
information.

Overview

Timeline

- Start: October 1, 2014
- End: Sept. 30, 2017
- Percent complete: 15%

Budget

- Total project funding
- FY15 - \$3000K (total project funding see parts 1 and 3)

Barriers

- Calendar/cycle life of lithium-ion cells being developed for PHEV and EV batteries that meet or exceed DOE/USABC goals

Partners

- Lead PI: Anthony K. Burrell
- Collaborators: ORNL, NREL
- Burrell, Anthony K.; Abraham, Daniel; Balasubramanian, Mahalingam; Bareno Garcia-Ontiveros, Javier; Bloom, Ira D.; Long, Brandon R.; Croy, Jason R.; Dees, Dennis W.; Dogan, Fulya; Gallagher, Kevin G.; Iddir, Hakim; Ingram, Brian J.; Johnson, Christopher; Lu, Wenquan; Ren, Yang; Vaughey, John T.; Wu, Huiming; Wu, Rinaldo, Steven G.; Jansen, Andy; Polzin, Bryant; Trask, Steven; Krumdick, Gregory; Shin, YoungHo; Zhang, Zhengcheng; Liao, Chen; Tenent, Robert, Ban, Chunmei; Wood, David; Daniel, Claus; Nanda, Jagjit, Li, Jianlin



Project objectives - Relevance

To understand the interfacial structures that lead to electrolyte/surface instabilities in nickel-rich electrodes for high energy density lithium-ion batteries and how they limit implementation into transportation technologies.

Project Areas:

- **Development of surface sensitive characterization tools** to determine the interfacial inorganic and organic compounds that make up the electrochemical surface of Ni-rich cathodes.
- **Ceramic coatings** - Investigate how coating methodology and electrochemical cycling affect the longevity of inorganic coatings on Ni-rich cathodes.
- **Design and synthesize novel electrolyte additives** that are stable to high voltage and high oxidation state metals.
- **Investigate and evaluate Ni(III)-rich cathodes** for capacity, stability and role of cation ordering on electrochemical performance.



Milestones

1. Evaluate the role of synthesis, coating method, and sample history of alumina coatings on baseline Ni-rich cathodes.
(Apr. 2015) *Completed*
2. Identify cathode compositions that contain predominately Ni(III) and the role of cation ordering on performance.
(Sep. 2015) *Ongoing*.
3. Identify interactions between the cell voltage, cathode surface, and electrolyte components that limit electrochemical performance.
(Sep. 2015) *Ongoing*.
4. Define criteria that limit stability of new high voltage electrolytes.
(Sep. 2015) *Ongoing*.



Approach - Strategy

Approach:

Devise chemical compositions, spectroscopic tools, and electrochemical models to better understand the limitations and breakdown mechanisms of high voltage-high energy cathodes in a lithium-ion battery cell configuration

Strategy:

Several phenomena contribute to the gradual breakdown in performance of lithium-ion batteries including surface degradation, cathode instability in the bulk, reactivity with organic electrolyte components, and surface films.

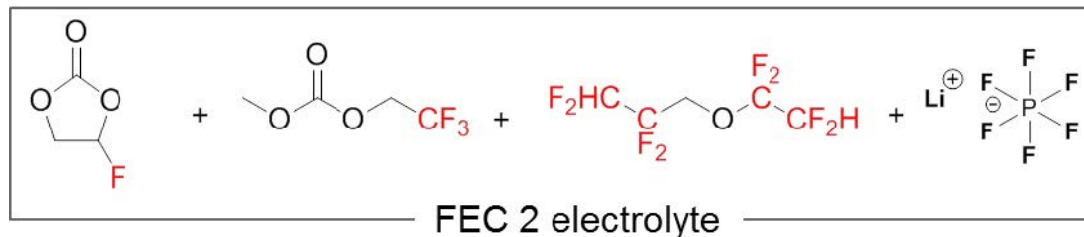
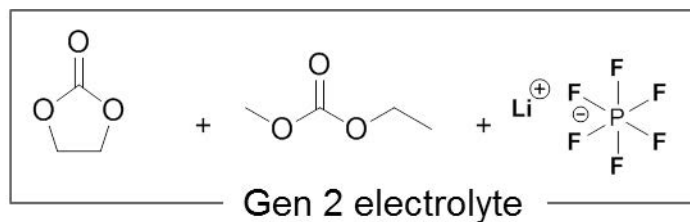
In Year 1 - utilizing several baseline systems – NCM523, NCA, and a low cobalt LMR-NMC, we will -

- 1) Investigate the effects of interfacial coating stability
- 2) Investigate the role of organic solvent electrolyte components – balancing high voltage stability and performance.
- 3) Determine the role of processing and sample history on performance
- 4) Initiate studies on new cathode formulations.



Electrolytes

As many of these high voltage systems appear limited by the ability of the electrolyte (salt and solvent) to resist oxidation against the charged cathode, we have initiated several studies on the implications of incorporating of fluorinated solvents. Selective fluorination can change decomposition pathways and increase stability due to the high strength of the C-F bond and its resistance to cleavage.



