HIGH ENERGY - HIGH VOLTAGE PROGRAM: MATERIALS

Project ID: ES254

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2016 U.S. DOE VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW AND PEER EVALUATION MEETING
June 8, 2016 Washington D.C.

OVERVIEW

Timeline

- Start: October 1, 2014
- End: Sept. 30, 2017
- Percent complete: 50%

Budget

- Total project funding:
  - FY15 - $3000K
  - FY16 - $4000K
- ES252, ES253, and ES254

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost, Performance, and Safety

Partners

- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

PROJECT OBJECTIVES - RELEVANCE

To understand the interfacial structures and reactions 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.

- **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.
- **Functionalized organic coatings** that are stable to high voltage and high oxidation state metals.
- **Investigate and evaluate Ni(III)-rich cathodes – 622, 811, NCA, 442, 523**

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MILESTONES

- Spectroscopic characterizations of pristine NCM 523 baseline cathode. **Completed**
    - Presence of surface proton and lithium bearing species (XPS, FTIR, NMR).
    - Effect of cycling on the bulk stability of 523 by XAS.
- Application of Al_2O_3 coating on baseline NCM 523 cathodes via wet coating and ALD method. ***Completed***
    - Effect of coating process on bulk and surface → ALD vs wet coating
    - Study of the effect of calcination temperature on wet coated NCM 523 and its effect on aluminum diffusion into the lattice.
    - Study the effect of calcination / calcination temperature on electrochemical performance of wet coated NCM 523.

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APPROACH - PROJECT

Approach: Devise materials strategies, utilize spectroscopic tools, and create electrochemical models that allow us 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. Utilizing NCM523 or NCA as initial baseline systems –

1. Investigate the effects of interfacial coating stability
2. Investigate the stability of organic coatings with regards to high voltage stability and performance.
3. Determine the role of processing and sample history on performance

MATERIALS SYNTHESIS AND CHARACTERIZATION

Bulk Nickel Rich Cathodes

- Electrodes provided by CAMP Facility (ANL)
- High temperature synthesis
- Thin films

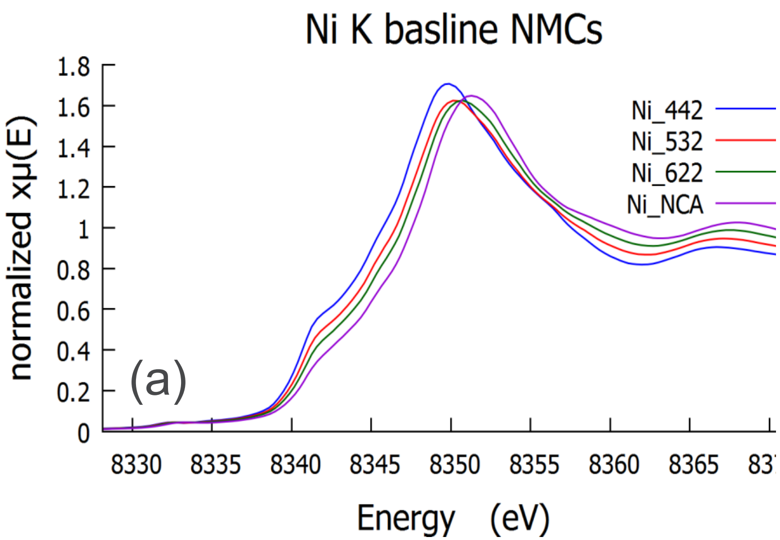
Organic Coatings

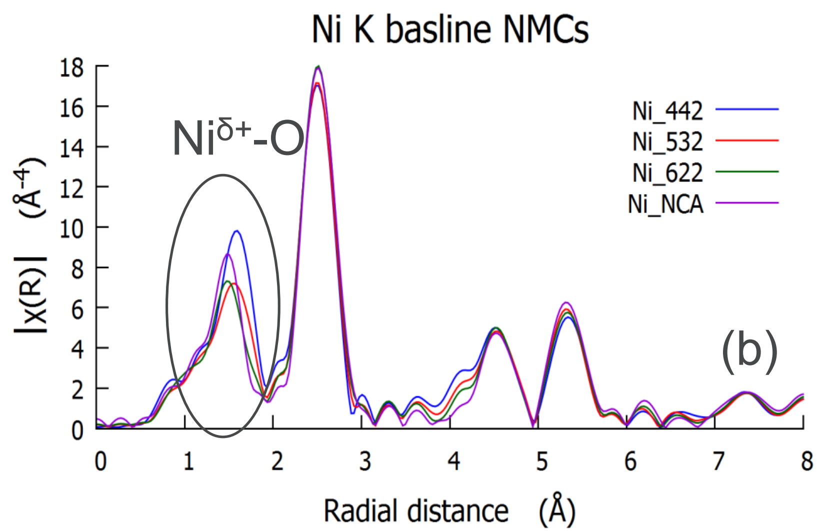
- Organic, Self-Assembled Monolayers (SAM)
- Characterization

