



ENABLING HIGH-ENERGY, HIGH-VOLTAGE LI-ION CELLS FOR TRANSPORTATION APPLICATIONS: MODELING AND ANALYSIS

Project ID: ES252

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2016 U.S. DOE HYDROGEN and FUEL CELLS
PROGRAM and VEHICLE TECHNOLOGIES
OFFICE ANNUAL MERIT REVIEW AND PEER
EVALUATION MEETING

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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

Energy fade during calendar-life and cycle-life aging limits the commercial viability of lithium-ion cells for transportation applications

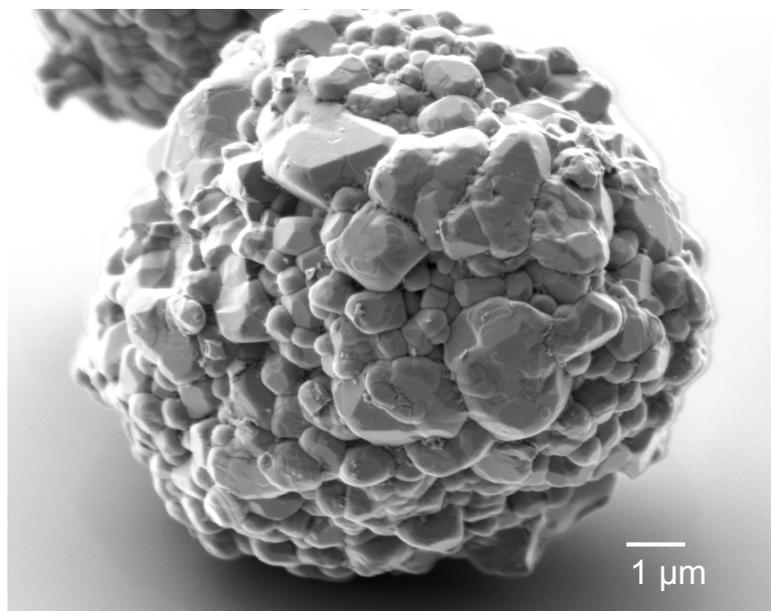
- High-performing, high-energy, safe and long-life batteries are needed to reduce petroleum consumption in vehicular applications
- Performance targets of plug-in electric vehicle (PEV) and electric vehicle (EV) batteries can be met by cells containing layered-oxide-based positive electrodes
- To achieve the energy and power density targets, cells with these electrodes must be cycled to voltages that exceed 4.5 V vs. Li/Li⁺
- On extended cycling at these voltages, capacity loss, impedance rise and voltage fade reduces the cell's energy and power output
- Mitigating these performance degradation characteristics is, therefore, critical to increasing longevity, thereby reducing lifetime cost of these high-energy batteries

APPROACH - PROJECT

- Determine factors that contribute to performance decline (capacity fade, impedance rise) in the baseline NCM523/Graphite cells
 - Use various diagnostic tools and techniques to determine cell constituents and reaction mechanisms associated with this performance loss
- Investigate oxide stability using first-principles density functional theory (DFT) and Ab-Initio Molecular Dynamics (AIMD) simulations
 - Perform DFT at GGA+U/HSE level and use AIMD to access activated states
 - Use techniques to explain data from techniques such as XAS and NMR
- Develop electrochemical models to explain electrode and cell performance and performance loss in high-energy/high-voltage lithium ion systems
 - Build on earlier successful characterization and modeling studies
 - Expand and improve data base and modeling capabilities
- Establish protocols to examine oxidative stability of electrolytes
 - Use protocols to identify electrolytes that are best suited at high voltages
 - Investigate and model the parasitic currents observed at high cell voltages
- Identify electrolyte systems that outperform the baseline Gen2 electrolyte
 - Examine fluorinated electrolytes which are known for high-voltage stability
 - Find electrolyte additives that mitigate loss of cell performance

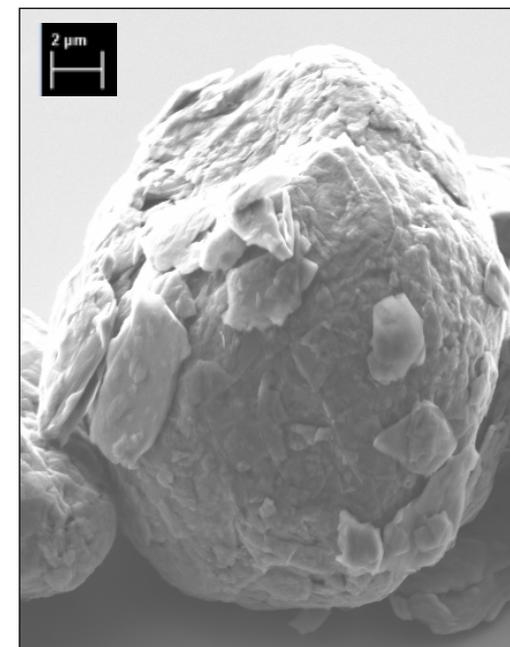
ELECTRODES FABRICATED AT THE CAMP FACILITY ARE USED FOR VARIOUS TESTS

Baseline Cells: NCM523-based positive & graphite-based negative electrodes



Baseline Electrolyte

- 1.2 M LiPF₆ in EC/EMC (3:7)



Positive Electrode contains

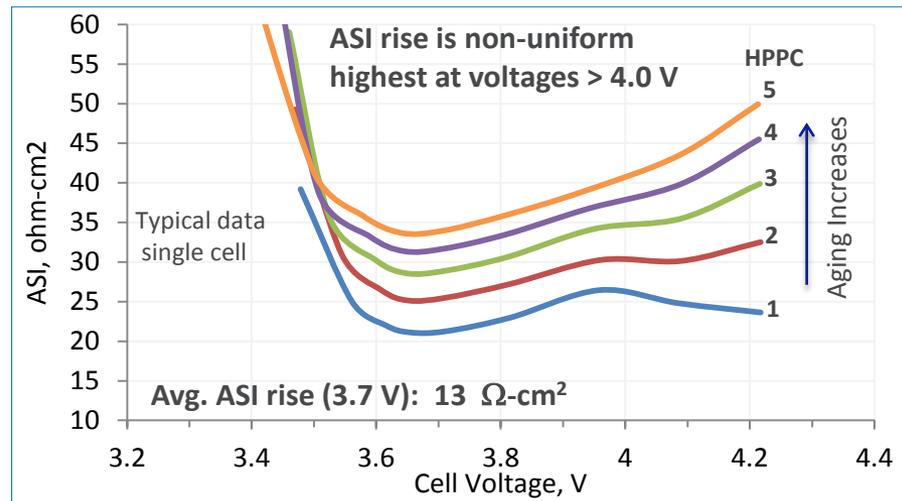
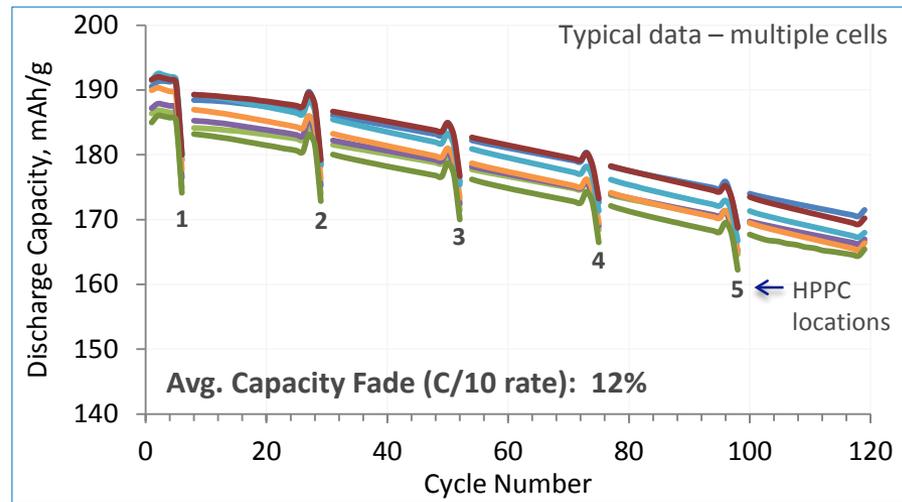
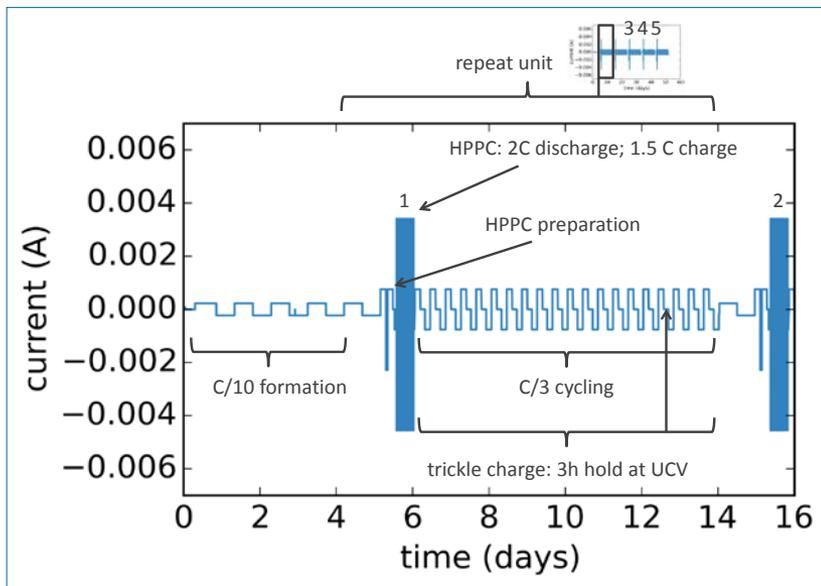
- 90 wt% NCM523 Oxide
- 5 wt% C45 carbon
- 5 wt% PVdF binder

