

Characterization of Voltage Fade in Lithium-ion Cells with Layered Oxides

Project ID: ES188

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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

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

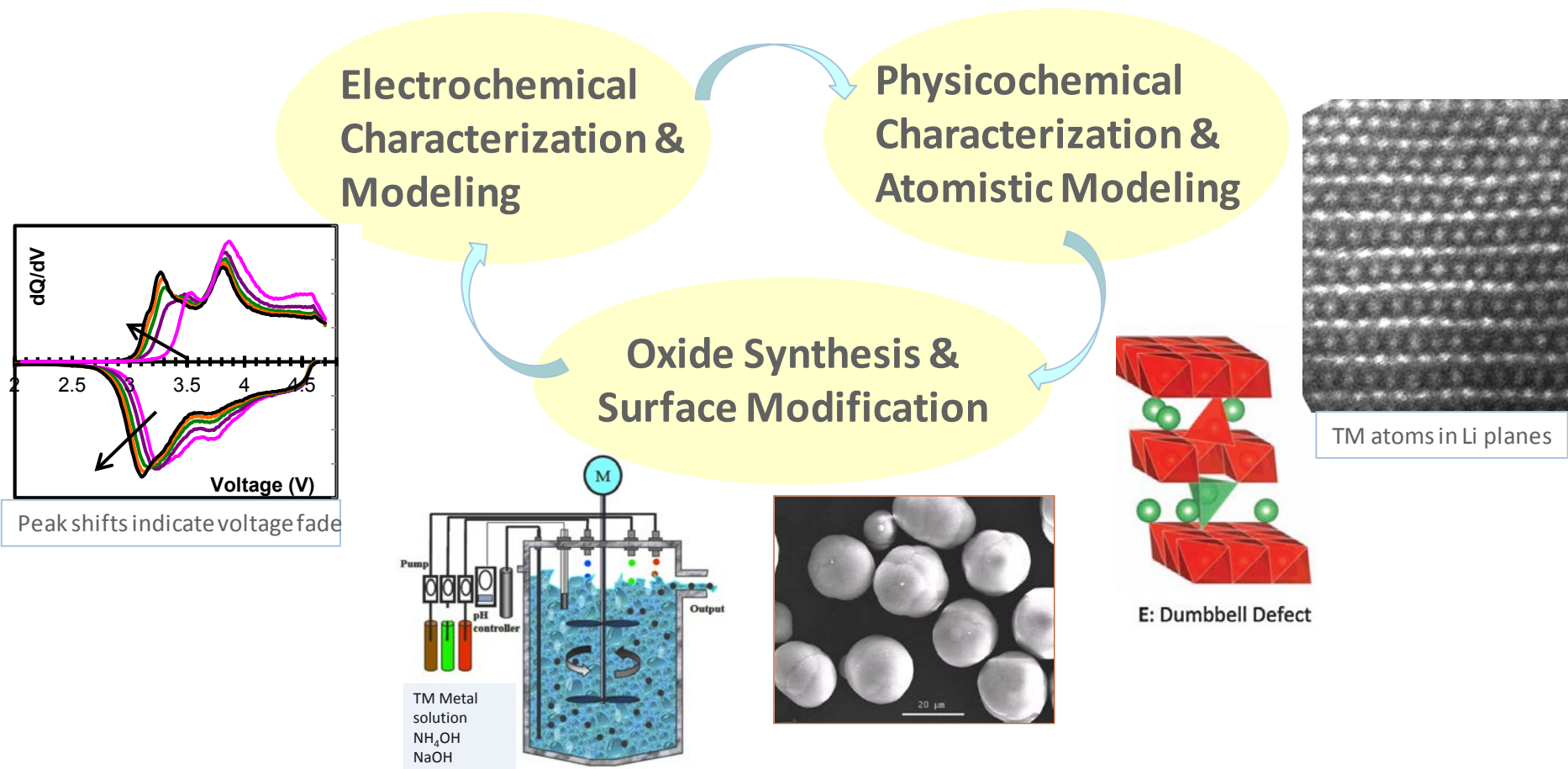
Voltage fade in lithium and manganese rich (LMR-NMC) oxides reduces energy density of lithium-ion cells during calendar-life and cycle-life aging

- 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 LMR-NMC based positive electrodes {LMR-NMC = $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ (M=Ni, Mn, Co)}
- To achieve the energy and power density targets these cells must be cycled to voltages that exceed 4.5 V vs. Li/Li⁺
- A continuous cycle-to-cycle decrease in positive electrode equilibrium voltage, termed voltage fade, reduces the cell's energy and power output under these cycling conditions
- Mitigating voltage fade in LMR-NMC oxides is, therefore, critical to increasing longevity, thereby reducing lifetime cost, of these high-energy batteries



Approach - Voltage Fade Team

- Multi-institution effort to identify factors that contribute to voltage fade in lithium and manganese rich NMC oxides (LMR-NMC)



Suggest/implement approaches to mitigate voltage fade

Approach - Project

Electrochemical characterization is essential to evaluate and benchmark voltage fade characteristics of potential positive electrode materials

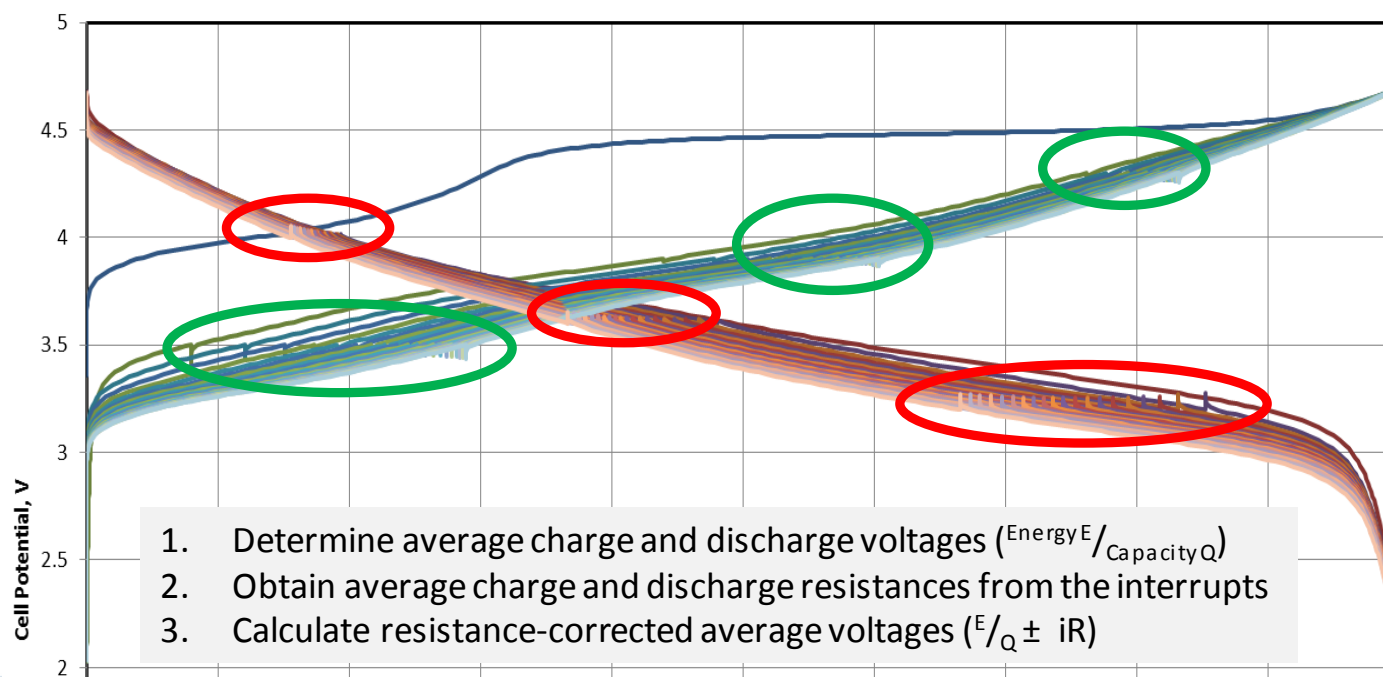
- Develop electrochemical protocols to track, quantify and characterize voltage fade in a reproducible and time-efficient manner
 - Disseminate protocols to partnering institutions and individuals to allow comparison of data generated at multiple laboratories
- Provide continuous feedback to team members for the development of electrochemical and atomistic models to explain voltage fade
 - Data from AC Impedance spectroscopy and galvanostatic intermittent titration experiments are used to develop models that explain diffusion and migration of lithium and transition metal atoms during oxide cycling
- Supply regular guidance to team members developing oxide materials to mitigate or minimize voltage fade during extended cycling
 - Electrochemical and material characterization data from cycling experiments form the basis for the selection of oxide synthesis techniques and oxide composition profiles that show reduced voltage fade



