Addressing the Voltage Fade Issue with Li-Mn Rich Oxide Cathode Materials

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Chemical Sciences and Engineering Division

Argonne National Laboratory

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Project ID# ES161

Vehicle Technologies Program

Overview

Timeline

- Start: October 2012
- Finish: September 2014

Budget

- FY2013: $4000 K

Barriers

- Development of a PHEV and EV batteries that meet or exceed DOE/USABC goals.

Partners (Collaborators)

- ORNL
- NREL
- BNL
- LBNL
- JPL

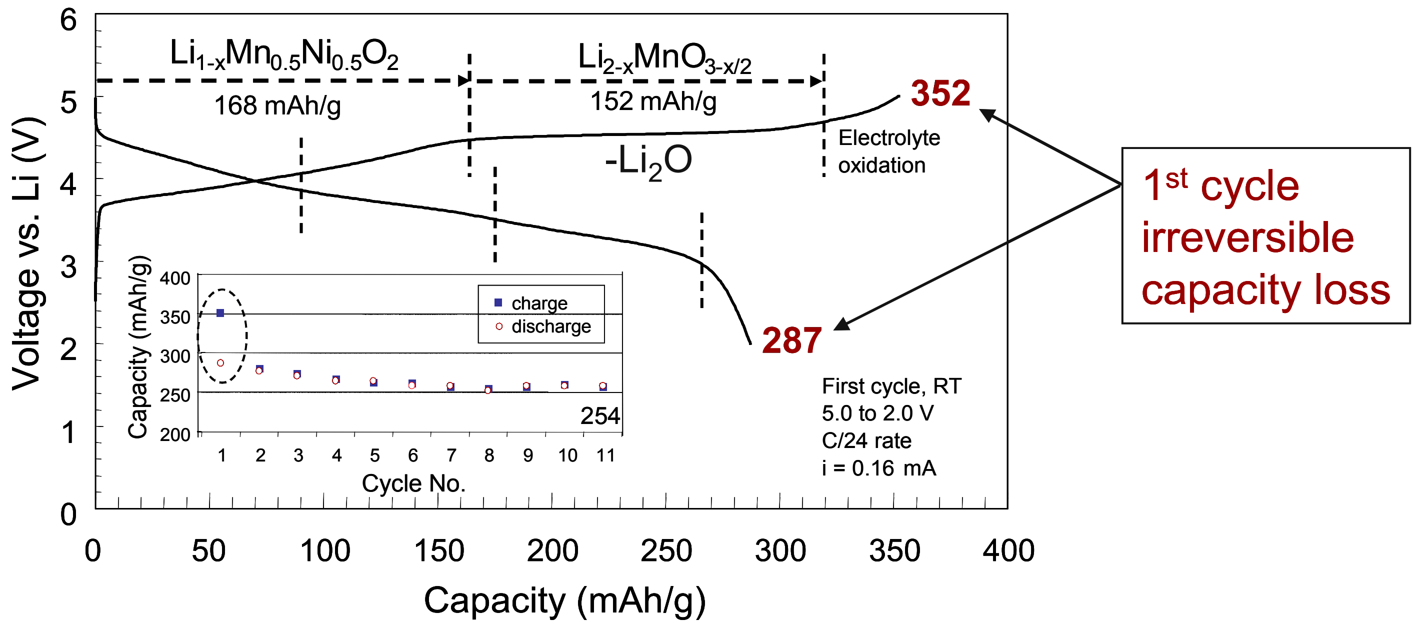
Project Objectives - Relevance

- Improve materials level performance of Li- and Mn-rich layered transition metal oxide cathodes (LMR-NMC) necessary to significantly improve upon existing Li-ion cathodes (pack level cost and energy density)
- Specific focus on the voltage fade phenomena present in the current generation of LMR-NMC materials.

Milestones

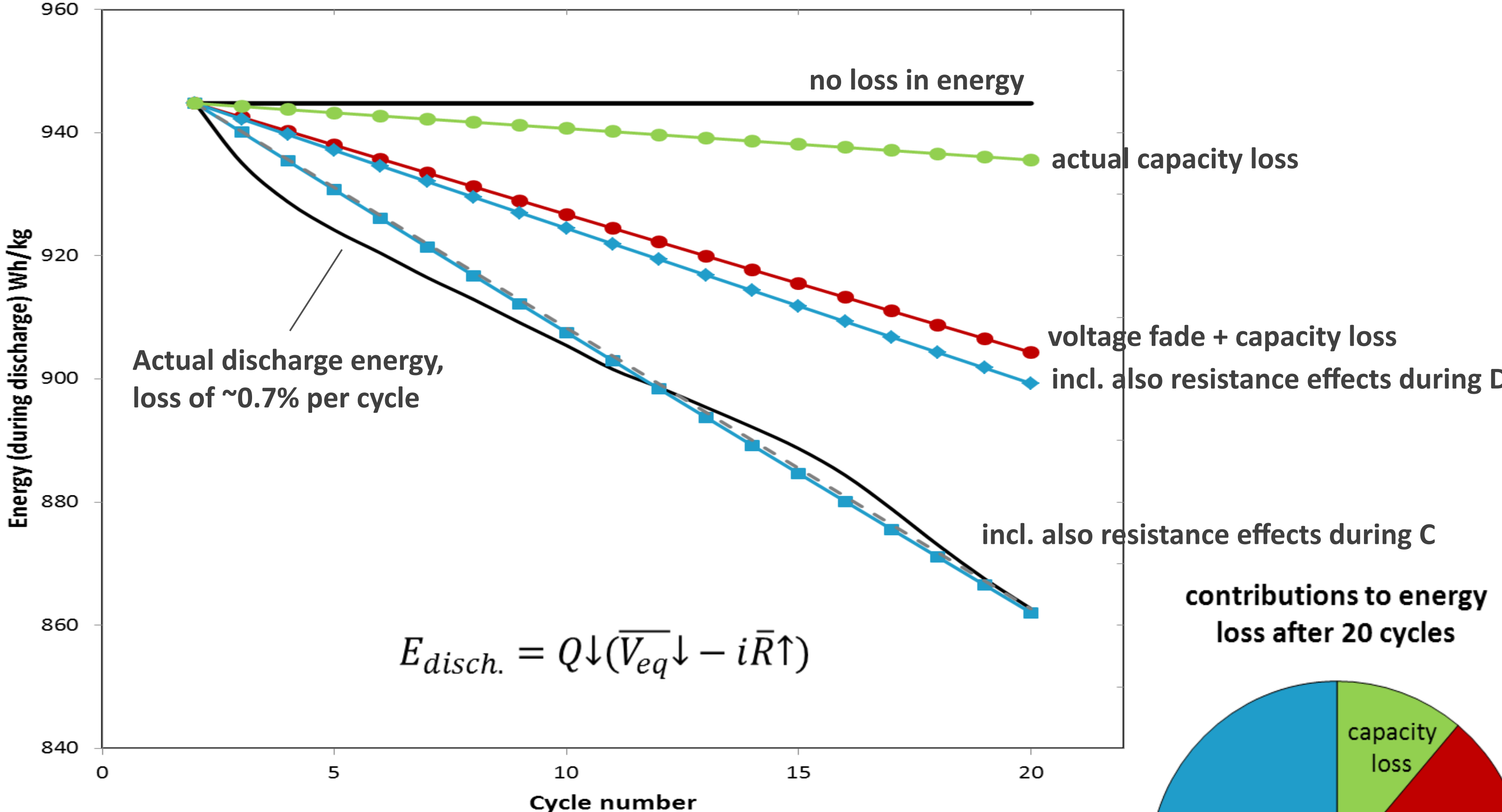
- Definition of the problem and workable limitations of the composite cathode materials (Dec 2012) **complete**
- Establish formal test protocols to determine and quantify voltage fade (Oct2012) **complete**
- Data collection and review of compositional variety available using combinatorial methods. (Oct 2013) **on target**
- Go/No-Go for post treatment/system level fixes. (March 2012) **complete**

Electrochemistry of a $Li/0.3Li_2MnO_3 \bullet 0.7LiMn_{0.5}Ni_{0.5}O_2$ Cell

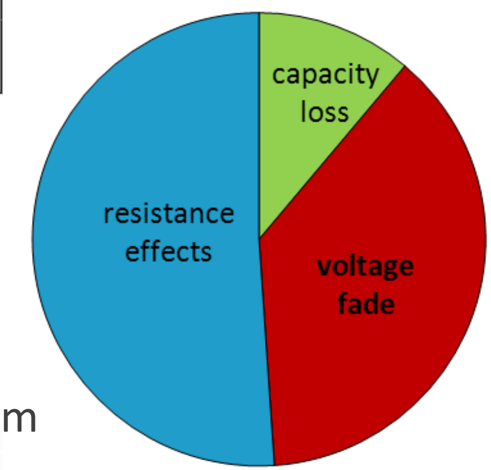


- Theoretical capacity of LiMn0.5Ni0.5O2 Component: 184 mAh/g
- Theoretical capacity of Li2MnO3 Component: 158 mAh/g
- Theoretical charge capacity (total): 342 mAh/g
- Coulombic efficiency: 82% (1st cycle); >99% (10th cycle)
- Capacity (10th cycle): 254 mAh/g

Energy output (discharge) for $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2$ *vs.* Li

