

Voltage Fade, an ABR Deep Dive Project: Status and Outcomes

Project ID: ES161

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Voltage Fade Team

Annual Merit Review

Washington DC, June 16-20, 2014

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

Overview

Timeline

- Start: October 1, 2012
- End: Sept. 30, 2014
- Percent complete: 75%

Budget

- Voltage Fade project
- \$3,900K

Barriers

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

Partners

- ORNL
- NREL
- ARL
- JPL



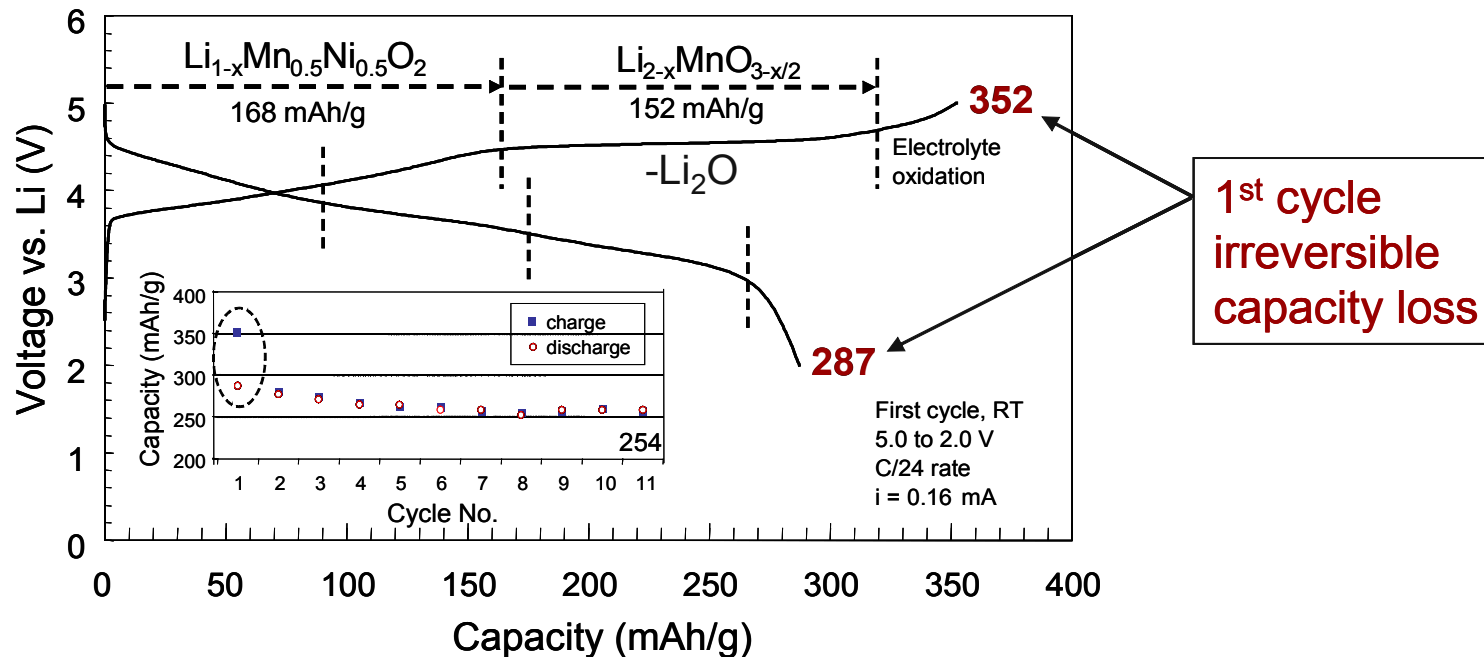
Project Objectives - Relevance

- 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 understanding the voltage fade phenomena present in the current generation of LMR-NMC materials.



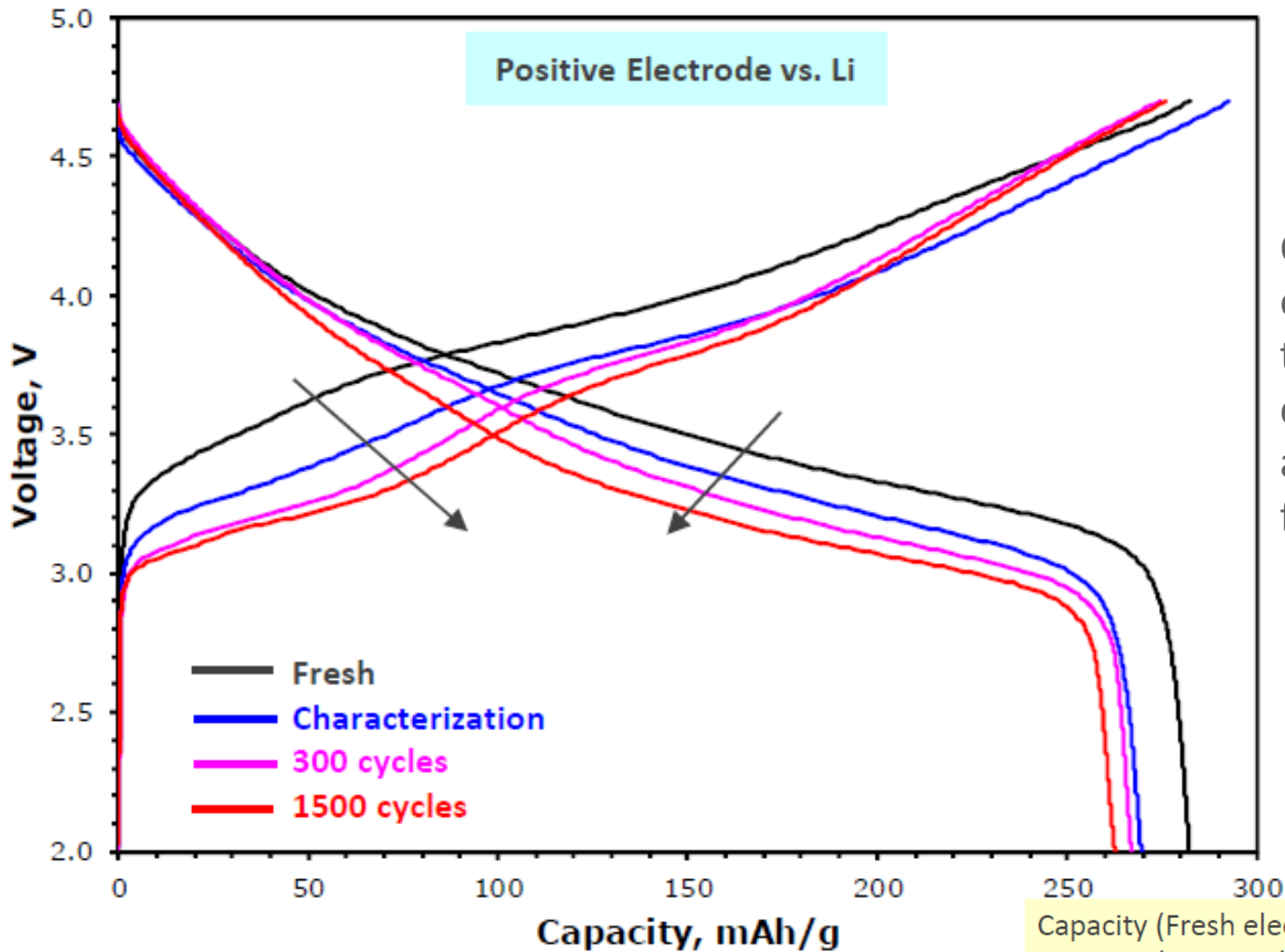
LMR-NMC $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$