Negative Electrode contains

- 92 wt% A12 Graphite
 - 2 wt% C45 carbon
 - 6 wt% PVdF binder

COIN CELL TESTS USING THE HEHV PROTOCOL SHOW CAPACITY FADE AND IMPEDANCE RISE

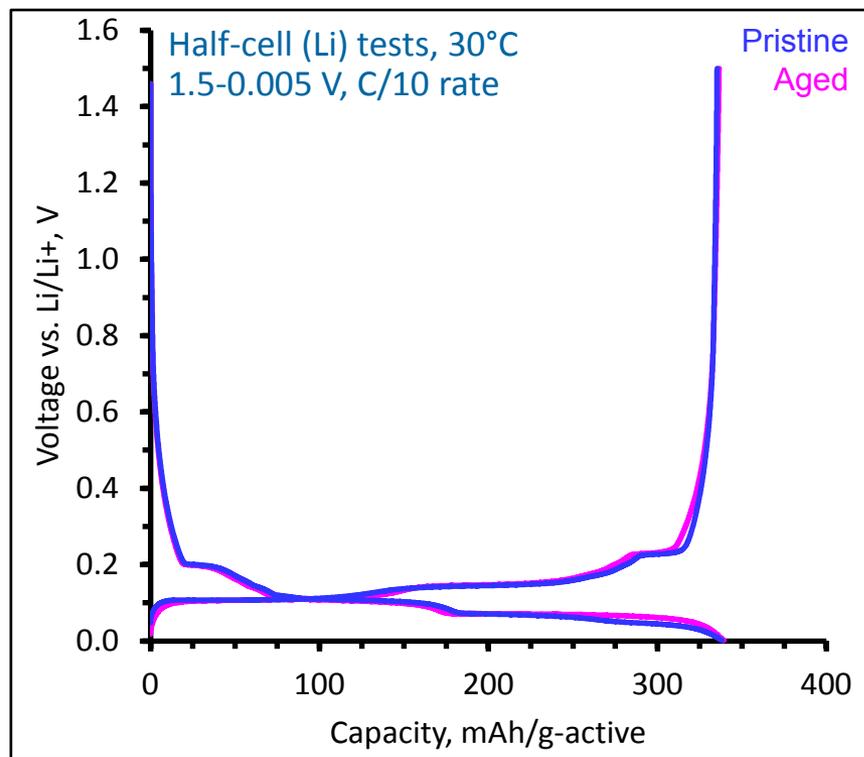
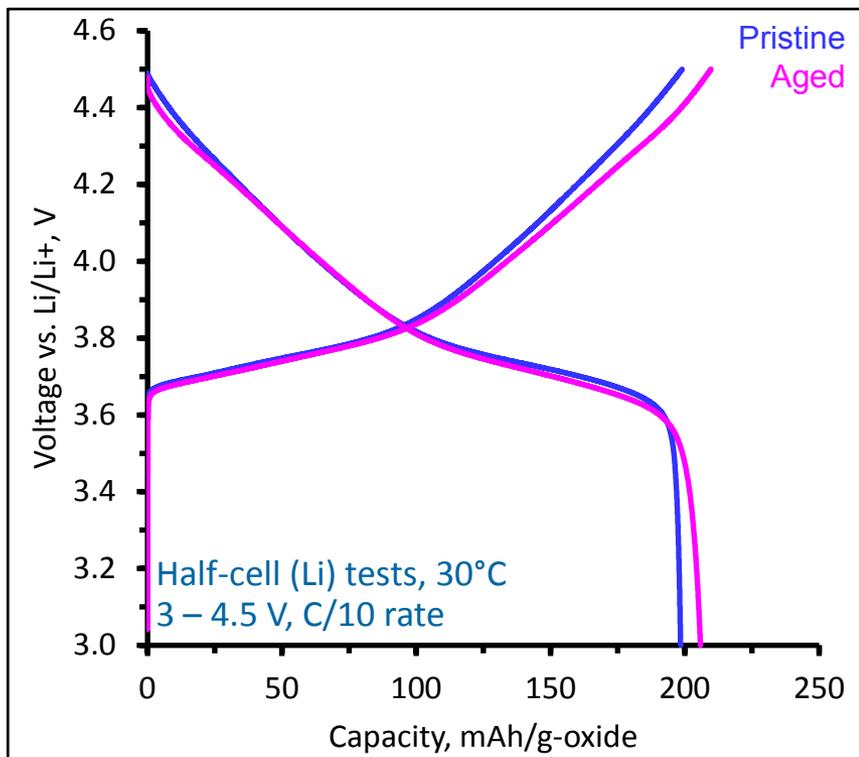
NCM523/Gr, 3-4.4 V, 30°C