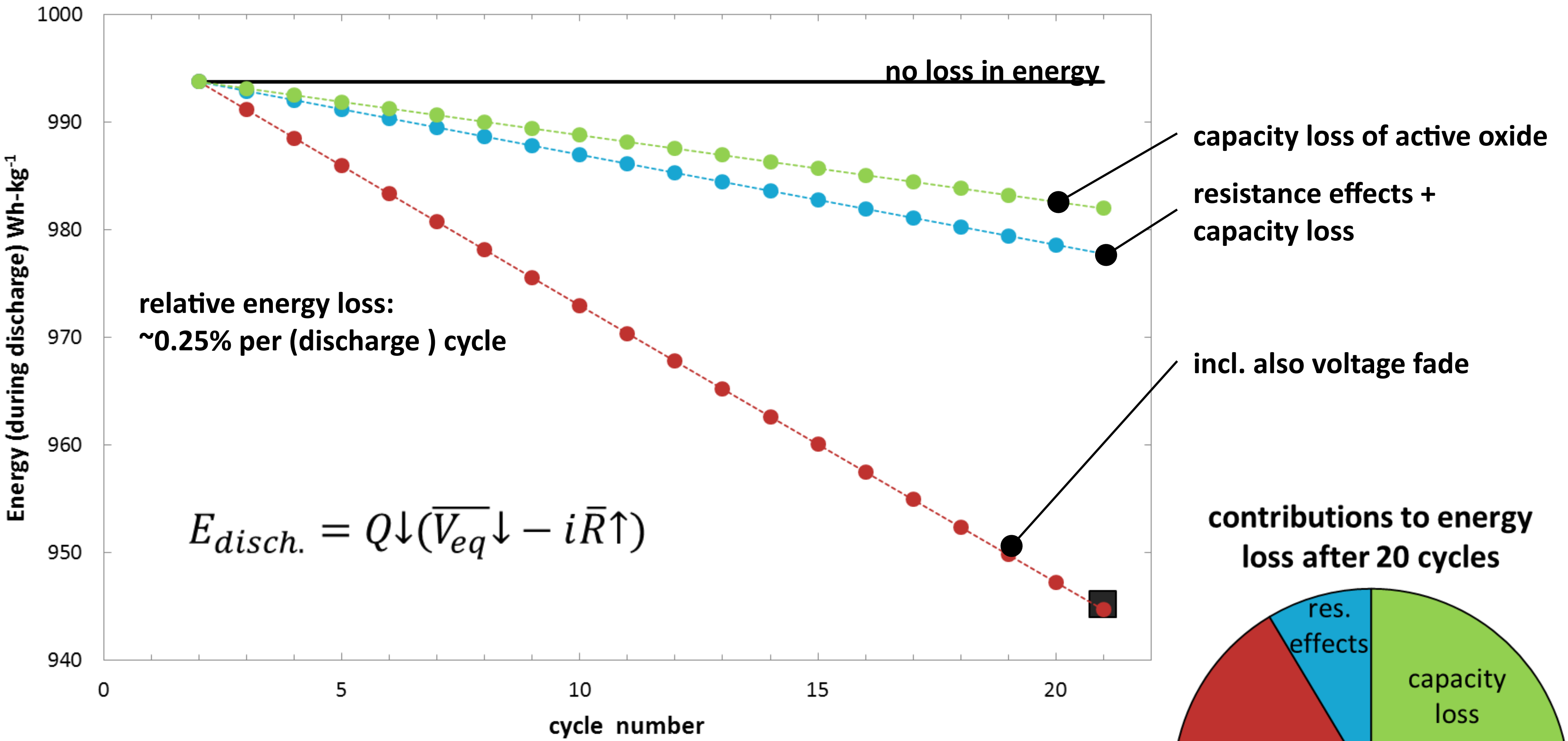


contributions to energy loss after 20 cycles



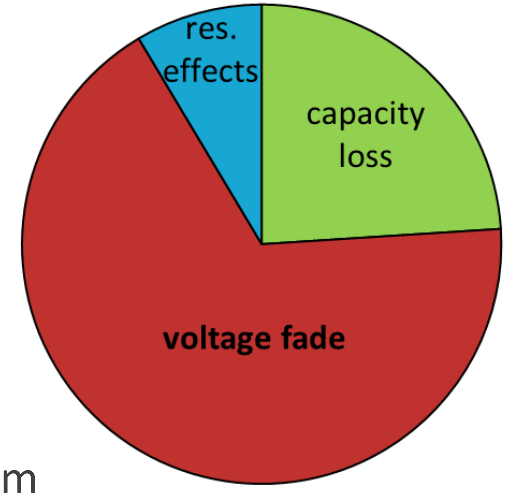
Energy loss is a serious problem in this material

Energy output (discharge) for $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2$ *vs.* Li



$$E_{disch.} = Q\downarrow(\overline{V_{eq}}\downarrow - i\bar{R}\uparrow)$$

contributions to energy loss after 20 cycles



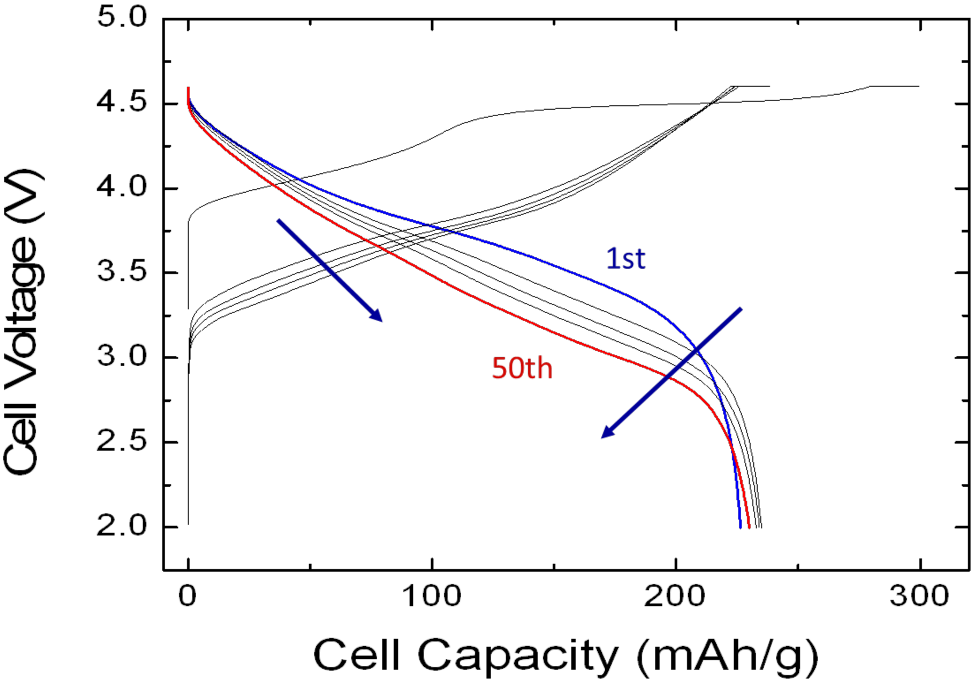
Voltage fade is the most pressing problem!

(positive resistances minimized by electrode design and additives)

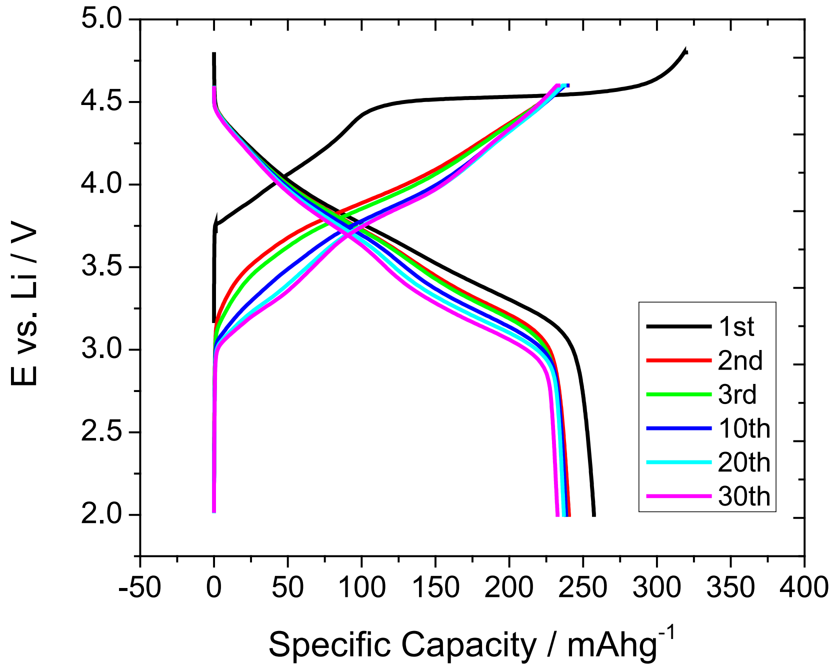
Voltage Profiles shape changes

LMR-NMC, 4.6-2.0 V, 16 mA/g, RT

$0.5Li_2MnO_3 \bullet 0.5LiMn_{0.31}Co_{0.25}Ni_{0.44}O_2$

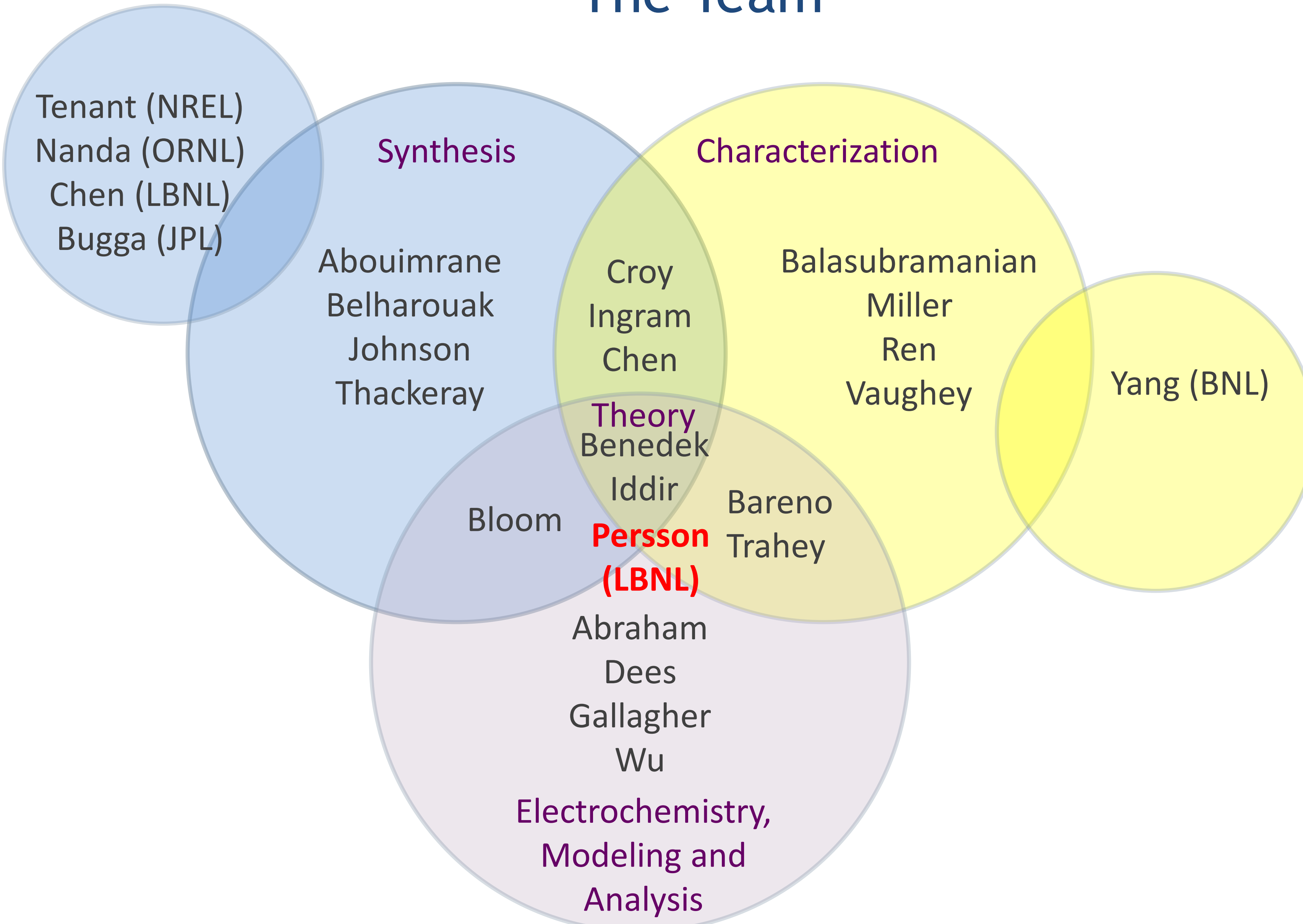


$Li_{1.7}Ni_{0.25}Mn_{0.75}O$



➢ This is not just **energy density** issue, but also **battery management** issue.

