

Synthetic Solutions for Correcting Voltage Fade in LMR-NMC Cathodes

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Project ID: ES190

Overview

Timeline

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

Budget

- Voltage Fade project

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



Relevance

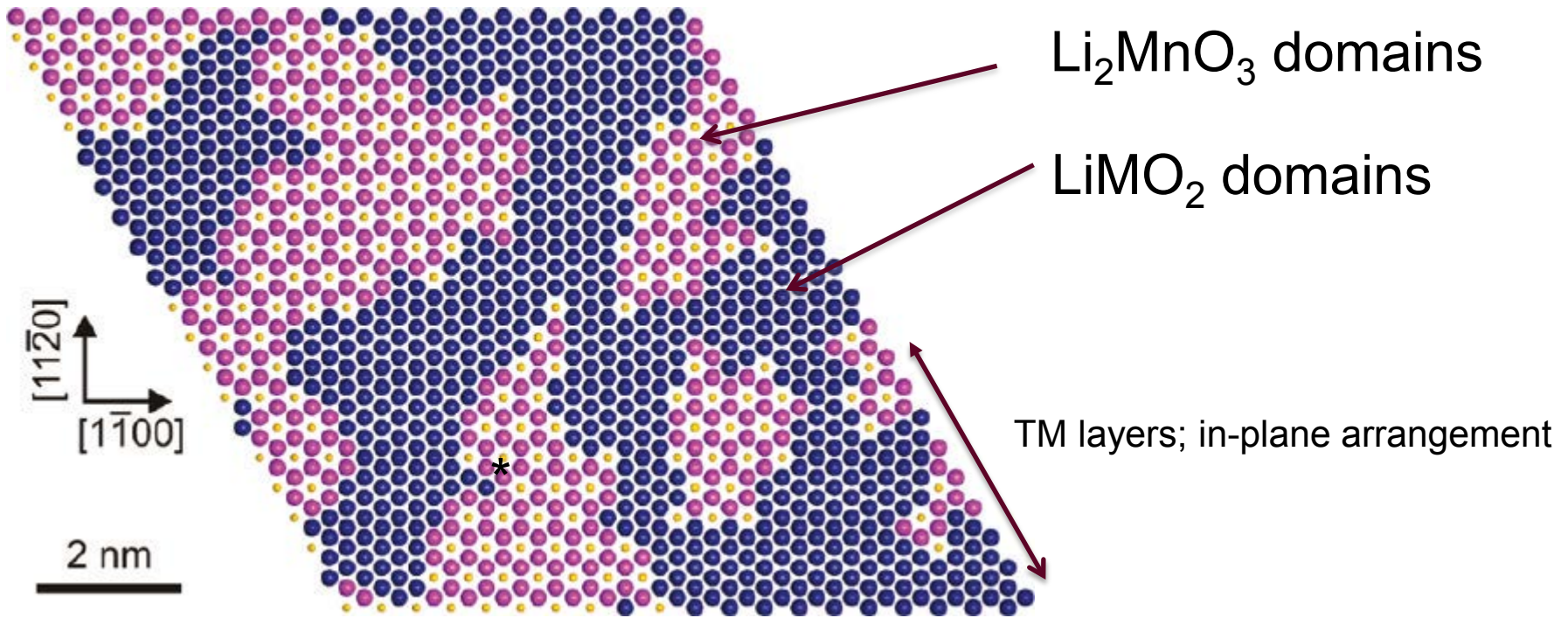
- **New cathode materials are required to improve the energy density of Li-ion cells for transportation technologies.**
- LMR-NMC class of layered compounds : Best known cathode option to date
- * 250 mAhg⁻¹ at high-charge voltages (4.7 – 2.0 V)
 - Energies approach 950 Whkg⁻¹
 - Capacity stable over 1000s of cycles
 - Low rate capability and low tap density
 - Energy loss over cycling duration due to **voltage fade**
- Need to solve structural and electrochemical performance problems
- Explore syntheses solutions towards VF-free cathode materials

* Abraham et al. (electrochemistry diagnostics ES188)





* Structural model



- Croy et al. ES194
- Iddir et al. ES193
- Key et al. ES187
- open literature

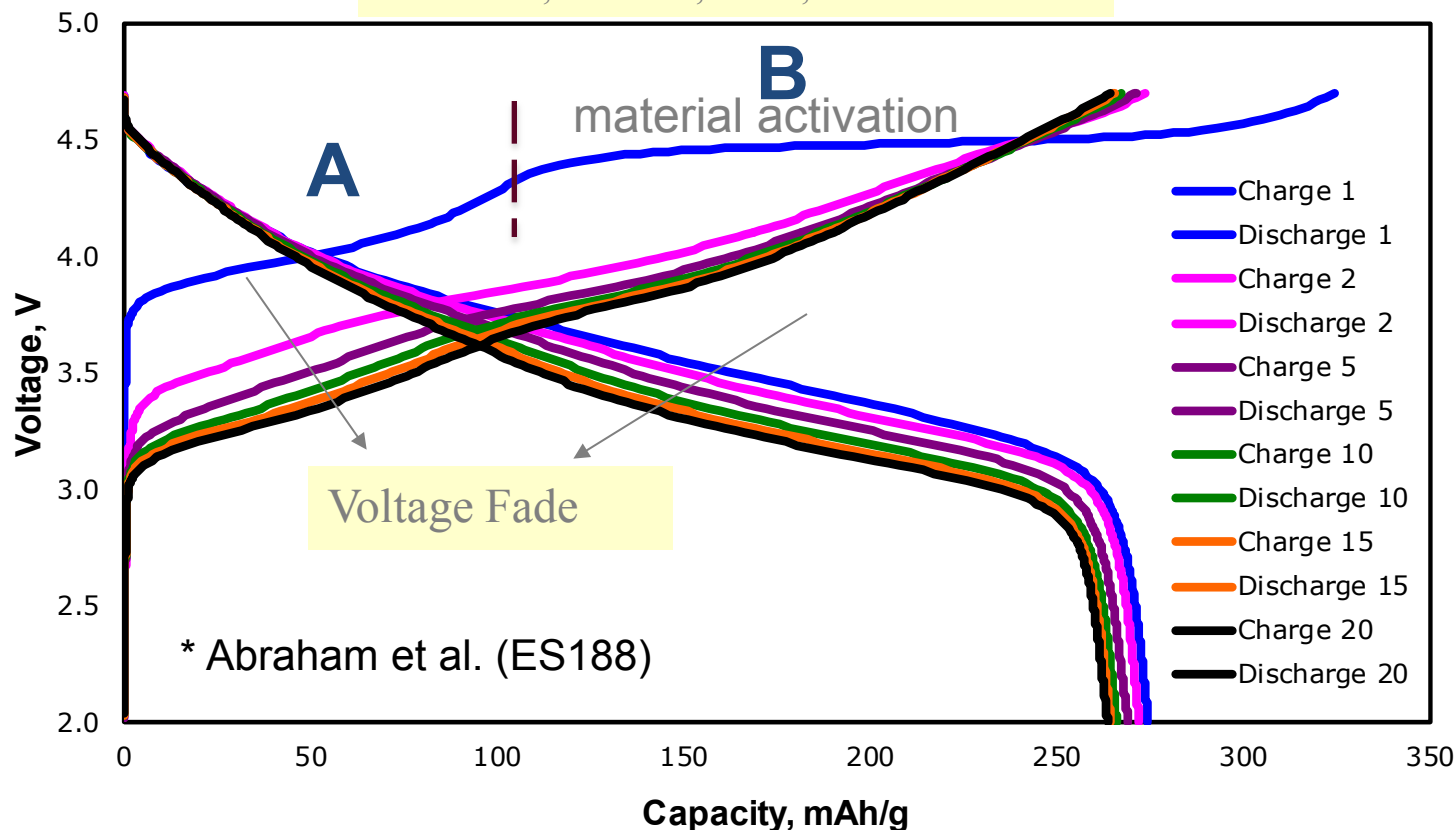
Initial state: Li-rich Mn-containing layered transition metal oxides: extra Li in the presence of Mn forms LiMn_6 domains in TM layer

* Schematic: Barenó et al. Chem. Mater. (2011)