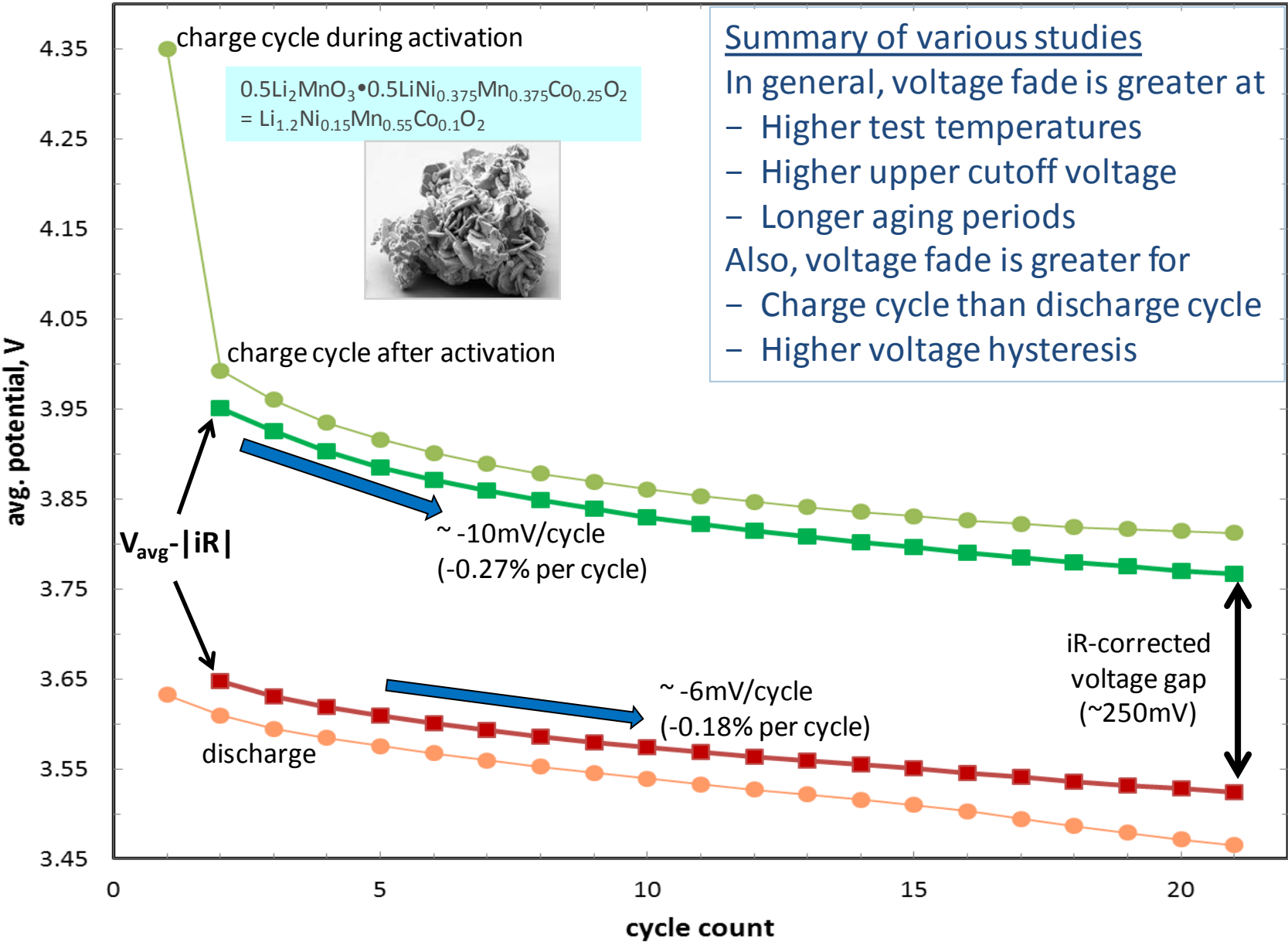
Established test protocol to measure and track voltage fade: use of an iR-corrected average voltage

Presented previously
in FY2013

- 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.



Typical voltage fade results for $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiNi}_{0.375}\text{Mn}_{0.375}\text{Co}_{0.25}\text{O}_2$



Summary of various studies

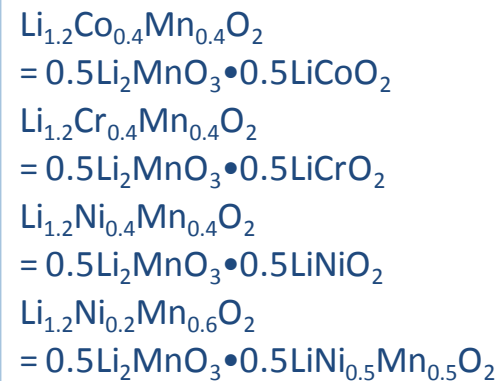
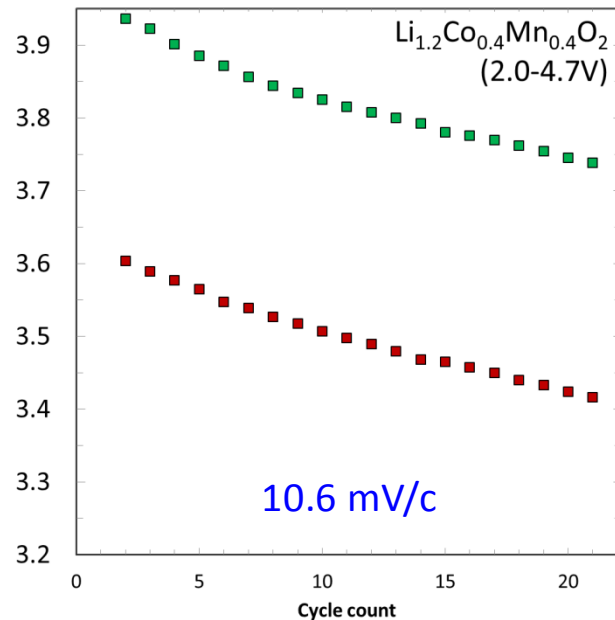
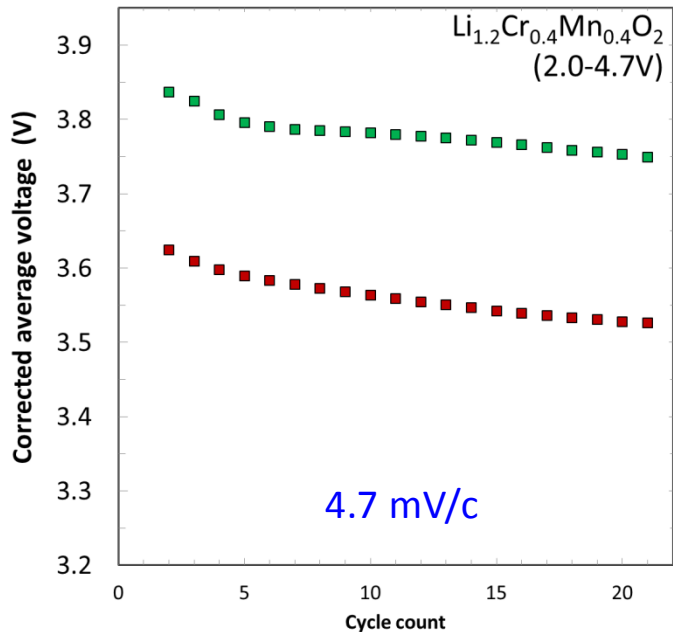
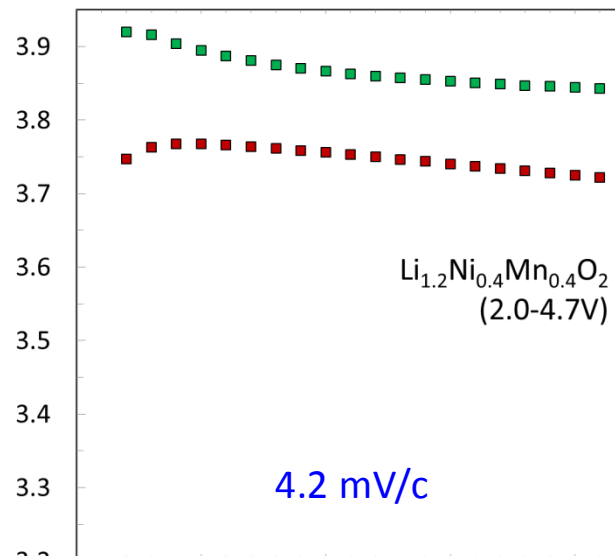
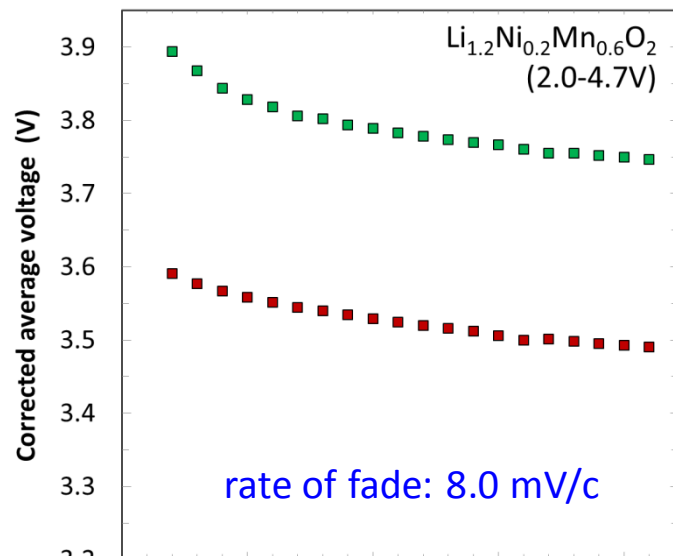
In general, voltage fade is greater at