Li half cell data. A very promising cathode material



- Theoretical capacity of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ Component: 184 mAh/g
- Theoretical capacity of Li_2MnO_3 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

Historical data taken from Johnson, Kim, Lefief, Li, Vaughey, Thackeray / Electrochemistry Communications 6 (2004) 1085–1091

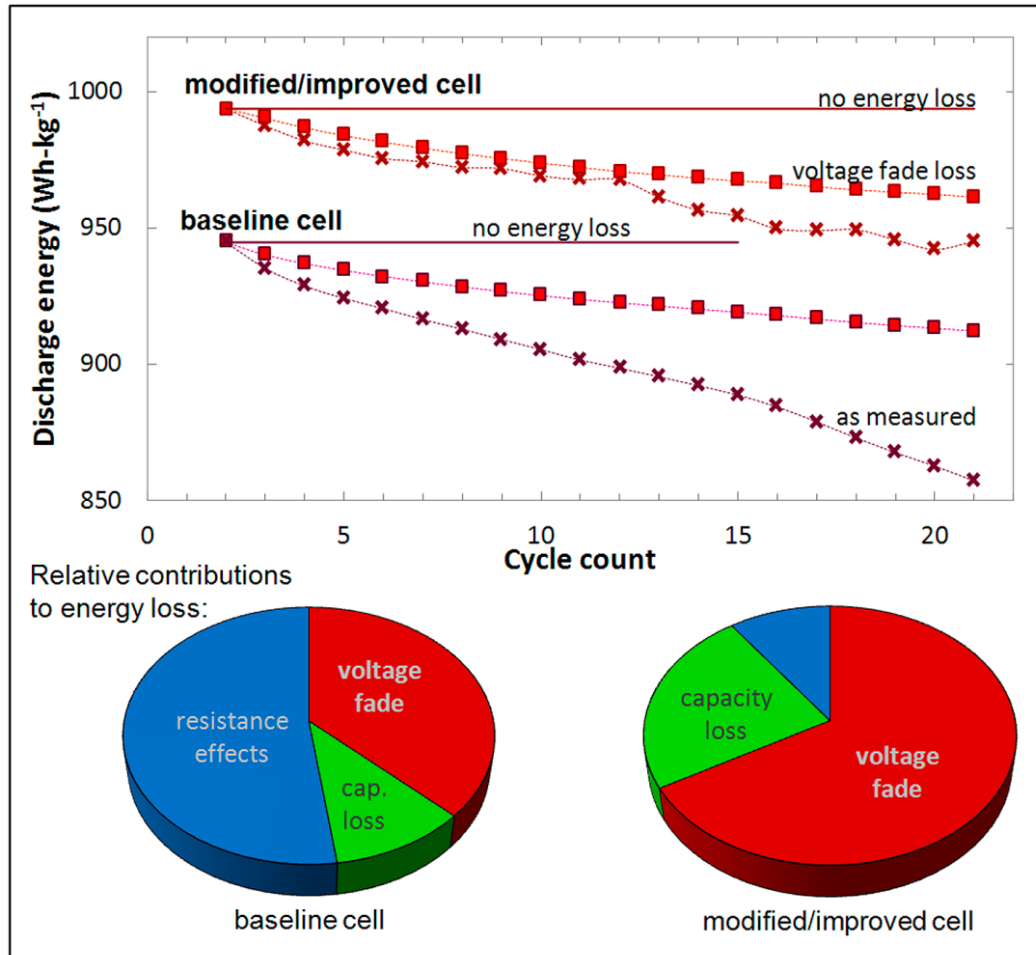


Cycling was carried out in full cell and then the harvested cathode was assembled into a fresh half cell

Capacity (Fresh electrode): 282 mAh/g
 Capacity (1500 cycle electrode): 262 mAh/g
 Some "true" capacity loss occurs on cycling – this could be due to oxide particle isolation that may result from loss of electronic connectivity (loss of oxide-carbon contact) or ionic connectivity (particle surface films or surface structure changes)

Cathode stability with respect to capacity is remarkable

Impact of voltage fade: discharge energy of $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.375}\text{Mn}_{0.375}\text{Co}_{0.25}\text{O}_2$ vs. Li



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

- Voltage fade represents the largest energy loss mechanism which cannot be mitigated using traditional strategies.

Initially energy loss was considered to be a major problem. However the real issue is cost. Voltage fade is a **battery management** issue

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 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.

In Fy12-13 we moved effort from other projects to create the voltage fade team.