Electrolyte oxidation pathway:

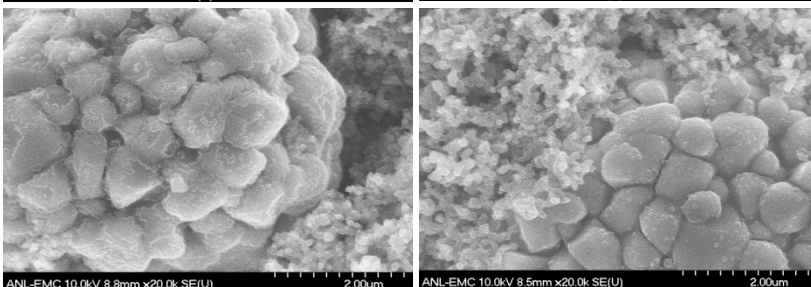
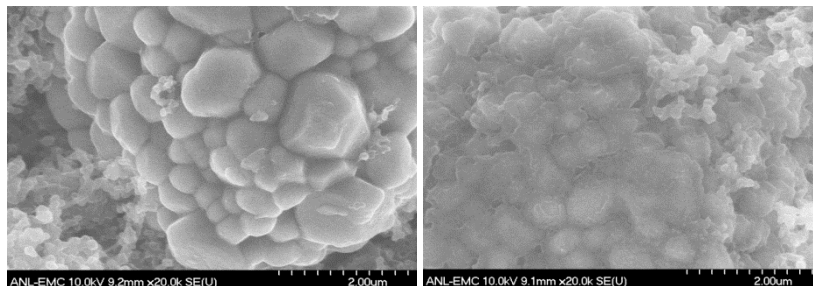


Electrolytes

4.3 V

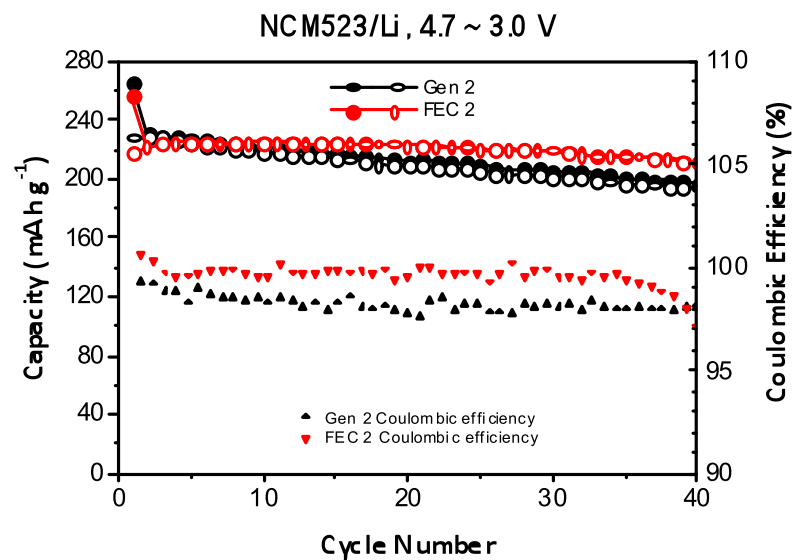
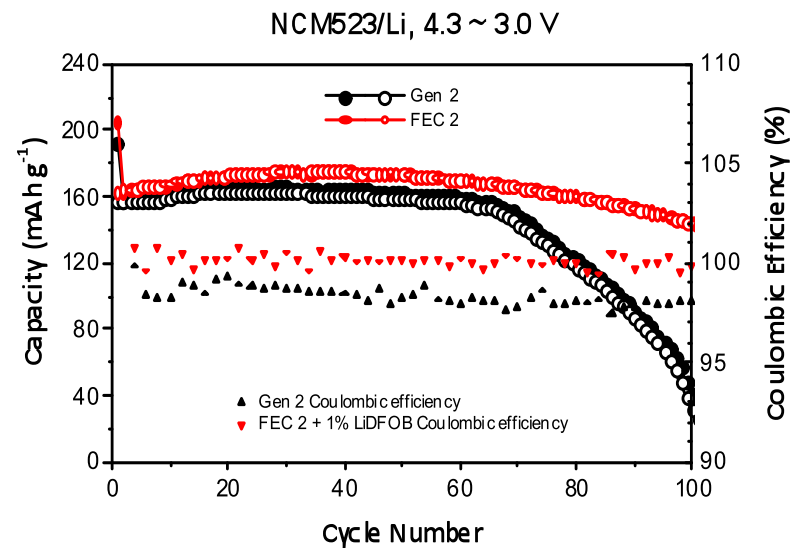
4.7 V