- Higher test temperatures
- Higher upper cutoff voltage
- Longer aging periods

Also, voltage fade is greater for

- Charge cycle than discharge cycle
- Higher voltage hysteresis

Voltage fade in various Li- and Mn- rich oxides



Bettge et al. JES 160 (2013) A2046

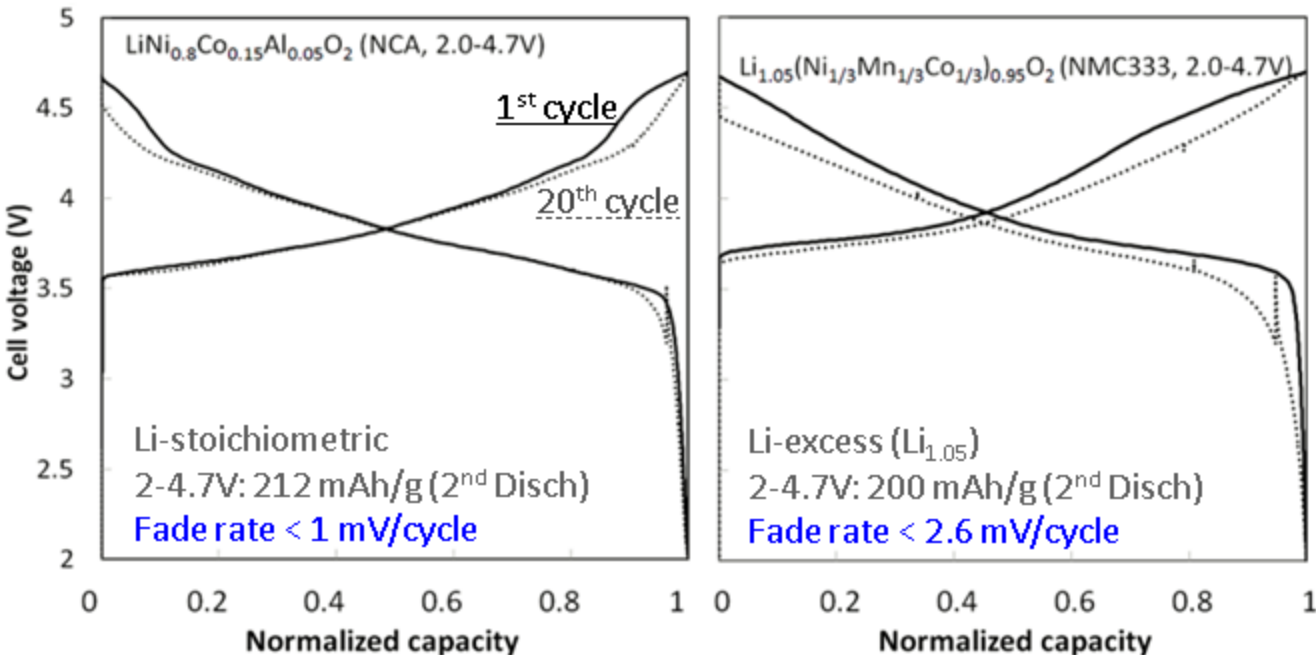
All Li- and Mn- rich oxides
studied display voltage
fade and hysteresis

Rate of fade depends on
oxide composition

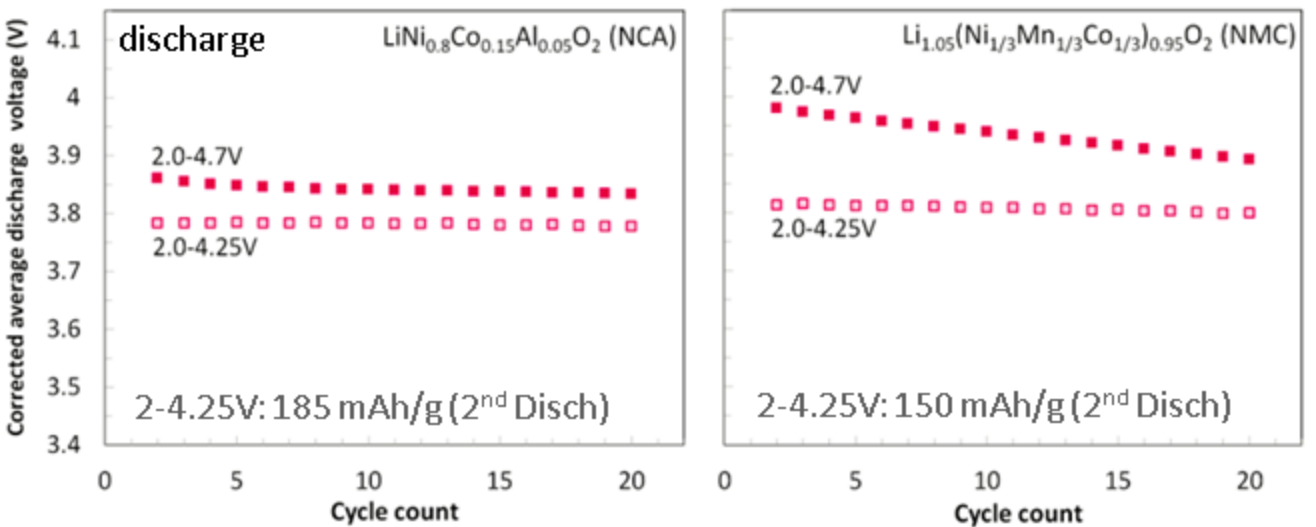
NCA & NCM333 oxide also display voltage fade (2-4.7V)