Inorganic Coatings

- Methods: Wet, Atomic Layer Deposition
- Characterization

PROGRESS – BULK STABILITY OF NMC CATHODES

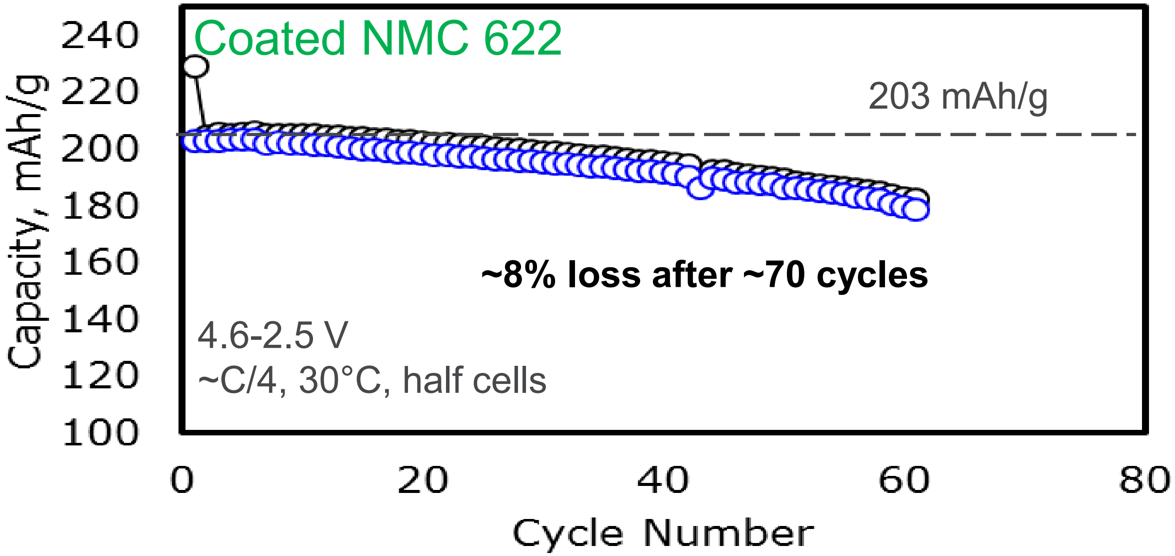




- Preliminary screening of stability vs. composition (442, 532, 622, NCA)
- C/4 cycling between 4.6-2.5 V vs. Li at 30°C
- XAS characterization of pristine and cycled electrodes (w&w/o coatings)

Objective: Prioritize surface vs. bulk instabilities of NMC cathodes

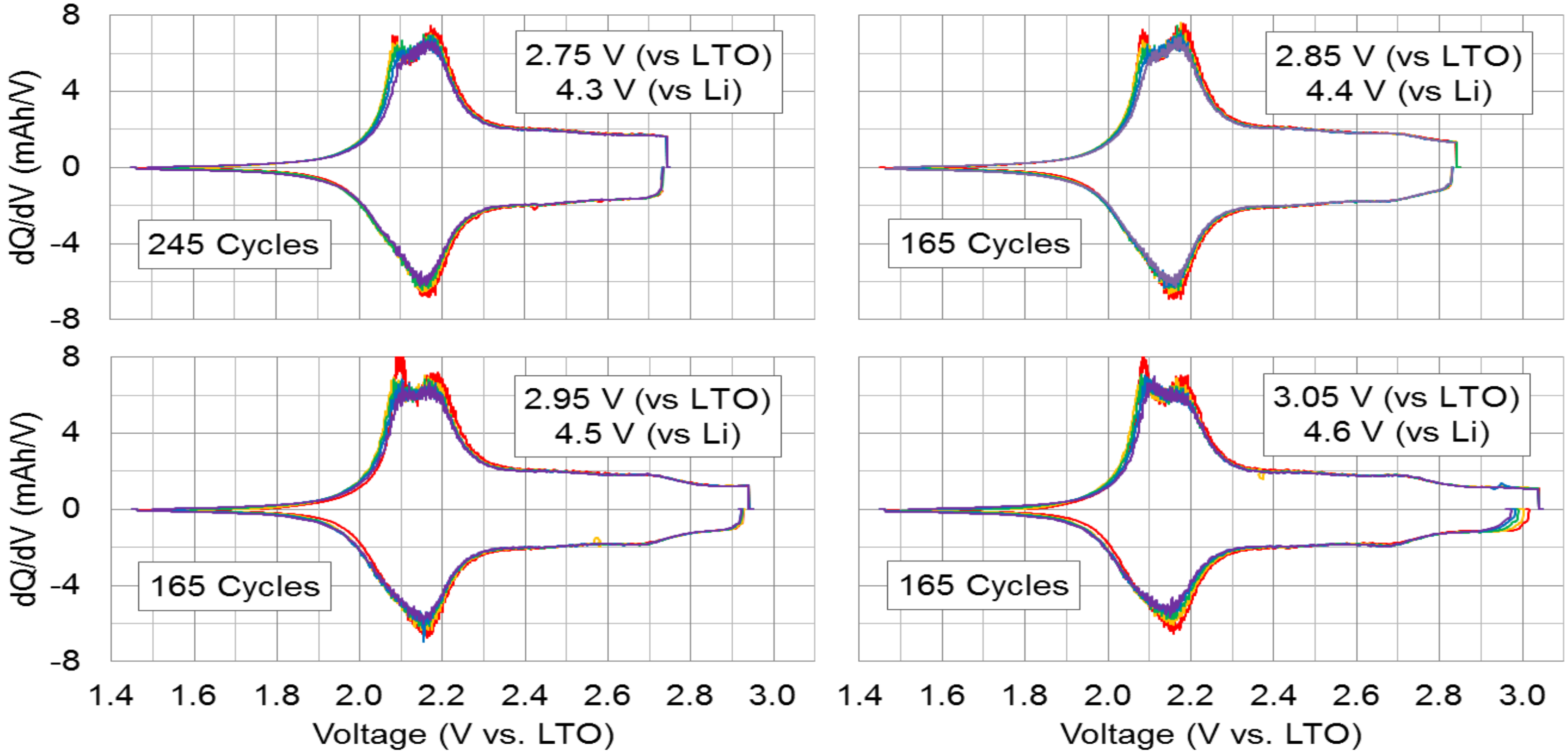
PROGRESS – BULK STABILITY OF NMC CATHODES