The Team


Tenant (NREL)
Nanda (ORNL)
Chen (LBNL)
Bugga (JPL)
Synthesis
Abouimrane
Belharouak
Johnson
Thackeray
Characterization
Croy
Ingram
Chen
Balasubramanian
Miller
Ren
Vaughey
Yang (BNL)
Theory
Benedek
Iddir
Bloom
Persson
(LBNL)
Bareno
Trahey
Abraham
Dees
Gallagher
Wu
Electrochemistry,
Modeling and
Analysis

The Approach

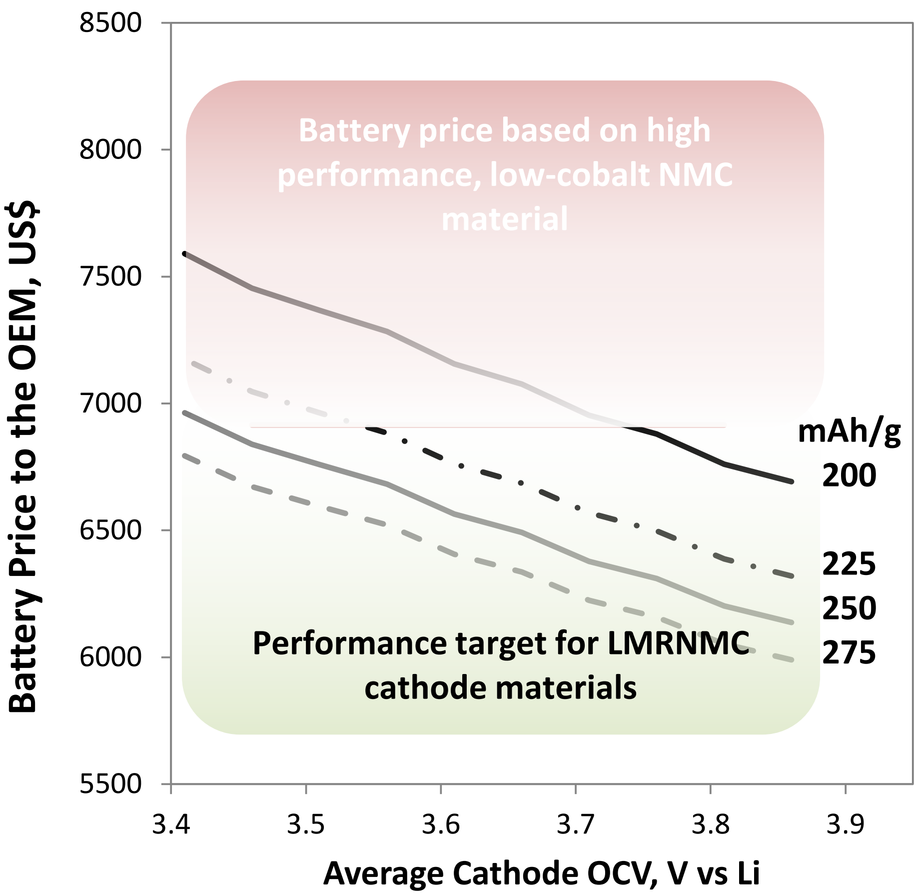
- A team that will share data and expertise to "fix" voltage fade in the LMR-NMC cathode materials. *This will be a single team effort – not multiple PI's working independently on the same problem.*

  - Definition of the problem and workable limitations of the composite cathode materials.
  - Data collection and review of compositional variety available using combinatorial methods.
  - Modeling and Theory.
  - Fundamental characterization of the composite cathode materials.
  - Understand the connections between electrochemistry and structure.
  - Synthesis.
  - Post treatment/system level fixes.

LMR-NMC cathode material performance targets

- Performance targets necessary to ensure final material is still valuable
  - Based on out-performing next best cathode option (red box)
- Higher capacity allows for slightly lower average OCV
- Cathode capacities and OCVs required for meaningful advance:
  - 225 mAh/g and V_{avg} > 3.55 V vs Li
  - 250 mAh/g and V_{avg} > 3.45 V vs Li
  - 275 mAh/g and V_{avg} > 3.35 V vs Li

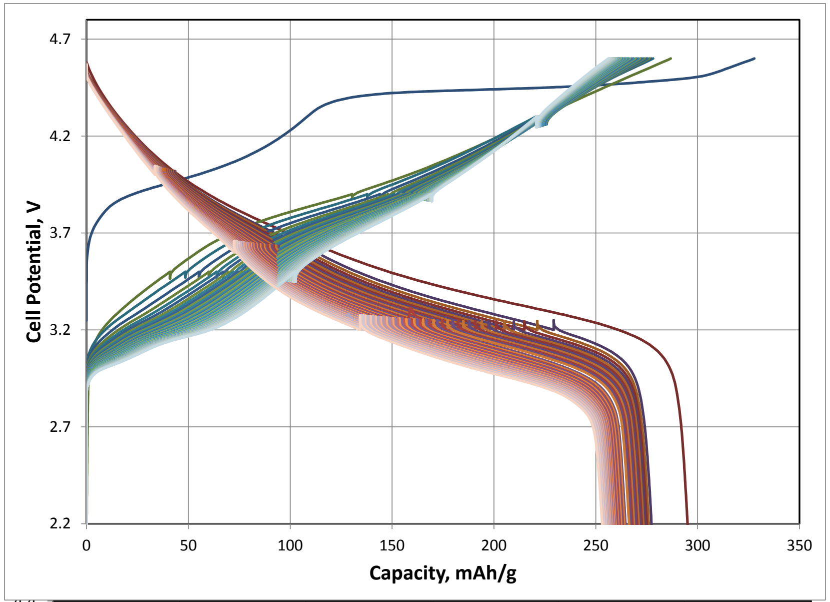
Target set at pack level: 40kWh, 100 kW 360V

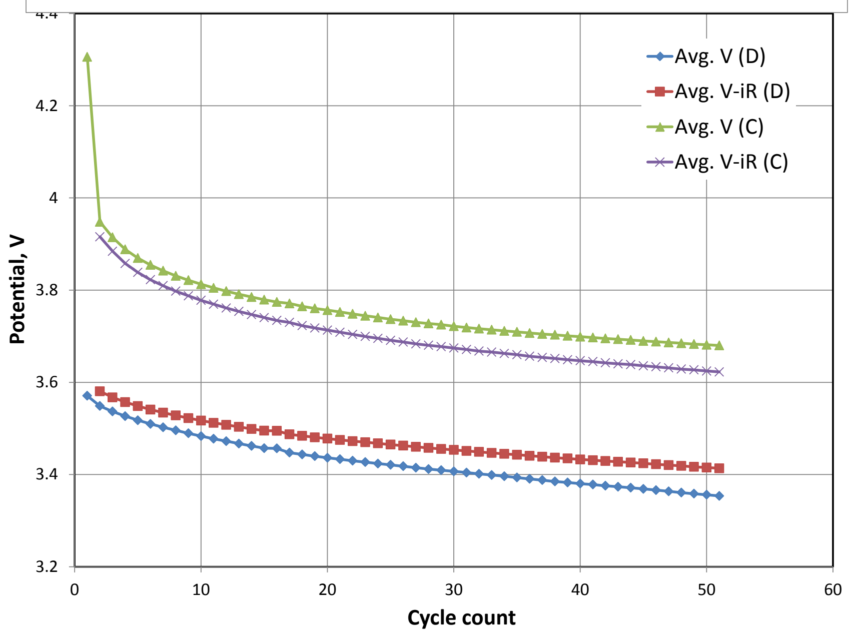


Battery price calculated using BatPaC for an advanced Li-ion battery with a silicon based anode material.

How Do We Measure Voltage Fade?

- Standardized test protocol
- Measure average voltage
  - Energy / Capacity = Avg Voltage
  - Estimates resistance contribution
  - Utilizes low currents w/ interrupts
- Excel Macro created to automate data analysis
- Fit fade to paralinear kinetics for comparisons
- Goal is to measure thermodynamic change in a reasonable time frame





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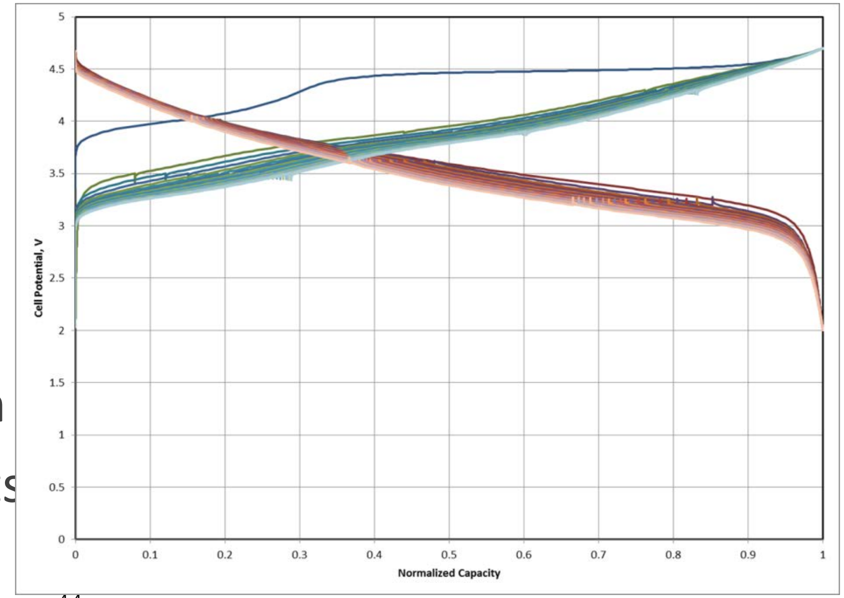
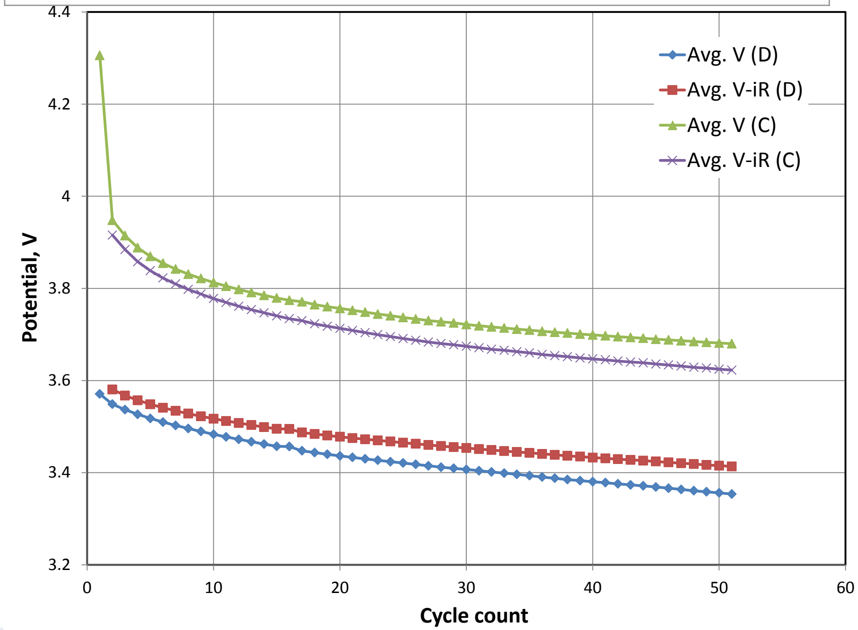
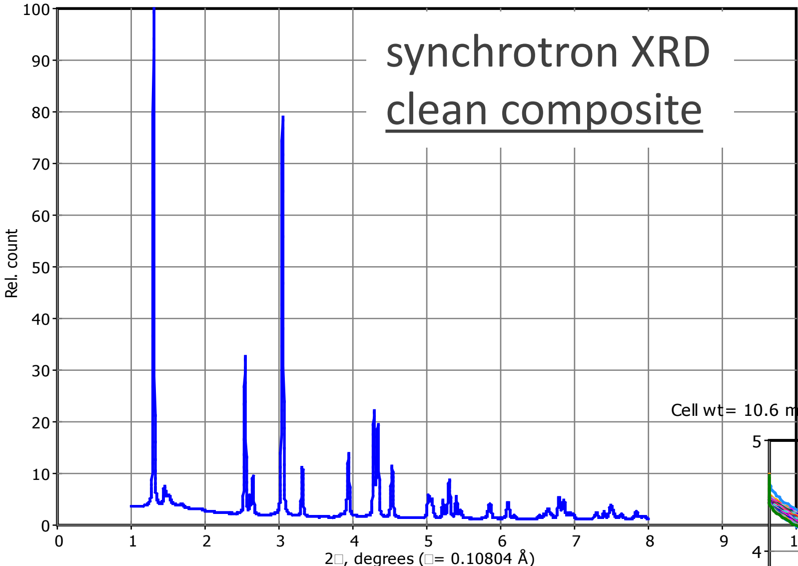
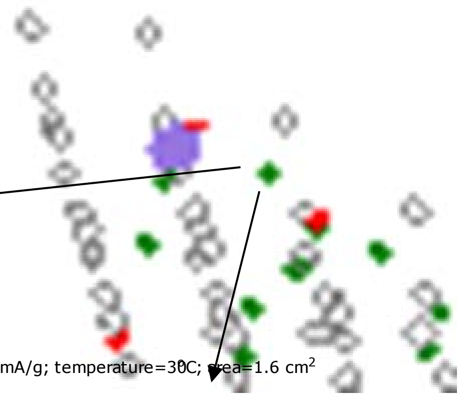