Voltage profile - electrochemical processes



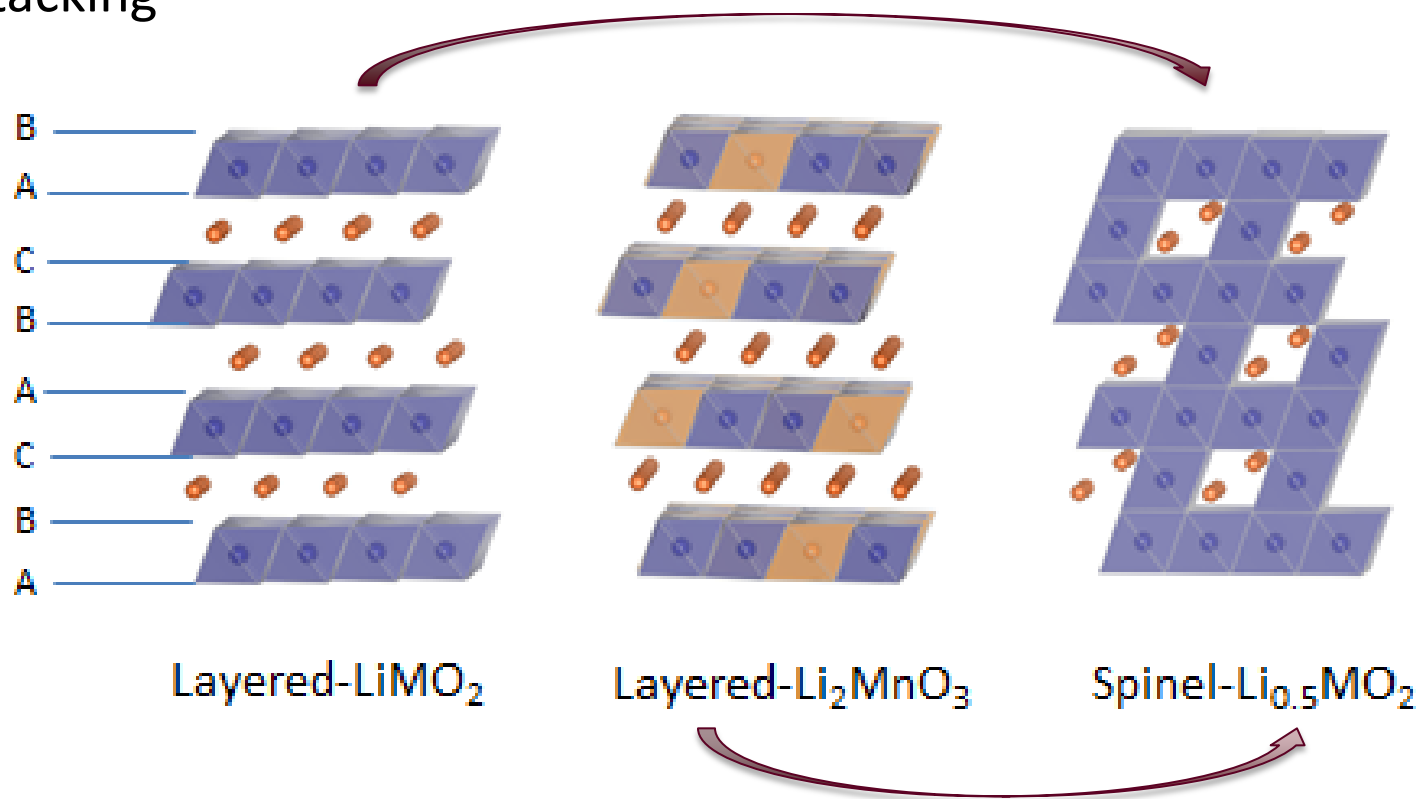
Li half cell; 2 – 4.7V, 30 °C; ~ C/25 Rate



- Voltage profile features are strongly correlated with composition
- Process A (Ni & Co redox); Process B (activation: Li removal from LiMn_6 domains in TM layer)
- Post-activation: VF (voltage fade) is manifested with full window cycling

Structural issue in voltage fade

- LiMO₂, Li₂MnO₃, and spinel-Li_{0.5}MO₂ share the O3 type oxygen layer stacking



- Significant proposed O-vacancy creation during activation
- Initiates Mn-dominated cation movement
 - Stable intermediate cation dumbbell structure configuration created
- Reversible and irreversible-type cation diffusion

Approach

- Study voltage fade mechanism
 - Apply knowledge to (1) composition and (2) structural design of cathode materials
- Use theory to help guide syntheses approaches and decisions
- Apply syntheses methods
 - Composition
 - pO_2 atmosphere
 - Sol-gel and co-precipitation routes
 - Establish best synthetic route to probe chemistry
 - Cation substitution
 - Structural alterations
- Use electrochemical voltage fade protocol for assessments

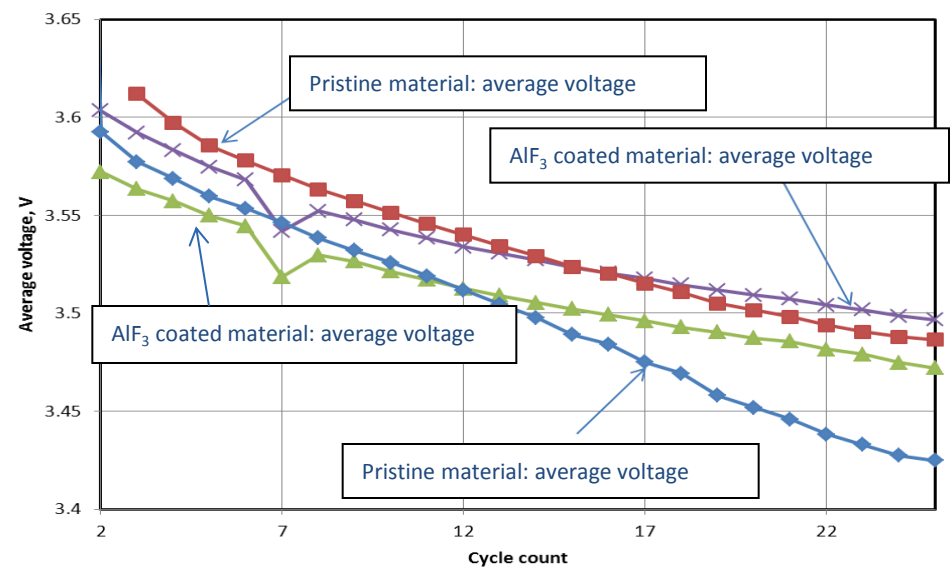
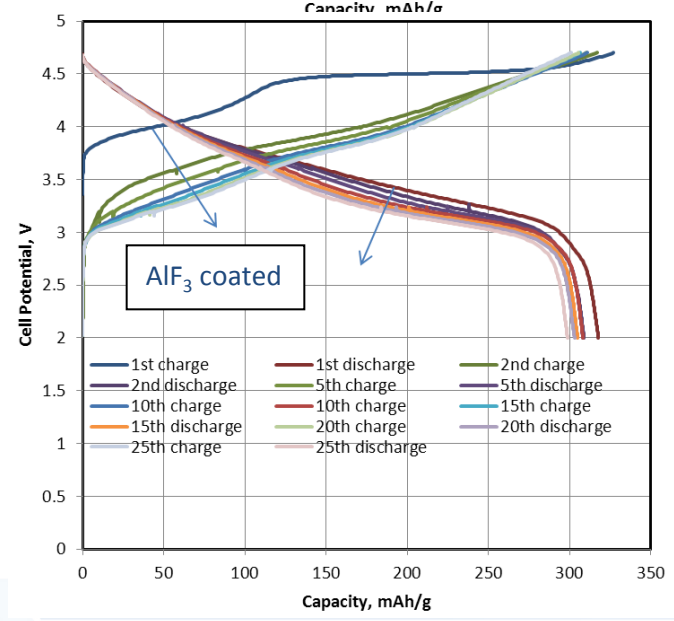
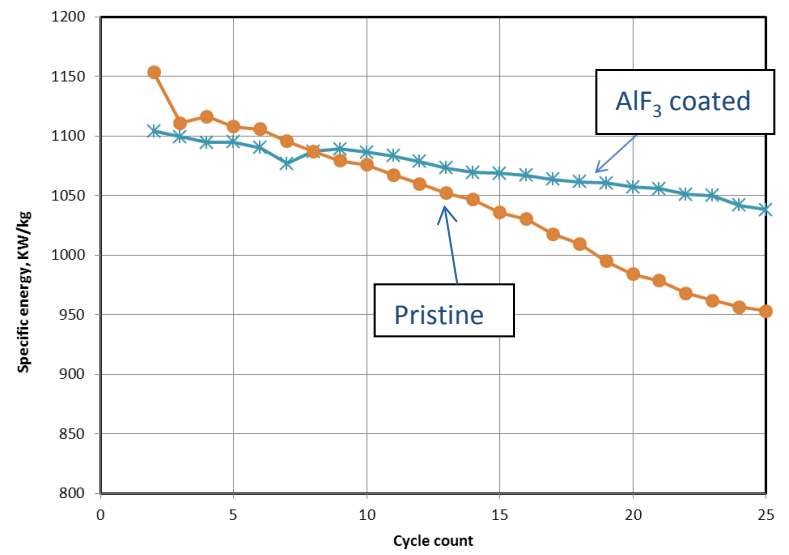
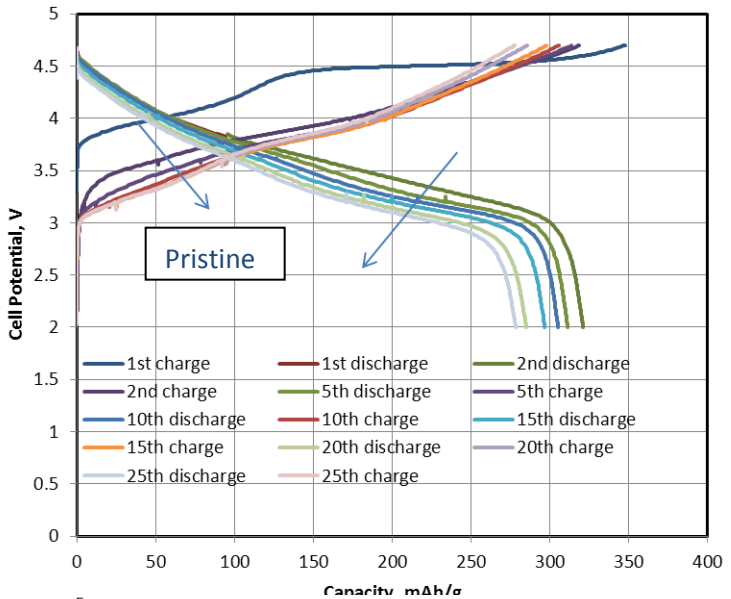