- All NMCs tested showed less than 15% loss after ~50 cycles
- All NMCs showed little to no change in average structures (XAS)
  additional bulk characterization is in progress…
- Capacity loss likely due to surface issues (electrolyte, Li anode losses)

Screening implies that bulk structures may be stable to 4.6 V vs. Li

PROGRESS – BULK STABILITY OF NMC CATHODES



- NMC 622 was chosen for a detailed study using LTO anodes at four different upper cutoff voltages (UCVs) to mitigate the effect of the anode in the study

Results indicate that NMC-622 is stable to at least ~4.4 V vs. graphite

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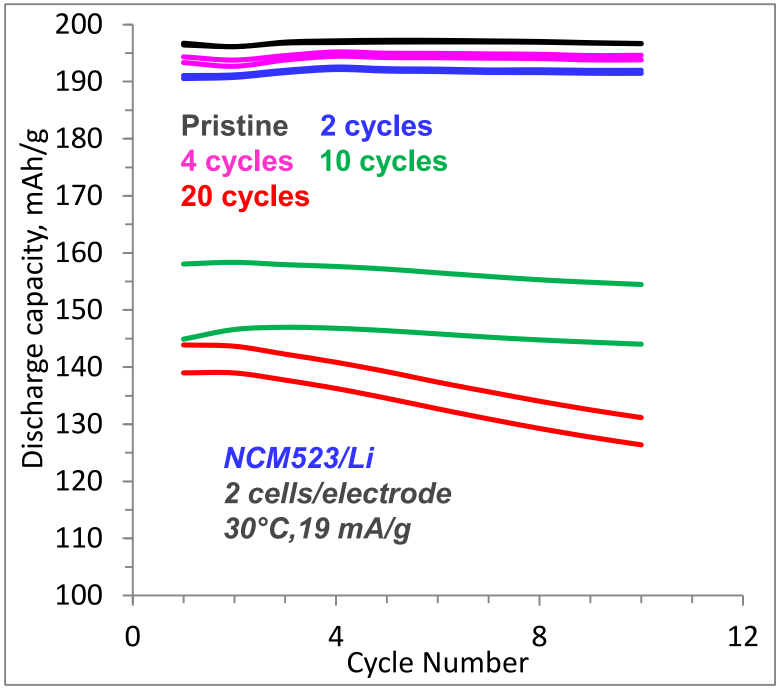
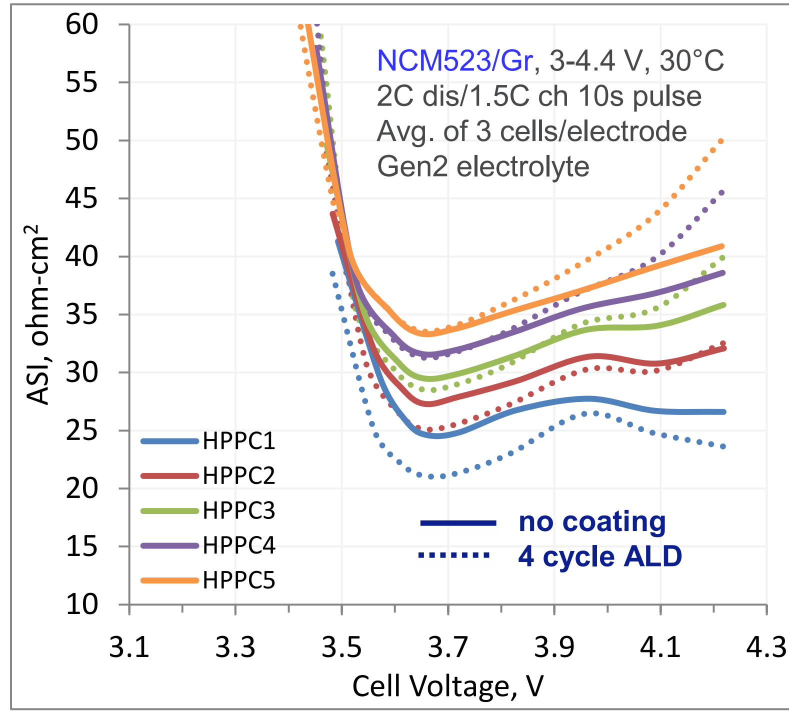
PERFORMANCE OF *ALD* Al_2O_3 COATED NCM523 OXIDE