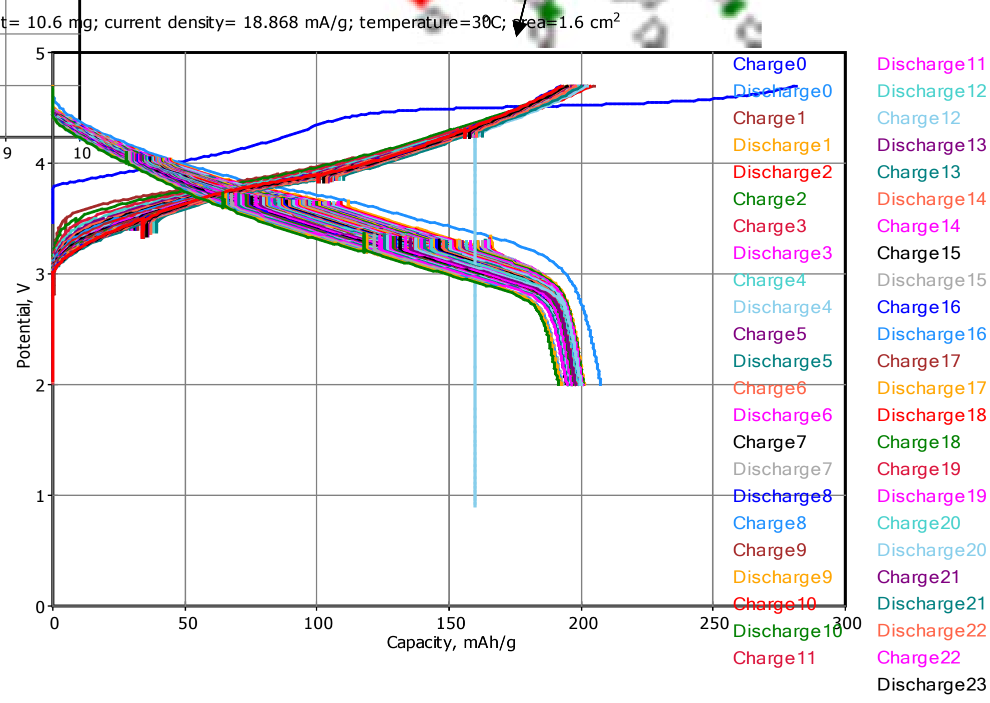


Combinatorial Sol-gel syntheses

$0.5Li_2MnO_3 \cdot 0.5LiNi_{0.40}Mn_{0.30}Co_{0.40}O_2$

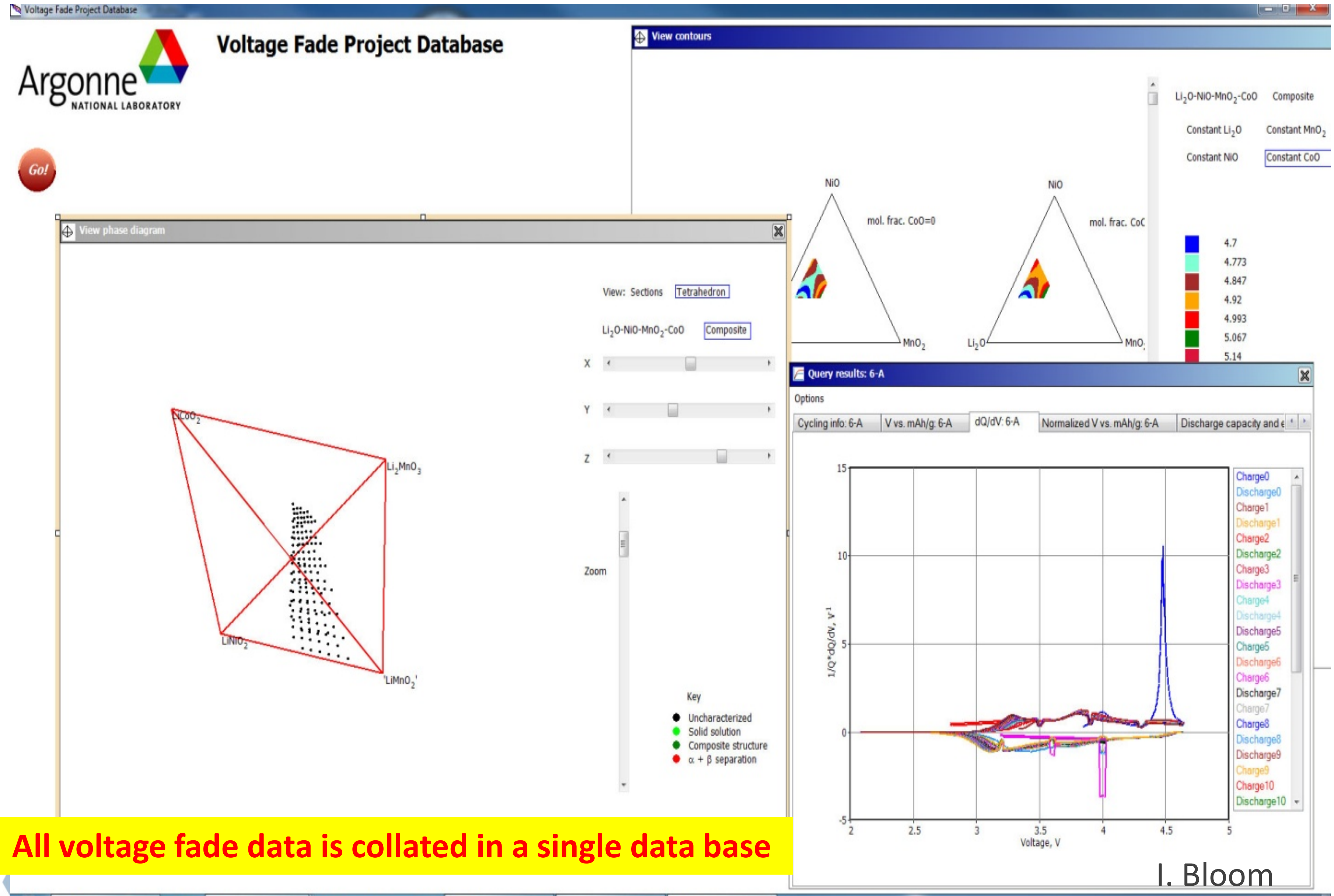






Looking for trends not solutions

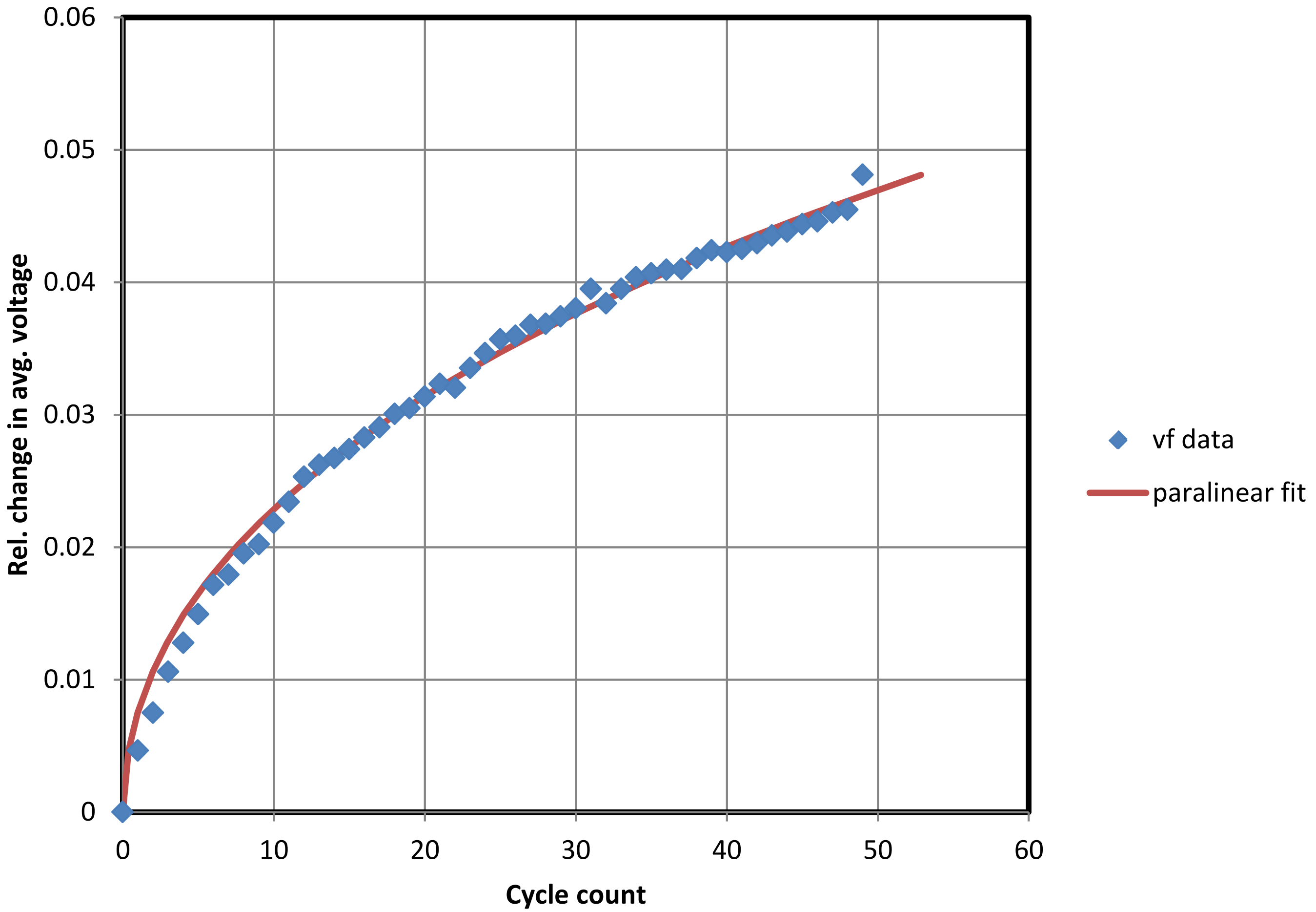
Database for ALL voltage fade systems



All voltage fade data is collated in a single data base

I. Bloom

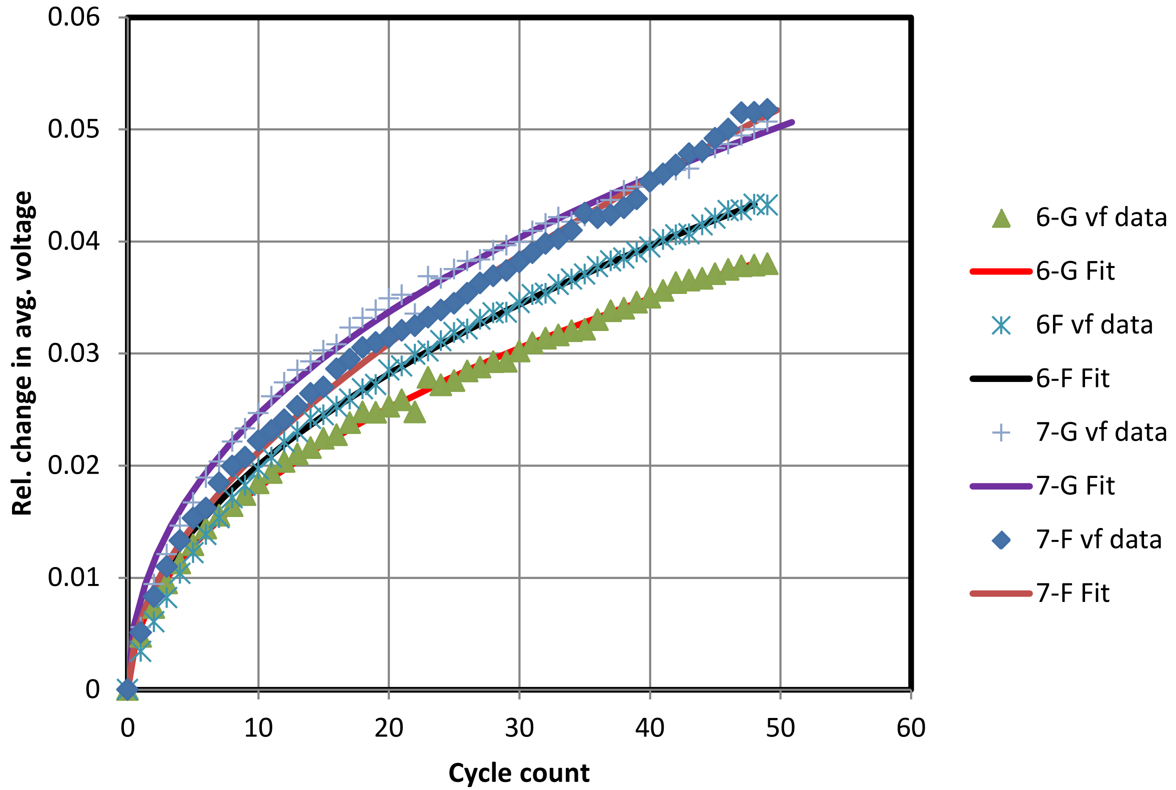
What are we learning?