Gen 2



SEM images of NCM523

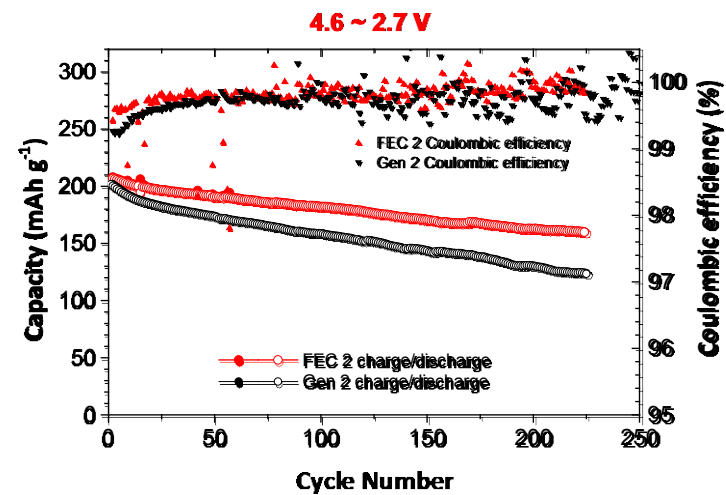
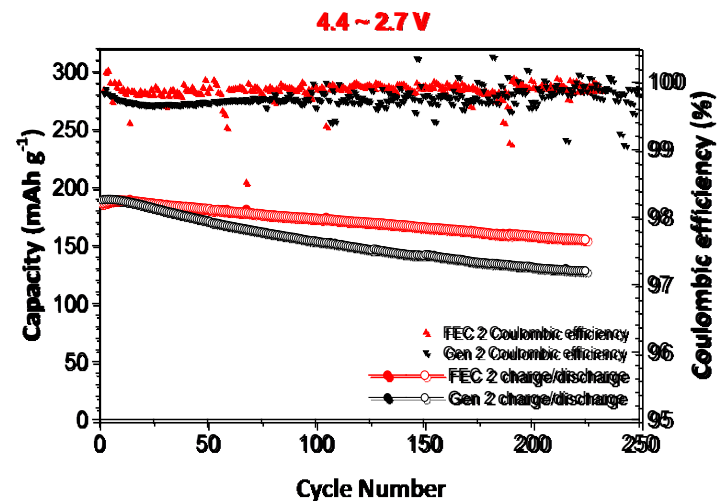
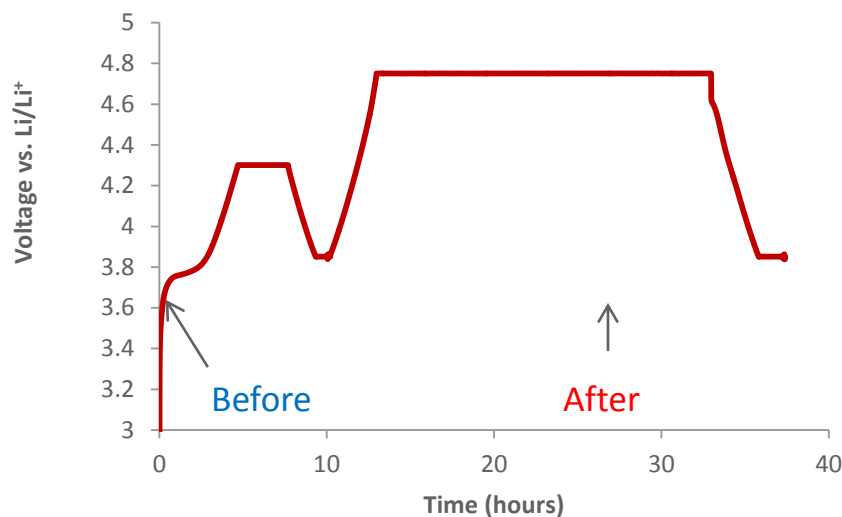
Changes in cathode surface morphology by incorporation of fluoride and voltage window



Electrolytes

Potentiostatic evaluation of electrolyte/additive effectiveness

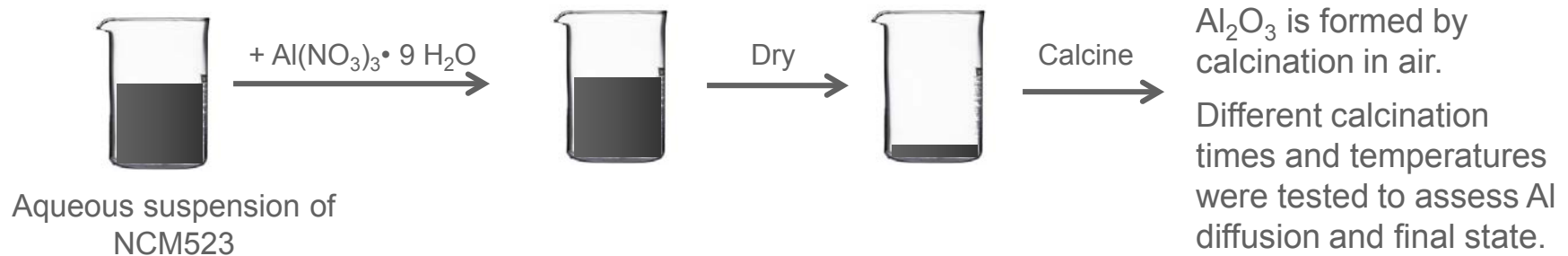
- NCM523/Graphite cell chemistry
- Cells are subjected to voltages where electrolytes are unstable
- Diagnostics of cell performance recorded both before and after high voltage hold
- Impedance change provides baseline for additive evaluation