Milestones of FY14

- Coating assessment _____ Completed:
no-go
- Composition variance _____ Completed
- Explore multiple synthesis routes _____ Completed
 - Firing Atmosphere used _____ Completed
 - Synthetic precursor effect _____ Completed
 - Doping/substitution _____ Completed
- ***Continue synthesis of materials*** _____ On-going
 - Focus: (1) structures***
 - (2) high-voltage redox reactions***
 - (3) linking theory/modeling to composition***



Coatings: effect of AlF_3 coating on the voltage fade of $\text{Li}_{1.2}\text{Ni}_{0.175}\text{Mn}_{0.525}\text{Co}_{0.1}\text{O}_2$

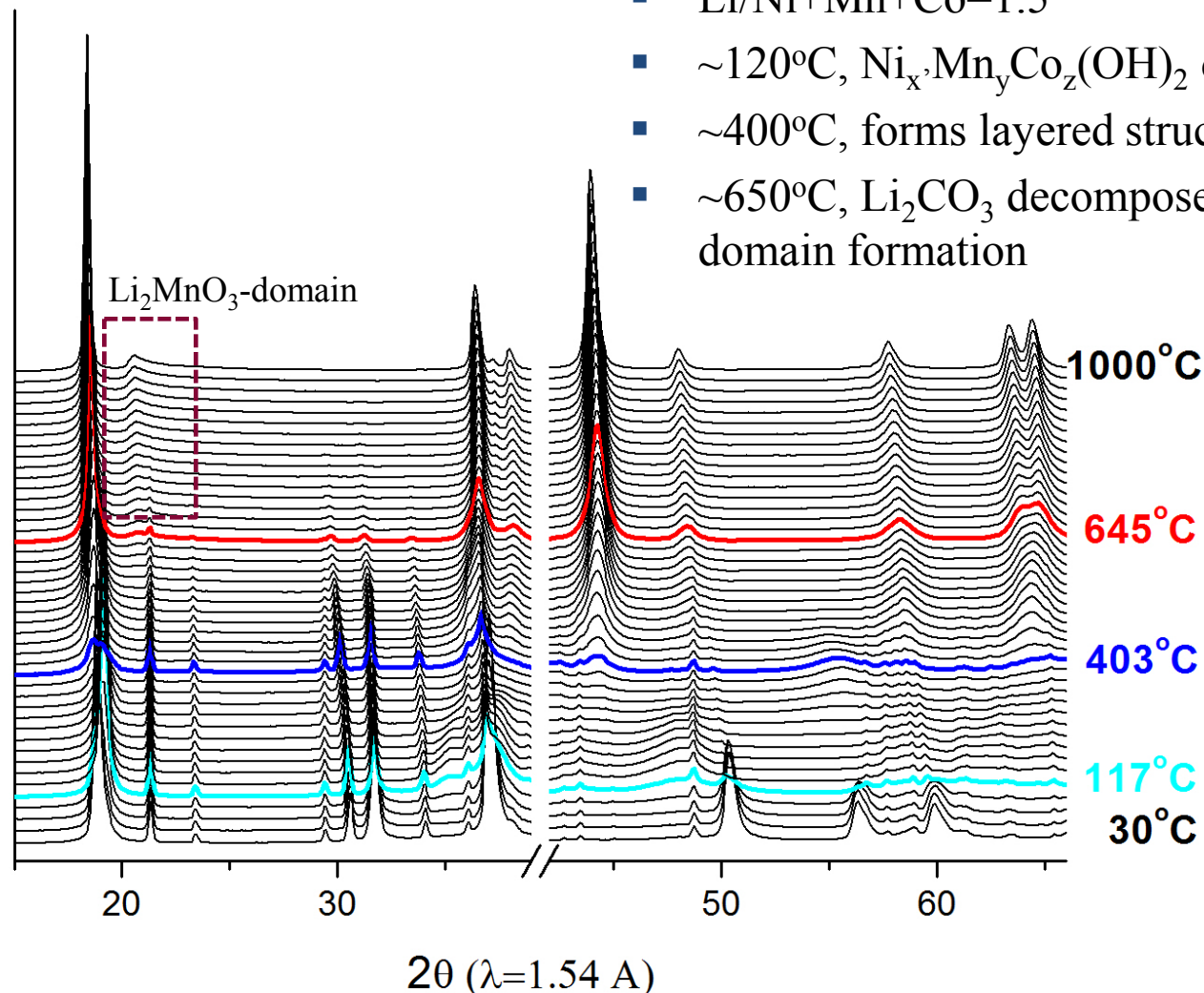


- Capacity retention better with AlF_3 coatings; but VF not curtailed
- Coatings: determined as no-go in FY'14



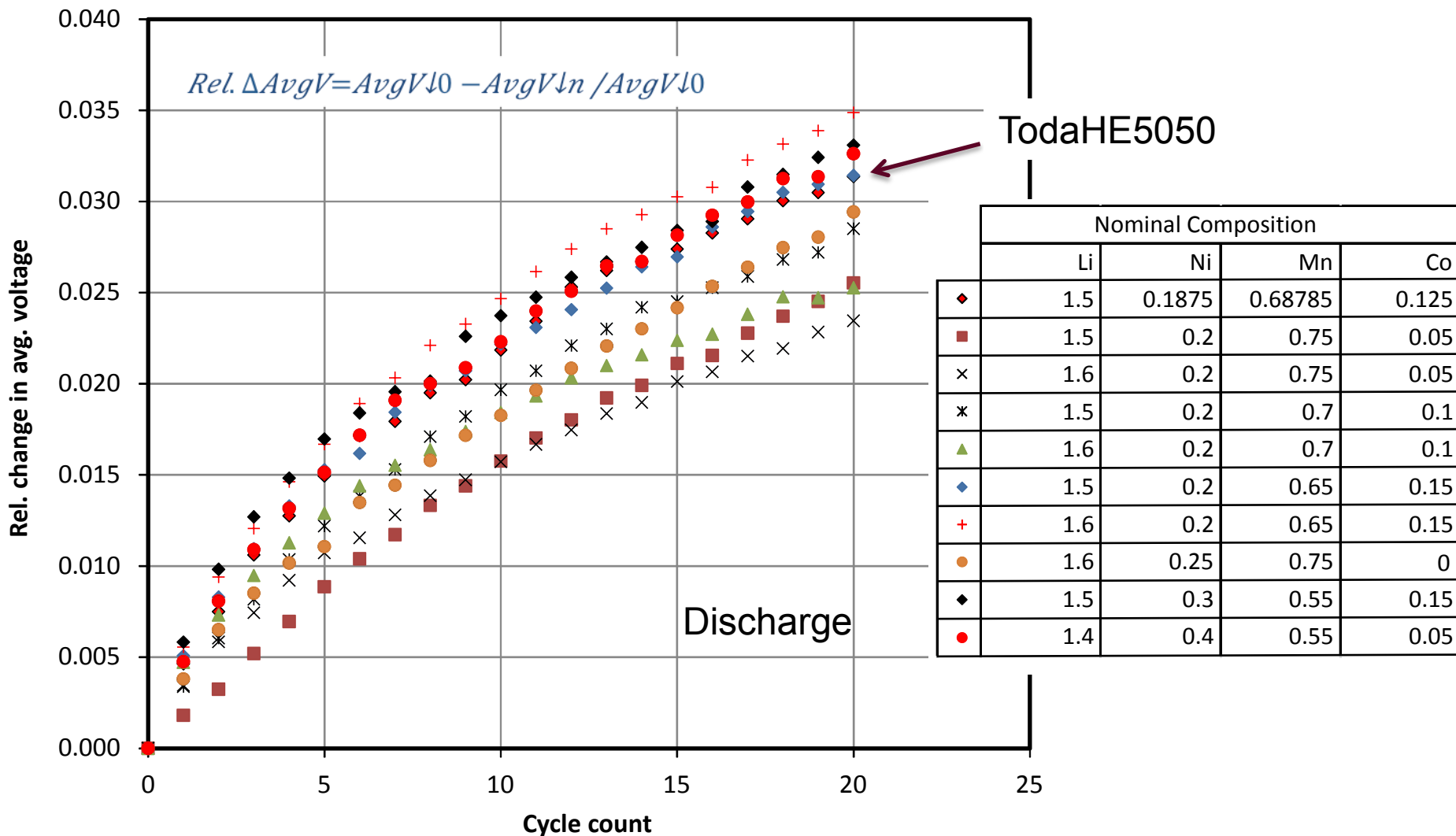
Li₂MnO₃ domains - preferential formation during LMR-NMC synthesis