Kinetics of voltage fade is not simple 1st or 2nd order reaction mechanism

I. Bloom

Kinetics of voltage fade depend on composition



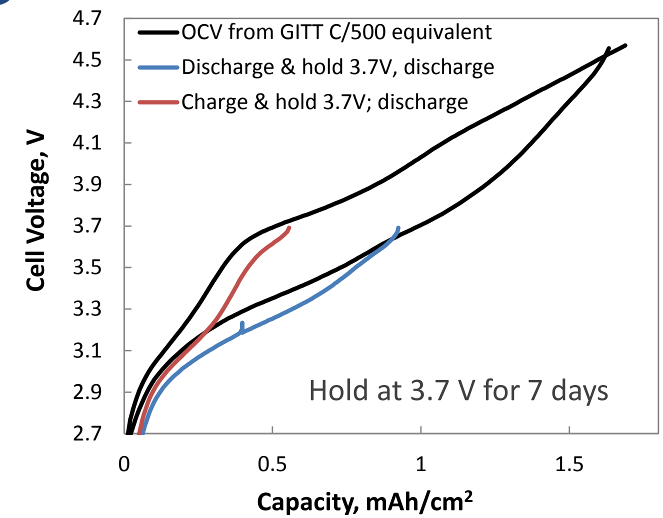
x=kp/kl*ln[kp / (kp-kl{x-kl*t})], where x is the dependent parameter (rel. change in avg V) and t is time (cycle count); kl=linear rate constant; kp=parabolic rate constant

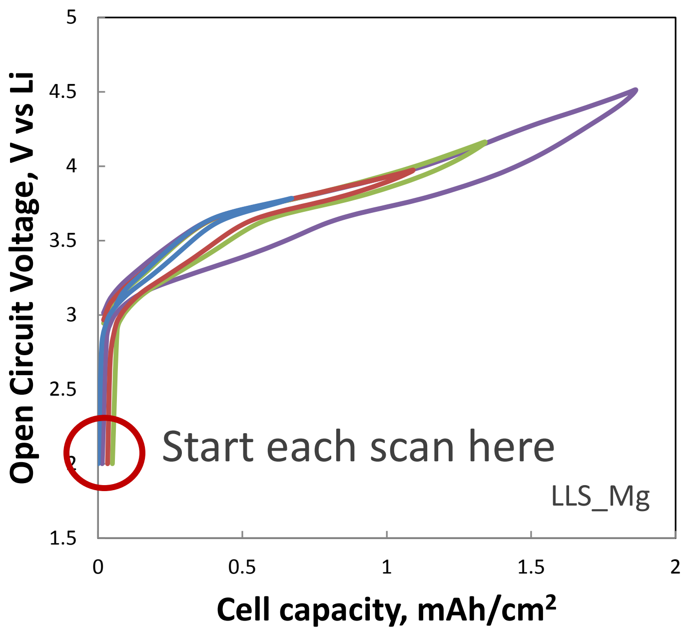
Modeling work is required to elucidate the mechanism

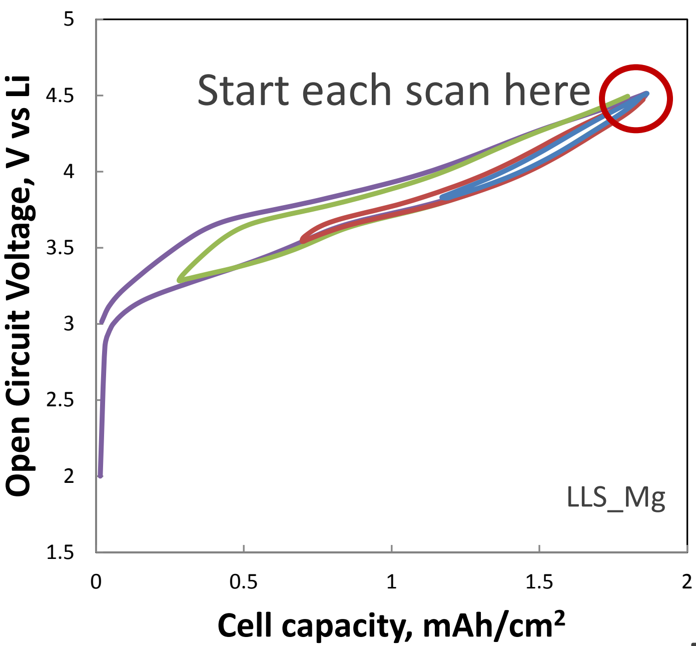
ES190

Does Hysteresis have anything to do with VF?

- Unknown physical process leading to stable hysteresis
- Scanning curves show shift from one boundary to other depends on voltage





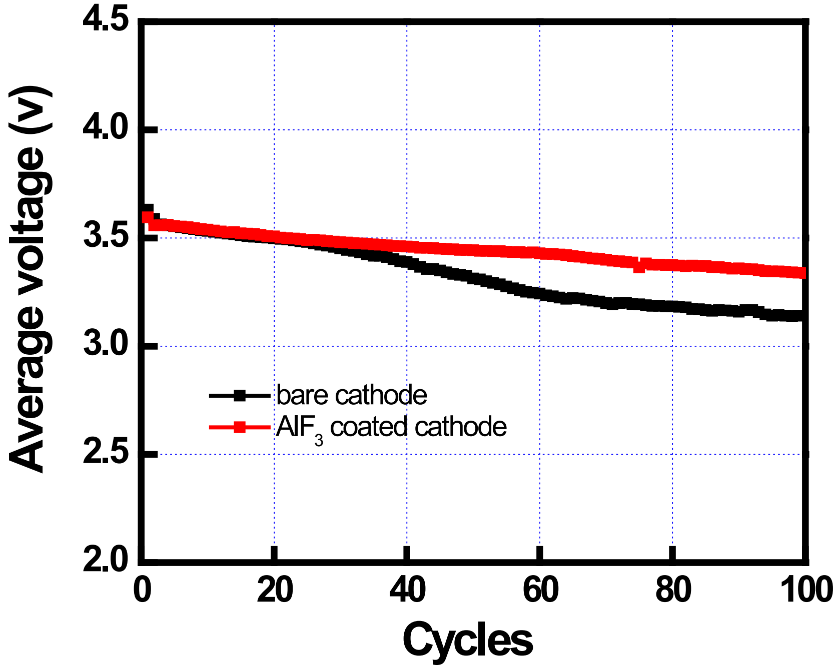


ES189

One current hypothesis says YES

Coatings - are they effective for VF?
Go No-Go for March 2012

Data will be collected with voltage fade protocols and analysis will be carried out using standard procedures.



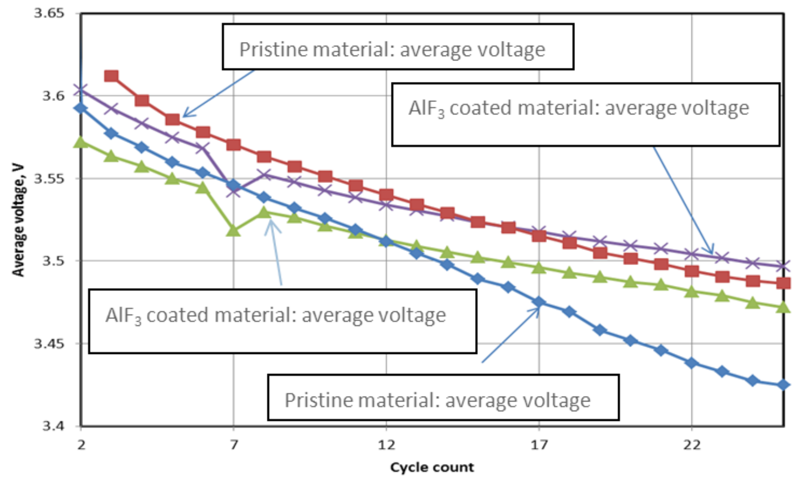
Average voltage vs. cycling of uncoated, and AlF_3 coated LMR-NMC

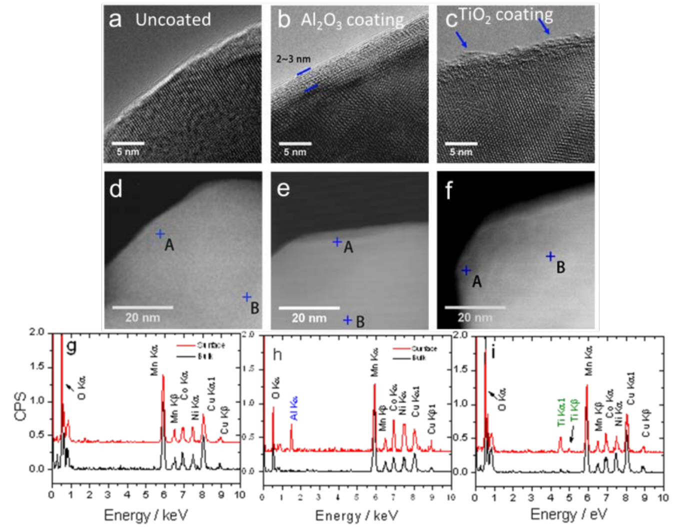
- Mn dissolution mitigated?
- Al surface doping ?

"some improvement in avg. voltage retention was observed with ***AlF_3*** coating"
- courtesy Amine DOE AMR 2012

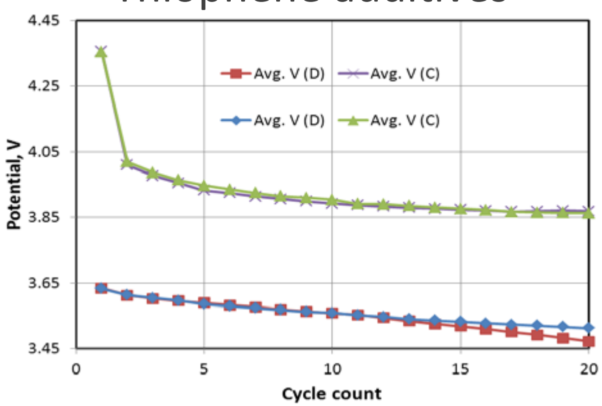
Data from multiple institutions was used for the down select

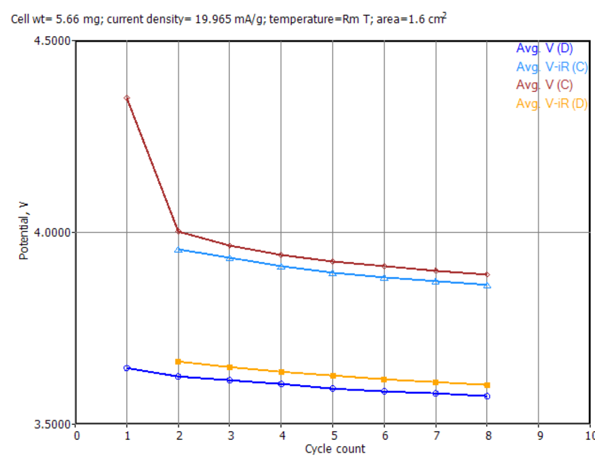
Surface treatments or Coatings – are they effective for VF? NO GO work stopped.