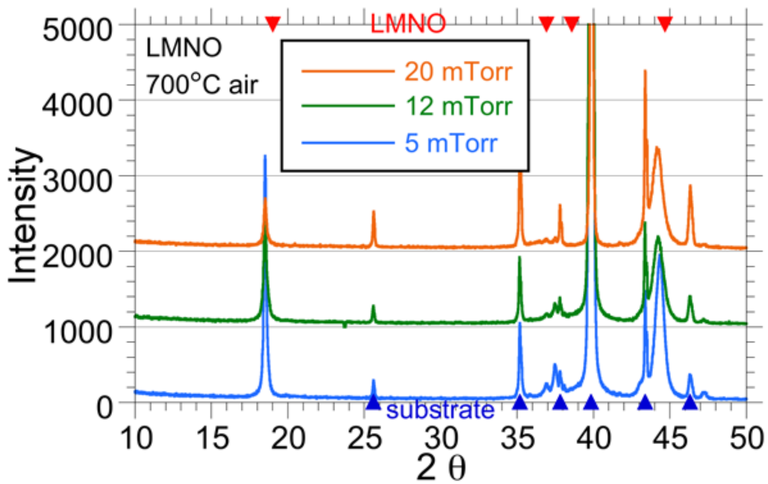


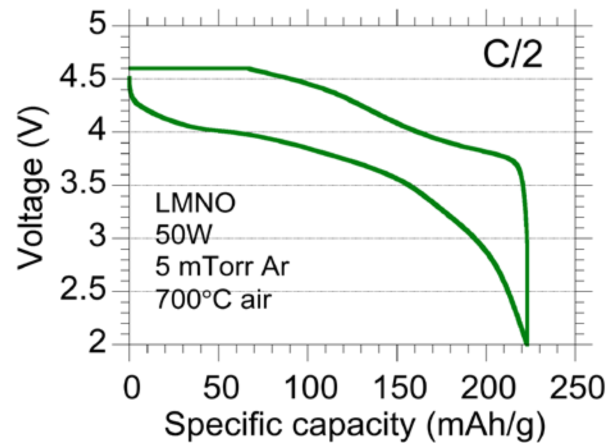
- Capacities of ALD alumina coated electrodes are lower than that of the pristine electrode.
- Thicker coated (10,20 cycle) electrodes showed (i) lower capacities, (ii) faster fade, and (iii) more variation.
- 4 cycle ALD electrode displayed the best cycling data among ALD samples.

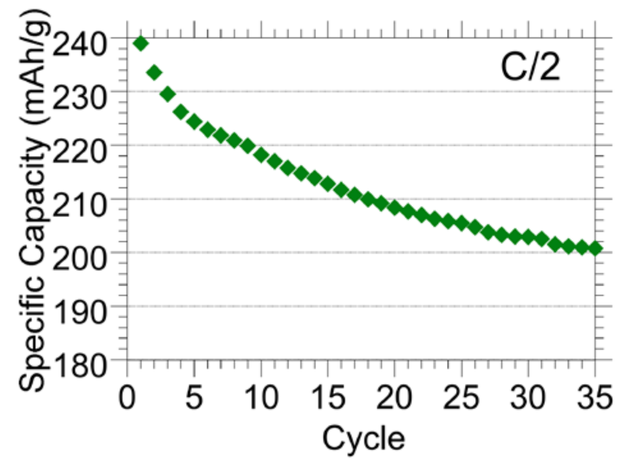
FULL cells with **4** Cycle ALD Alumina

- Capacities and capacity retentions similar to the pristine electrode.
- The area specific impedance of the coated electrode is initially higher, but the impedance rise is lower at voltages > 3.8 V.
- For all cells the rapid ASI rise at voltages < 3.55 V arises from the positive electrode.

PROGRESS - THIN FILM CATHODES





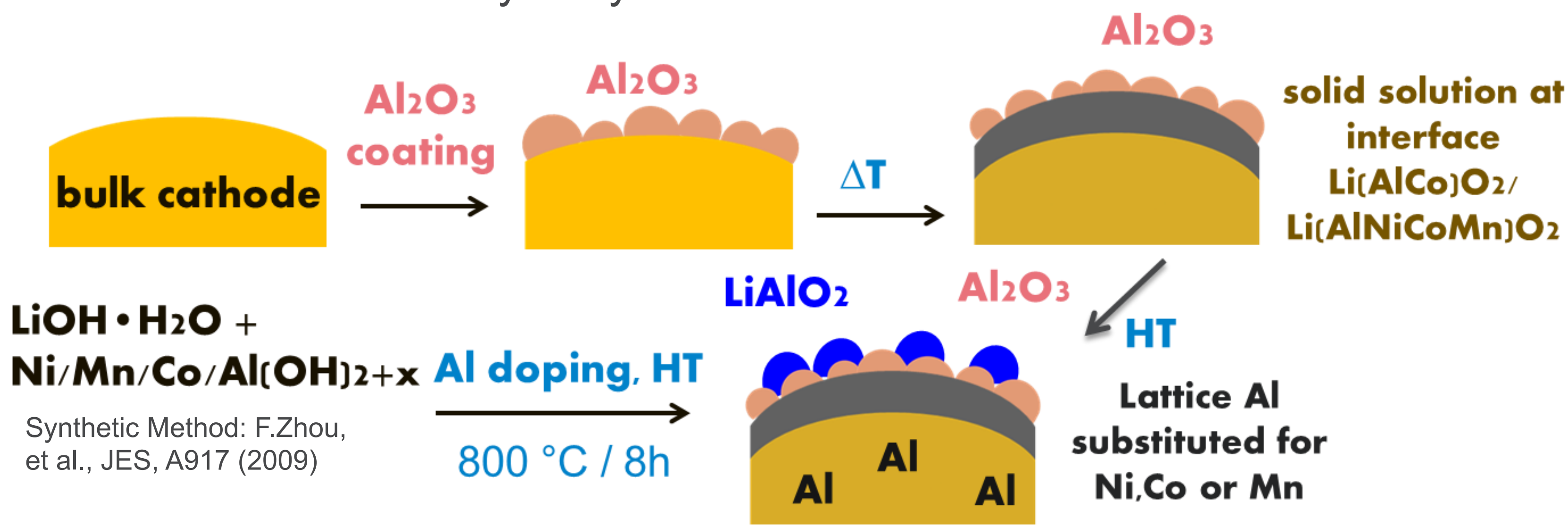


- Allows study of idealized interfaces and eliminates binders and carbon
- Initial cathode work has focused on the layered oxide $Li(Ni_{0.5}Mn_{0.5})O_2$ (LMNO) (ORNL).