Timeline

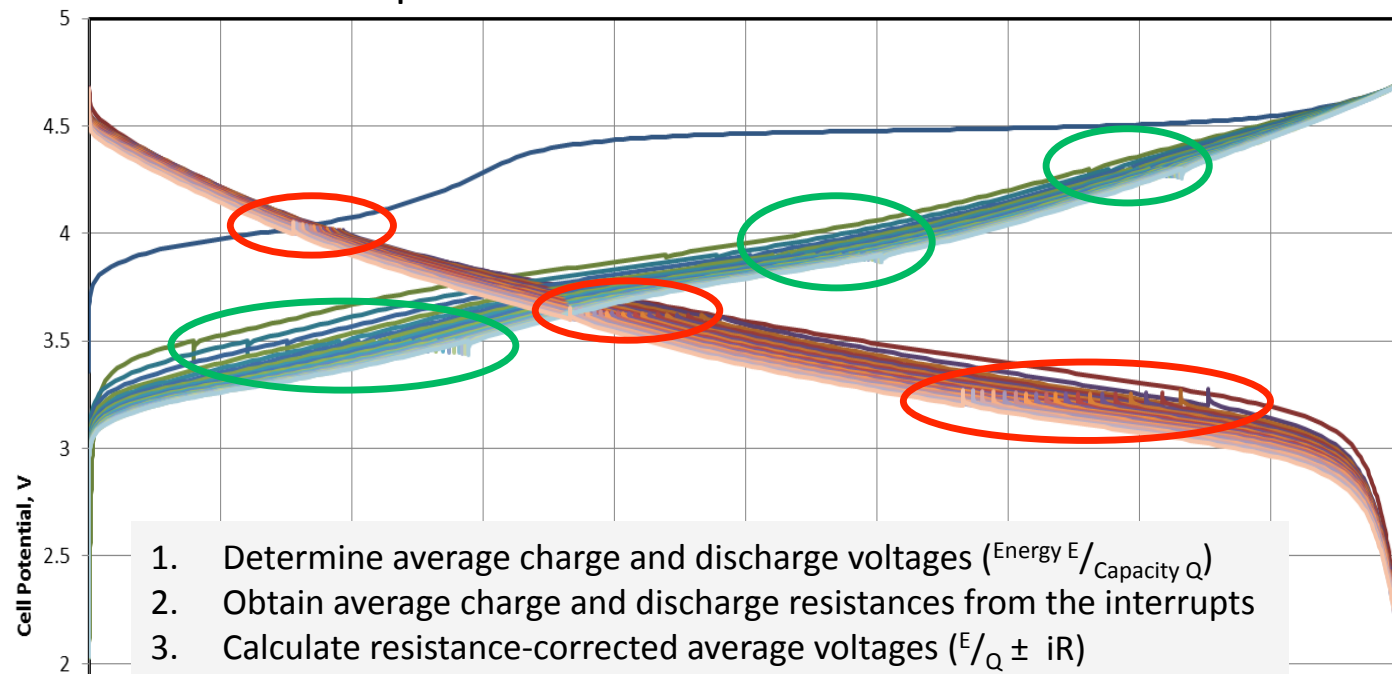
- Early 2012 realization that voltage fade was not something that was going to be fixed quickly or simply
- Work with DOE to determine a path forward shifting resources from existing disparate efforts and adding capabilities by halting some activates and shifting their resources.
- May 2012 propose new work scope. Initial work plan presented at AMR-2012 (ES161). (initial estimate 3 year project)
- May – Oct roll out of voltage fade and close down of other projects
- Oct 2012 full project is underway
- By AMR 2013 (ES161) Project is well underway with many milestones completed.
 - Targets defined
 - Testing procedures established
 - No Go on coating and post treatment
- **Sept 2014 Project to close after only 2 years.**



Common test protocol to measure and track voltage fade: A critical component to success

- Cell configuration: oxide as positive, Li metal as negative
- Temperature: 30°C (also 55°C)
- Initial activation cycle: 2-4.7V @ 10 mA/g followed by 2-4.7V @ 20 mA/g cycles
- Number of cycles: 20; Test time: ~20 days
- Total of 6 current interrupts implemented to obtain quasi-OCVs & DC cell resistances during charge at 3.5V, 3.9V, 4.3V, and during discharge at 4.0V, 3.6V, 3.2V. Each interrupt is a 10 minute monitored rest.

Presented previously
in FY2013



You need to have a
common protocol to
make real choices in
research directions
and down selects

1. Determine average charge and discharge voltages ($\frac{\text{Energy } E}{\text{Capacity } Q}$)
2. Obtain average charge and discharge resistances from the interrupts
3. Calculate resistance-corrected average voltages ($\frac{E}{Q} \pm iR$)

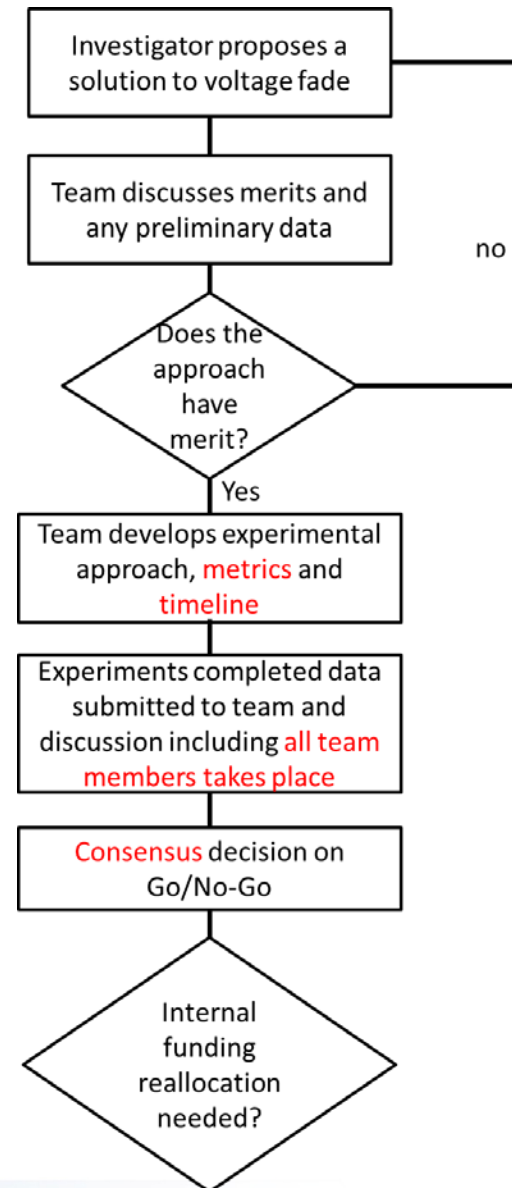


Now we can measure it, how do we fix it?