Standard protocol developed to track performance changes

CAPACITIES OF HARVESTED ELECTRODES ARE SIMILAR TO THAT OF PRISTINE ELECTRODES

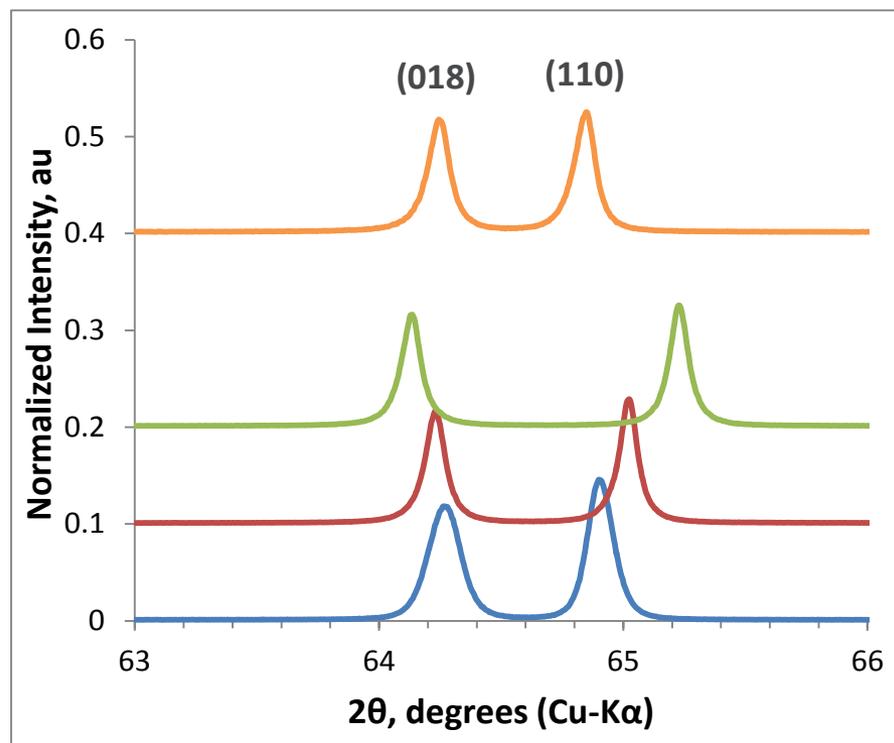
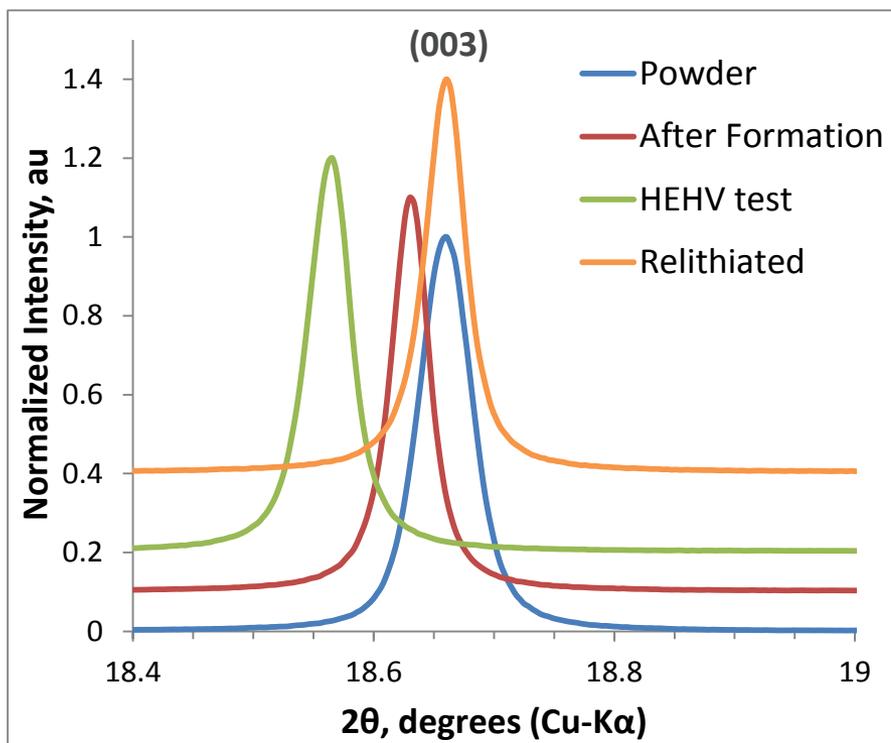
Electrodes harvested from NCM523/Gr cells cycled using HEHV protocol



Data show that there is no obvious “loss” of active material

XRD DATA ARE CONSISTENT WITH HARVESTED ELECTRODE ELECTROCHEMISTRY DATA

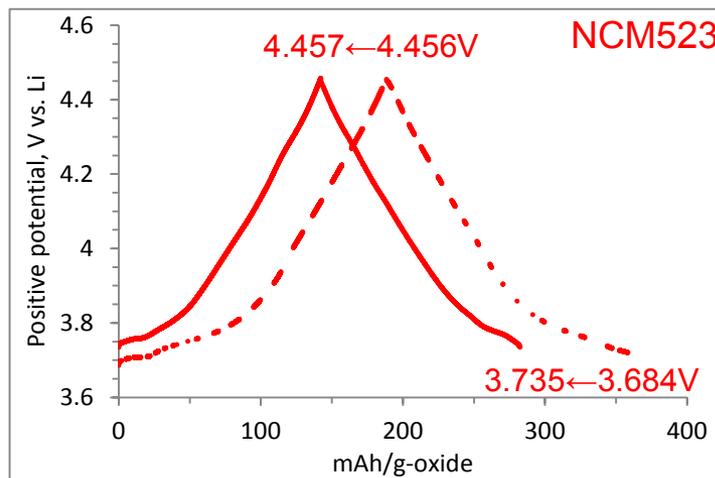
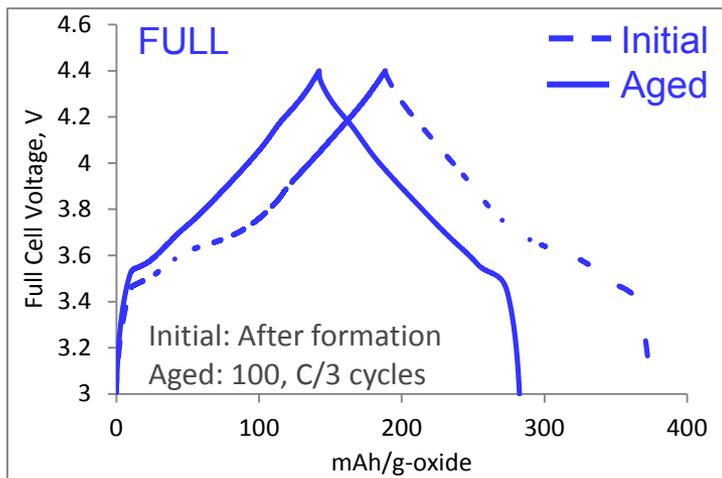
NCM523 oxide patterns collected at the Advanced Photon Source



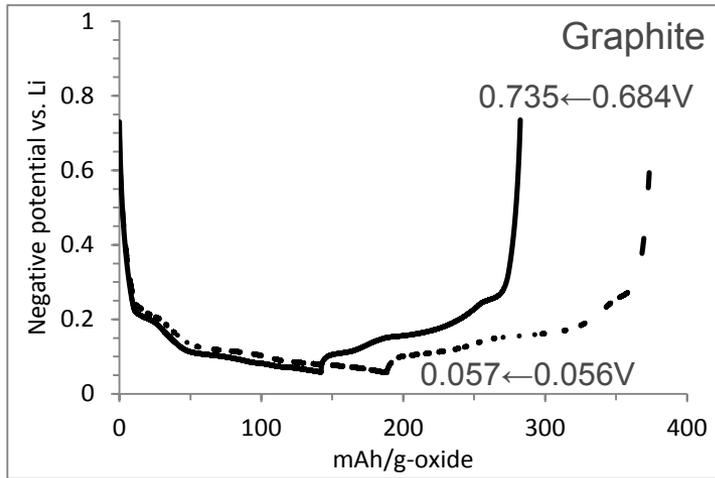
XRD patterns indicate c-axis expansion and a-axis contraction that are consistent with oxide delithiation during progressive aging. Relithiated oxide pattern is similar to that of the pristine powder, which indicates that the oxide bulk structure is maintained after HEHV cycling.

DATA FROM CELLS WITH REFERENCE ELECTRODES COMPLEMENT DATA FROM COIN CELLS

NCM523/Gr, Li-metal RE, 3-4.4 V, 30°C, Data shown at ~ C/10 rate



Full cell capacity decreases during the 3-4.4 V cycling. The positive electrode UCV shows minimal change, whereas the LCV changes by 51 mV, reducing the voltage cycling window. Corresponding changes are seen in the negative electrode plots.



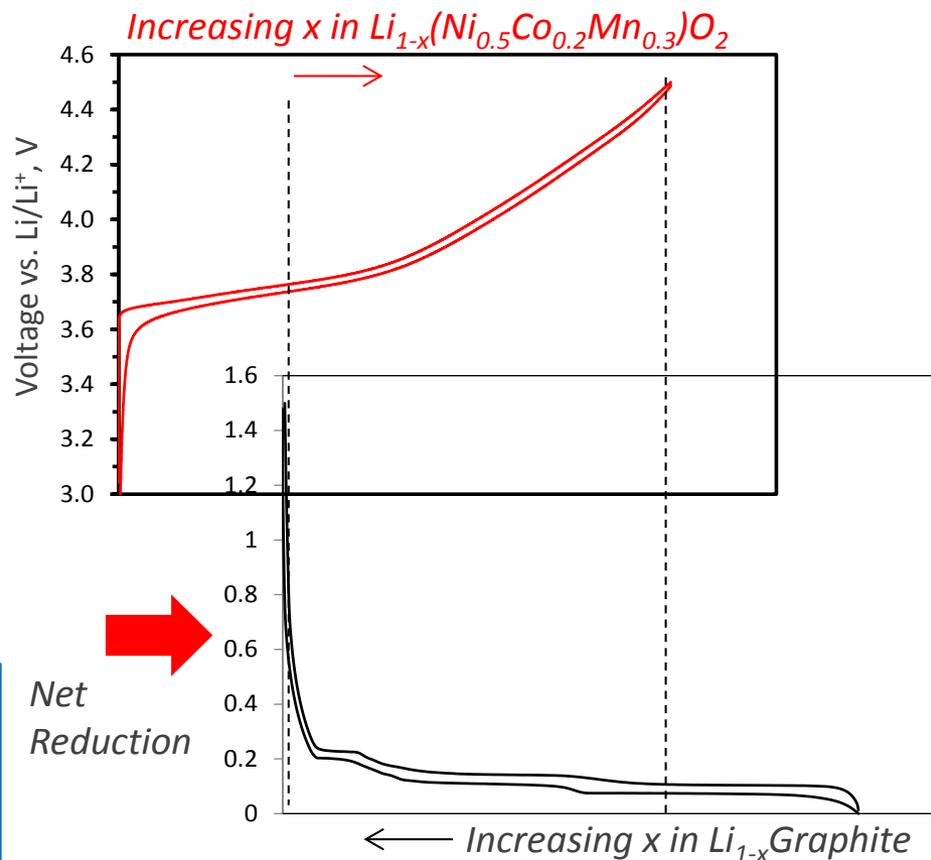
SCHEMATIC ILLUSTRATION OF ELECTRODE POTENTIAL WINDOW SHIFTS AND FULL CELL VOLTAGE AFTER CYCLING