- Li/Ni+Mn+Co=1.5
- ~120°C, Ni_xMn_yCo_z(OH)₂ decomposition
- ~400°C, forms layered structure
- ~650°C, Li₂CO₃ decomposes: initiates Li₂MnO₃ domain formation



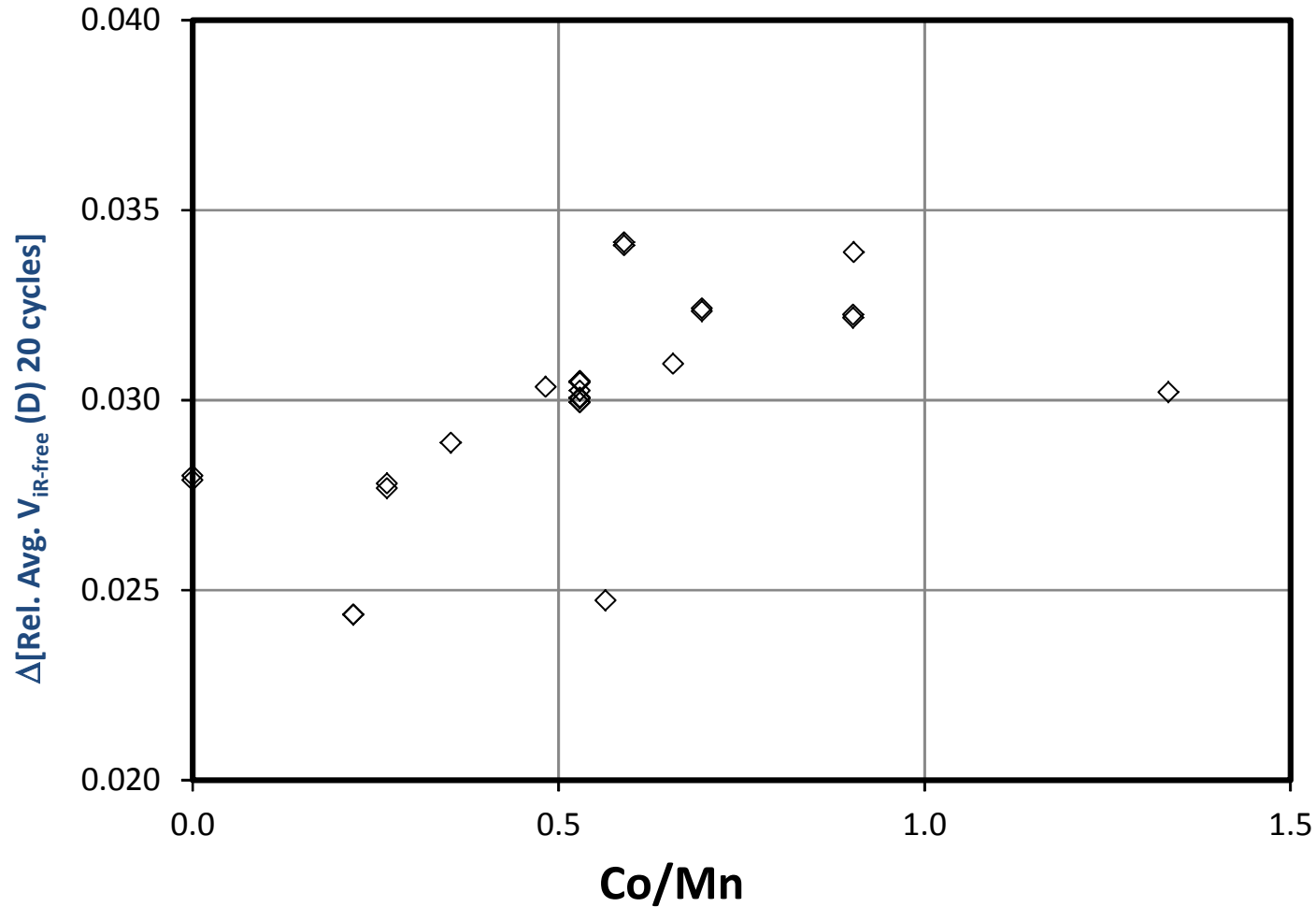
Synthetically we must take into account strong tendency to make LiMn₆ units in TM plane

Effect of bulk composition on voltage fade



Voltage fade not stopped, but rate of voltage fade changed as a function of LMR-NMC composition

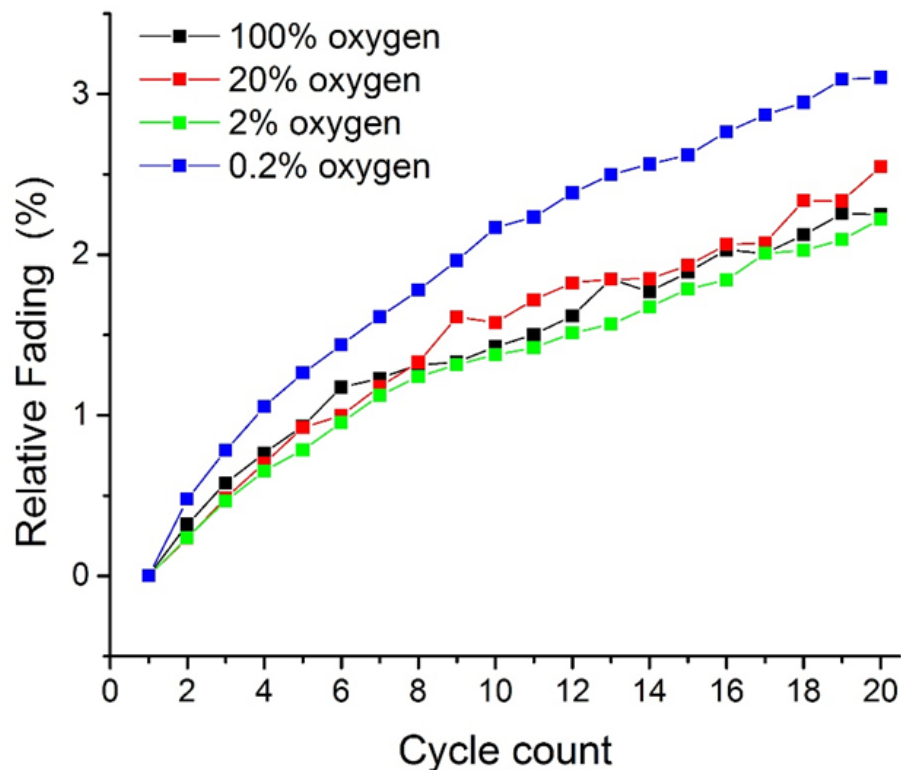
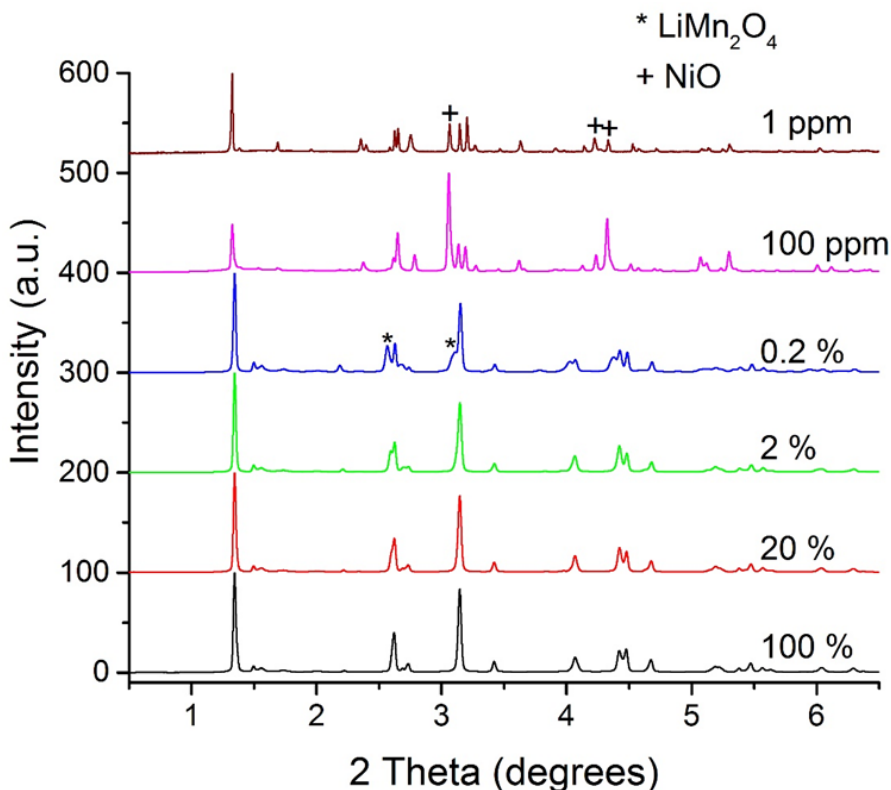
Result: composition effect- Co/Mn ratio