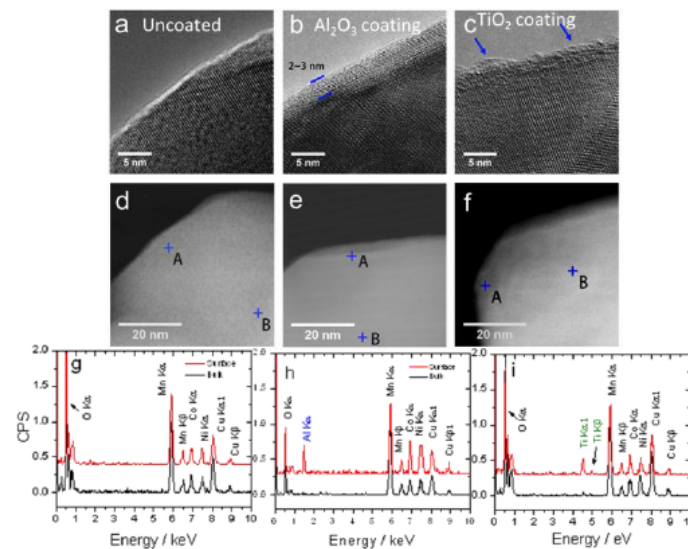
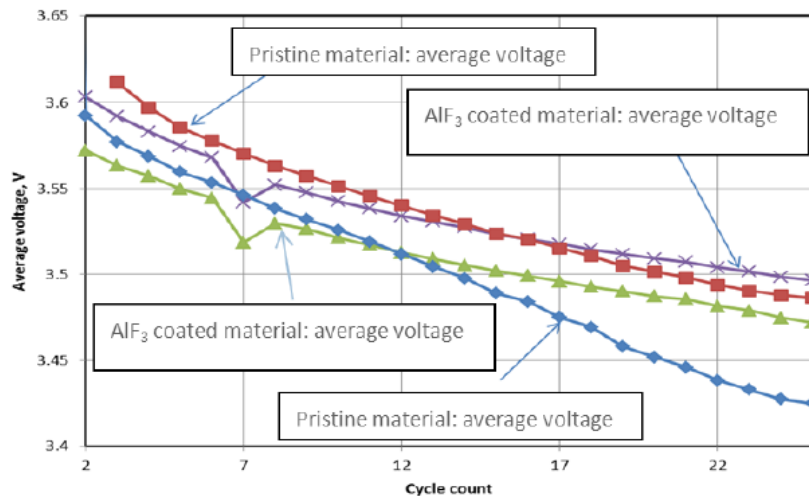
Initial “solutions” proposed at beginning of project

- Type of Synthesis
- Composition
- Surface Treatments
- Cycling protocols
- Electrolytes
- Morphology

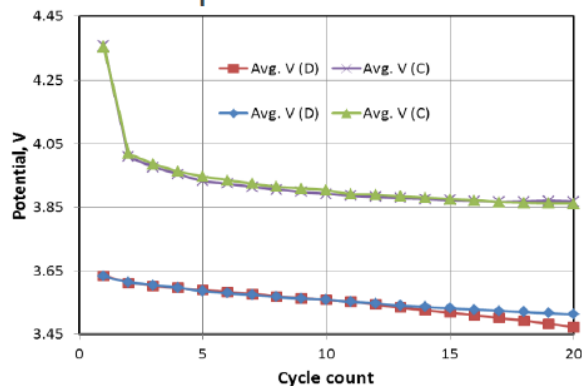
We follow a team approach to decisions using a process including data (from as many sources as possible), metrics and finally consensus.



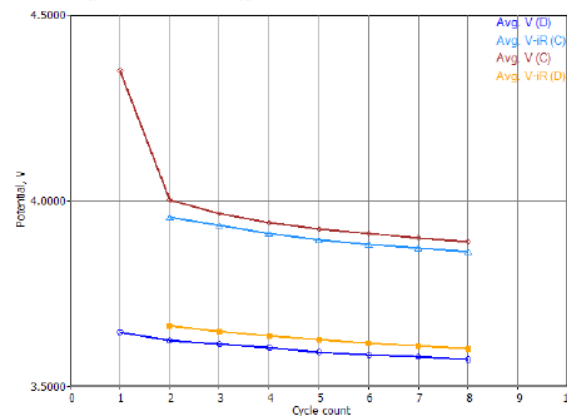
Common test protocol and our process let us: NO GO post synthesis treatments, coatings and additives