Fade rate is lower than for Li- and Mn- rich oxides

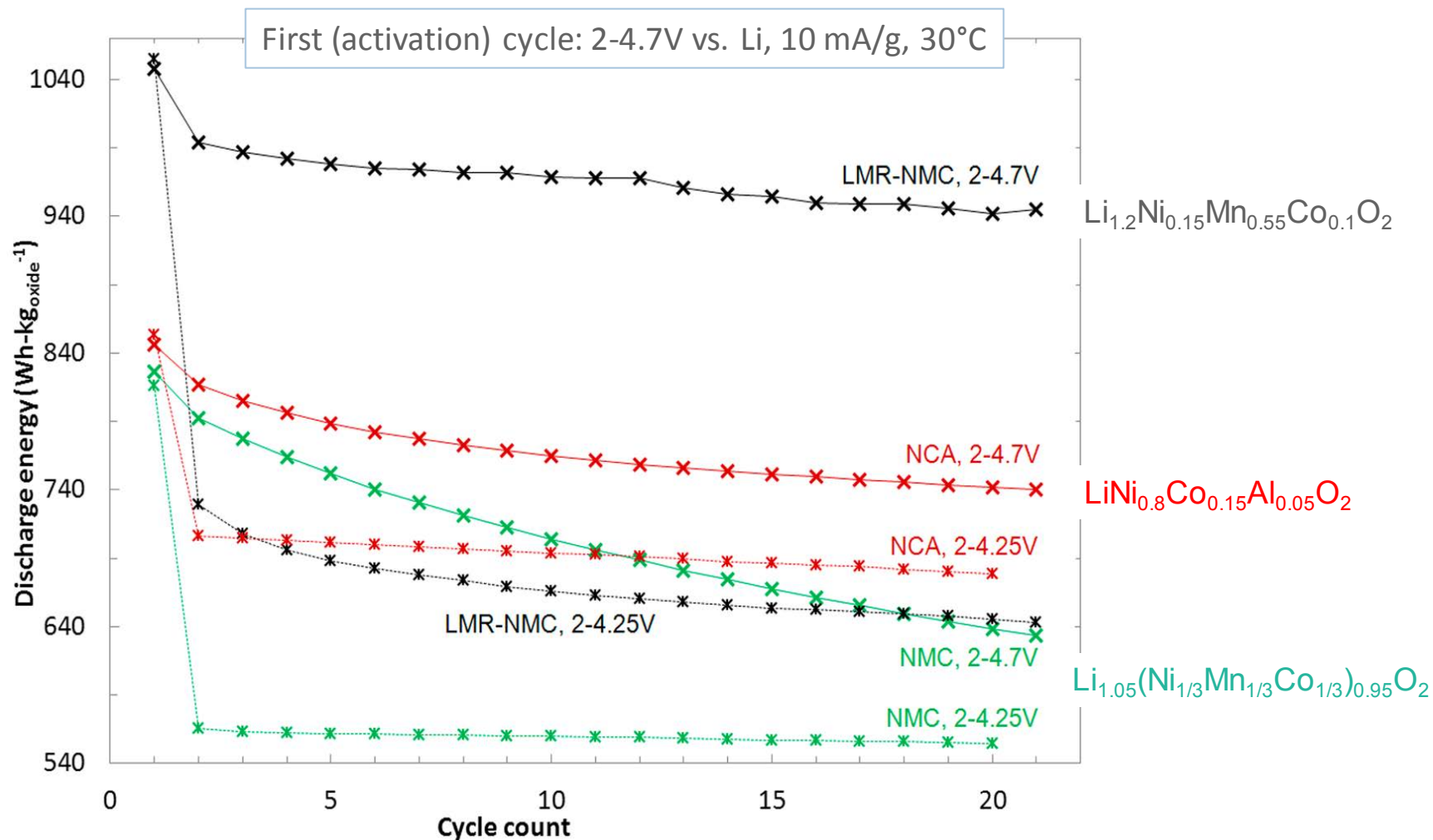
Bettge et al. JES 160 (2013) A2046



No measurable fade during 2-4.25V cycles

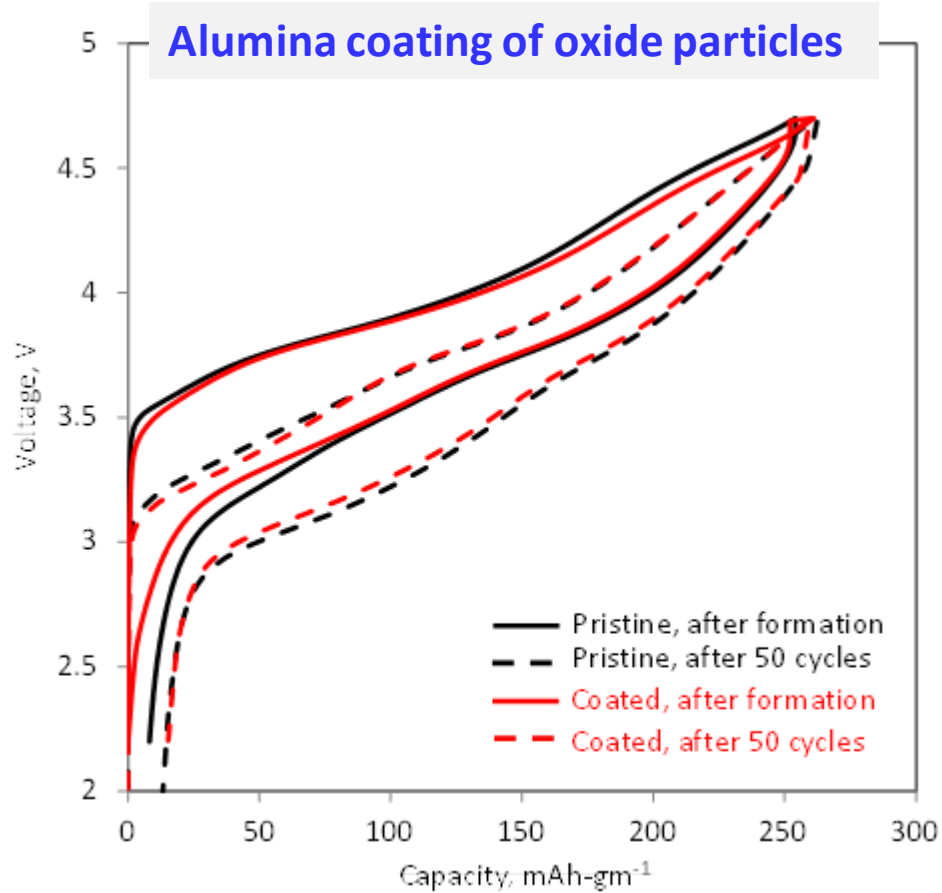


In 2-4.7 V cycling window $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ shows highest energy density



In 2-4.25 V range $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ shows higher energy density

No mitigation of voltage fade by select electrolyte additives or select oxide/electrode coatings (*tests vs. Li counter electrode*)



Pol et al, JPS258 (2014) 46

Relative change in average voltage in baseline cells and in cells containing an electrolyte additive or a coated cathode.

Coating/additive	100 × rel. change in average voltage after 20 cycles (100 × s.e.)	100 × rel. change in average voltage after 50 cycles (100 × s.e.)
Discharge		
Baseline	3.14 (0.10)	4.81
3-Hexylthiophene	2.88	4.52
LiDFOB	3.38	
Al ₂ O ₃ (5 ALD cycles)	3.40	5.30
Al ₂ O ₃ (100 ALD cycles)	3.22	5.47
AlPO ₄	3.68	5.48
LiAlO _x	3.32 (0.07)	
TiO ₂ (100 °C)	3.14 (0.04)	
TiO ₂ (150 °C)	3.20 (0.07)	
ZrO ₂ (100 °C)	3.17 (0.01)	
ZrO ₂ (150 °C)	3.26 (0.03)	
LiPON (1 h)	2.69	
LiPON (2 h)	2.60	
LiPON (3 h)	5.20	
Charge		
Baseline	3.97 (0.49)	4.52
3-Hexylthiophene	3.16	4.20
LiDFOB	4.89	
Al ₂ O ₃ (5 ALD cycles)	3.52	5.15
Al ₂ O ₃ (100 ALD cycles)	3.14	4.70
AlPO ₄	3.66	5.03
LiAlO _x	5.21 (0.05)	
TiO ₂ (100 °C)	4.39 (0.01)	
TiO ₂ (150 °C)	4.60 (0.01)	
ZrO ₂ (100 °C)	4.62 (0.02)	
ZrO ₂ (150 °C)	4.85 (0.03)	
LiPON (1 h)	3.67	
LiPON (2 h)	3.75	
LiPON (3 h)	7.97	

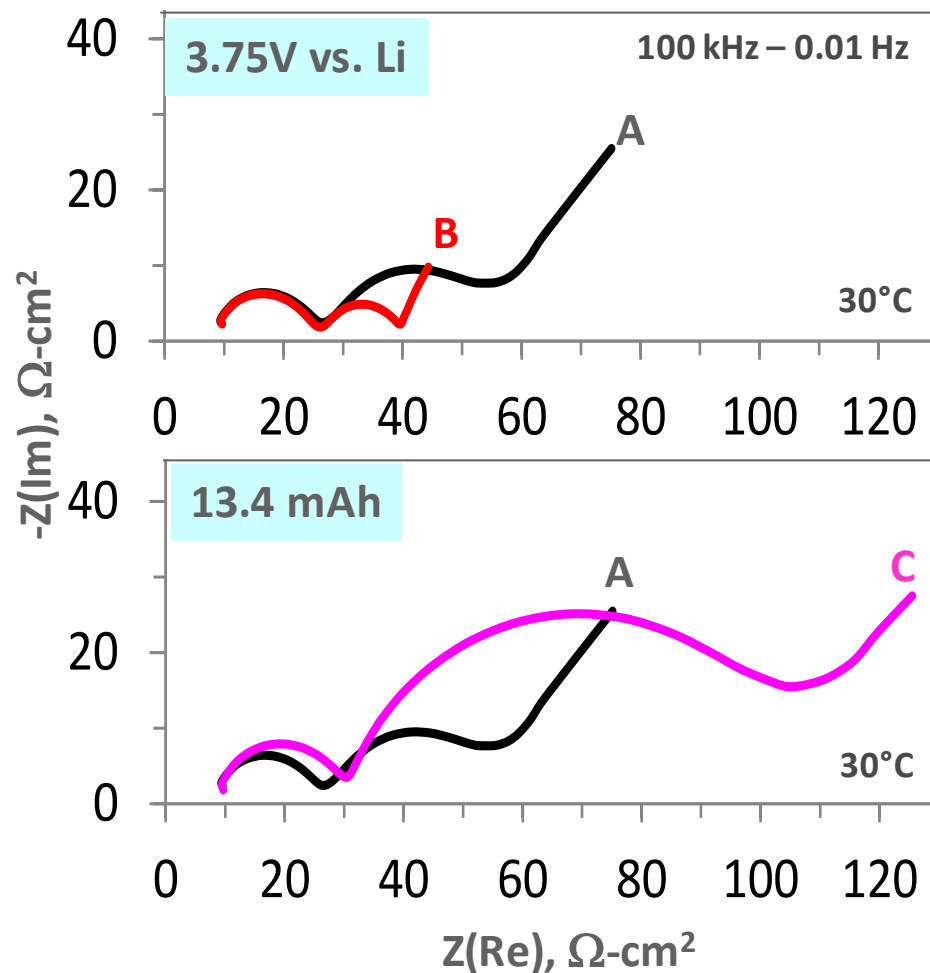
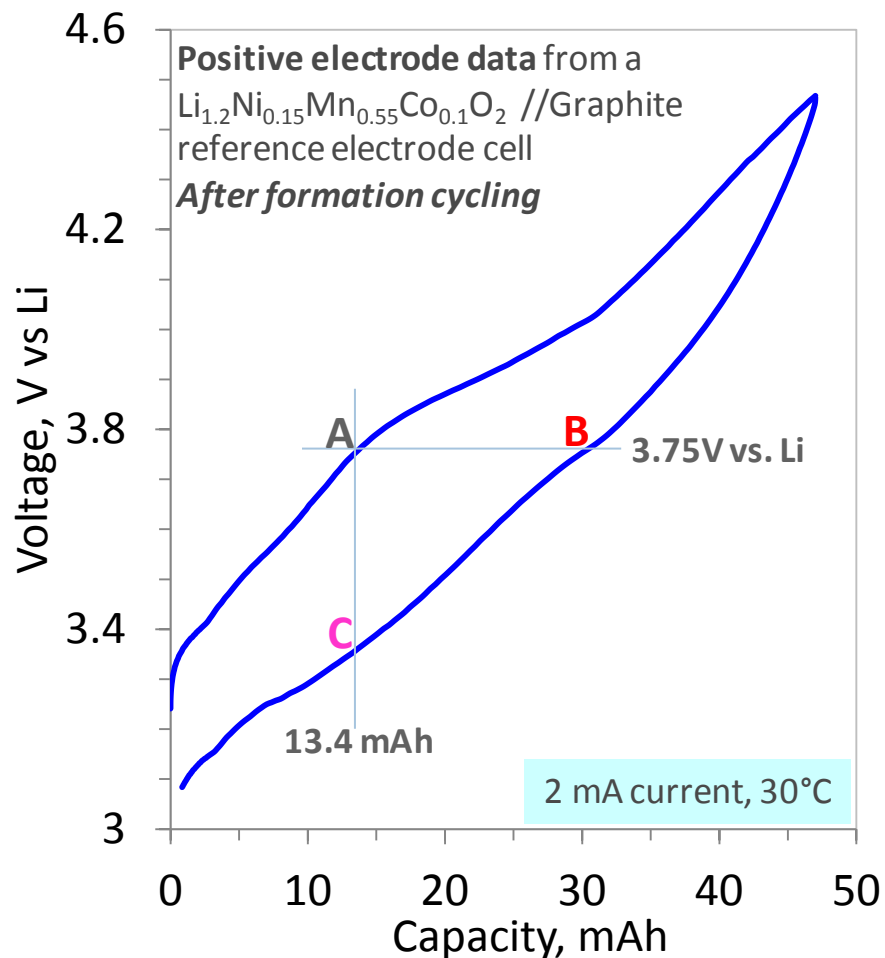
Bloom et al., JPS 249 (2013) 509