NCM523/Gr, Li-metal RE, 3-4.4 V, 30°C, Data shown at ~ C/10 rate

- Electrode potential window shifts during cycling
 - Reduces utilization of electrode active material
 - Causes positive electrode to cycle at higher SOC
 - Increases potential at negative electrode during cell discharge

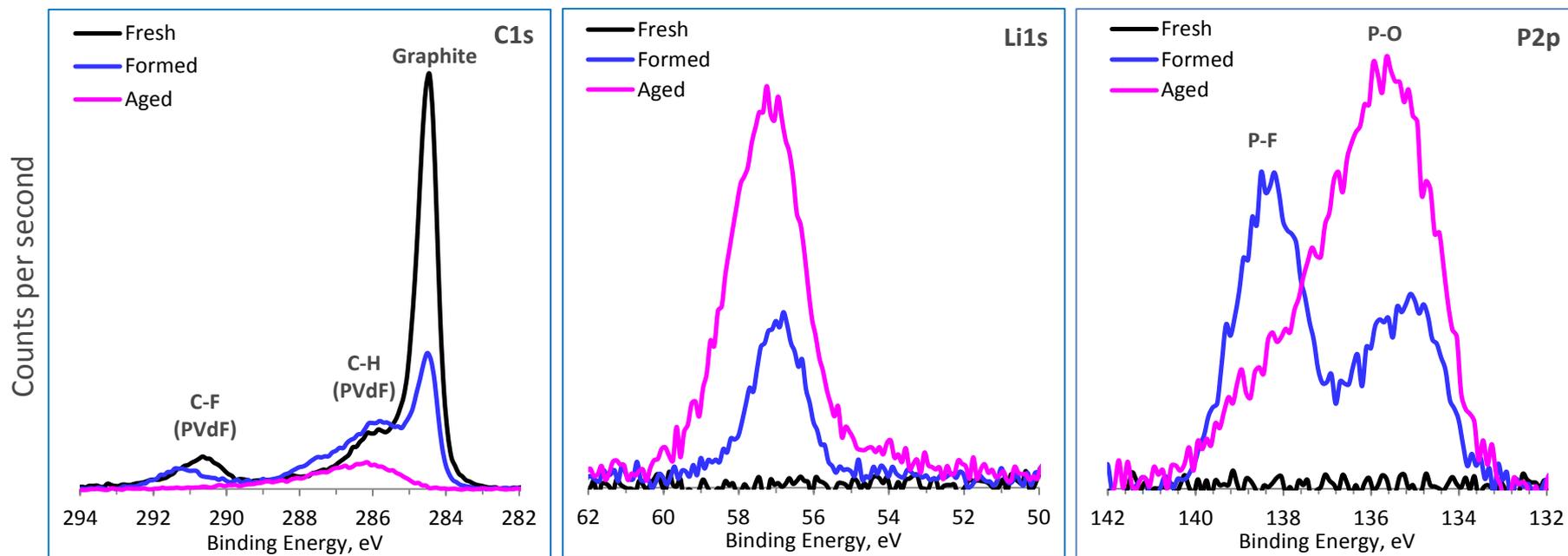
Li-trapping in negative SEI is main contributor to cell capacity fade

Electrolyte additives that enhance SEI stability should reduce fade



XPS/SIMS DATA ARE CONSISTENT WITH LITHIUM TRAPPING IN NEGATIVE ELECTRODE SEI

NCM523/Gr cells - XPS data of graphite electrodes from the Post-Test Facility

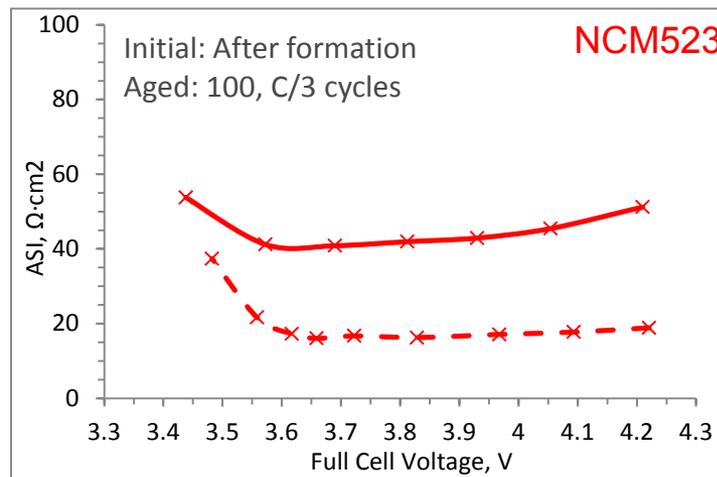
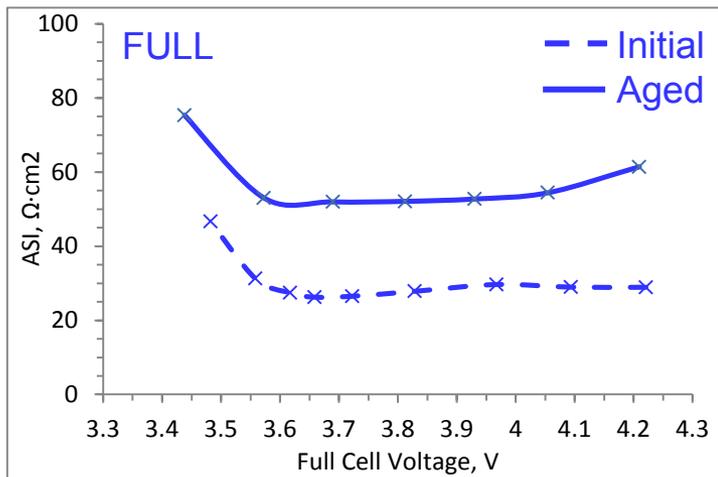


Note: Y-axis scale is different for each element
All samples were lightly rinsed in DMC before study

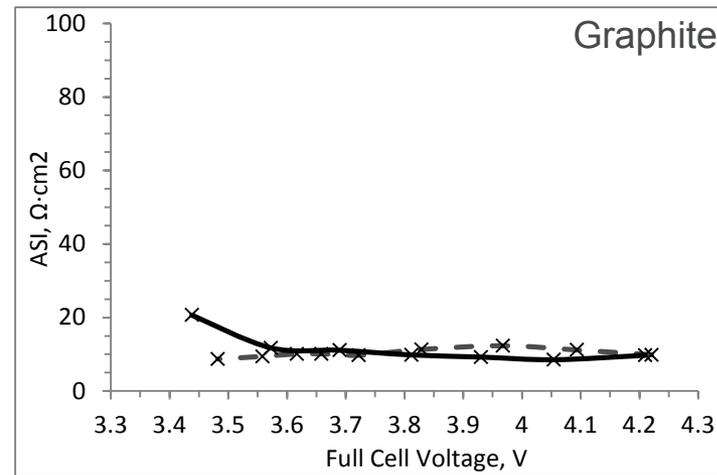
The C1s spectra show a reduction in graphite and binder peak intensities on cycling indicating SEI presence, which appears to get thicker on aging. There is a corresponding increase in Li1s, P2p, O1s (not shown) and F1s (not shown) peak intensities. In general, the aged sample SEI appears more inorganic, i.e., dominated by salt-decomposition products.