LMNO films show expected plateaus, stability, and capacity

ALUMINA ON THE NMC SURFACE

- What are the surface species after coating process ?
- How does elevated temperature affect the coating ?
- Is there any solid solution formation or lattice Al ?
- 523 surface is ~15% hydroxy-terminated.



Synthetic Method: F.Zhou, et al., JES, A917 (2009)

- Characterization: XRD, SEM, FTIR, XPS and solid state NMR
- ALD coated samples show no $LiAlO_2$ formation on annealing due to low Al content and the lower amount of surface protons compared to wet coating

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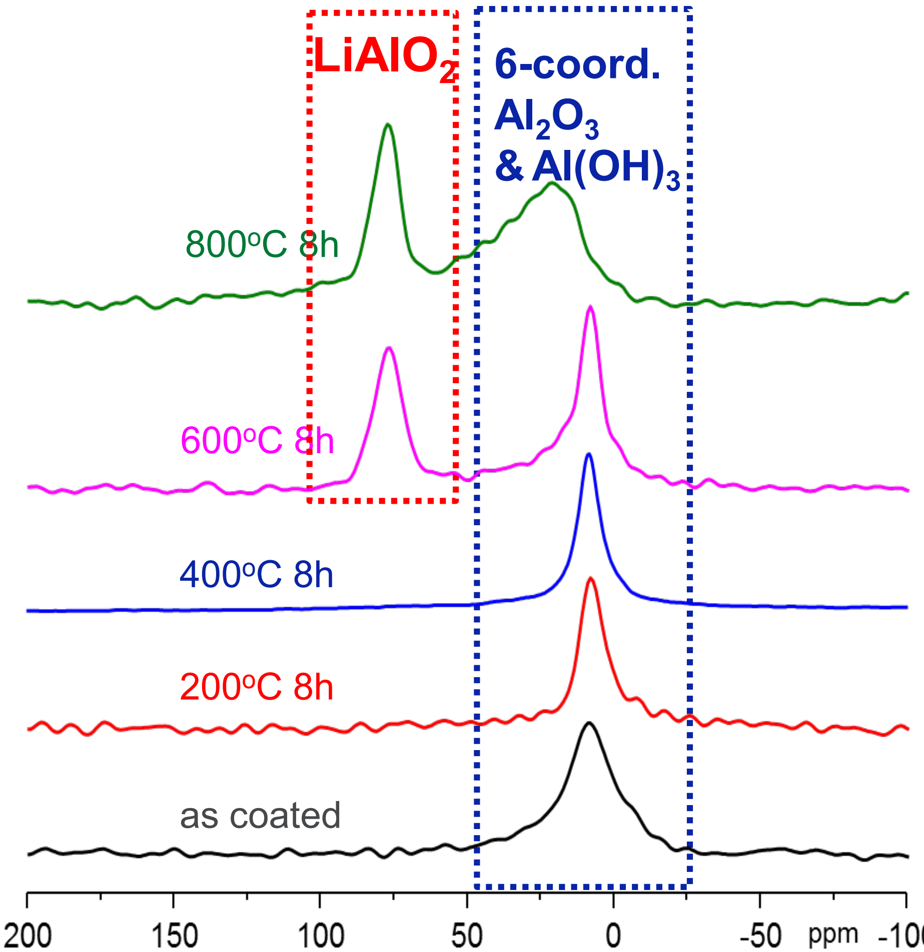
AL(III) IN THE LATTICE AND SURFACE

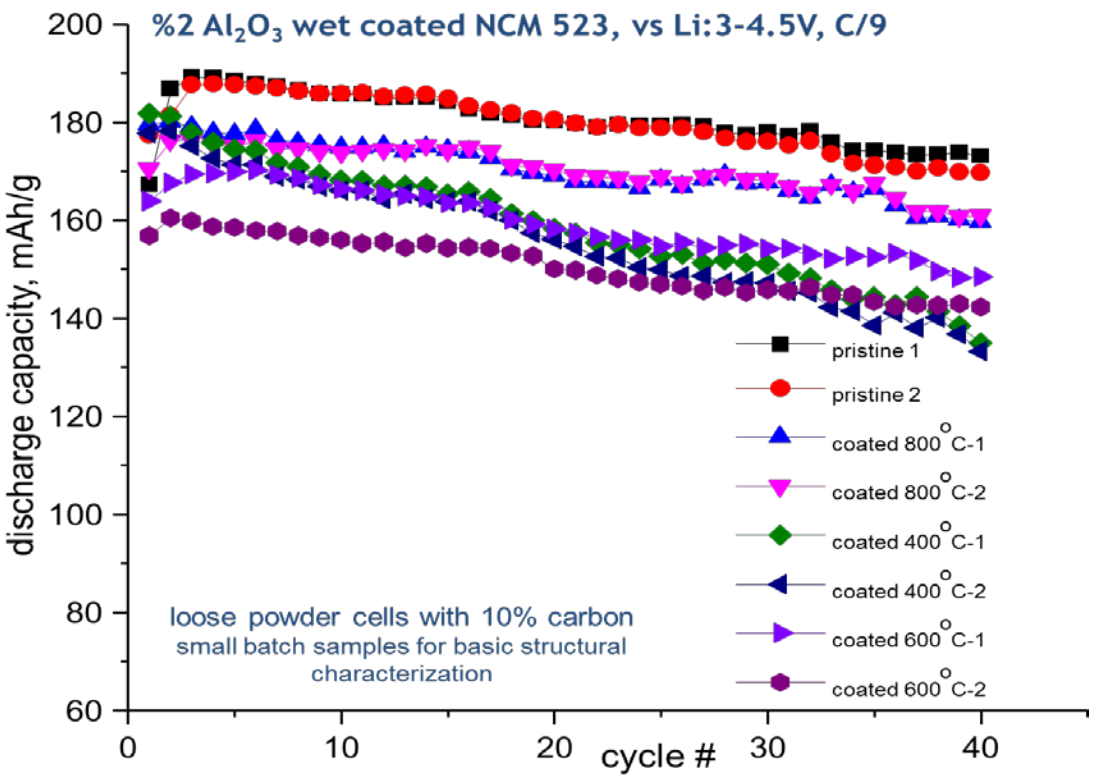
- With annealing at high temperature - coating gets well dispersed and more uniform.
- Annealing higher than 600 °C, results in formation of $LiAlO_2$.
- Wet coating process forms surface proton and lithium bearing species, ALD does not