Impedance data affected by oxide voltage hysteresis

(in agreement with XAS, NMR and Neutron data)

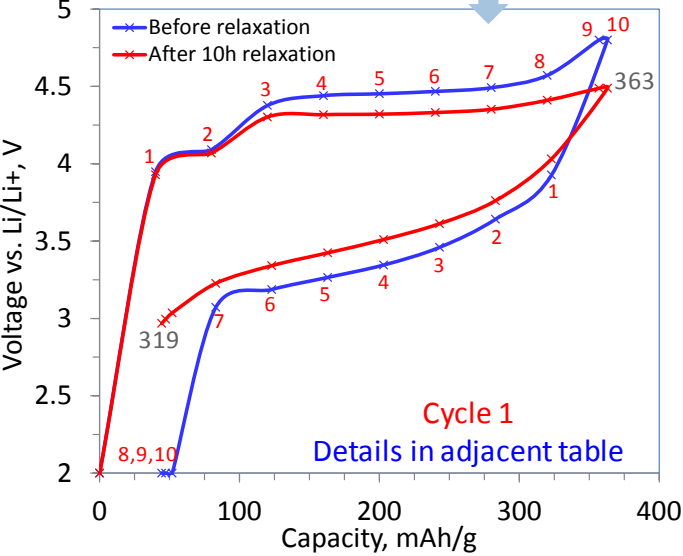
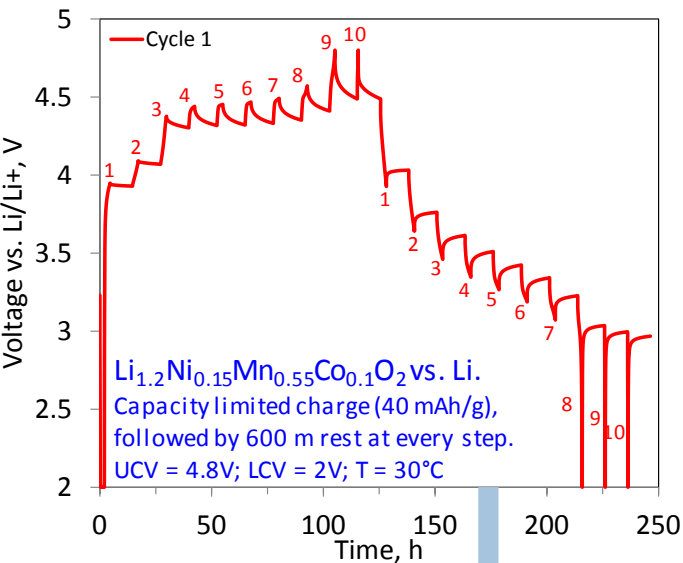
Y. Li, unpublished data



Impedance data differences indicate that Li atoms occupy different oxide sites during charge and discharge for same voltage and/or capacity

Slow voltage relaxation during current interrupts

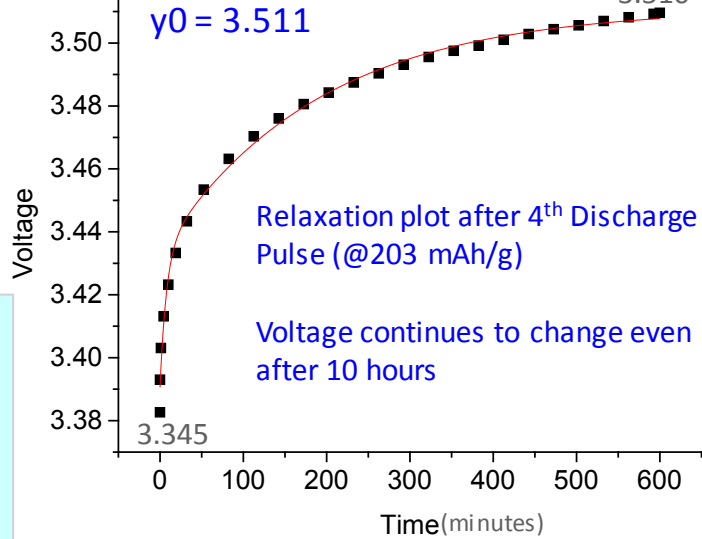
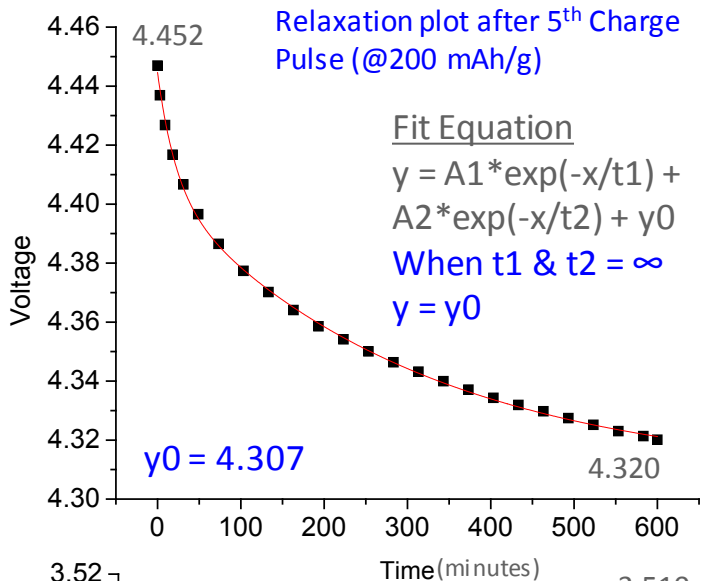
Induces differences between data obtained by *ex situ* and *in situ* techniques



Cycle 1 – activation cycle

Pulse No.	Capacity mAh/g	Before V vs. Li	After V vs. Li
C_0	0	2	2
C_1	40	3.948	3.928
C_2	80	4.091	4.069
C_3	120	4.376	4.302
C_4	160	4.440	4.317
C_5	200	4.452	4.320
C_6	240	4.467	4.331
C_7	280	4.491	4.351
C_8	320	4.571	4.410
C_9	357	4.800	4.488
C_10	363	4.800	4.488
D_1	323	3.927	4.031
D_2	283	3.642	3.761
D_3	243	3.460	3.612
D_4	203	3.345	3.510
D_5	163	3.265	3.424
D_6	123	3.187	3.341
D_7	83	3.071	3.226
D_8	52	2	3.035
D_9	47	2	2.995
D_10	44	2	2.968