CELL IMPEDANCE RISE MAINLY ARISES AT THE POSITIVE ELECTRODE - HPPC (10S, 3C DISCHARGE PULSE)

NCM523/Gr, Li_xSn RE, 3-4.4 V, 30°C, cycling based on HEHV protocol

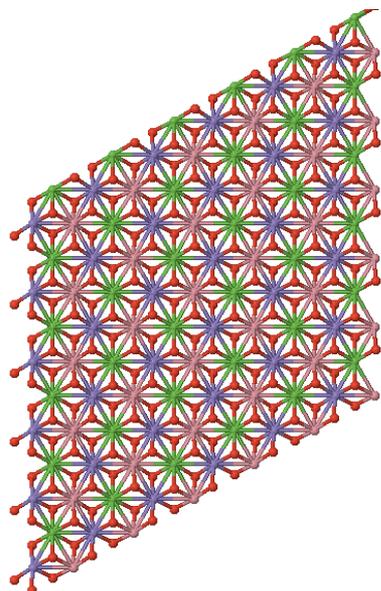


Full cell impedance increases during the 3-4.4 V cycling. The positive electrode is the main contributor to this impedance rise. The negative electrode contribution is minimal. Similar conclusions were drawn from studies on electrodes harvested from cells tested using the HEHV protocol.



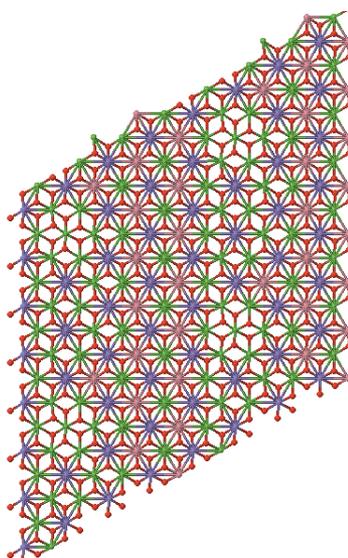
DFT AND AIMD MODELS BEING DEVELOPED TO EXAMINE OXIDE STRUCTURE AND STABILITY

Atomic Structures of pristine NCM333, NCM523 and NCM622 shown



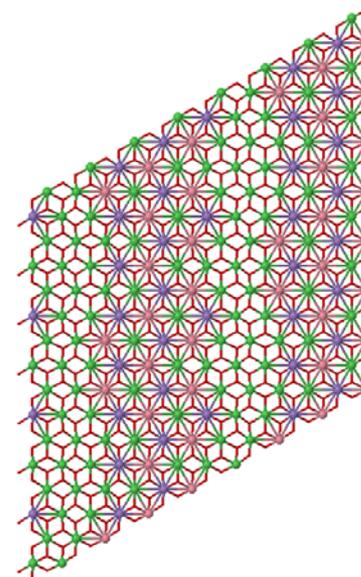
Low energy configuration NCM333

Ni²⁺, Mn⁴⁺, Co³⁺



Low energy configuration NCM523

Ni(2+,3+,4+), Mn⁴⁺, Co³⁺



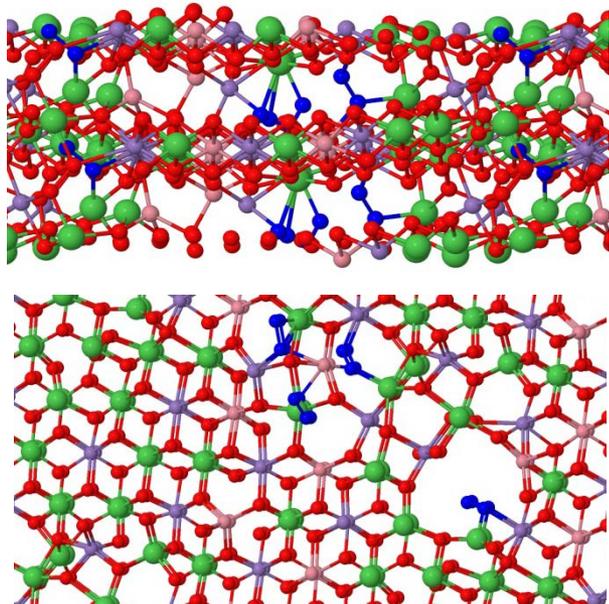
Low energy configuration NCM622

- Ni
- Mn
- Co
- Li

Ni clustering increases with increasing Ni content and oxidation state

MODELS INDICATE THAT NCM523 OXIDE BULK STRUCTURE IS STABLE UP TO ~70% DELITHIATION

Oxide surfaces are more likely to show structural transformations



NCM523 - All Li removed AIMD+DFT

Top panel: view along TM planes.

Bottom panel: view along the c-axis perpendicular to the TM planes.

O is in red, Ni in green, Co in pink, and Mn in purple.

O-O bonds are shown in blue

→ **Signature of O participation in the charge compensation mechanism**

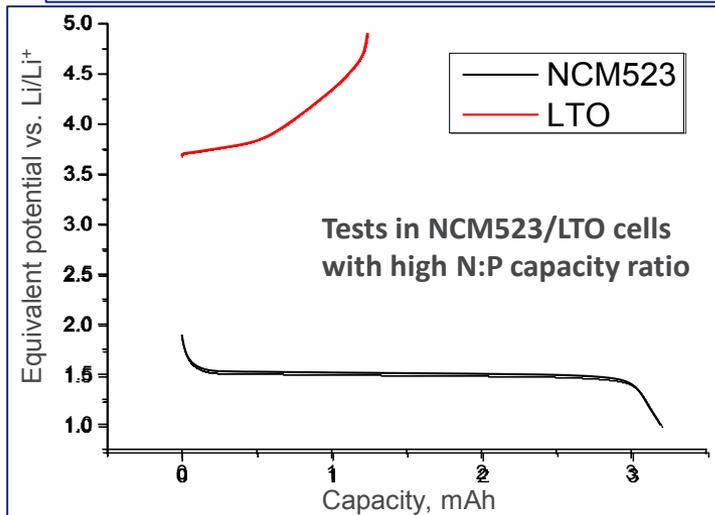
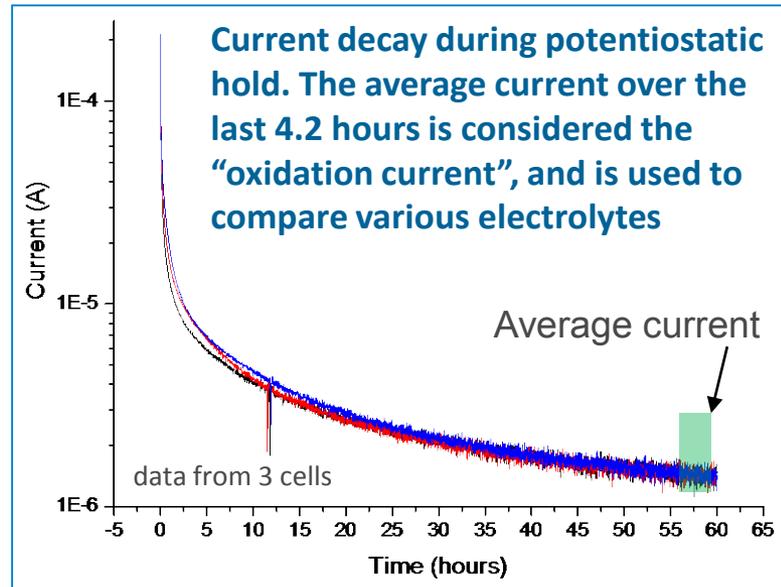
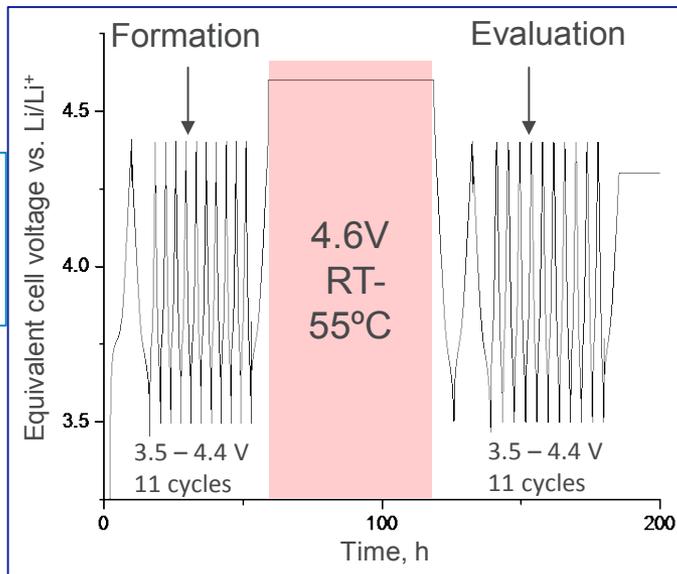
AIMD simulations (state of charge) are being conducted to explore possible structural transformations that could result from oxide delithiation