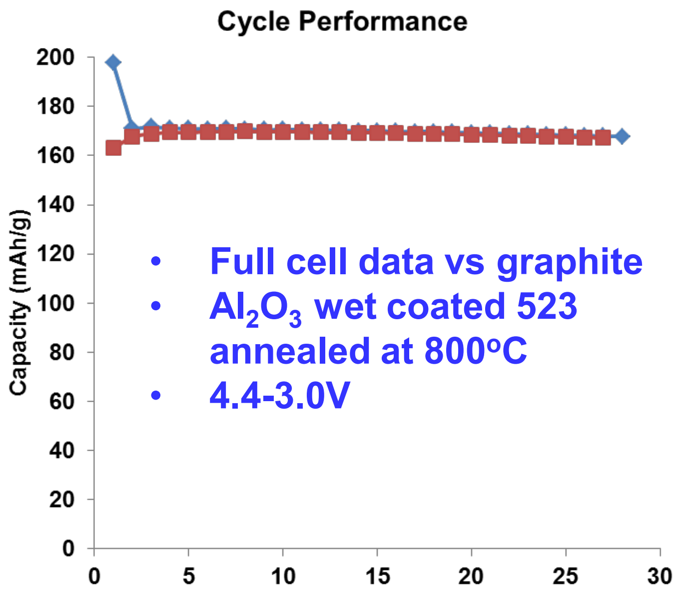
- **No signs of Al(III) incorporation into the lattice. In agreement with predictions by Ceder, et al. (JES, 4335 (1999))**
- **Solid solution formation hindered by Mn(IV)**