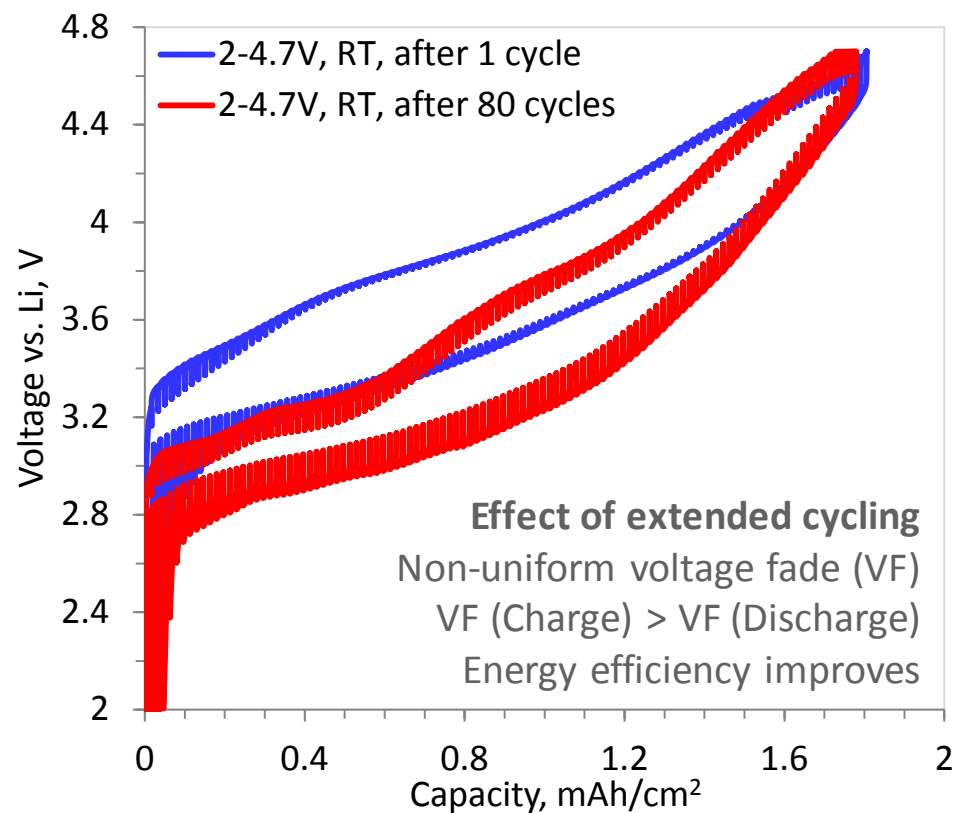
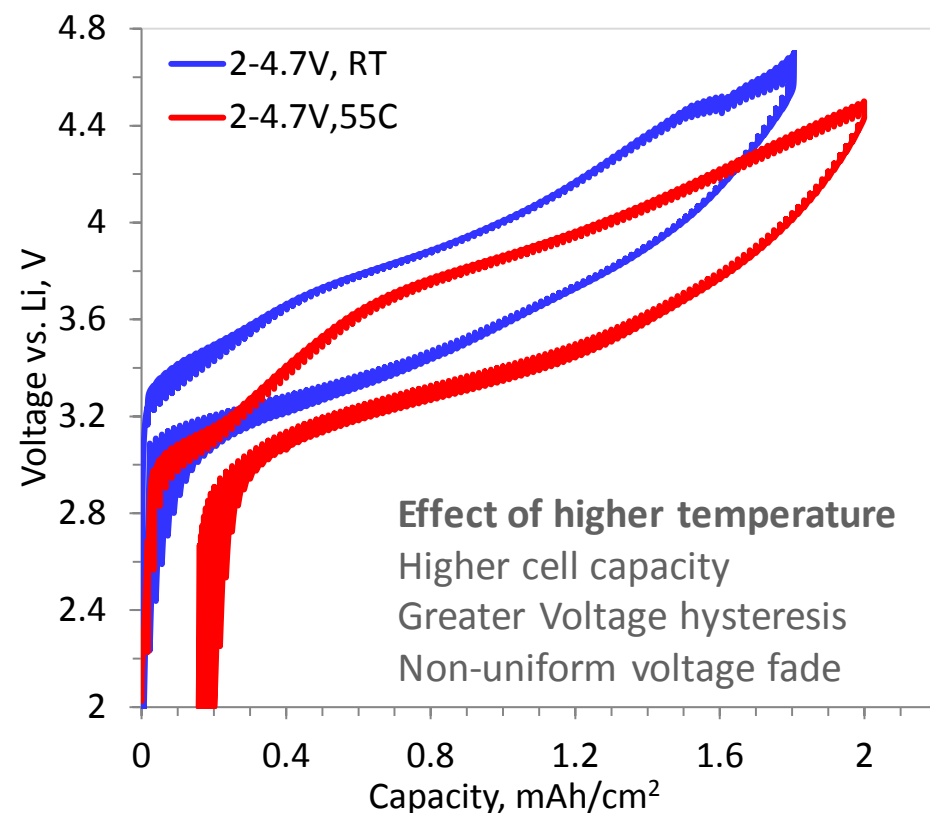
Slow relaxation consistent with TM atom (e.g., Mn, Co, Ni) migration into Li planes



Voltage Hysteresis observed in $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$

vs. Li. One activation cycle (2-4.7V) followed by GITT cycling (0.1 mA/cm² current for 600s, followed by 6000s rest. Total time @ RT ~ 22 days/cycle ~ C/250 rate)

Y. Li, unpublished data



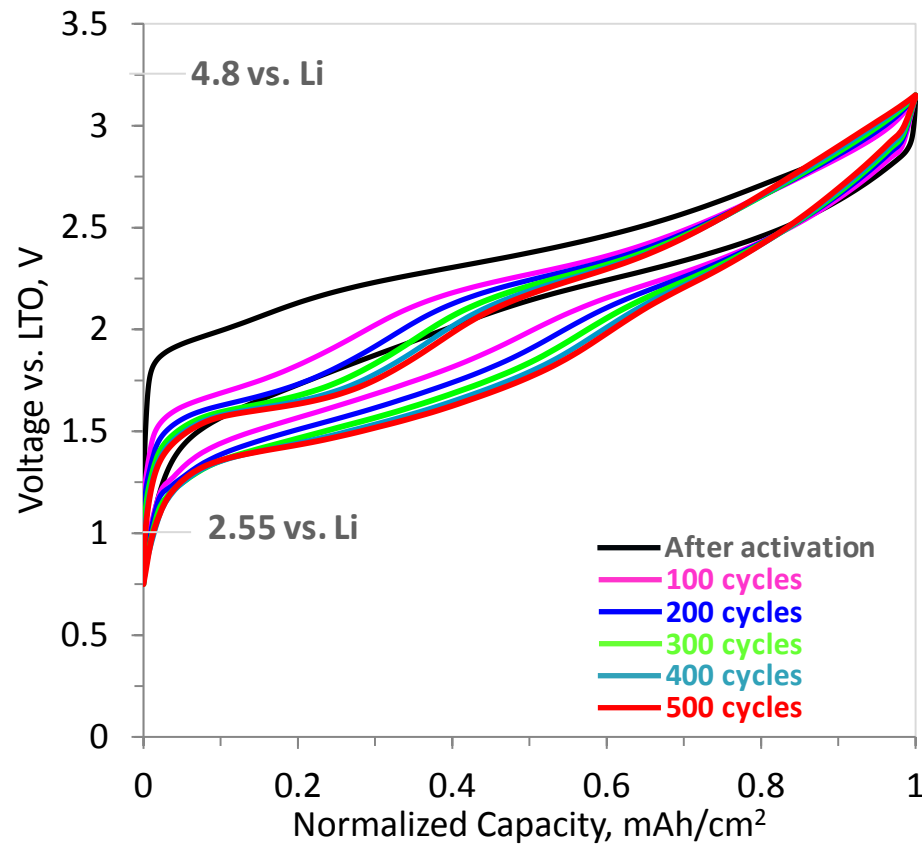
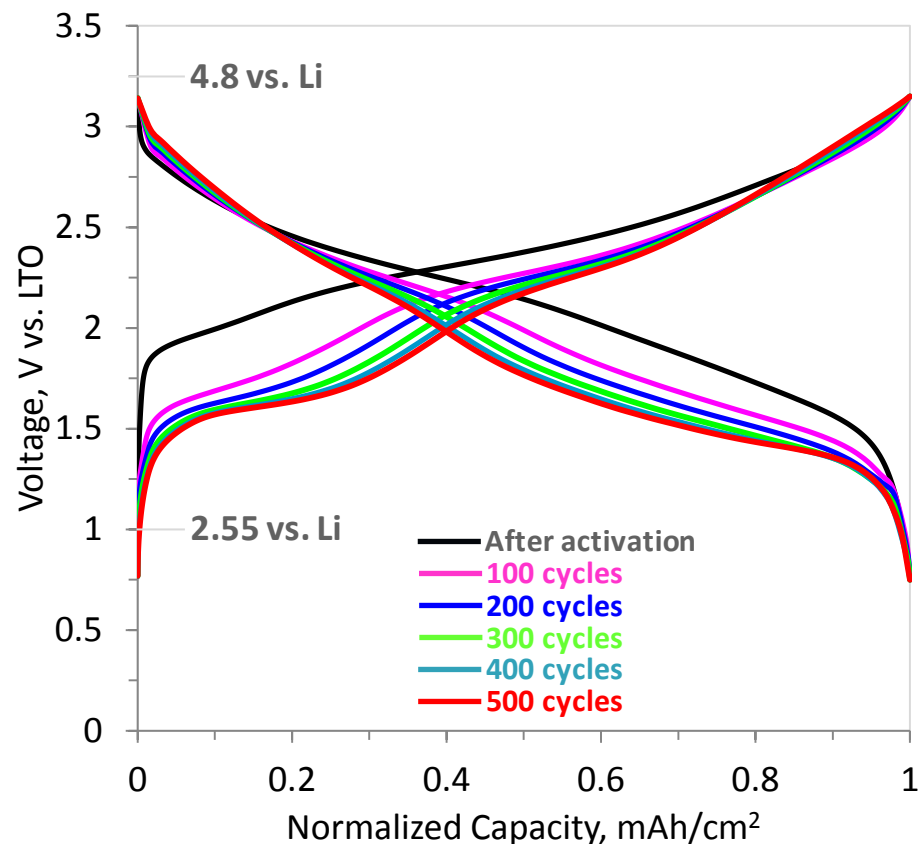
Voltage Hysteresis observed under all cycling conditions
Hysteresis decreases on cycling but does not disappear