Data indicate that Ni-rich domains are less stable and undergo structural transformations, starting with O loss, then Ni migration to Li layer, followed by Mn and Co migration (to a lesser extent)

Also see
ES254

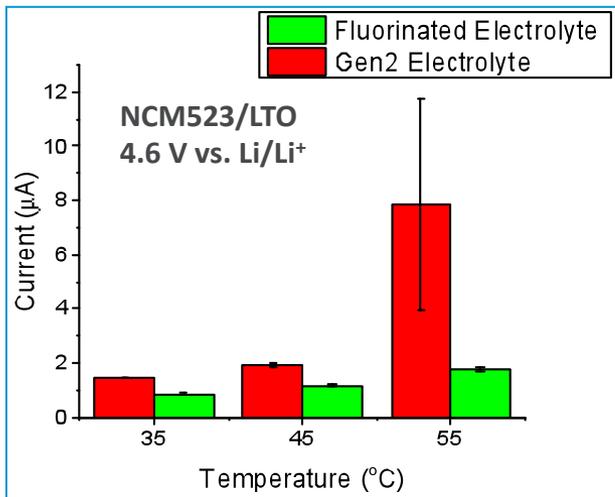
NEW PROTOCOL DEVELOPED TO EVALUATE OXIDATIVE STABILITY OF ELECTROLYTES

Protocol consists of formation cycling, potentiostatic hold, post-test cycling



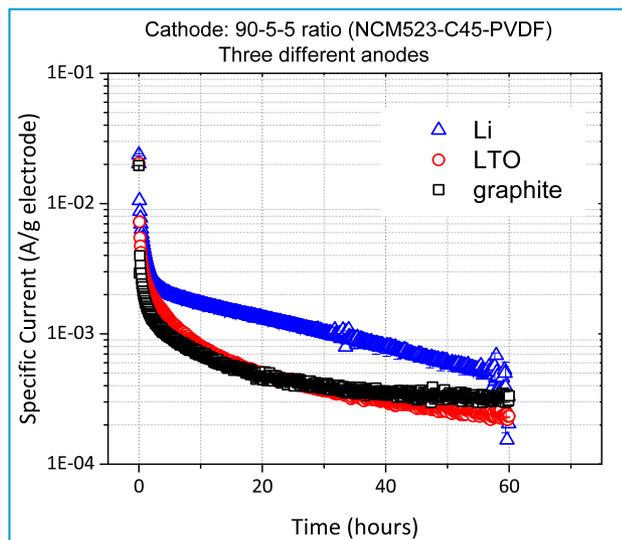
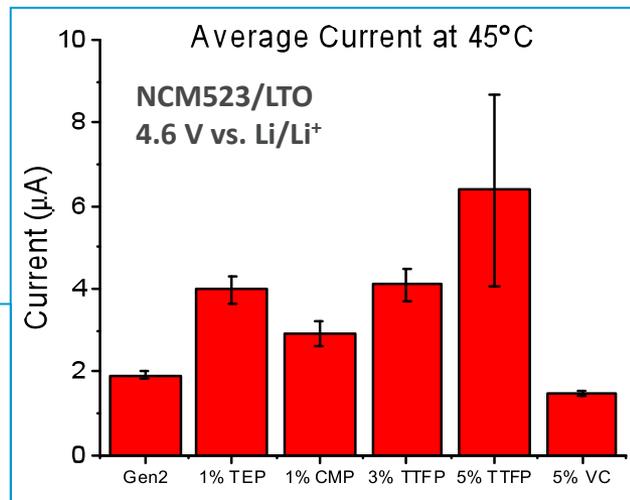
- Multiple contributions to the decaying current
 - Active material relaxation
 - Loss of oxidizable component
 - Changes at the interface
 - Loss of electrolyte lithium

OXIDATIVE STABILITY – ELECTRODES, ELECTROLYTES AND TEMPERATURE ALL AFFECT THE DATA

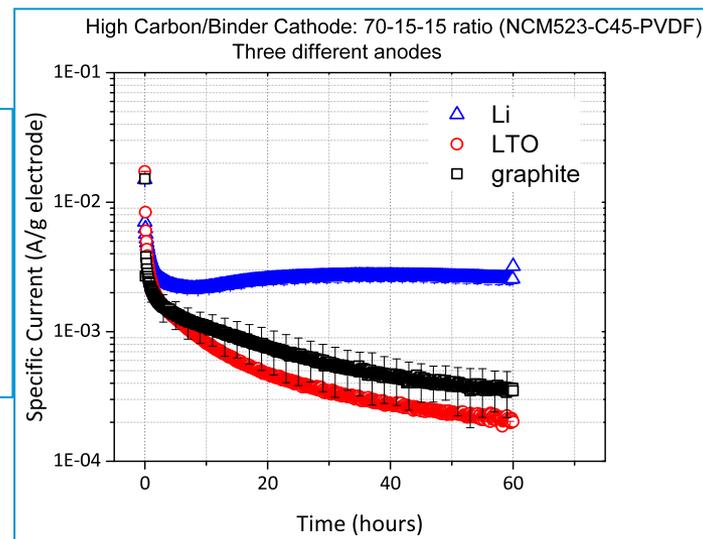


The oxidation current for the fluorinated electrolyte is smaller than that for the Gen2 electrolyte

Of the various electrolyte additives studied, cells with 5 wt% VC show the lowest oxidation current

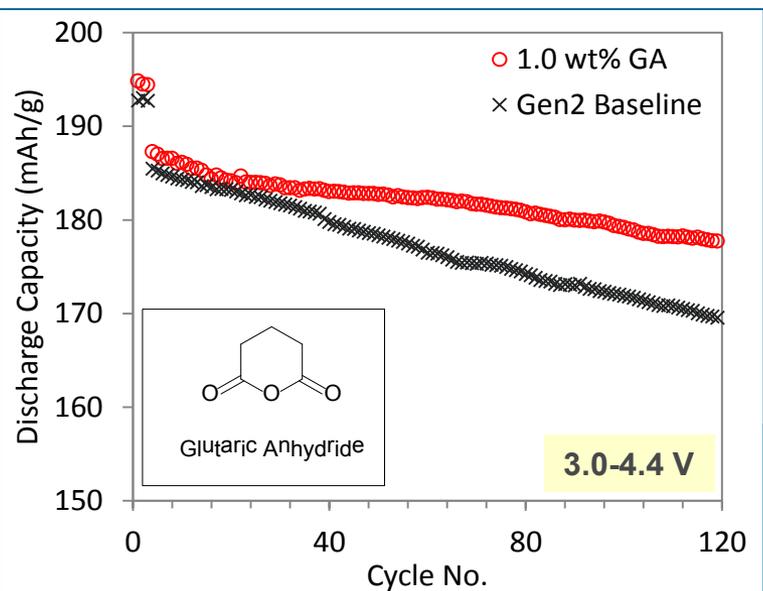
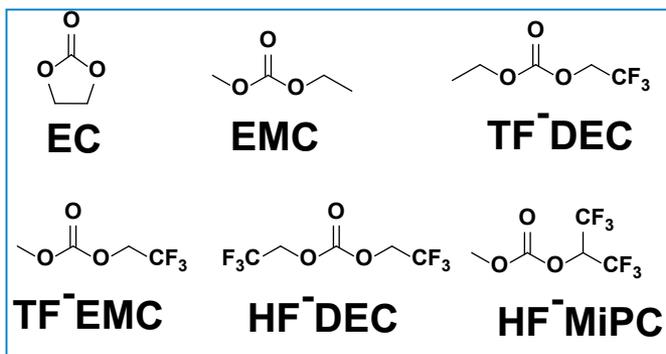