^{27}Al MAS NMR, 2wt% Al_2O_3 on NMC 532

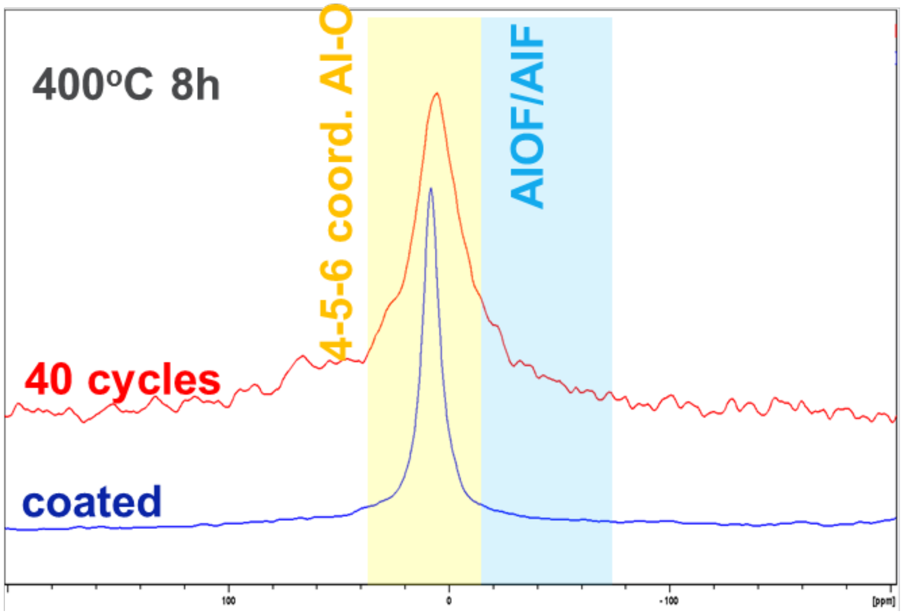
EFFECT OF CYCLING ON ALUMINA COATINGS

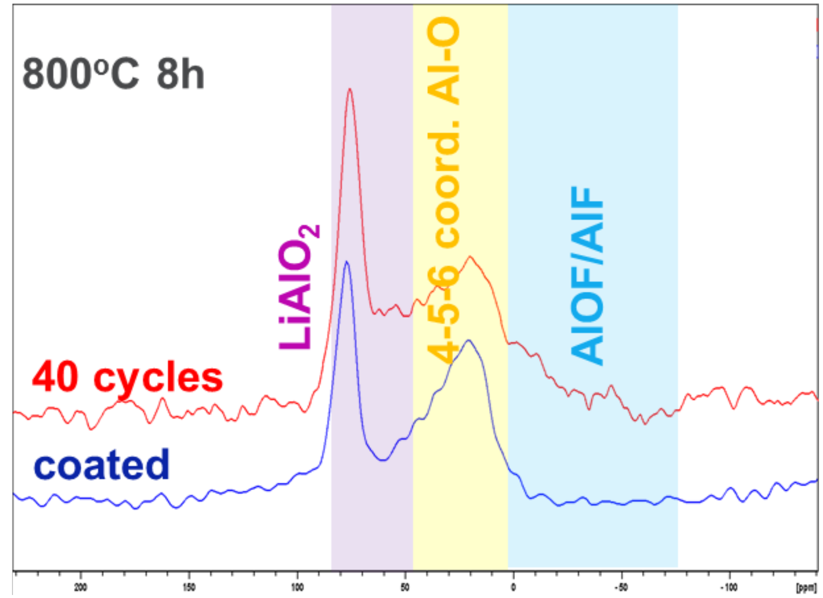




- Lower capacity in comparison with non-coated baseline material
- Higher annealing temperature provides better electrochemistry compared with lower annealing temperatures

EFFECT OF CYCLING ON ALUMINA COATINGS





^{27}Al MAS NMR 2% Al_2O_3

$$Al_2O_3 + 2HF \rightarrow Al_2O_2F_2 + H_2O$$

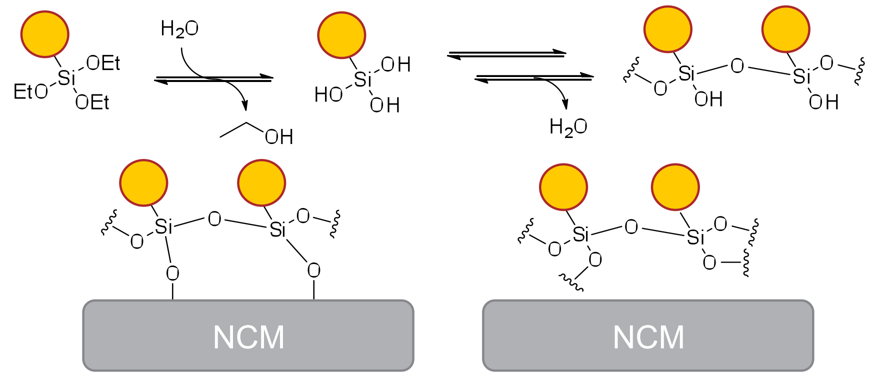
$$Al_2O_2F_2 + 2HF \rightarrow Al_2OF_4 + H_2O$$

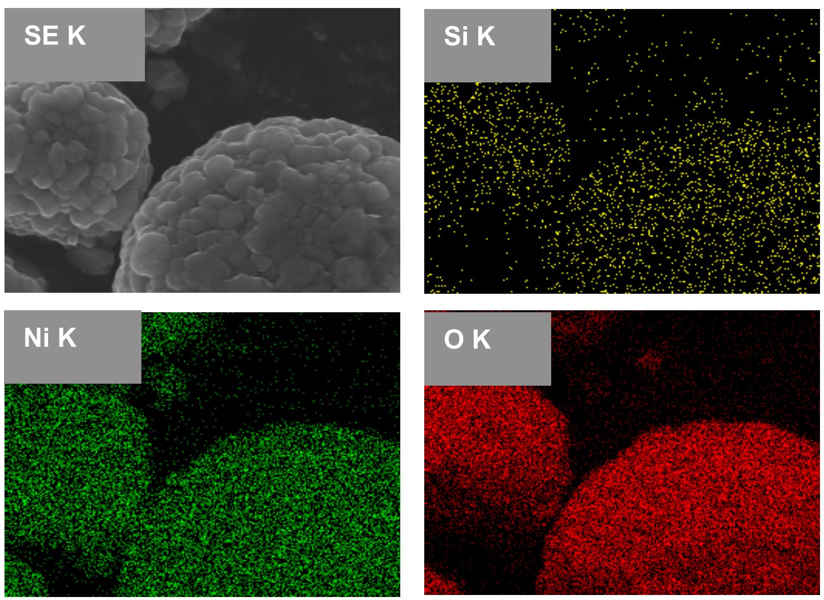
$$Al_2OF_4 + 2HF \rightarrow 2AlF_3 + H_2O$$

- **No** pronounced change in $LiAlO_2$ after cycling
- Possible formation of Al(OF)/AlF_3 environments due to reaction with electrolyte salts

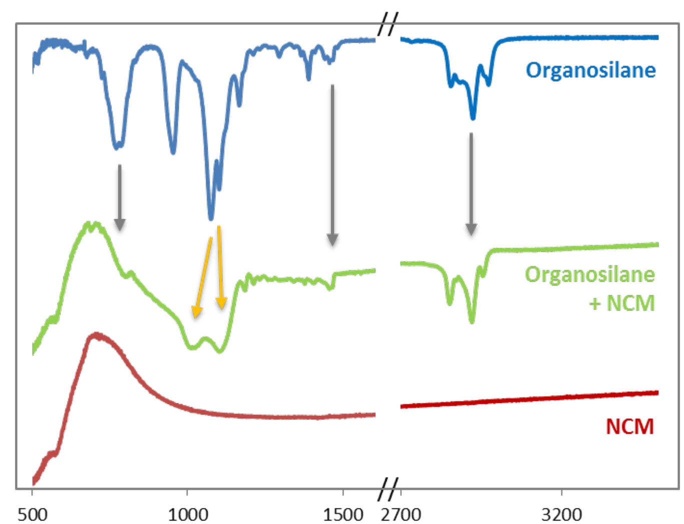
ORGANIC COATINGS

Characterization of coating synthesis by EDX shows a homogenous distribution of Si-species on NCM523 particle EDX. The formation of an **organosilane** polymer is suggested by FTIR and solid state NMR.