Greater content of Co in composite the greater the voltage fade

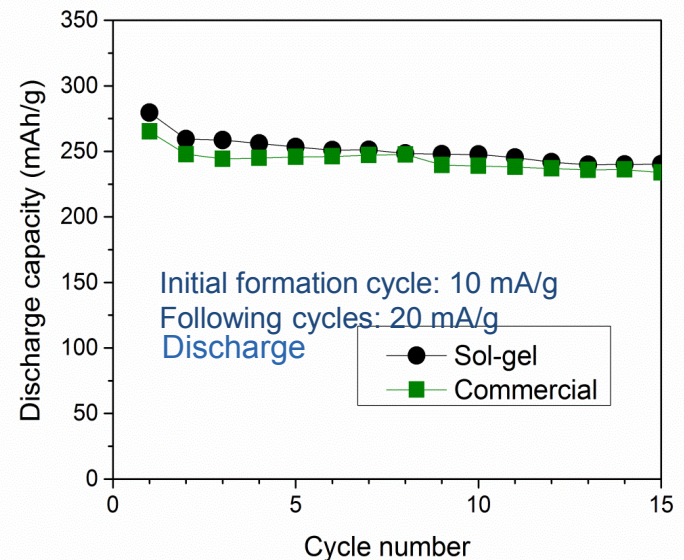
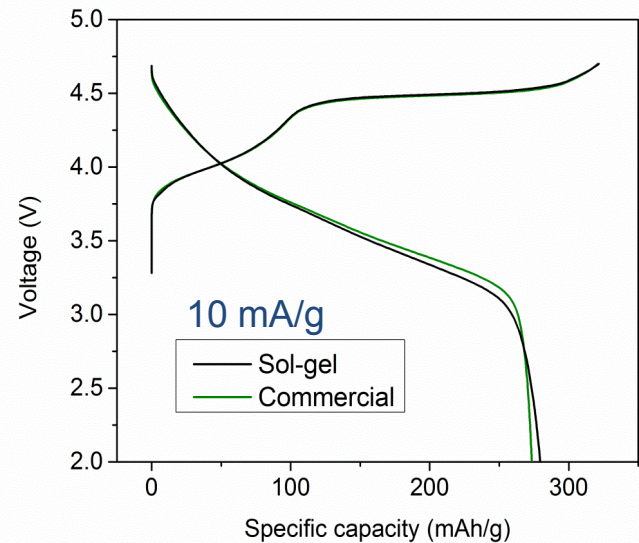
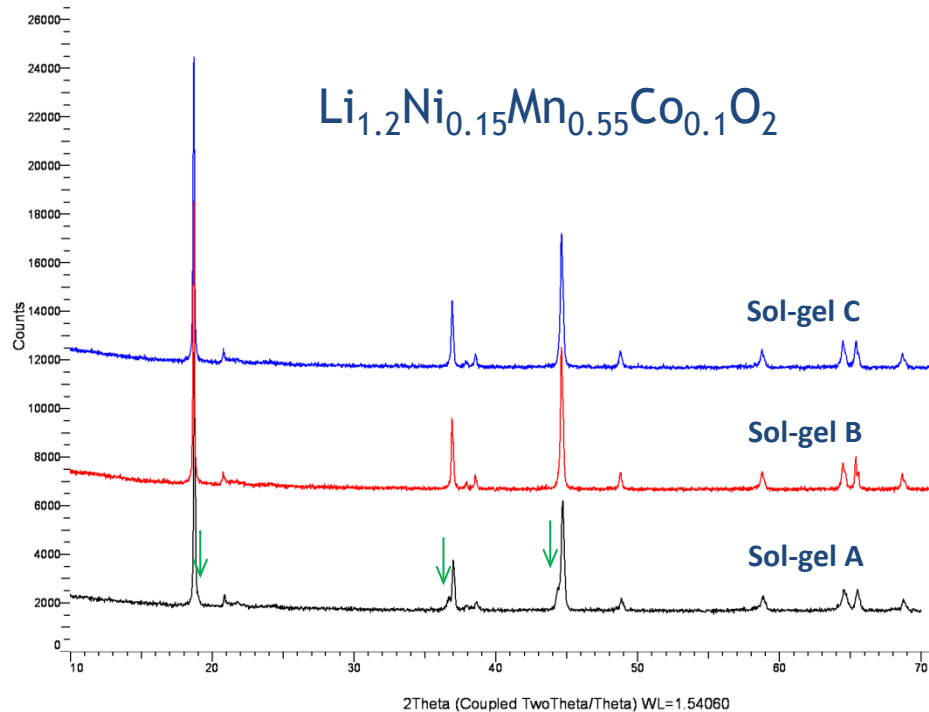
Synthesis atmosphere: effect of pO₂

Targeted nominal composition: $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{Li}[\text{Ni}_{0.375}\text{Mn}_{0.375}\text{Co}_{0.25}]\text{O}_2$
layered notation: $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$



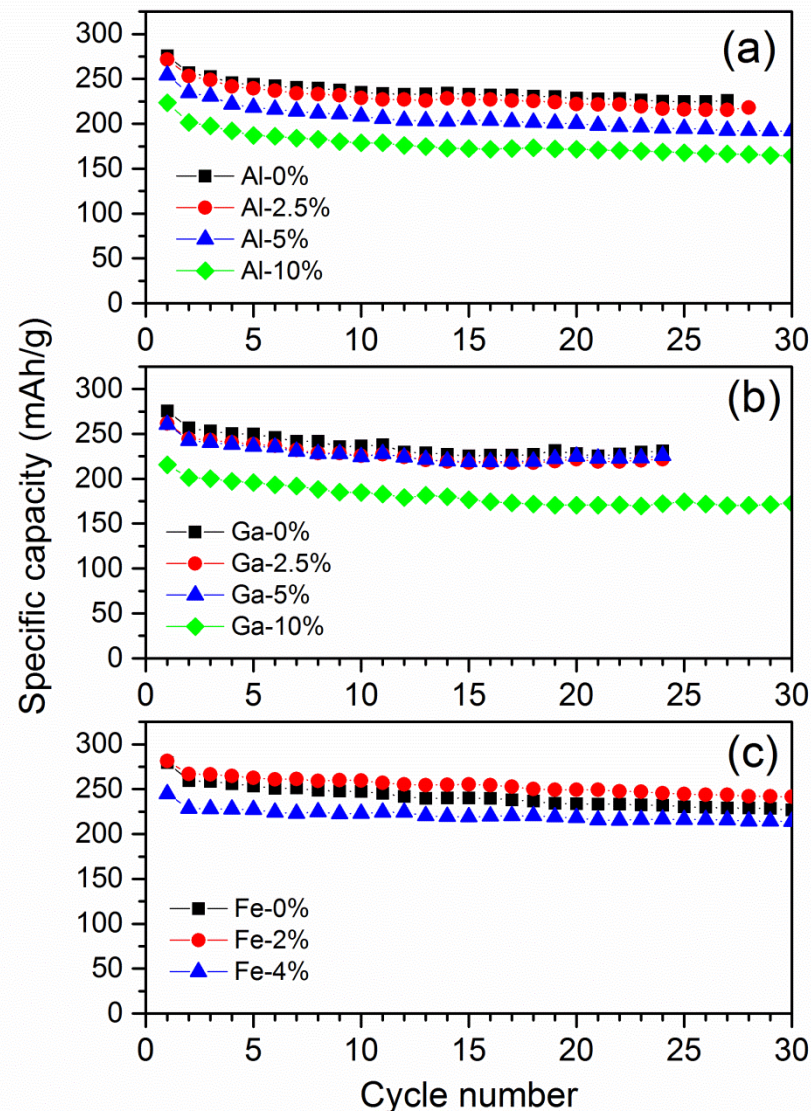
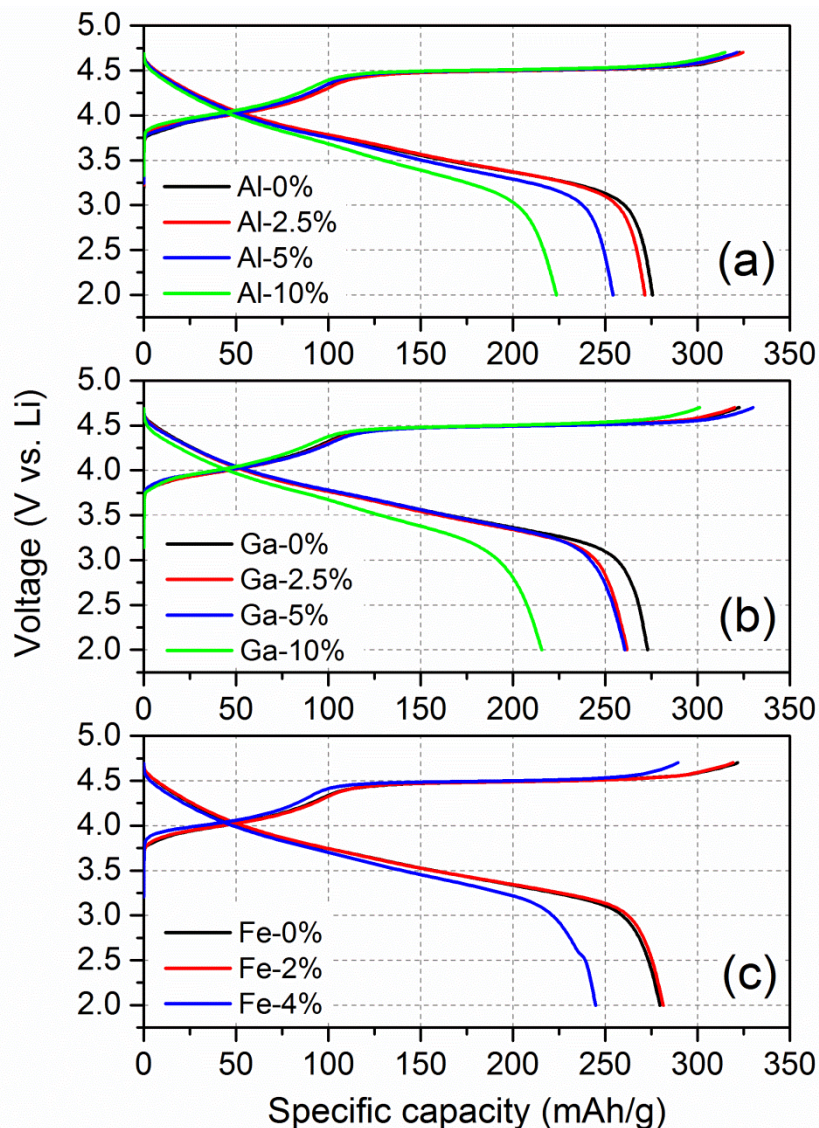
- Pechini process used to form Li-containing precursor materials
- Precursor material calcined in 100% oxygen shows voltage fade