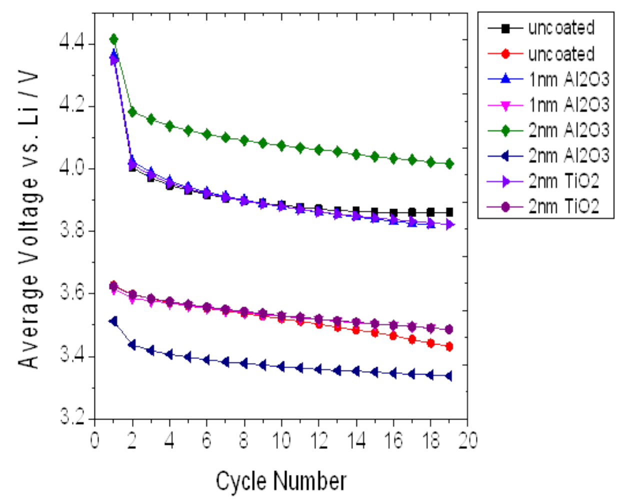




Thiophene additives



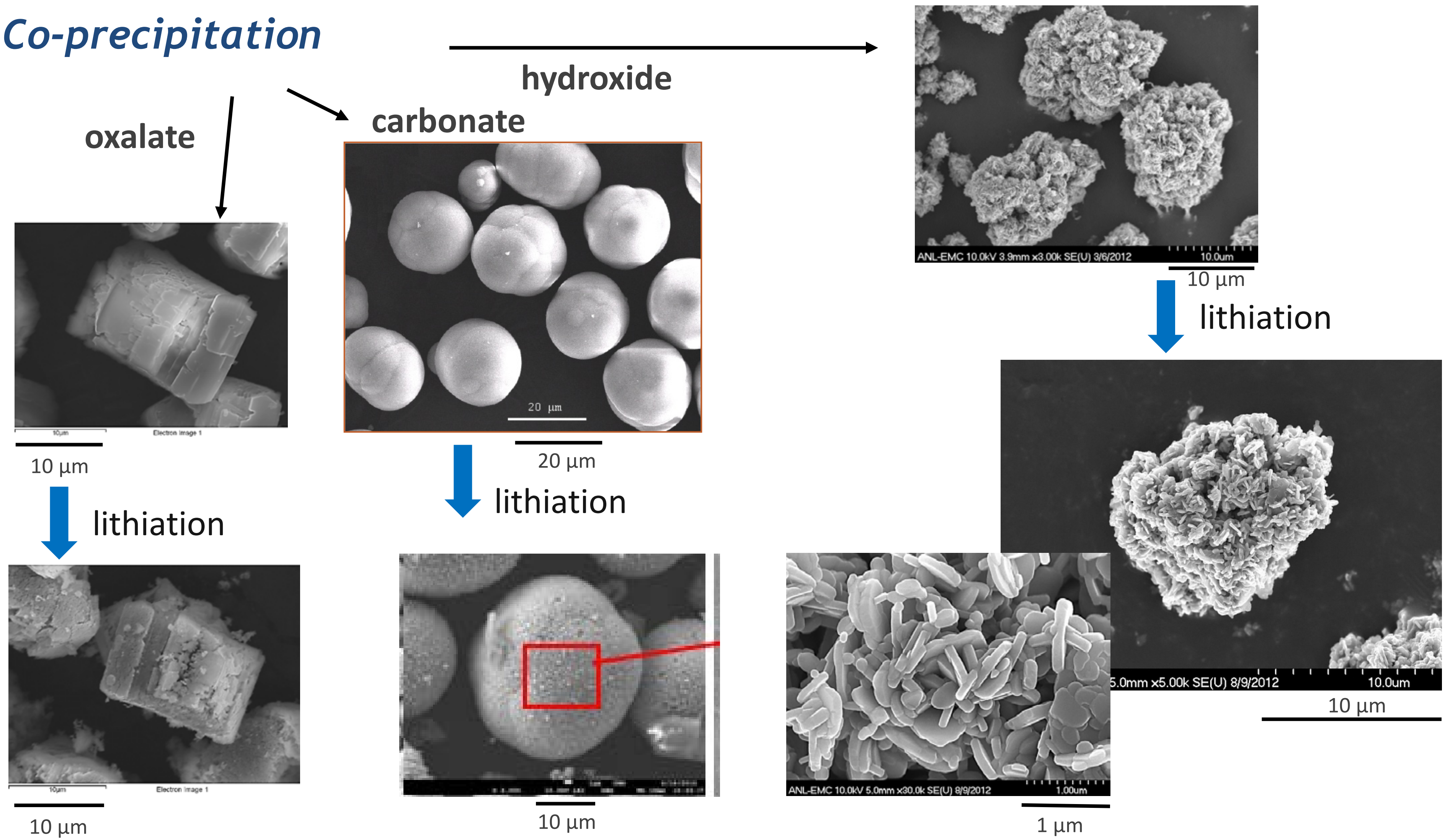




No evidence for Additives or coatings affecting voltage fade

See es191 for complete description

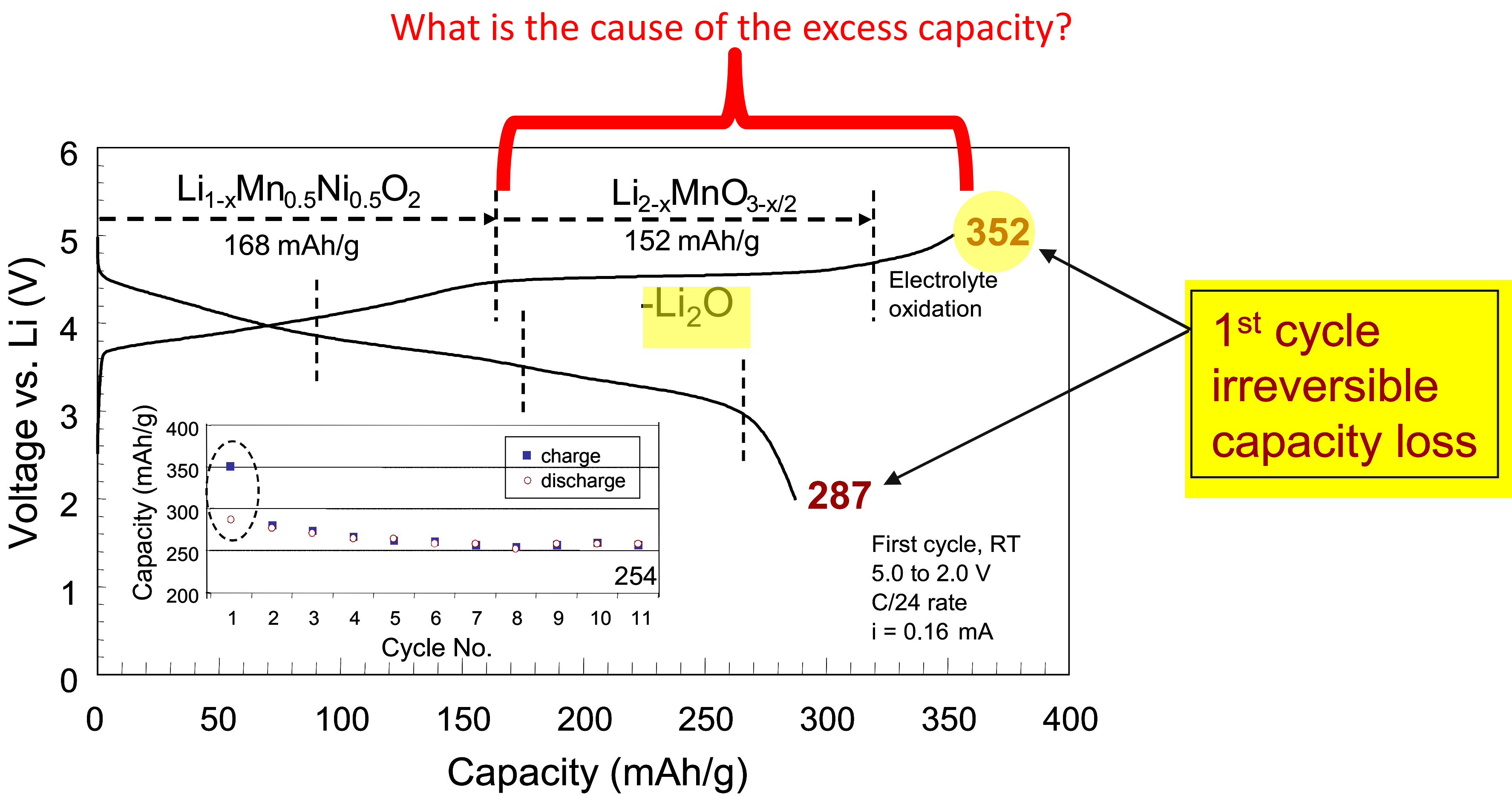
Next Go No-Go - Synthesis Method does it matter?



- ❑ **Others: sol-gel, combustion (glycine-nitrate), & direct solid state**

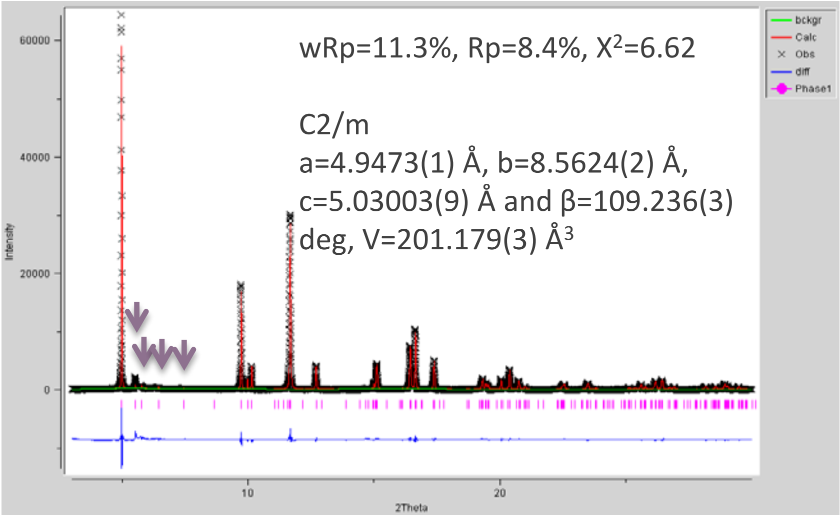
I. Belharouak, D. Kim, H. Wu
Help from Chen (LBNL)

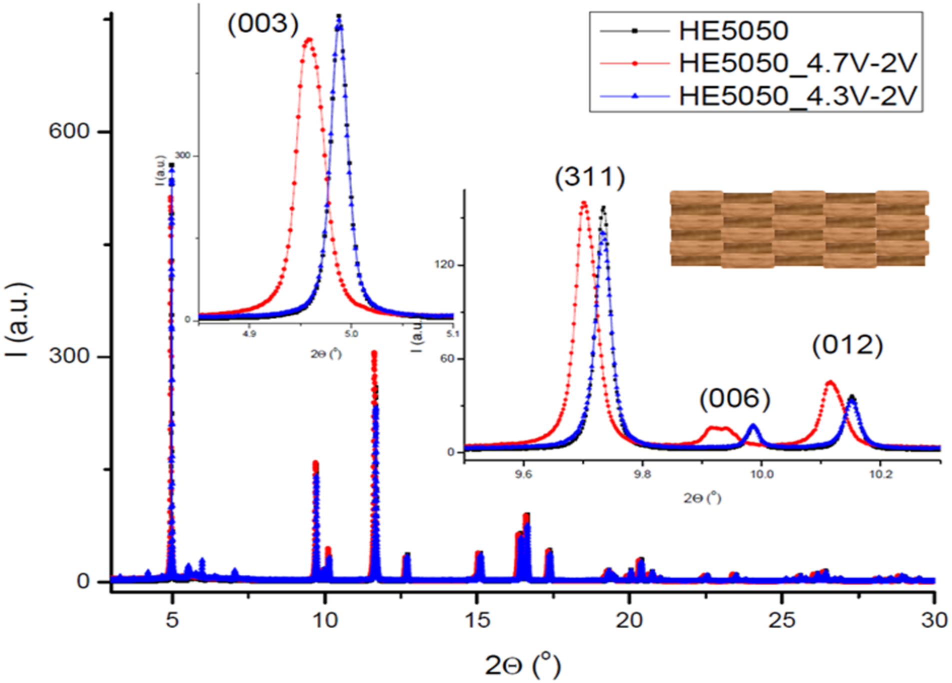
Things we need to understand.