SEM/EDX



FTIR

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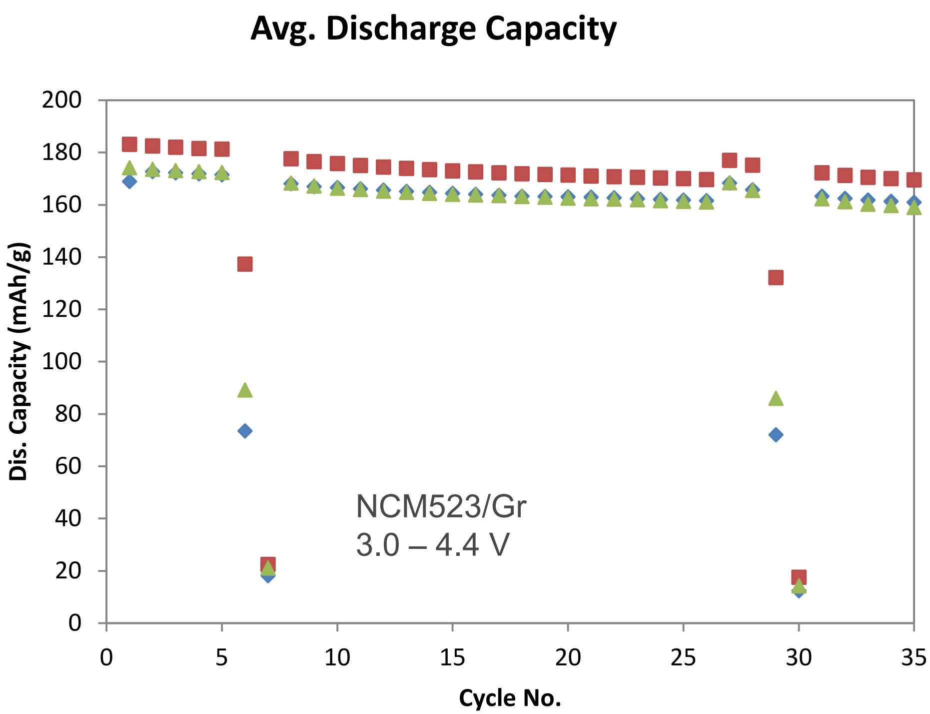
ORGANIC COATINGS



- Organosilane-coating NCM523 had no detrimental impact on performance (w/ Li-anode).
- EIS on cycling showed slightly higher rise in impedance for coated samples when compared to uncoated samples.
- Cycling in graphite full cells is similar to performance of non-coated baseline material.

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SUMMARY

- Al_2O_3 coated NCM forms $LiAlO_2$ above 600^{o}C and stays as Al_2O_3 at lower temperature
- With annealing at high temperature - coatings get well dispersed and more uniform (NCM)
- Annealing temperature has an affect on electrochemical performance of wet coated samples
- Wet coating and ALD coating result in differences in electrochemical performance

FUTURE WORK

- Investigate role of functionalizing the organosilane coatings to increase protective capability and lithium conductivity.
- Develop synthetic processes for $Li(NMC)O_2$ films.
- Identify and evaluate inorganic coatings that coat in a low-surface proton environment.
- Utilizing complimentary bulk characterization tools, investigate the subtle changes in the bulk that occur on cycling.
- Understand the surface-electrolyte reactions with regard to the surface cation reorganization.

PUBLICATIONS AND PRESENTATIONS

- Fulya Dogan, John T. Vaughey, Hakim Iddir and Baris Key, “Direct Observation of Lattice Aluminum Environments in Li-ion Cathodes NCA and Al-doped NMC via ^{27}Al MAS NMR Spectroscopy”, submitted, ACS Applied Materials and Interfaces, 2016.

- Fulya Dogan, J. - S. Park, J. Croy, B. Key, J. T. Vaughey “Investigation of Aluminum Environments in Al_2O_3 coated cathodes: The Effect of Cathode Composition on Electrochemical Performance and Aluminum Local Environments” Gordon Conference on Batteries, Ventura, CA, February 2016.

- A. Hubaud, F. Dogan, C. Pebbles, C. Liao, J. Vaughey “Interfacial Stability of Ni-rich Layered Oxide Cathodes” IBA2016, Nantes, France, March 2016.

- Adam Tornheim, Meinan He, Chi-Cheung Su, Chen Liao, Javier Bareno, Ira Bloom, Zhengcheng Zhang “Temperature Dependence of Electrolyte Oxidation at a Charged NCM Cathode Surface” MRS, Phoenix, AZ March 2016

- C. Peebles, M. He, F. Dogan, A. A. Hubaud, J. T. Vaughey, C. Liao “Organosilane Cathode Coatings for High-Voltage Lithium Ion Batteries” 18th International Meeting on Lithium Batteries, Chicago, IL, USA, June 2016.

- C. Peebles, F. Dogan, A. A. Hubaud, J. T. Vaughey, C. Liao “Organosilane Coatings for Ni-Rich High-Voltage Lithium Ion Batteries” 229th Meeting of the Electrochemical Society, San Diego, CA June 2016.