Surface coatings

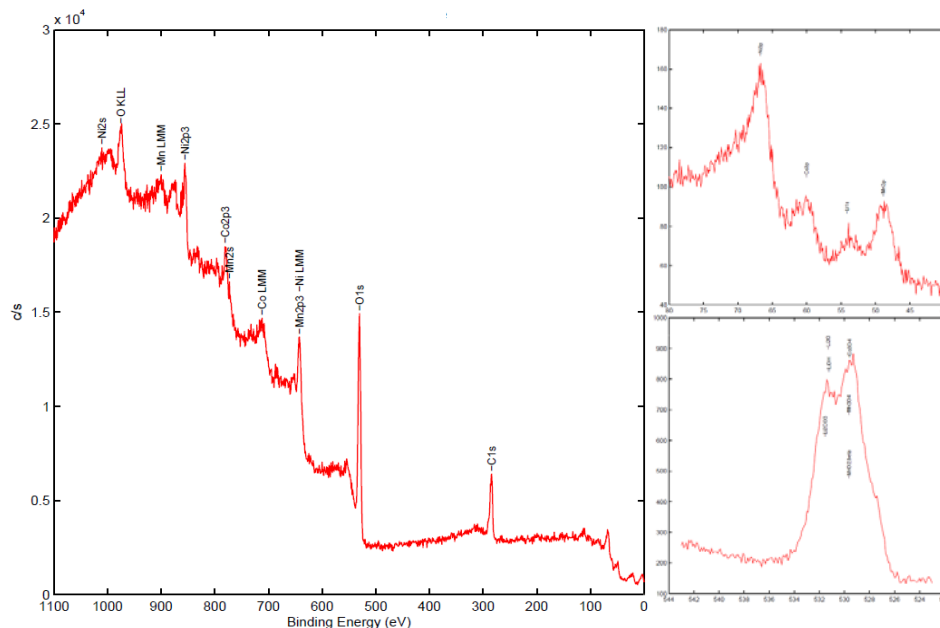
- Recent reports have shown that degradation at high voltages of cathode material NCM523 may be related to the formation of an interfacial rock salt phase that is suspected to increase the charge transfer resistance.
- The most commonly proposed strategy to improve the stability and performance of the cathode is the fabrication of a surface coating to protect it from the electrolyte. Coating materials tested for NCM523 include Al_2O_3 , TiO_2 , CuO , ZnO , AlF_3 , LaPO_4 .
- In addition to the coating material and thickness, the coating technique and conditions should be carefully examined.

Al_2O_3 wet coating process:

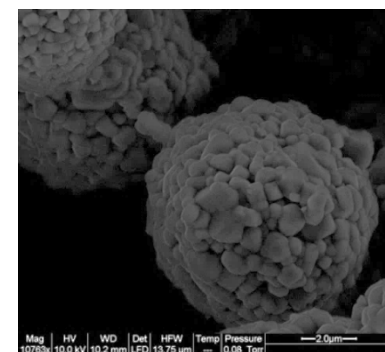
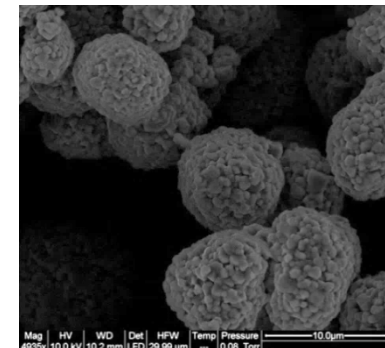
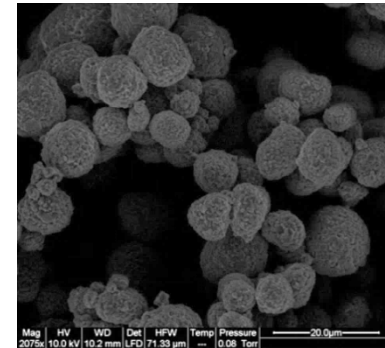


Surface coatings

- Several batches of Al_2O_3 -coated NCM523 have been prepared via different methods (wet coating, ALD, PVD) and in various conditions.
- Coated and uncoated NMC523 samples have been characterized with different techniques (XRD, SEM/EDS, NMR, IR, XPS) and evaluated electrochemically.
- EDS and XPS of uncoated NCM523 show some evidence of Li surface residues that may affect the coating process.