Current decay is affected by the electrode couple being studied. These “parasitic” currents are especially higher for cells with Li metal anodes

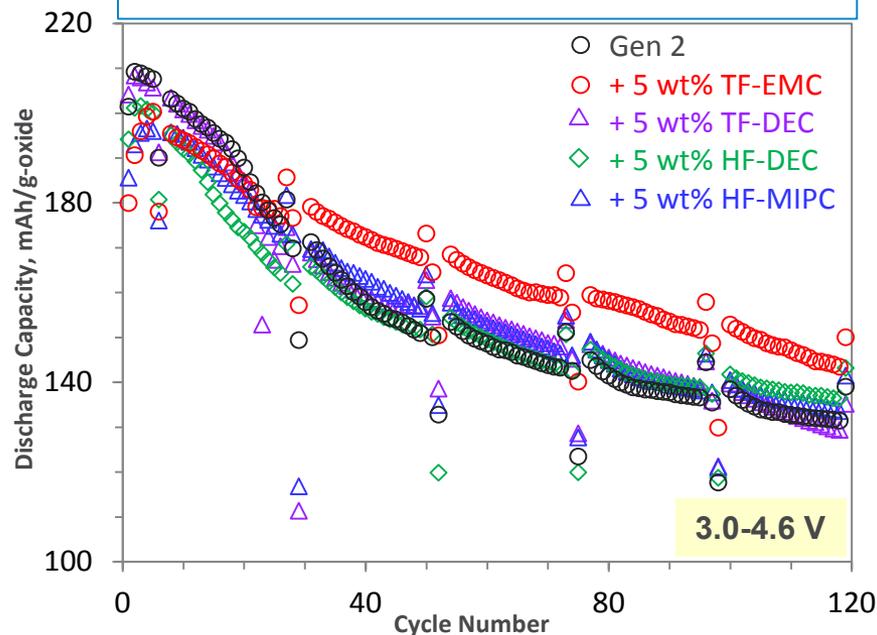


FLUORINATED CARBONATES AND OTHER COMPOUNDS ARE BEING EXAMINED AS ELECTROLYTE ADDITIVES

NCM523/Gr, 30°C, cycling based on HEHV protocol



Capacity retention is marginally better in cells with 5.0 wt% TF-EMC

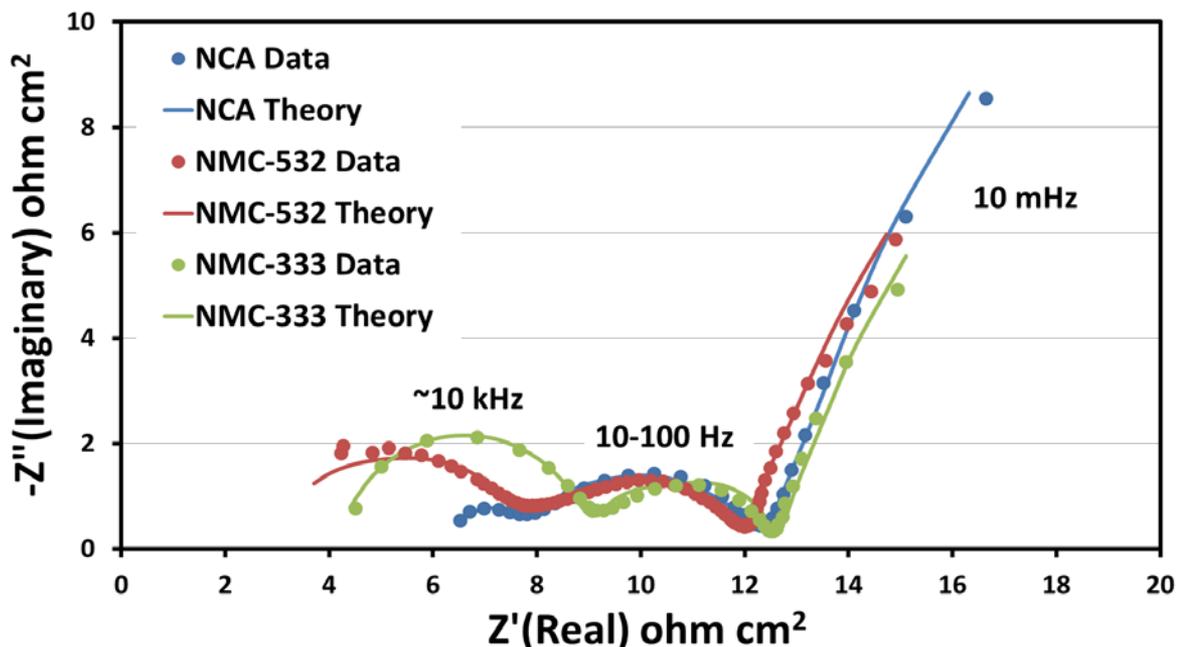


Addition of 1 wt% Glutaric Anhydride improves cell capacity retention but also increases cell impedance

EIS ELECTROCHEMICAL MODELING VALUABLE FOR EXAMINING INTERFACIAL PHENOMENA

EIS Studies on NCM523 Standard Electrodes Similar to Earlier Work on NCA and NCM333

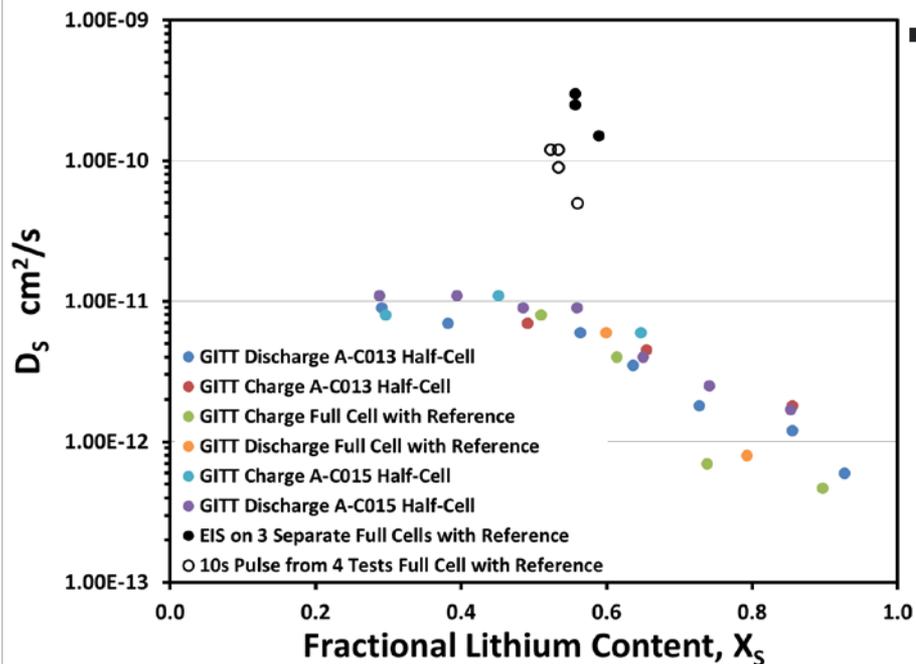
- EIS model analysis of micro-reference electrode cell studies are able to track changes in interfacial transport and kinetic parameters with SEI and surface modifications.
- Characteristic large high frequency circular arc on NMC materials associated with electronic particle contact resistance.
- Bulk lithium diffusion coefficient (D_S) for NCM523 is relatively high (i.e. on the order of 10^{-10} cm²/s).



Description of electrochemical model in *Journal of The Electrochemical Society*, **162** (4) A559 (2015)

ELECTROCHEMICAL MODEL APPLIED TO VARIOUS NCM523 STUDIES TO OBTAIN D_S

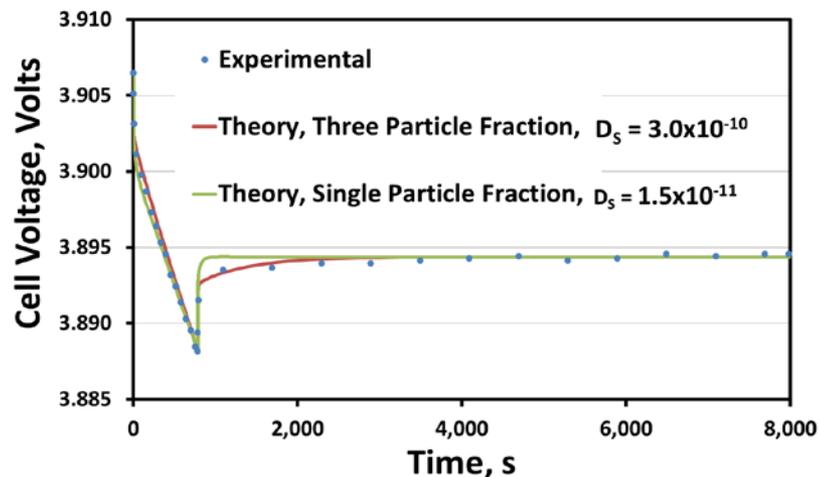
Slow Relaxation (~900s TC) Observed in Galvanostatic Intermittent Titration Technique (GITT) Studies on NCM523 vs. NCA & NCM333



■ A large variation in the D_S was obtained depending on the type of electrochemical study (e.g. EIS, Short Pulse Current, and GITT) modeled using original lithium intercalation model.