HR-SXRD study of activated HE5050

- HE5050 has the C2/m symmetry.
- The material that was charged to 4.3 V and discharged to 2.0 V showed almost identical XRD pattern to the HE5050, except slightly broadened peaks.





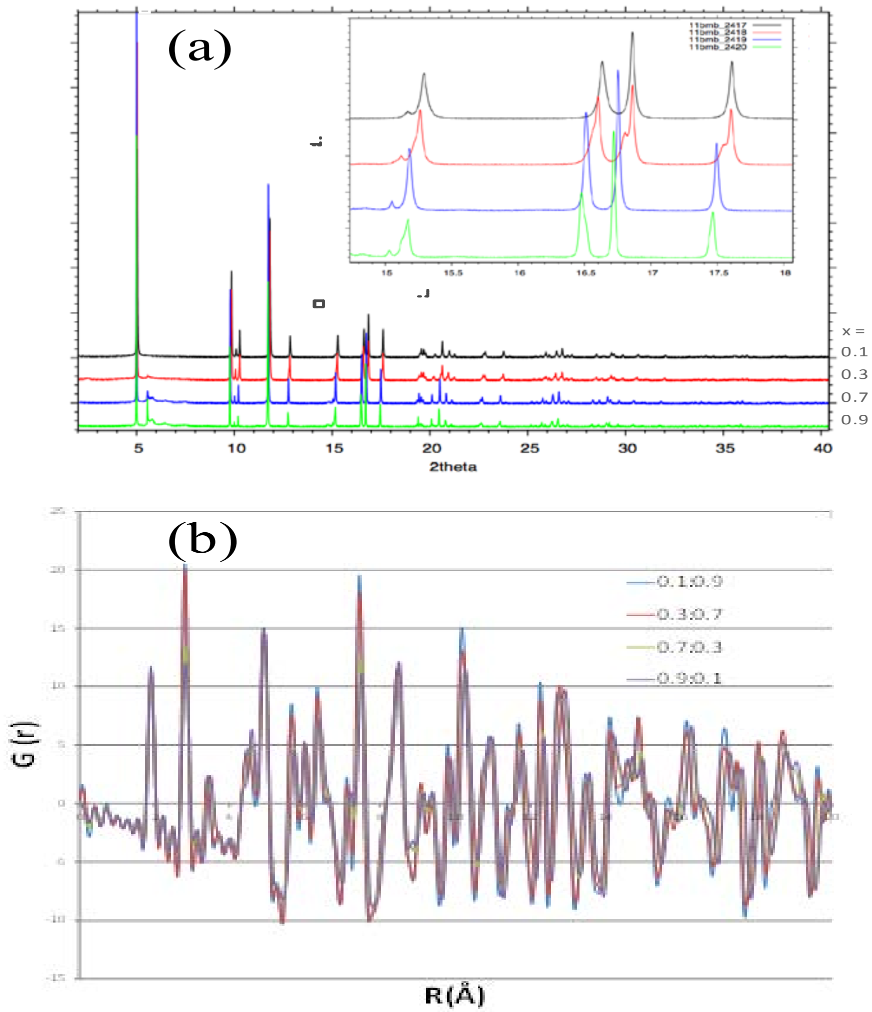
➤ ***The activated [HE5050(4.7V-2V)] become structurally heterogeneous, or phase separated.***

ES189, ES194 and ES190

Neutron pair-distribution-function (NPDF) study

- Neutrons are sensitive to transition-metal elements and Li ions

➢ NPDF study showed that not only the *local structure* but also the *long-range structural coherence* may play an important role in the electrochemical performance.



ES189, ES194 and ES190

Future Work on characterization will be at single particle level

Develop and exploit ***coordinated characterization*** **to correlate electrochemical behavior and structure at the micro- and nano-scale**

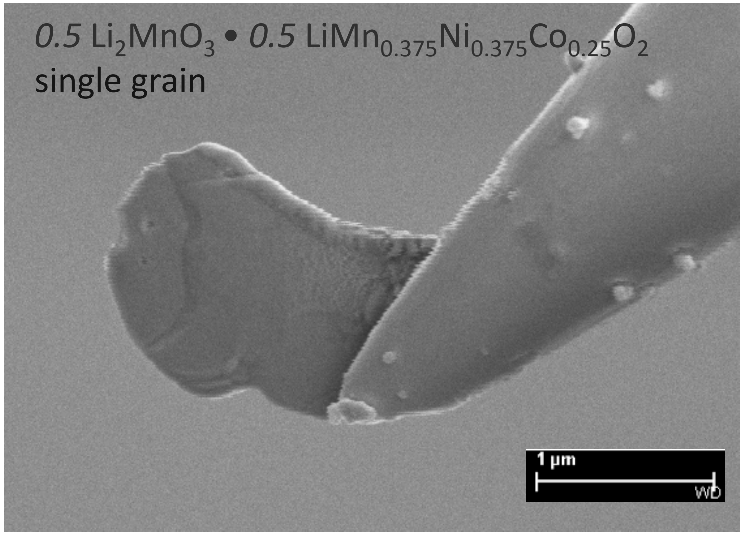
- obtain statistically reliable cycling data from single particles of

0.5 Li_2MnO_3 • *0.5* $LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$

- assess voltage fade in single particles and particle-to-particle variations, use insight to help interpretation of full cell measurements

- implement *operando* approach for characterization of single grains during electrochemical cycling, especially at the TEM scale, to correlate with structural evolution

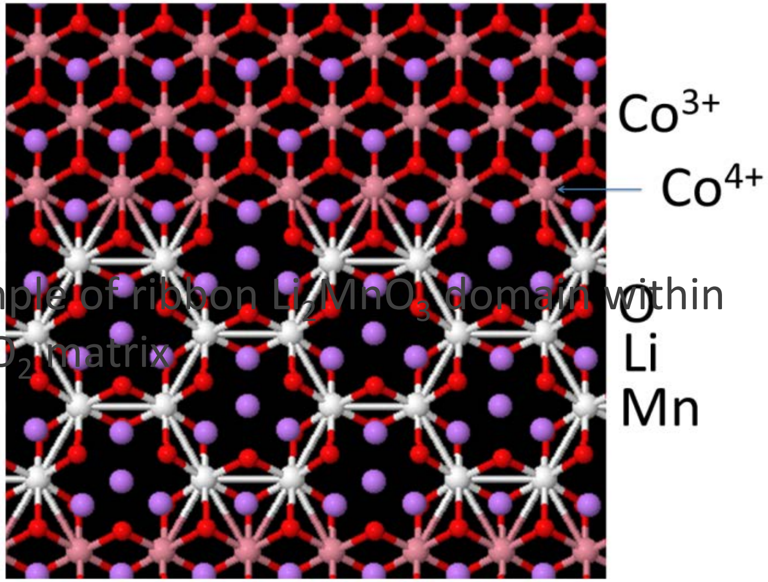
- move the challenge for characterization from billions of particles in a coin cell to the single particle & single grain level



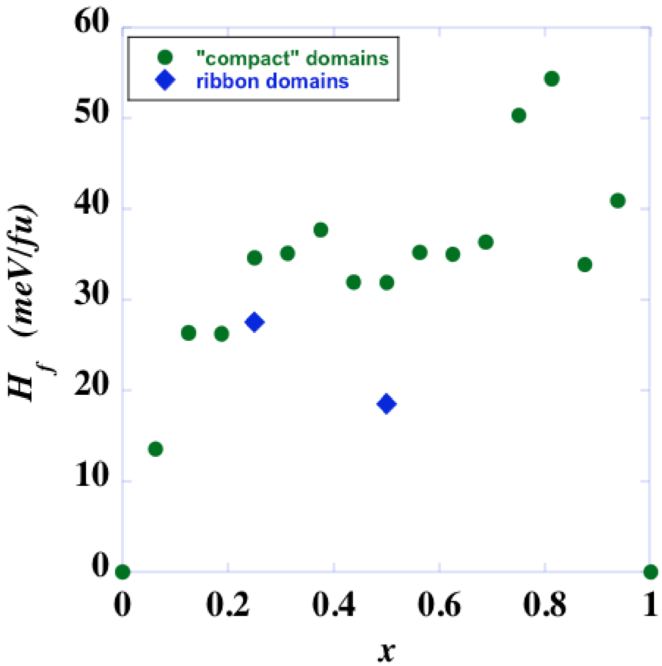
Project Id: ES 186

Theory is helping discriminate different possible mechanisms for Voltage fade.

e.g. Domain size and shape influence VF?



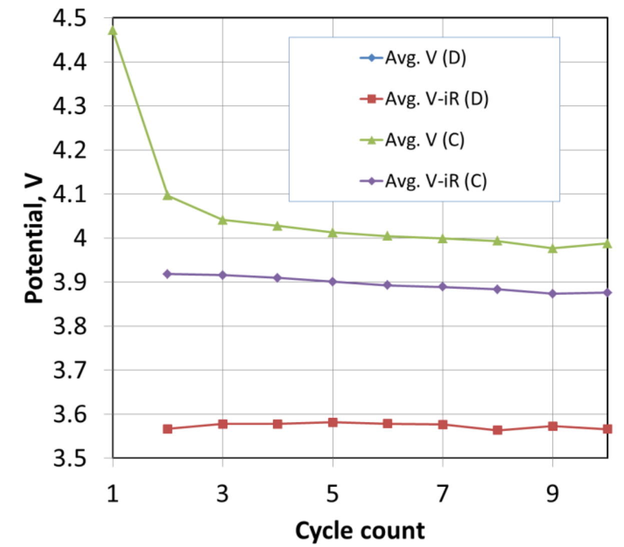
Example of ribbon Li_2MnO_3 domain within $LiCoO_2$ matrix



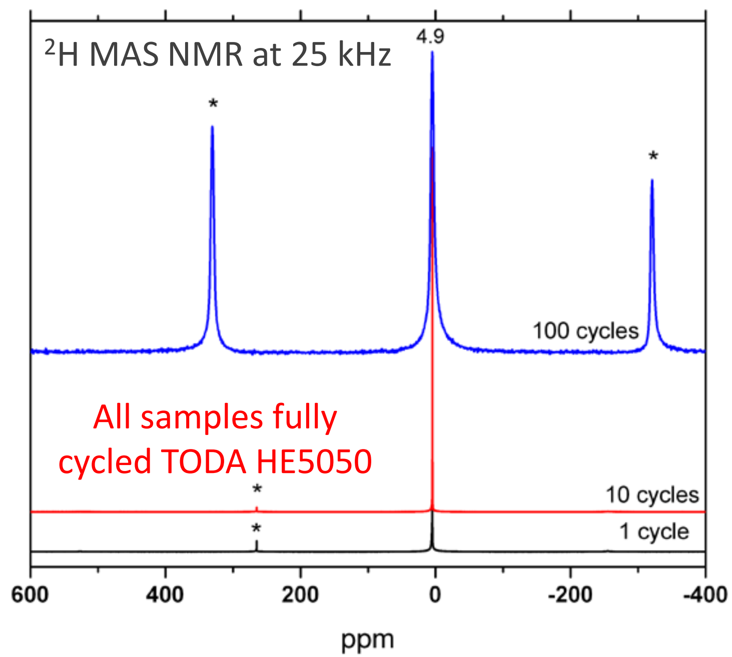
Calculated formation enthalpy vs. domain size for $xLi_2MnO_3.(1-x)LiCoO_2$

Electrochemical insertion of ^{2}H ?