XPS spectrum of NCM523



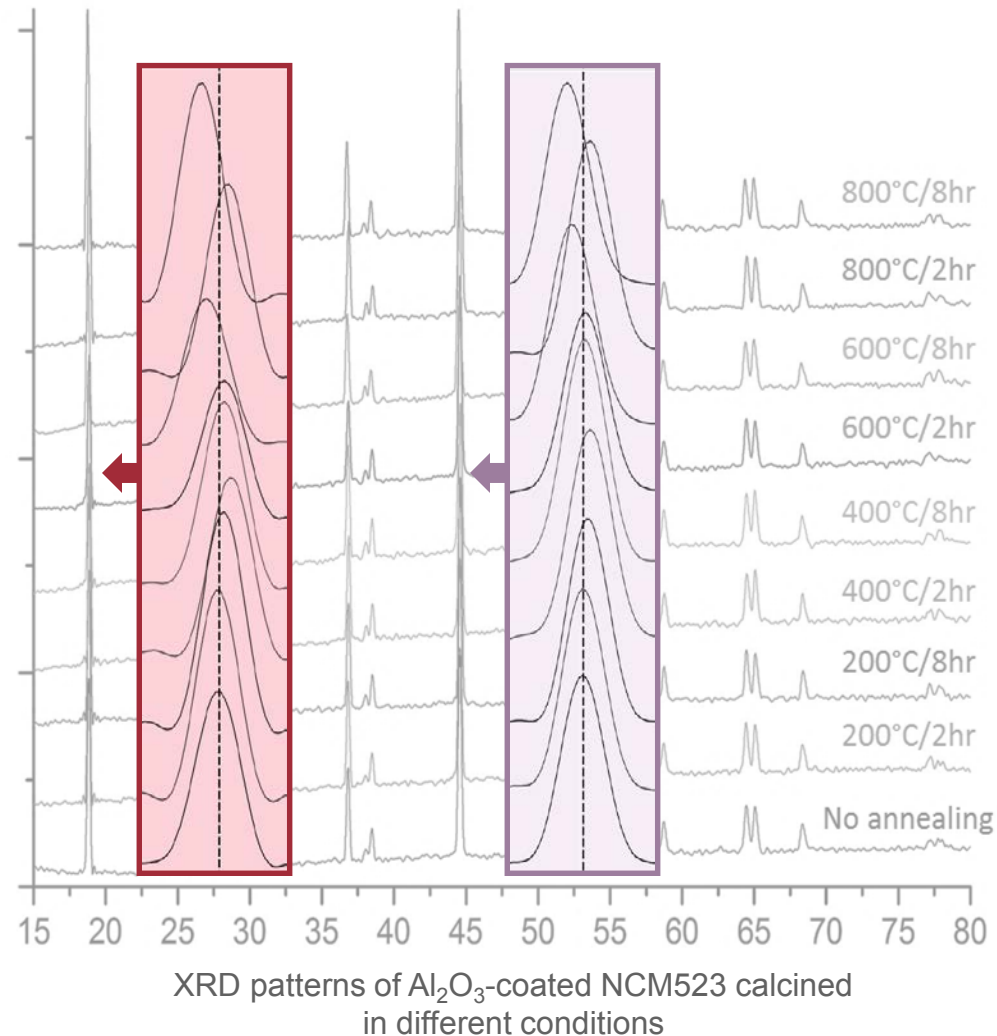
SEM images of NCM523

Surface coatings

- XRD data for Al_2O_3 -coated NCM523 (wet coating, 2 wt.%) show that the coating process can induce small changes in the crystal structure and therefore could have an effect on the electrochemical performance of the material.

T (°C)	t (hr)	a
0	0	2.8718
200	2	2.8718
200	8	2.8710
400	2	2.8717
400	8	2.8738
600	2	2.8718
600	8	2.8753
800	2	2.8711
800	8	2.8762

Lattice constant of Al_2O_3 -coated NCM523 calcined in different conditions

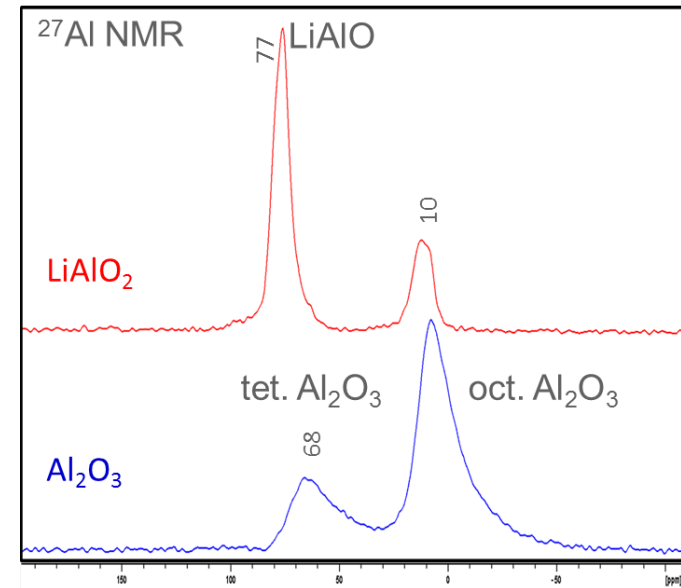
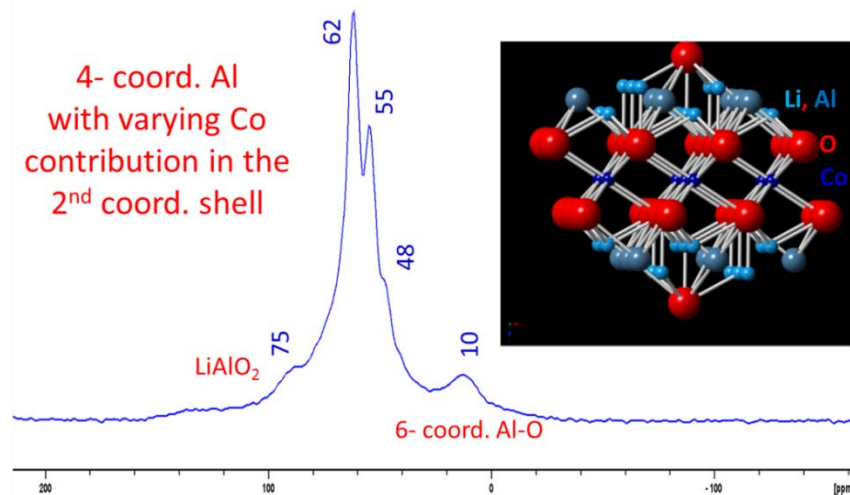


Surface coatings

- NMR is a local probe for both surface and bulk species to study the effect of coating process /conditions and interaction of coating with electrolyte and additives.
- For Al_2O_3 -coated NCM523 a combination of ^7Li and ^{27}Al MAS NMR applications can be used to investigate:
 - Coordination/composition of Al species at the interface and coating layer
 - Possible Al diffusion into the bulk
 - Surface morphology
 - Possible lithium loss from the bulk

With coating technique, loading level, annealing conditions.