Thiophene additives



Cell wt= 5.66 mg; current density= 19.965 mA/g; temperature=Rm T; area=1.6 cm²



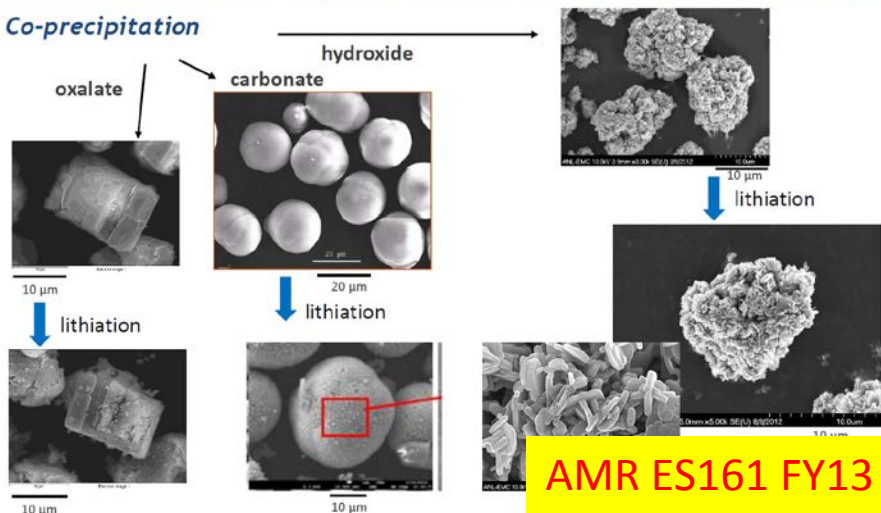
Presented previously
in FY2013

voltage fade is unaffected by coatings and additives

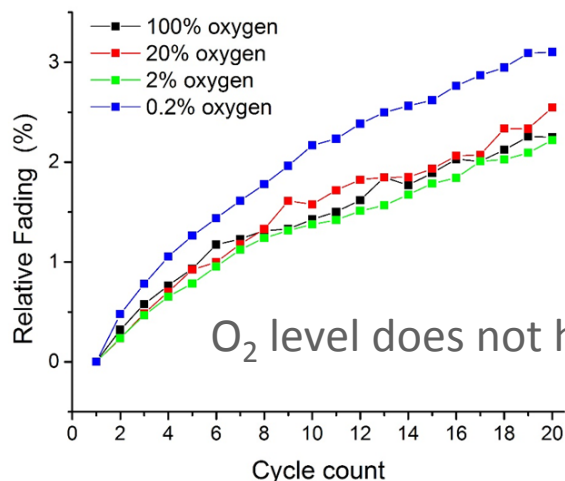
Common test protocol and our process let us :NO GO synthesis method

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

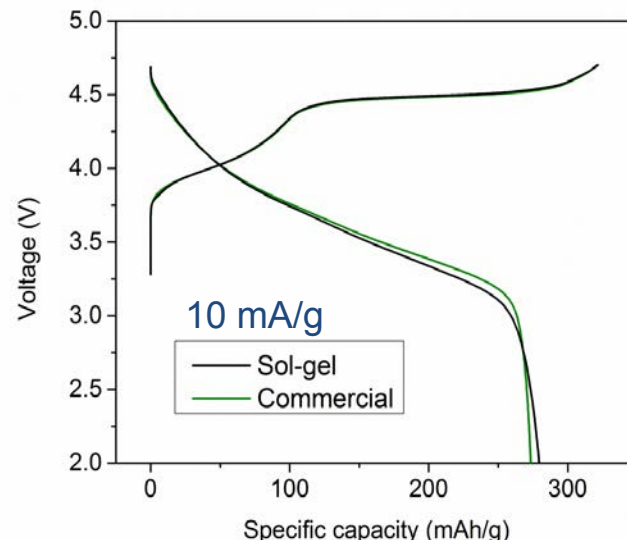
Co-precipitation



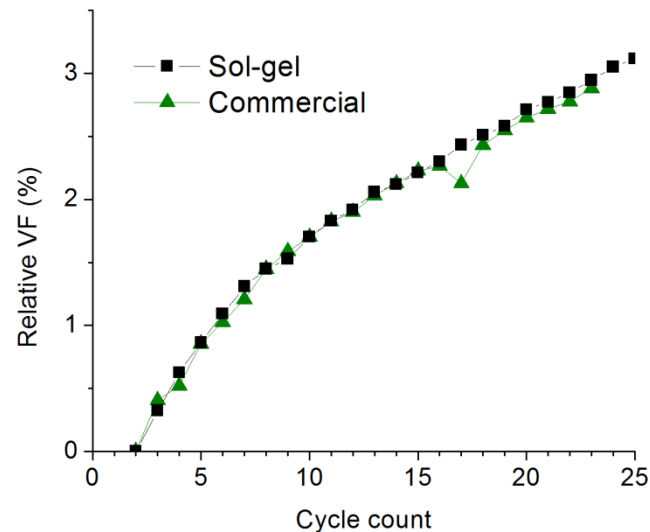
Others: sol-gel, combustion (glycine-nitrate), & direct solid state



O₂ level does not have an effect



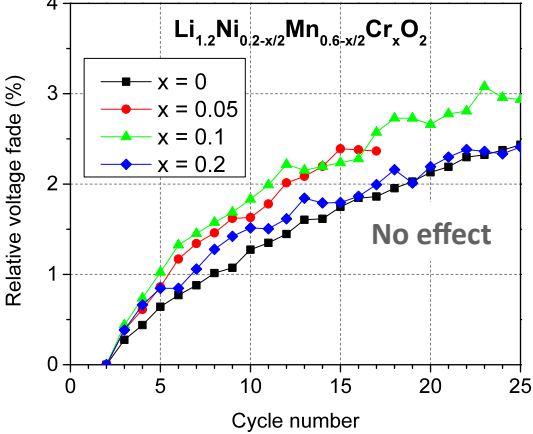
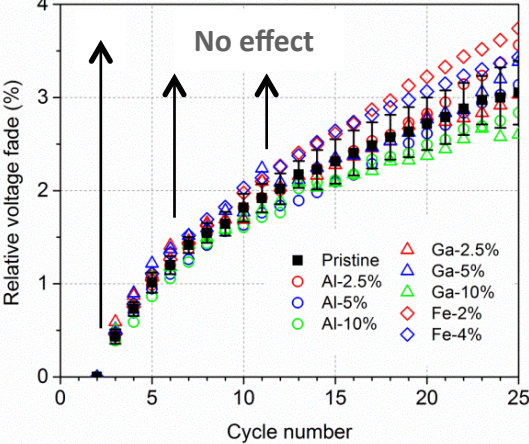
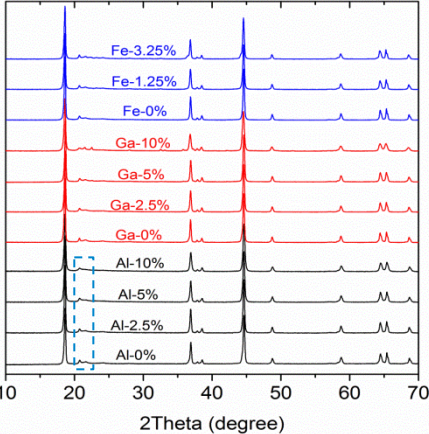
Type of synthesis does not have an effect



If you make equivalent material (capacity, voltage etc) the voltage fade rate is unaffected by the synthesis method

Common test protocol and our process let us conclude that composition has an effect, BUT has not lead to a fix (yet)