- No structural ^{2}H detected after cycling for Toda HE5050 (Voltage Fade present)
- Significant accumulation of diamagnetic (surface) deuterium bearing species detected consistent with impedance rise and SEI build-up

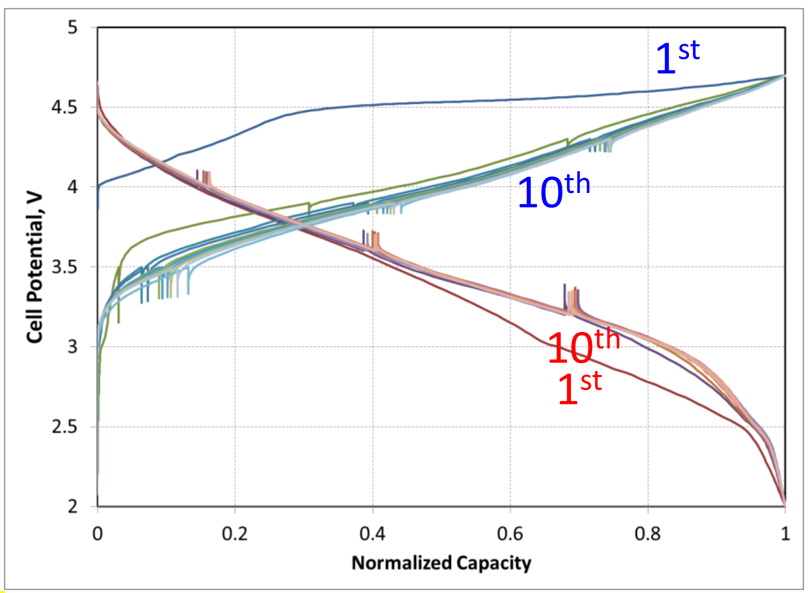


($0.5Li_2MnO_3 \bullet 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2$)



* indicates spinning sidebands due to MAS

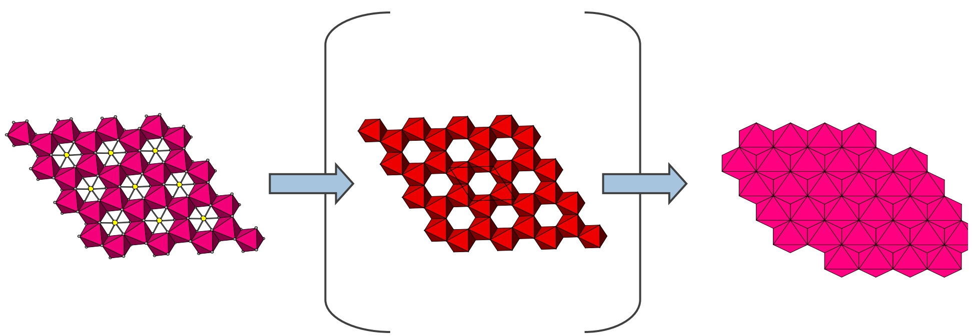
Voltage profile of TODA HE5050 after 10 cycles



Voltage fade is not caused by protons

Theory-Synthesis interaction. How can dopants help? Theory predicts and then we make.

- $Li_2M'O_3$ doping
  - Modulate oxygen loss (lattice instability) and retard spinel conversion in domain
    - Ti doping; strong Ti-O bonds
    - Ru doping; Ru not known to form spinels
- $LiMO_2$ doping
  - Li_2MnO_3 domain to BiI_3 prototype structure followed to CdI_2 layered structure
  - Effect the diffusion of TM cations into back-fill of vacancies left by Li removal

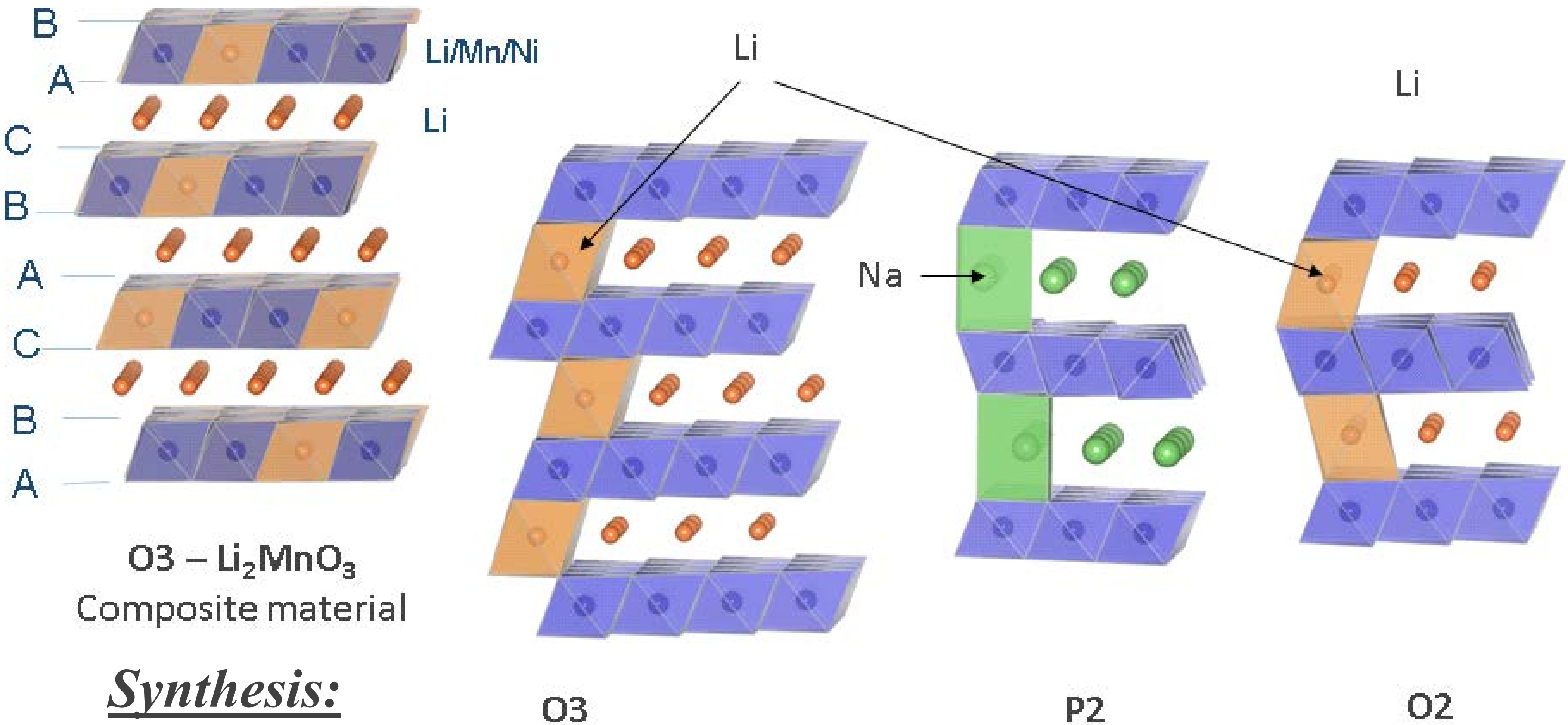


Li_2MnO_3 $[BiI_3]$ CdI_2

(- 2 Li) (-O)

ES190 and ES193

Example is the Design of systems that prevent spinel transformation via Na exchange.



Synthesis:

(2) $Na_{1.0}[Li_{0.2}Ni_{0.25}Mn_{0.75}]O_y + LiBr \longrightarrow Li_{1.0}[Li_{0.2}Ni_{0.25}Mn_{0.75}]O_y + NaBr$

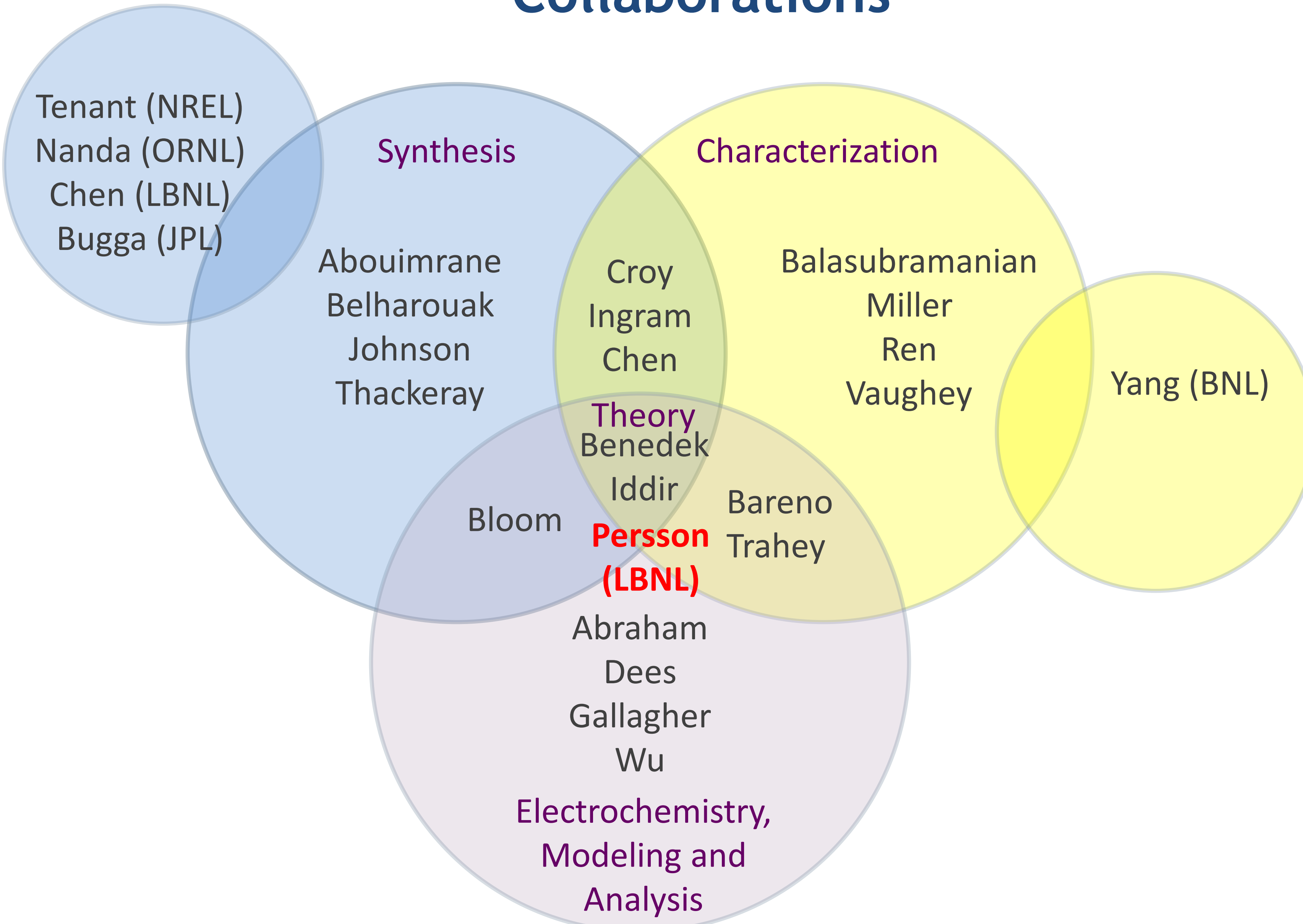
P2 refluxing hexanol O2

(O2stacked) $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.5}Mn_{0.5}O_2$

Future work

- Understand the cause of voltage fade.
  - Determine the origin of the high capacity in the LMR-NMC materials.
  - Continue aggressive down selects focused on voltage fade issues.
  - What does hysteresis have to do with Voltage Fade ?
  - Understand compositional control of voltage fade.

Collaborations



Acknowledgements

- Support for this work from DOE-EERE, Office of Vehicle Technologies is gratefully acknowledged
  - David Howell, Peter Faguy & Tien Duong

- The voltage fade team
- Industrial Partners
- All of ABR/BATT community