Does oxide voltage stabilize after extended cycling?

Tests in $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2 // \text{Li}_4\text{Ti}_5\text{O}_{12}$ cells; Li unsuitable for long-term cycling

500 cycles, 30 °C, 0.75 - 3.15 V vs. LTO (2.3 - 4.7 V vs. Li/Li^+)

Also see ES187 (Key)



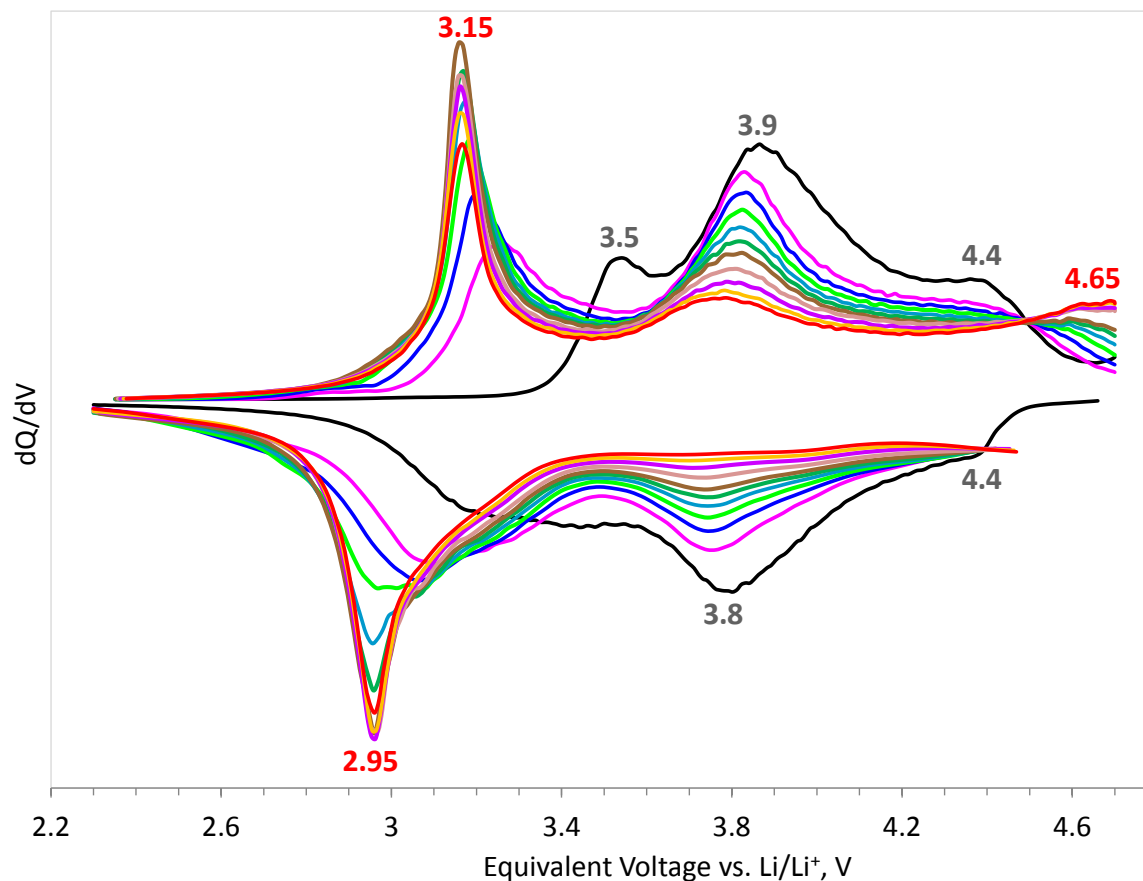
Negligible capacity loss even after 500 cycles – justifies capacity normalization

Voltage hysteresis decreases but persists even after 500 cycles

Voltage fade rate decreases and voltage profile stabilizes around 400 cycles

dQ/dV plot - voltage fade peaks stabilize around 400 cycles

$\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2 // \text{Li}_4\text{Ti}_5\text{O}_{12}$ cells; 1000 cycles, 30 °C, 0.75 - 3.15 V vs. LTO (2.3 - 4.7 V vs. Li/Li^+)



Changes on cycling

Continuous shift of 3.5V charge peak to 3.15 V

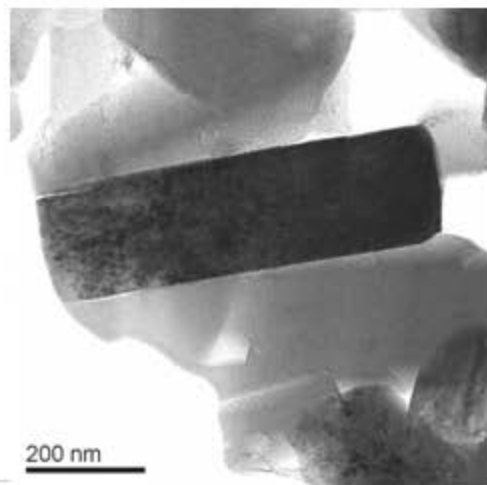
(corresponding peak on discharge shifts to 2.95 V)

Continuous decrease in 3.9 V charge (3.8 V discharge) peak

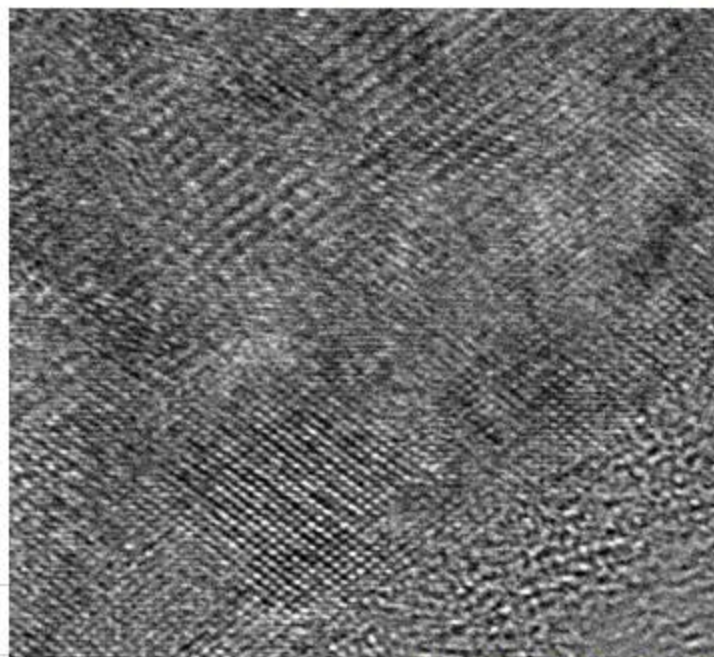
Gradual growth of 4.65 V charge peak

Also see ES187 (Key), ES194 (Croy)

High-resolution electron microscopy of aged oxide samples (after 1000 cycles) show coexistence of multiple crystal structures including areas with layered, spinel, and Li_2MnO_3 characteristics