^{27}Al MAS NMR LiAlCoO_2



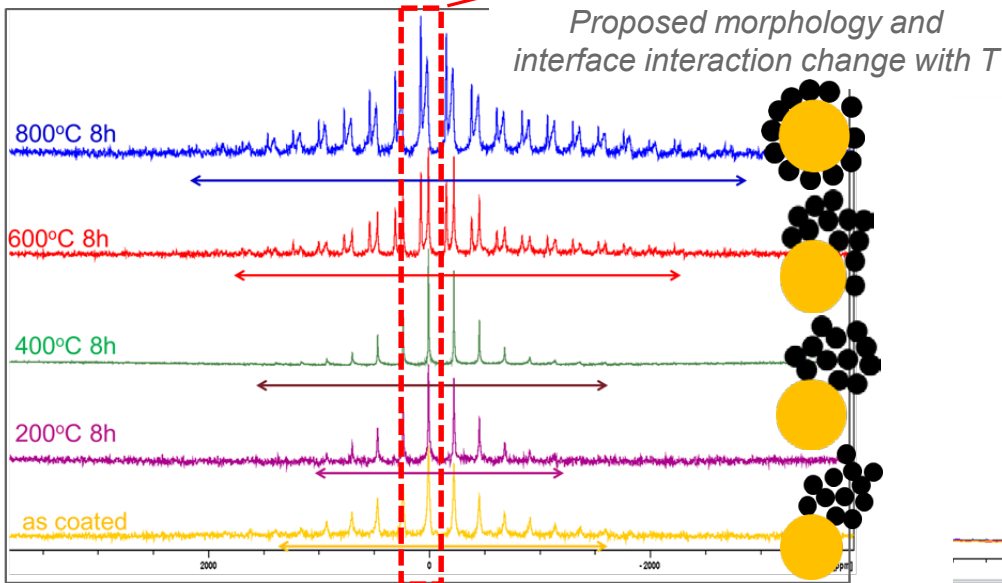
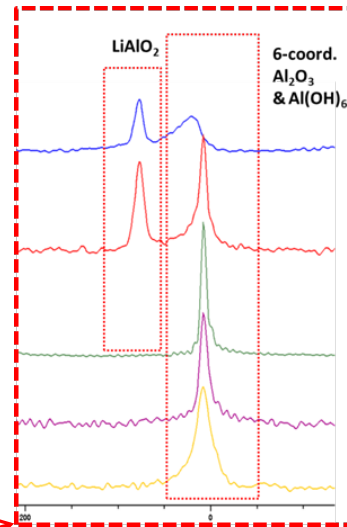
Model comparison and systematic study on lattice aluminum NMR signature in different composition of coated cathodes to be compared with the coated cathode materials

Surface coatings

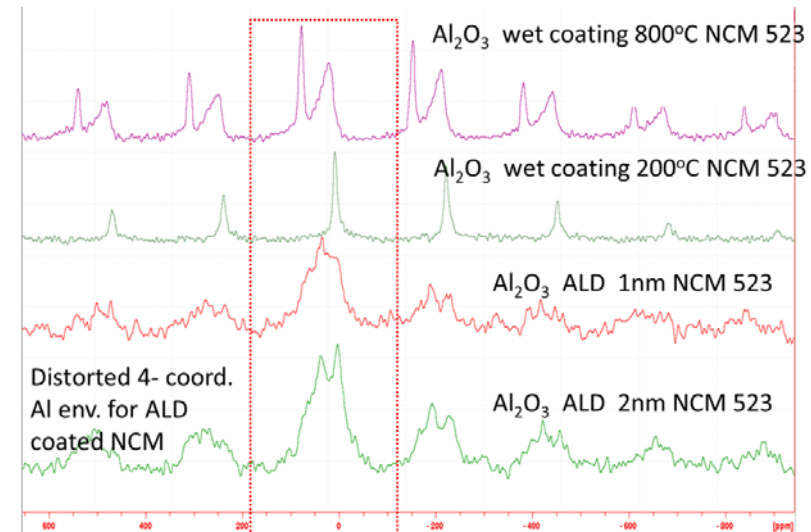
^{27}Al MAS NMR of Al_2O_3 -coated NCM523 calcined at different temperatures.