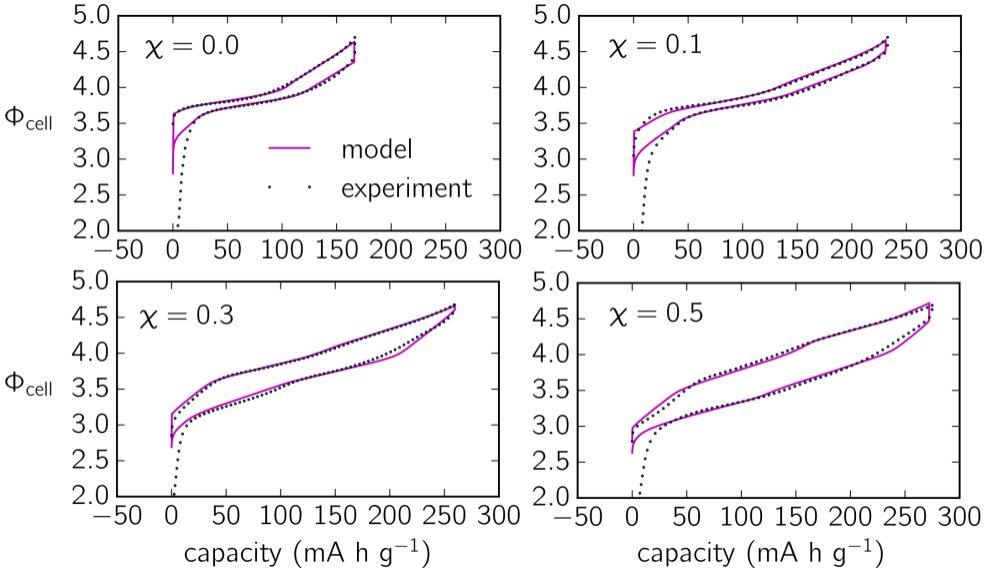
Redox active Cr substituted (Cr for Ni + Mn)



o Voltage fade was not suppressed for either cation doping or substitution in this study

LMR-NMC Electrode Half-Cells slow cycling compositional Dependence which can be modeled ES189, enabling further optimization.

- ES190, C. Johnson
- ES189, D. Dees
- ES194, Croy



The process worked: NO GO's and down selected were made using data from multiple sources and a unified testing-analysis process. **Most importantly the whole team was involved in the decisions.**

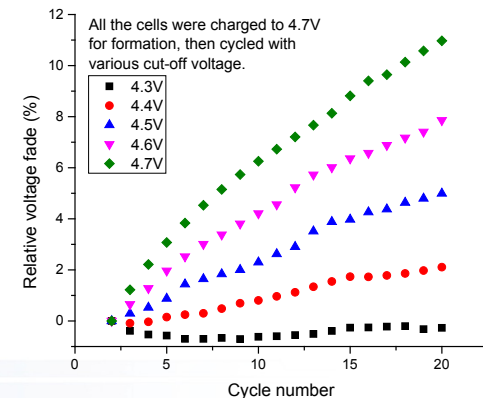
Now we can measure it, how do we fix it?

- ~~Type of Synthesis~~
- Composition ←
- ~~Surface Treatments~~
- Cycling protocols ←
- ~~Electrolytes~~
- ~~Morphology~~

Chemical composition affects rate of fade but no example where voltage fade is eliminated at in 2-4.7 V range

The lower the cycling cut-off voltage, the less voltage fade. No voltage fade when upper cutoff voltage of **4.3V** was used as cycling voltage.

Voltage fade rate is effectively zero in cells cycled 2-4.3V or less



The decision making process works.

- Collecting data the same way – comparisons possible
- Data is presented the same way and all data is uploaded to the data base – leads to real debate and overall understanding
- Others in the team validate the results
- Consensus outcomes
- **Result: this project ends one year early!**



So what is going on?

Proposed Mechanism: Voltage Fade and Hysteresis

- VF/hysteresis are related, charge/discharge energetics differ.
- Any model for this class of materials must account for both

Current Conceptual Interpretation of VF and Hysteresis

Gallagher et al., *Electrochem. Comm.*, (2013)