Sol-Gel synthesis route



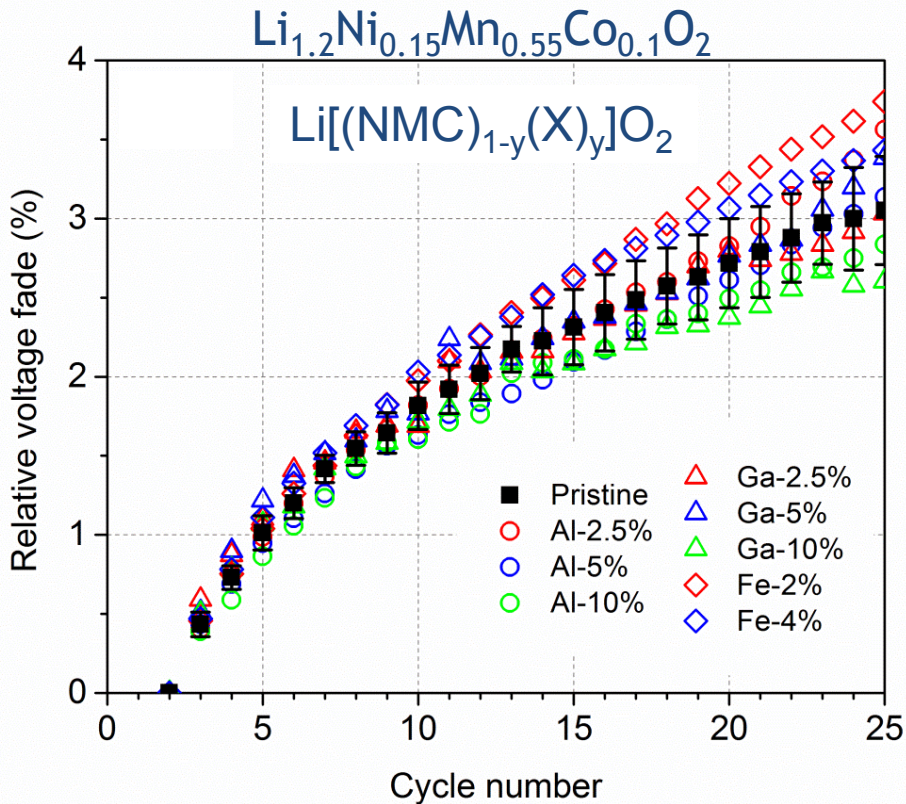
- Successful synthesis of HE5050 (Toda) via sol-gel reactions
- Expected capacity obtained
- Good syntheses method for exploring substitution chemistry

Cation-substituted (Al, Ga, Fe) Electrochemistry

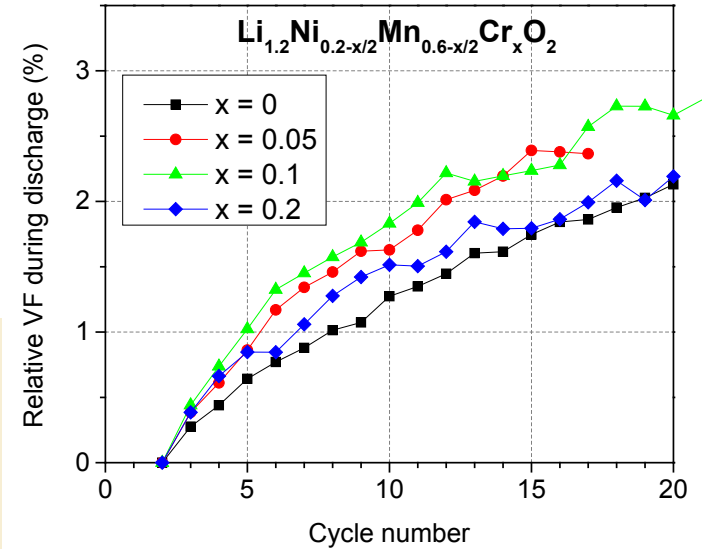
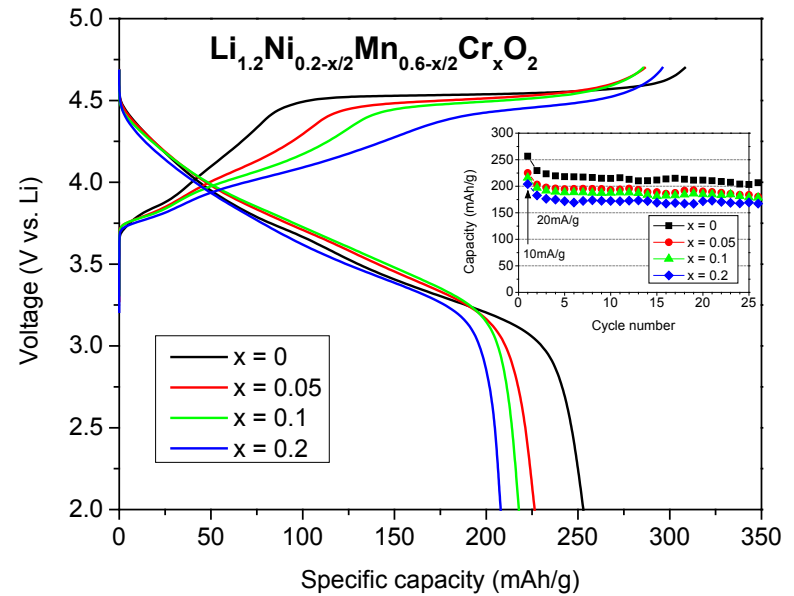


Stable capacities $\sim 250 \text{ mAhg}^{-1}$ \rightarrow similar Li quantity cycled in samples