Wider sideband envelope and increase in sideband intensity with increasing temperature and formation of a LiAlO_2

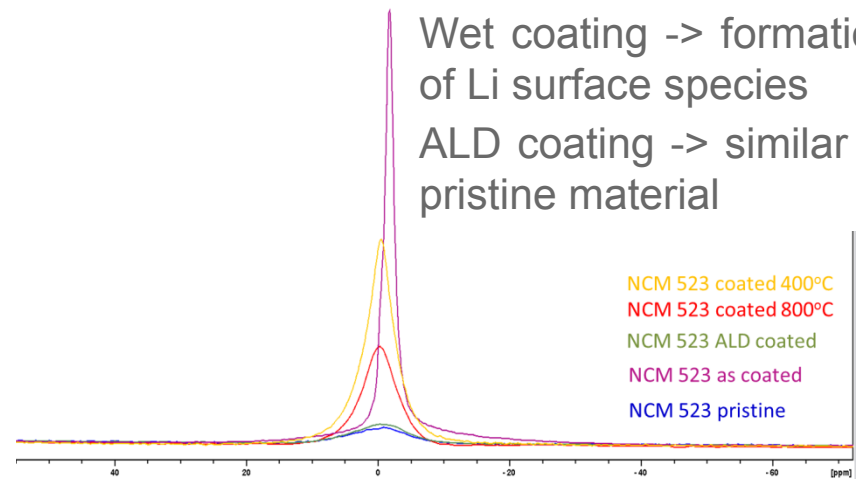
No major change in Al environments up to 400°C



^{27}Al MAS NMR of Al_2O_3 -coated NCM523: wet vs ALD coating



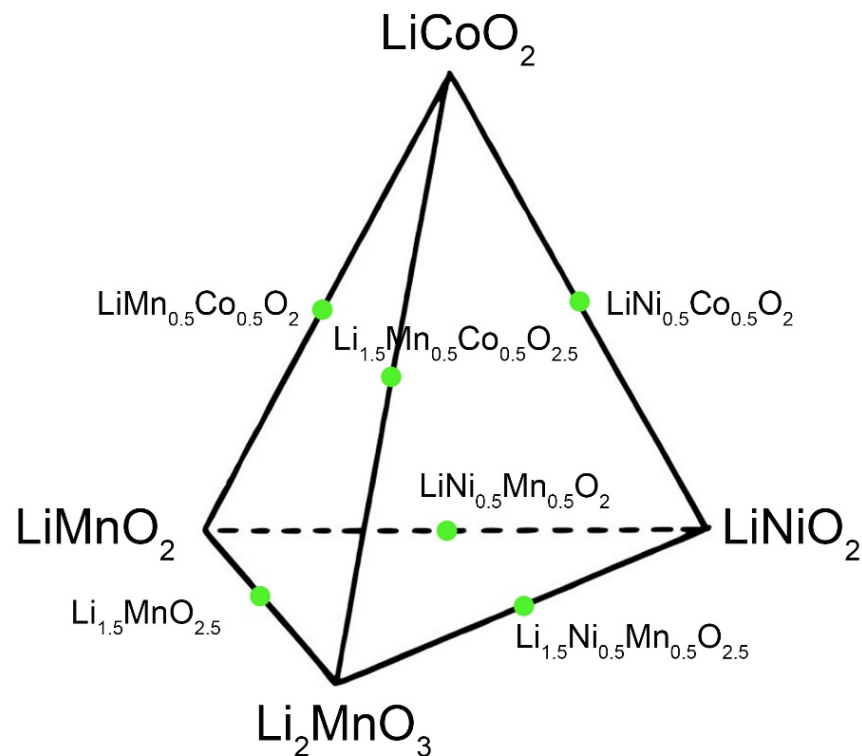
Wet coating $\rightarrow$ formation of Li surface species
ALD coating $\rightarrow$ similar to pristine material



Ni(III) Rich Cathode Materials

In designing high energy cathode materials it is important to know the behavior and the interactions between the primitive components at high potential.

Primitive compounds and their 50 % mixture are prepared and tested.