Discharged



Hysteresis



Charged

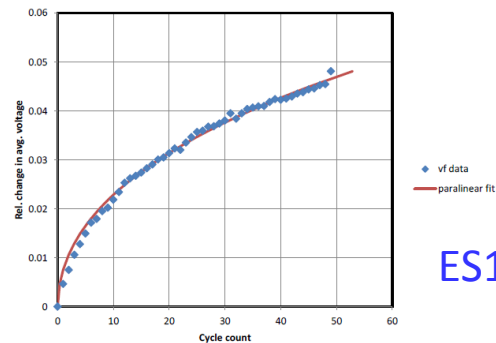
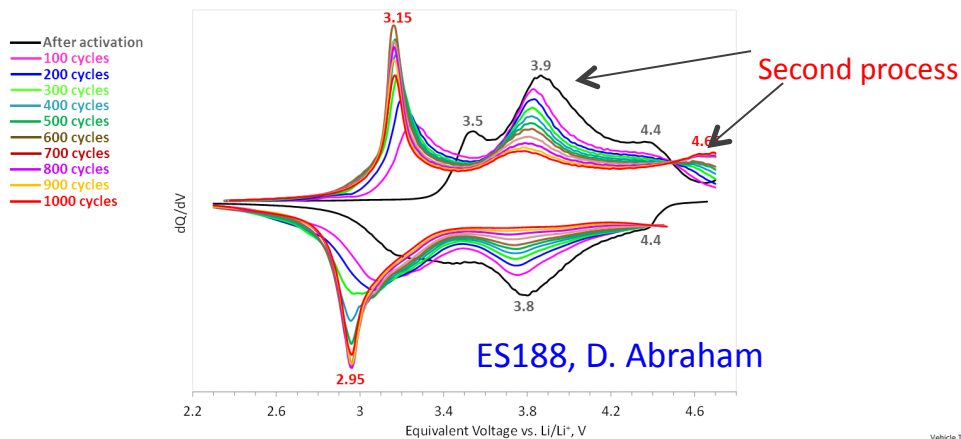
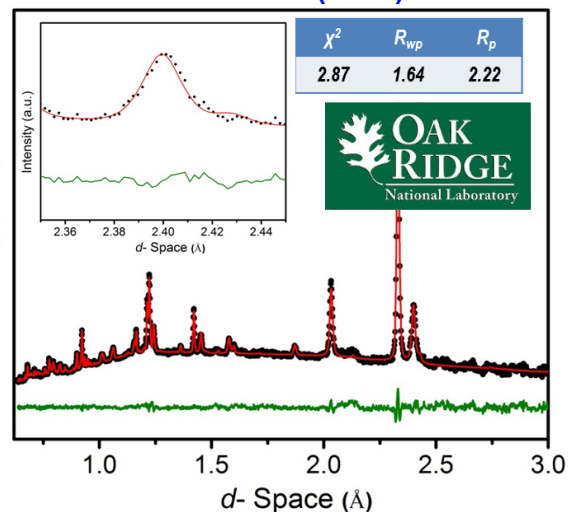
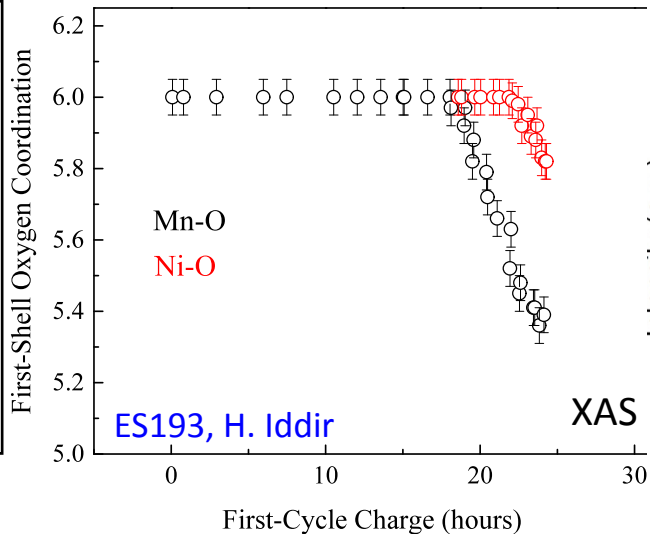
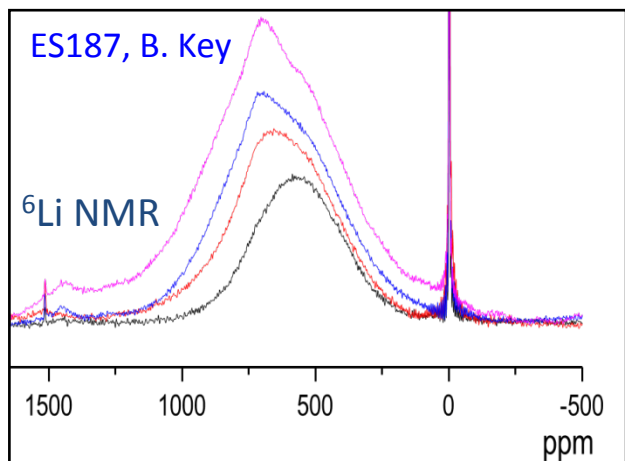
Voltage Fade



Discharged

- Charging to ~ 3.8 V and above induces migration to tetrahedral sites
- Cations are 'stuck' in that site until a critical Li content is reached on discharge (~ 3.2 V)
- At the critical lithium content cations can:
 - migrate back to original site (hysteresis)
 - continue on to the lithium layer (voltage fade)
 - remain 'stuck' – capacity loss, impedance rise

Proposed Mechanism: So far data is consistent with hypothesis



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

However a second process is also present ES187 (Key), ES194 (Croy), ES188 (Abraham)

Conclusions.

- The LMR-NMC is a truly remarkable material which is not perfect, but cathode capacity fade is effectively zero. [ES188 D. Abraham](#)
- Voltage fade appears to be a fundamental property of the materials class. [All voltage fade talks](#)
- Lower Li/Mn excess is better. [ES190 C. Johnson](#), [ES194 Croy](#), [ES187 B. Key](#)
- Understanding the properties of this system has lead to new materials. [ES190 C. Johnson](#), [ES194 Croy](#)
- **Team approach worked.**
 - Concentrated effort gave the answer in two years instead of (many) years of individual effort.
- There is no easy fix to voltage fade but it can be mitigated or lived with.

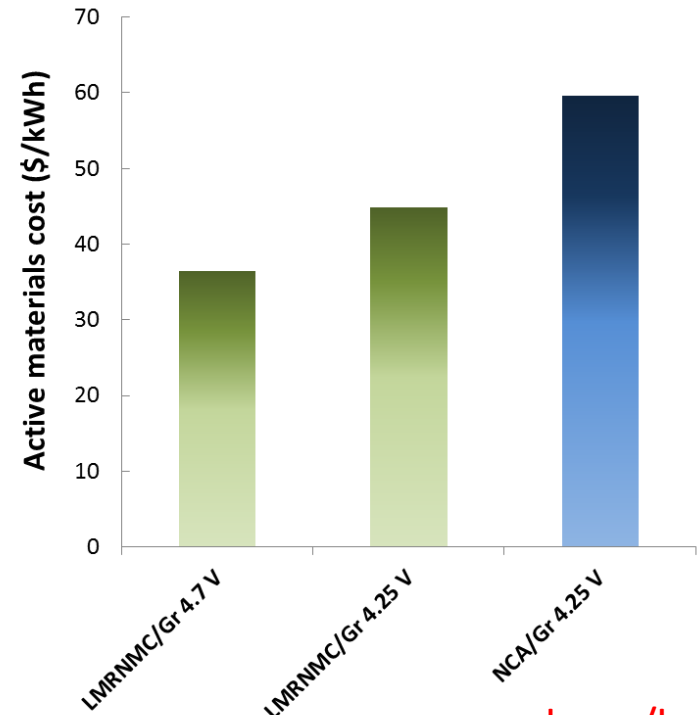
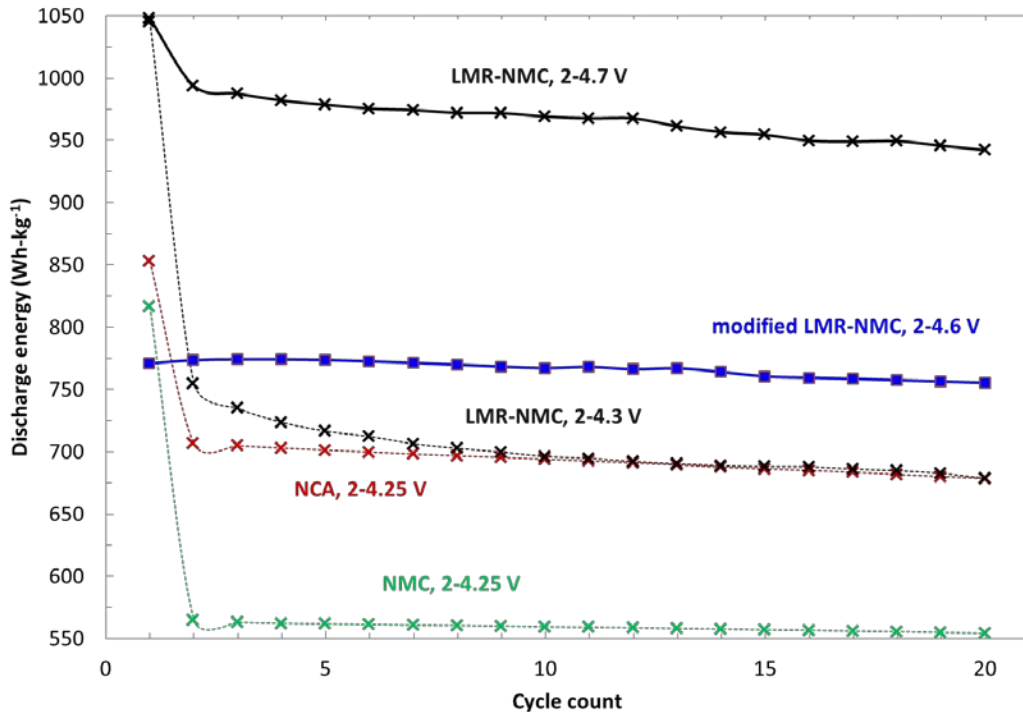
Caveats.