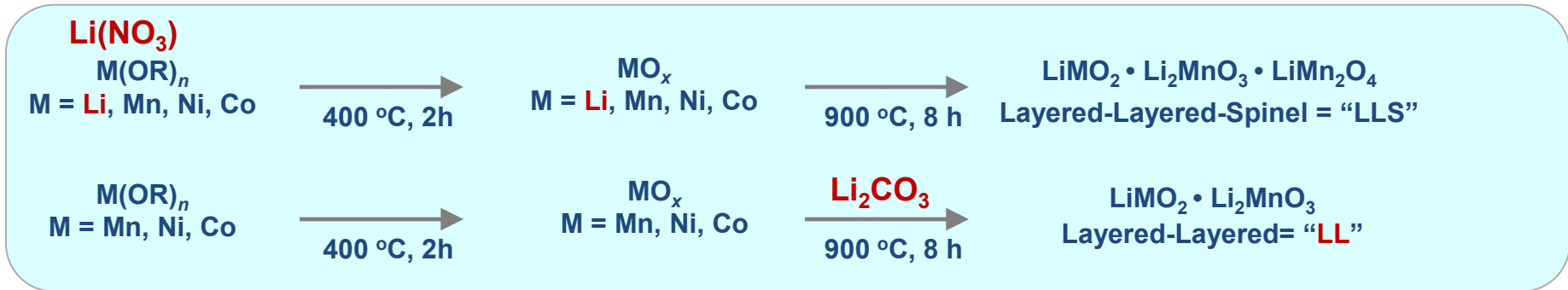
Al, Ga, Fe-substituted



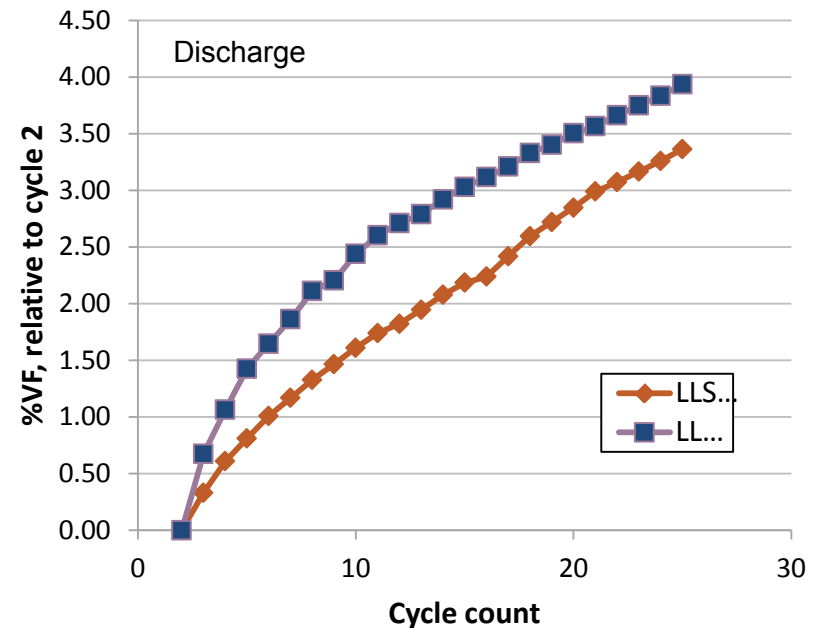
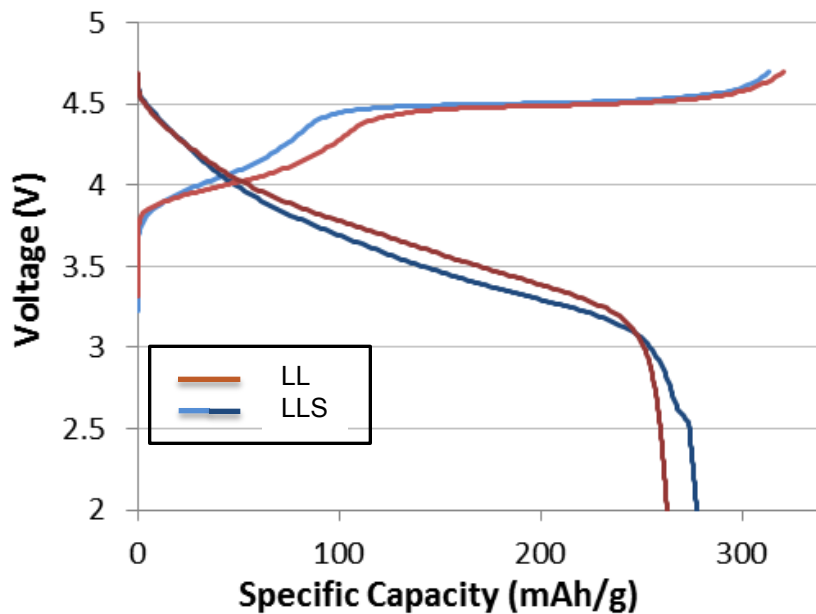
- Spectator cations (Al & Ga)- no VF effect
- Substituted Fe cation (redox active) – no VF effect
 - surmise Fe migration to surface during synthesis
- Substituted Cr cation (redox active)
 - activation plateau altered
 - VF not retarded



Order of Li-addition in Sol-gel synthesis



LL vs. LLS of same nominal composition: $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$



- Phase distribution in product depends on when Li is introduced in the synthetic process
- Possible synthetic approach to structure control; VF not mitigated however in this example



Summary - Synthetic approaches to VF-free materials

- As-prepared Li-rich/Mn-rich synthesized materials strongly form Li_2MnO_3 domains
 - LiMn_6 units in TM-plane
 - Composition
 - Variance of Li, Ni, Mn and Co – no effect
 - Voltage fade rate can be changed by as much as ~36%
 - Percentage of Co increases, then VF increases
 - Method of synthesis
 - Pechini, Sol-Gel and Co-precip. routes evaluated – no effect
 - Oxygen firing – no effect on VF
 - Sol-Gel reactions
 - Cycling performance/features equivalent to commercial materials
 - Successful cation doping/substitutions – Al, Ga, Fe, Cr
 - Spectators and redox cations
 - No effect on VF – rate of change affected only
 - Order of Li addition
 - Can create spinel component in as-prepared material
 - Structural control may be possible – but no effect on VF in example herein
- Various synthetic approaches did not stop voltage fade
 - Arresting voltage fade in these class of Li-rich Mn-rich 'layered-layered' composites appears unobtainable



Remaining Challenges and Barriers

- Can we find a new synthesis route not yet used that will stop voltage fade
- Must determine location of Li, TM cations in LMR-NMC composites to direct syntheses going forward
 - Total understanding of structural changes of LMR-NMC during first charge ('activation' plateau)
 - Total understanding of TM cation movements during cycling
- Must prove charge compensation in these LMR-NMC cathode materials
 - May lead to new novel synthesis approaches
 - May lead to totally new materials for cathodes



Future Plans

- Optimize Li, and TM cation distribution in domains
 - Control domain size?
 - Try glycine-nitrate combustion reaction
 - Is a solid solution possible?
 - Quenching with compositions that show lowest voltage fade rate
 - Control movement of TM cations in Li-rich layered structures at high-states of charge
 - Combination of dopants
 - Use redox active cations – replace Mn with Ru
 - Incorporate Ti – more covalency imparted to the structure
- Lower initial Li_2MnO_3 component in ‘layered-layered’ composite needed
 - Evaluate other structural components like spinel in composite (i.e. LLS)
- Finish off the synthesis plans in the project wrap-up
 - Provide suggestions to the voltage fade (high-voltage/high energy team) going forward into next year’s project
 - Can we stop condensation of structure – vacancy distribution; make material more ‘flexible’



Acknowledgments and Collaborations

Argonne Voltage Fade Team: Anthony Burrell (PI), Andrew Jansen, Ali Abouimrane, Daniel Abraham, Khalil Amine, Bachir Aoun, Mahalingam Balasubramanian, Javier Bareno Garcia-Ontiveros, Ilias Belharouak, Roy Benedek, Martin Bettge, Ira Bloom, Zonghai Chen, Jason Croy, Dennis Dees, Fulya Dogan, Kevin Gallagher, Gary Henriksen, Hakim Iddir, Brian Ingram, Christopher Johnson, Baris Key, Eungje Lee, Yan Li, Chi-Kai Lin, Brandon Long, Wenquan Lu, Dean Miller, Bryant Polzin, Yang Ren, Steven Rinaldo, Michael Slater, Michael Thackeray, Stephen Trask, John Vaughey, Anh Vu, Huiming Wu, Qingliu Wu, Zhenzhen Yang, Ye Zhu

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

Responses to Previous Year Reviewers' Comments

- Majority of comments were favorable and do not require a response
- Reviewer 4: Conduct investigation on temperature effect on VF
 - Response: this work is outside the scope of a synthetic study
- Reviewer 4: Add more analytical resources; both outside and inside Argonne
 - Response: this task is a synthetic effort
- Reviewer 3: Evaluate Cr, Mo; also evaluate Co effect on layering
 - Response: Cr was substituted into structure –alterations occurred on activation plateau, but ultimately no VF was stopped in these materials; Mo was not looked at; Co changes were looked at – VF not stopped, but rate of changed altered
- Reviewer 4: additional resources needed
 - Response: the VF team redirected ANL individuals to assist in focused synthesis efforts