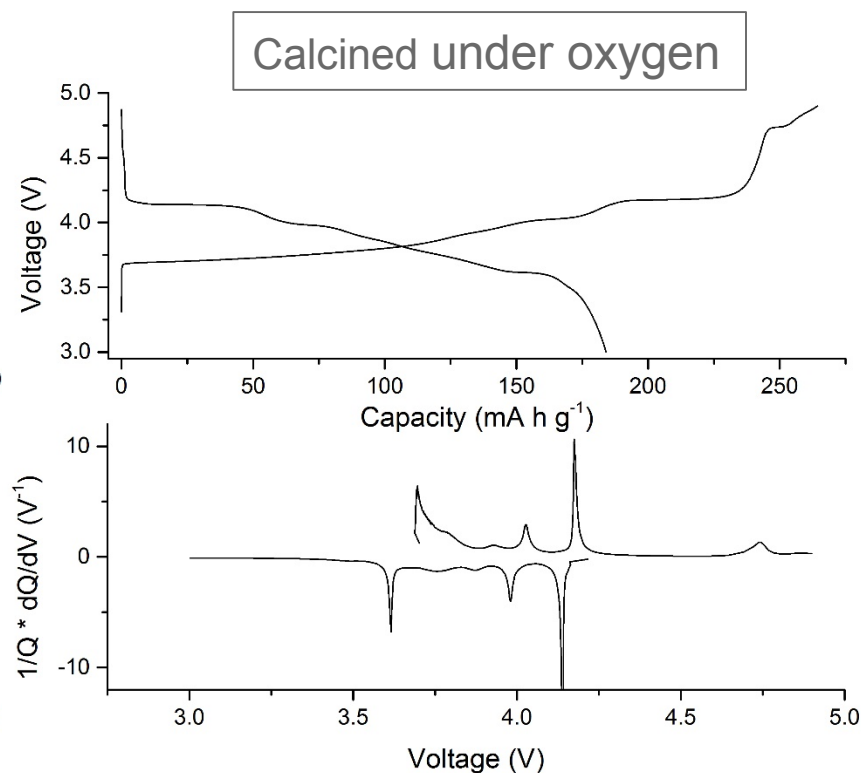
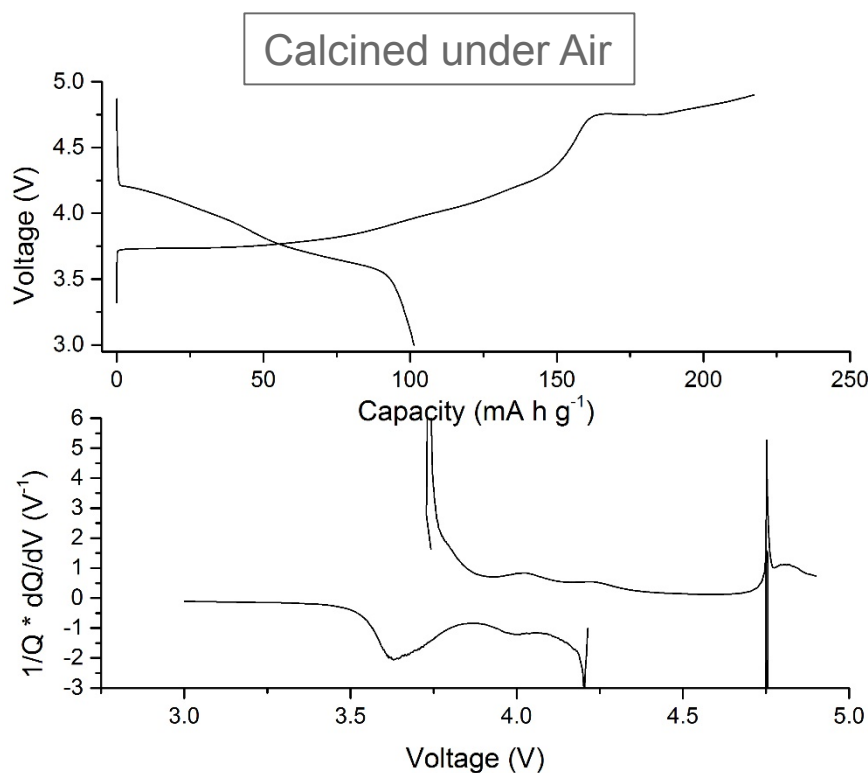


Green dots: 50 % mixed of the two compounds at the two ends of the line



Ni(III) Rich Cathode Materials

LiNiO₂: Synthetic Conditions – First Cycle



- Chemistry of LiNiO₂ is quite complicated with at least 4 active electrochemical processes during charge
- Sample calcined under oxygen shows better performance



Summary

We have initiated a new program to study the interactions between charged high voltage cathodes, liquid electrolytes and additives, and the role of interfaces, diffusion, and electrochemical performance.

- Initial studies are focused on baseline cathodes NCM523. Our initial work involved studying Al_2O_3 coatings and looking at the point the coating becomes a dopant using several spectroscopic techniques. Using wet-coated samples we note that above 400 °C, the ^{27}Al NMR spectra shows changes indicative of a change in coordination and a more paramagnetic environment for the Al(III)
- This was consistent with Powder X-Ray Diffraction (PXRD) which showed unit cell changes above 400 °C with expansion along the c-axis.
- Adding fluoride anions to the electrolyte components was found to increase stability to higher voltage giving higher cycling efficiency when compared to the non-modified solvent.
- Collaborations with ORNL and NREL to coat NCM523 via different methods have been established.



Collaborations and Coordination with Other Institutions

Thin Film Coatings

- Gabriel Vieth, Jagjit Nanda (ORNL)
- Dave Schroeder (NIU)

ALD Coatings

- Chunmei Ban, Robert Tenent (NREL)

Electrode Coating Methods

- Ana Kiricova, Youngho Shin, Greg Krumdick (ANL-MERF)

Characterization

- PNNL/EMSL (Karl Mueller, NMR)
- ANL/CNM – Electron Microscopy Center



Future work

- Work with organic electrolyte group to balance the properties of the materials used with the oxidative power of the charged cathodes. Develop methods to investigate a variety of charged cathodes against the electrolyte systems developed.
- Explore more Ni(III) rich areas of phase space to identify cathode formulations that possess the required electrochemical properties and can act as a model system for the characterization, modeling, and diagnostics groups.
- Attempt to understand how the method of coating the cathode material affects the electrochemical properties of the electrode materials.
- Utilize and develop spectroscopic techniques to guide the coatings and interfaces, electrolyte, and synthesis teams to develop more robust and stable high voltage high energy storage systems.