■ Including multiple particle fractions in DC active material lithium intercalation model results in an improved fit and a higher D_S .

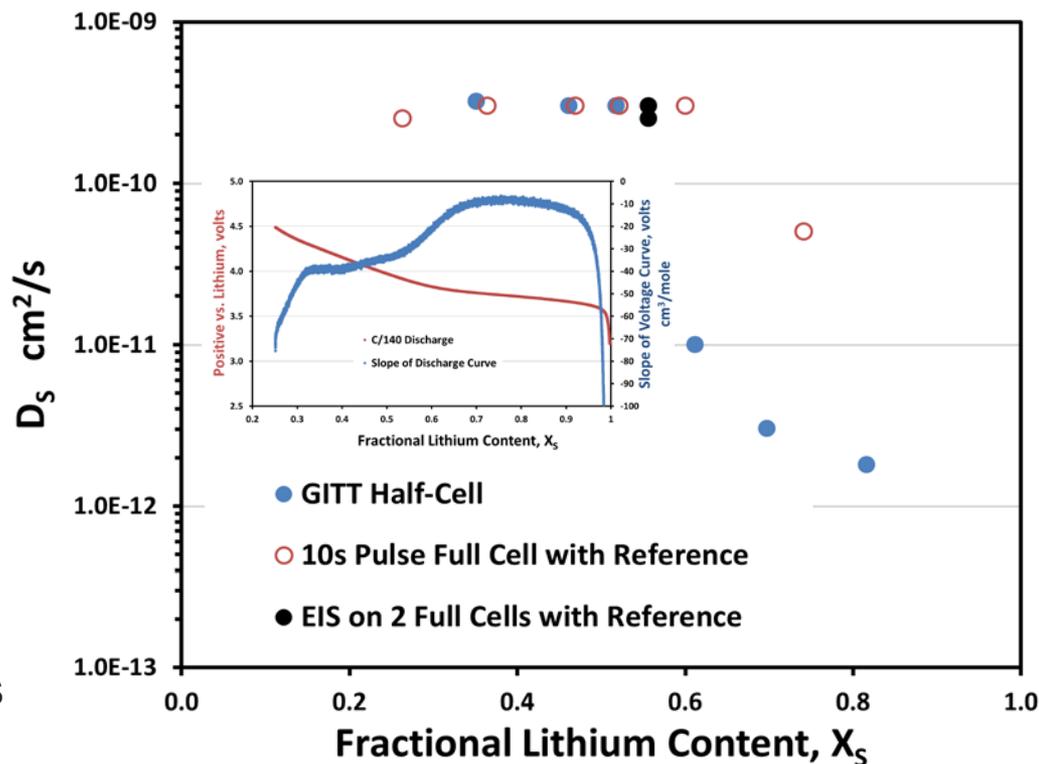
NMC-532 Half-Cell GITT ($X_S = 0.52$)
13m C/21 Discharge Followed by Long Rest



D_s FROM NCM523 STUDIES USING MULTIPLE PARTICLE FRACTION INTERCALATION MODEL

D_s the Same at Higher SOC, but Varies at Lower SOC. Variation Occurs at Inflection in OCV Curve.

- Alternative active material transport models were examined to address the observed sudden change in D_s .
 - Using a thermodynamic rather than a concentration driving force in model shows some improvement.
 - Modeling the bulk NMC active material as dual-domains can greatly reduce the variation, but introduces new parameters that are difficult to determine.
- Further work needs to be done to specifically examine the impact of the phase change that causes the inflection in the NCM523 OCV curve.



CONTRIBUTORS AND ACKNOWLEDGMENT

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- Post-Test Facility (PTF)
- Materials Engineering Research Facility (MERF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Advanced Photon Source (APS)

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PUBLICATIONS AND PRESENTATIONS

- A. Tornheim, S.E. Trask, Z. Zhang, J. Electrochemical Society, Article under review, J. Electrochemical Society 160 (2016)
 - Title: Evaluation of Electrolyte Oxidation Stability on Charged $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ Cathode Surface through Potentiostatic Holds.
- D.P. Abraham, Invited Presentation, Lithium Battery Power 2015, Baltimore, MD, November 19, 2015.
 - Title: Enabling Long-Life High Energy Density Lithium-Ion Cells”
- J.A. Gilbert, M. Klett, J. Bareno, D. Miller, V.A. Maroni, D.P. Abraham, Abstract, International Meeting of Lithium Batteries (2016), Chicago, IL
 - Title: Performance Changes in NCM523//Graphite Cells Resulting from High-Voltage Cycling
- C. C. Su, M. He, C. Peebles, Z. Zhang, Abstract, International Meeting of Lithium Batteries (2016), Chicago, IL
 - Title: The Impact of Different Substituents in Fluorinated Cyclic Carbonates in the Performance of High Voltage Lithium-Ion Battery Electrolyte
- N.R. Vadivel, K.G. Gallagher, D.W. Dees, Abstract, International Meeting of Lithium Batteries (2016), Chicago, IL
 - Title: Modeling the Positive Electrode Side Reaction for a High Voltage Lithium-Ion Battery
- R. Benedek and H. Iddir, Abstract, International Meeting of Lithium Batteries (2016), Chicago, IL
 - Title: Energy-Density Optimization in Lithium-Rich Layered-Oxide Cathode Materials
- M. He, C. C. Su, Y. Wang, Z. Zhang, C. Peebles, Abstract, International Meeting of Lithium Batteries (2016), Chicago, IL
 - Title: Mechanistic Studies of Fluorinated Electrolyte for High Voltage Lithium-Ion Battery

FUTURE WORK AND WORK IN PROGRESS

- “Sprints” in progress to identify electrolyte systems that outperform the baseline electrolyte at high voltages
 - Fluorinated systems and various additives are being examined
 - Details will be reported in future publications/presentations
 - Mechanistic details of promising systems will be investigated
- Continue development of electrochemical models
 - Utilize EIS electrochemical model to study changes in interfacial transport and kinetic parameters with SEI and surface modifications
 - Complete examination of lithium transport in NCM523, including the (a) Impact of phase changes; (b) Influence of top-of-charge voltage
 - Complete modeling the parasitic current behavior at high cell voltages
- Extend development of DFT and AIMD models
 - Use NMC333 low energy surfaces as model systems to investigate oxide interactions with the electrolyte and additives
 - Investigate the effect of increased Ni content on the stability of the low energy surfaces and their interactions with the electrolyte

SUMMARY

- NCM523/Gr and NCA/Gr cells tested using the HEHV protocol in the 3-4.4 V range show capacity loss and impedance rise
 - Data from harvested electrodes show that Li-trapping in negative electrode SEI is main contributor to capacity fade
 - Data from Reference Electrode cells show that (i) the positive electrode is main contributor to impedance rise, and (ii) electrode potential window shifts during cycling reduces utilization of electrode active material
- Models examining low energy configurations in pristine NCM oxides show that Ni clustering increases with increasing Ni content and oxidation state
 - AIMD simulations indicate that Ni-rich domains are less stable and prone to structural transformations
 - Oxide surfaces are far less stable than the bulk, and undergo major structural transformation resulting from oxygen loss
- An electrochemical test protocol was developed to determine electrolyte oxidation rates at high voltages
 - Many additives do not passivate the cathode surface as previously suggested
- Electrochemical modeling studies show that lithium transport in NCM523 oxides is more complex compared to NCA and NCM333
 - NCM523 exhibits an extremely long time constant which complicates analysis