- We did not turn over every rock or exhaust every possible option. However, the current level of effort is not justified for a further year.



Path Forward: Voltage fade in LMR-NMC requires trade offs.

- High energy cells will require different electronics for management.
- Lower energy cells = no voltage fade



www.cse.anl.gov/batpac

LMR-NMC with no voltage fade has same energy density as NCA but is less expensive. LMR-NMR with voltage fade is still outstanding, but will require a cost benefit analysis for specific applications.

Project rap up and future

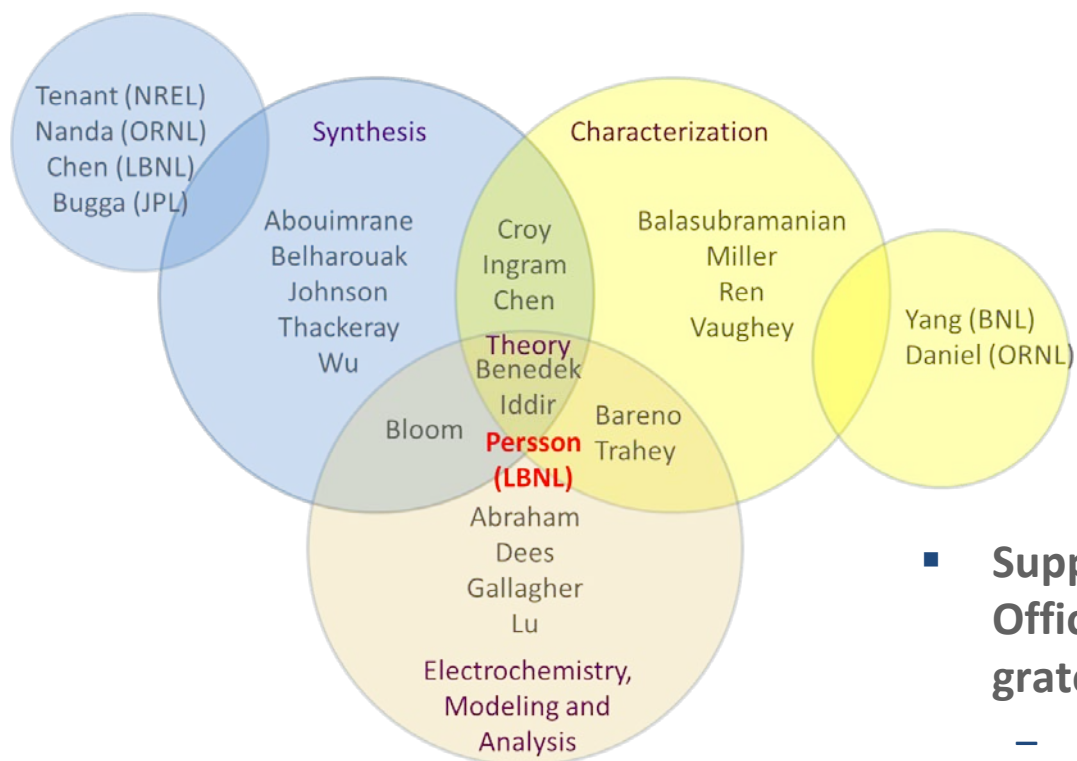
- Complete work on existing approaches to mitigation.
- Complete understanding of the “activation of the material”.
- Determine the other mechanisms of change in LMR-NMC.
- Deliver workable solutions to high energy cells using LMR-NMC.

- Even if we can live with voltage fade, to obtain highest energy density from LMR-NMC we still need to have cells that function at 4.7 V vs graphite (or silicon) for extended cycling.



Collaborations and Acknowledgment

Burrell, Anthony K.; Abouimrane, Ali; Abraham, Daniel; Amine, Khalil; Balasubramanian, Mahalingam; Bareno Garcia-Ontiveros, Javier; Belharouak, Ilias; Benedek, Roy; Bettge, Martin; Bloom, Ira D.; Long, Brandon R.; Chen, Zonghai; Croy, Jason R.; Dees, Dennis W.; Dogan, Fulya; Gallagher, Kevin G.; Henriksen, Gary L.; Iddir, Hakim; Ingram, Brian J.; Johnson, Christopher; Key, Baris; Li, Yan; Lu, Wenquan; Miller, Dean J.; Ren, Yang; Slater, Michael D.; Thackeray, Michael M.; Vaughey, John T.; Wu, Huiming; Wu, Qingliu; Zhu, Ye; Yang, Zhenzhen; Lee, Eungje; Aoun, Bachir; Vu, Anh D.; Lin, Chi-Kai; Rinaldo, Steven G.



Cell Analysis, Modeling, and Prototyping (CAMP) Facility

Posttest Facility

Materials Engineering Research Facility

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