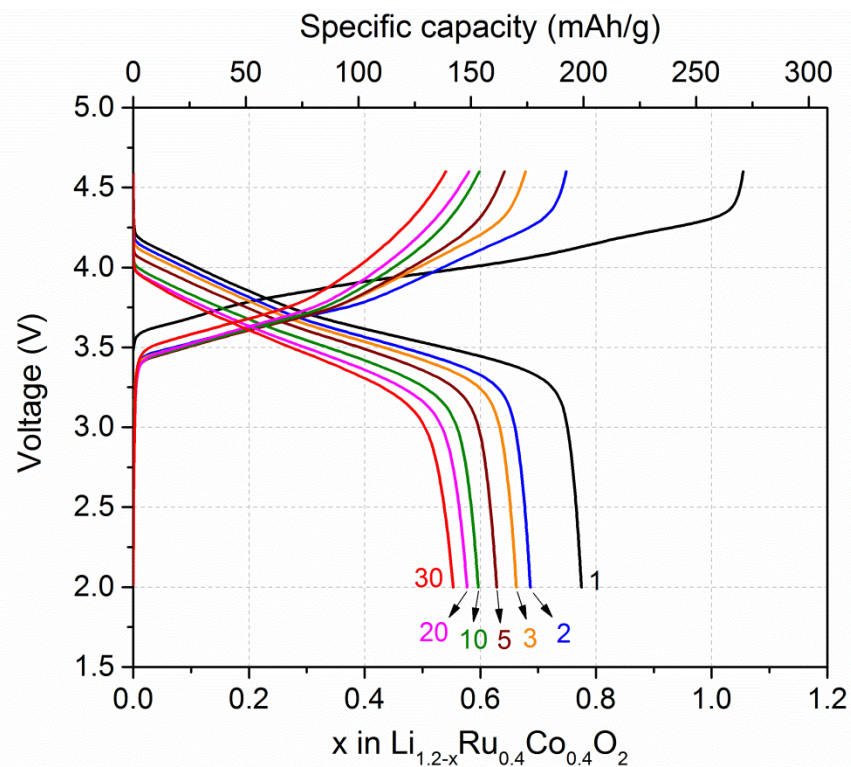
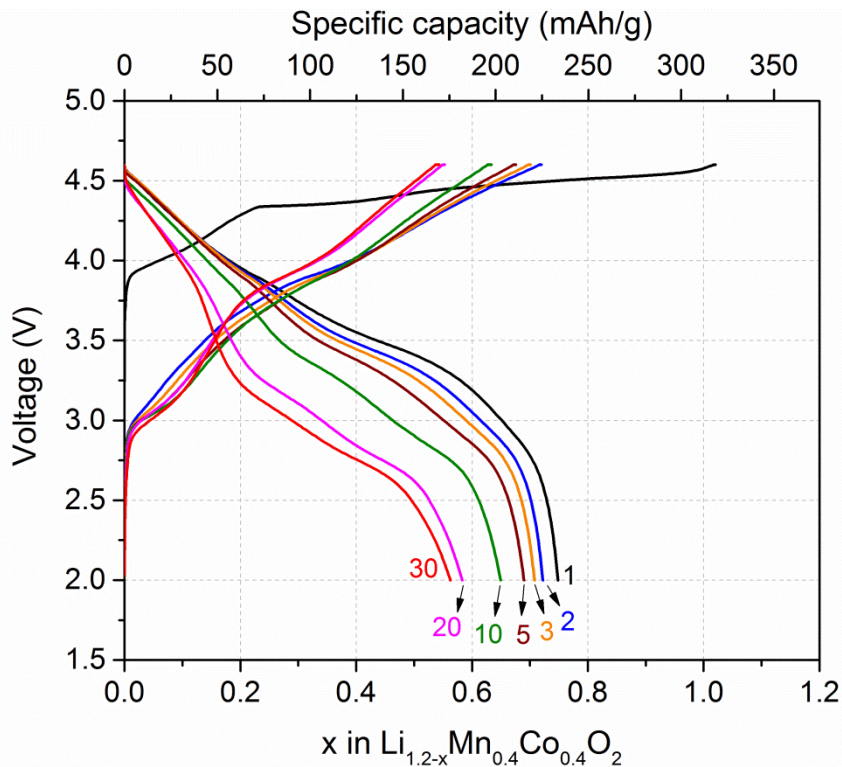
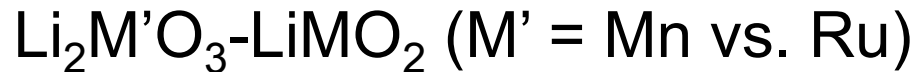
Publications and Presentations

- 225th ECS meeting, May 11-15, 2014, Orlando, FL
Title: Structure and electrochemistry of cation substituted “layered-layered composite” cathode materials for Li-ion batteries, Oral presentation
- The 17th International Meeting on Lithium Batteries, June 10-14, 2014, Como, Italy
Title: P2 layered Na transition metal oxides: A synthetic precursor to new O_2 $xLi_2MnO_3 \cdot (1-x)LiMO_2$ ion exchanged ‘layered-layered’ cathode materials.
Poster presentation
- “Li-Ion Composite Cathode Materials: Influence of Initial Nanophase Distribution on Structural Evolution During Cycling,” *poster presentation*, M. Slater, E. Lee, and C. Johnson, Gordon Research Conference: Batteries, San Buenaventura, CA, March 2014.
- “Comparison of Voltage Fade in Two Different Polymorphs of ${}^6Li_{1.2}Mn_{0.55}Co_{0.1}Ni_{0.15}O_2$,” *poster presentation*, M. D. Slater and C. S. Johnson, Advanced Lithium Batteries for Automobile Applications 6, Argonne, IL, September 2013.
- Eungje Lee et al., “Effect of Cation (Al or Ga) substitution on voltage fade in $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ cathode for Li-ion batteries,” (*submitted*)

Technical Back-Up Slides

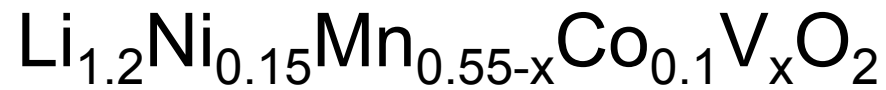


Ruthenium

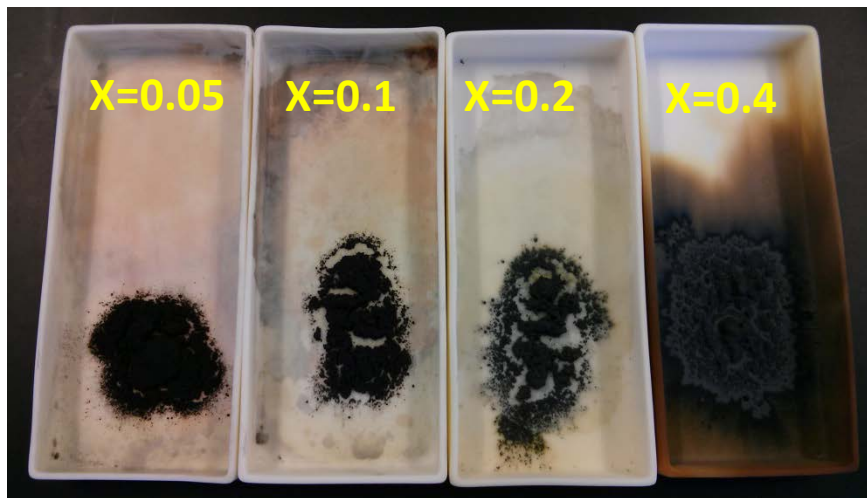


Li_2RuO_3 based sample (IR-free result) does not show typical voltage fade as in Li_2MnO_3 based materials, in spite of capacity fade.

Vanadium



(a)



(b)

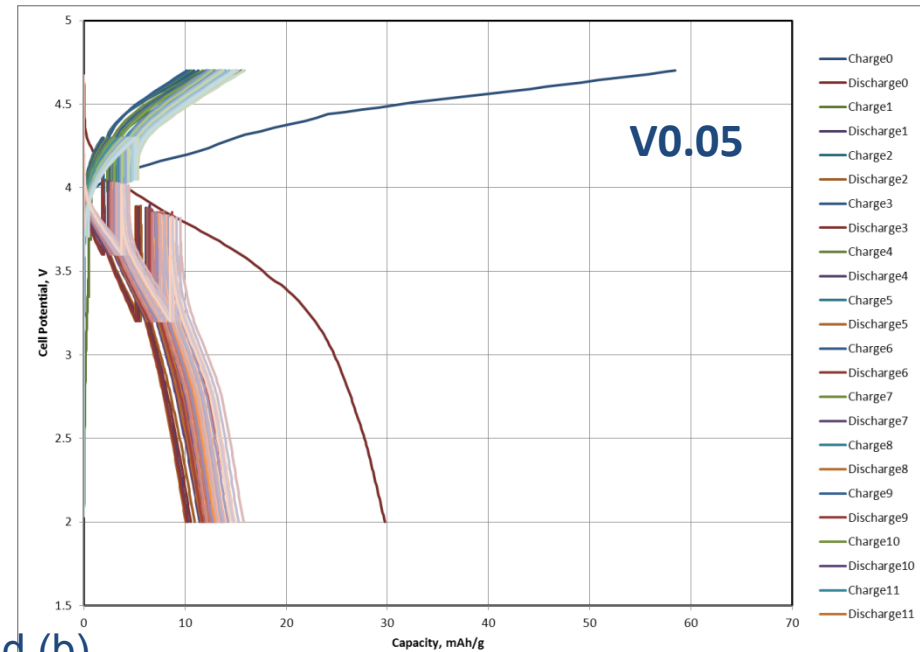


Fig. 2. V dopant: (a) photo of the products, and (b) coin cell voltage profiles