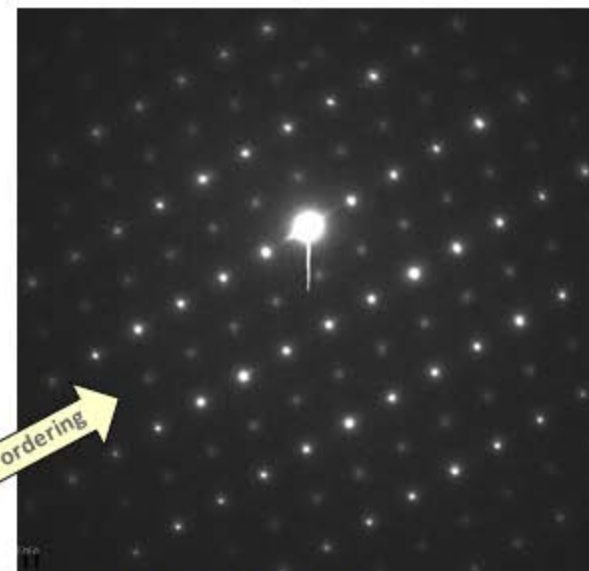
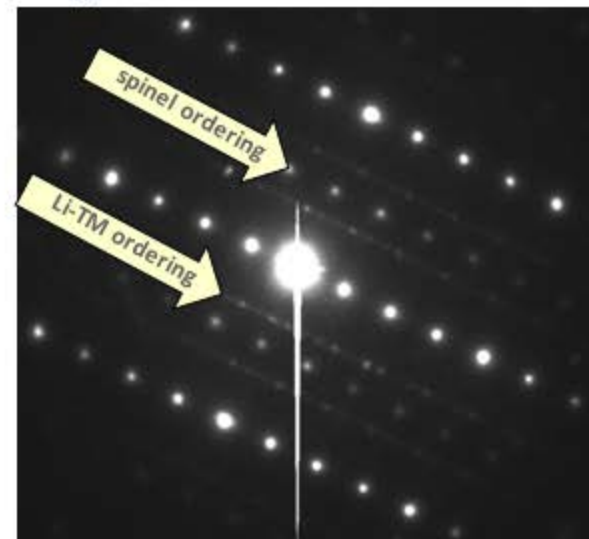
Several particles studied



High-resolution image



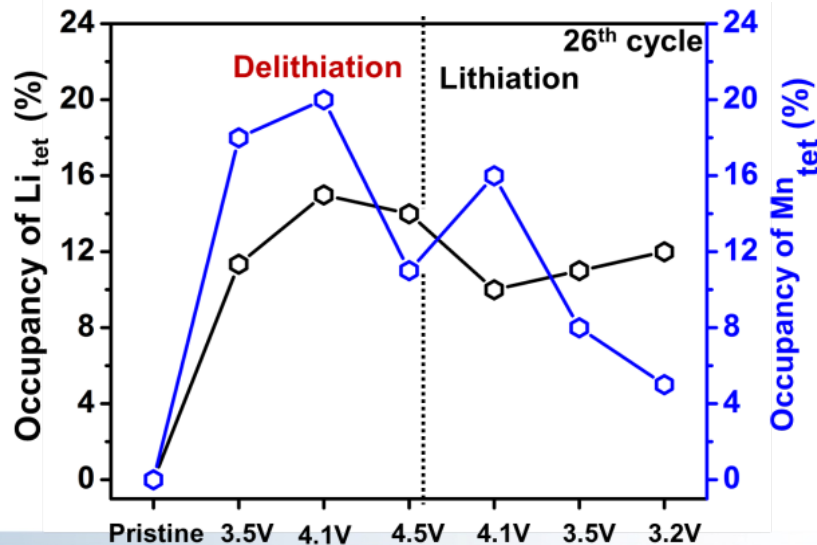
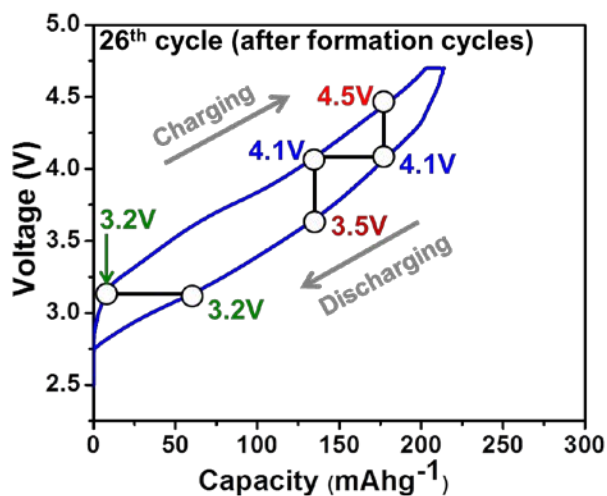
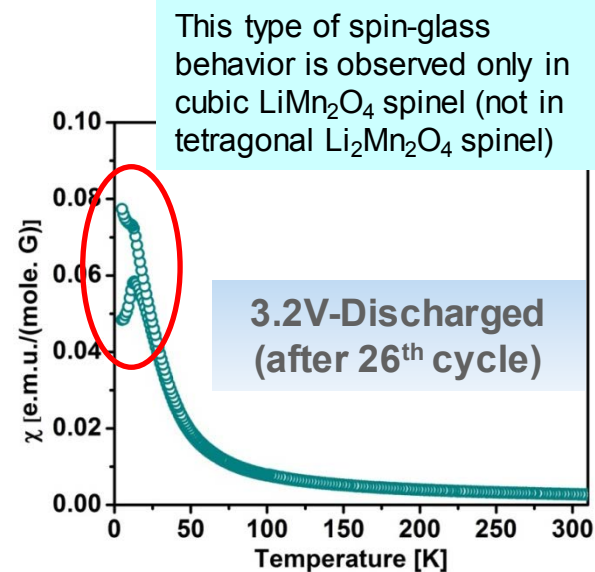
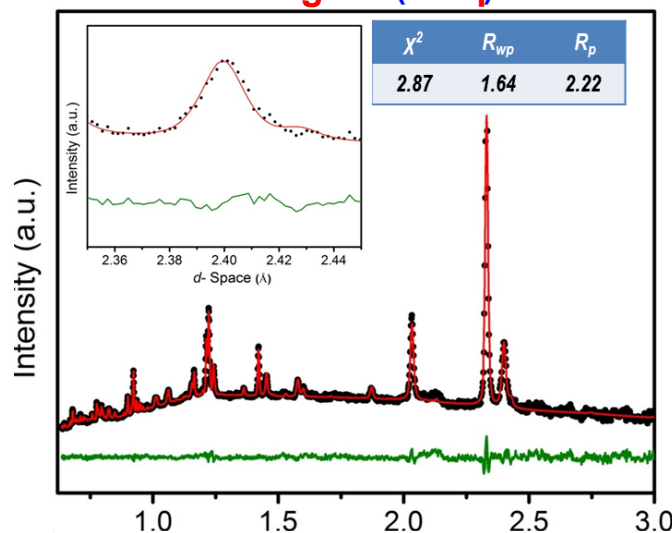
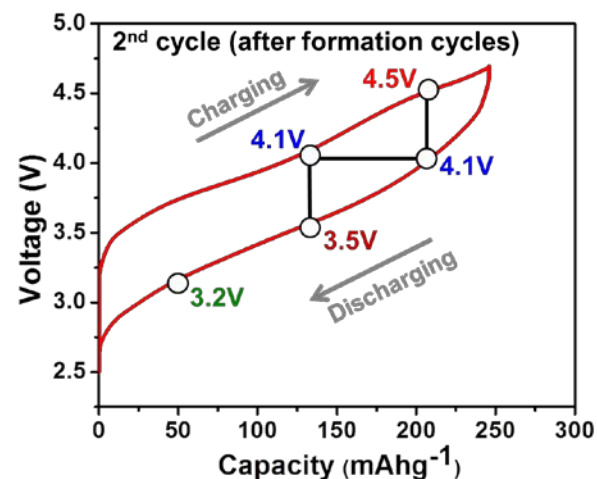
- Particle-to-particle variations in structure
 - generally similar, but crystal structure fractions vary
- Electron diffraction patterns comprise
 - strong layered fundamental reflections
 - super reflections due to spinel ordering
 - super reflections from Li-TM ordering (Li_2MnO_3 -like)



Miller, unpublished data

Neutron diffraction and magnetic property data on $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ consistent with spinel ordering

**Lithium in tetrahedral (0 0 x) site
Shows better agreement parameter**



Mn in tetrahedral sites of Li layer

See ES193 (Idir)

Data from Oak Ridge National Laboratory
Also see Publications & Presentations

Responses to Previous Year Reviewers' Comments

Relevance

Comments – “aligned with DOE objectives to reduce dependence on petroleum”, “project involves understanding voltage fade in LMR-NMC, a material of appreciable interest to reach EV goals”,

Response – positive comments, project direction maintained.

Approach

Comments – “quantifying and benchmarking electrochemical performance of LMR-NMC”, “focusses on definition of baseline and its characterization”

Response – This is not a stand-alone project but part of a team approach/effort to identify materials that have the potential to minimize or eliminate voltage fade

Technical Accomplishments

Comments – “project demonstrated that VF is unaffected by changes in electrode constitution and electrolyte additives”, “VF shown to not depend on electrode kinetics”, “unsure if resistance-corrected voltage approach is accurate because of voltage relaxation during current interruption”

Response – positive comments. Resistance-corrected voltage is *one* approach to examine voltage fade. The experimental conditions (current interrupt locations, relaxation times, voltage windows, etc.) need to be adjusted based on material tested to obtain reliable and consistent data.

Future Research

Comments – “test new LMR-NMC compositions, with dopants, from ANL and elsewhere”, “recommend that the team adopt impedance spectroscopy to gain more information”

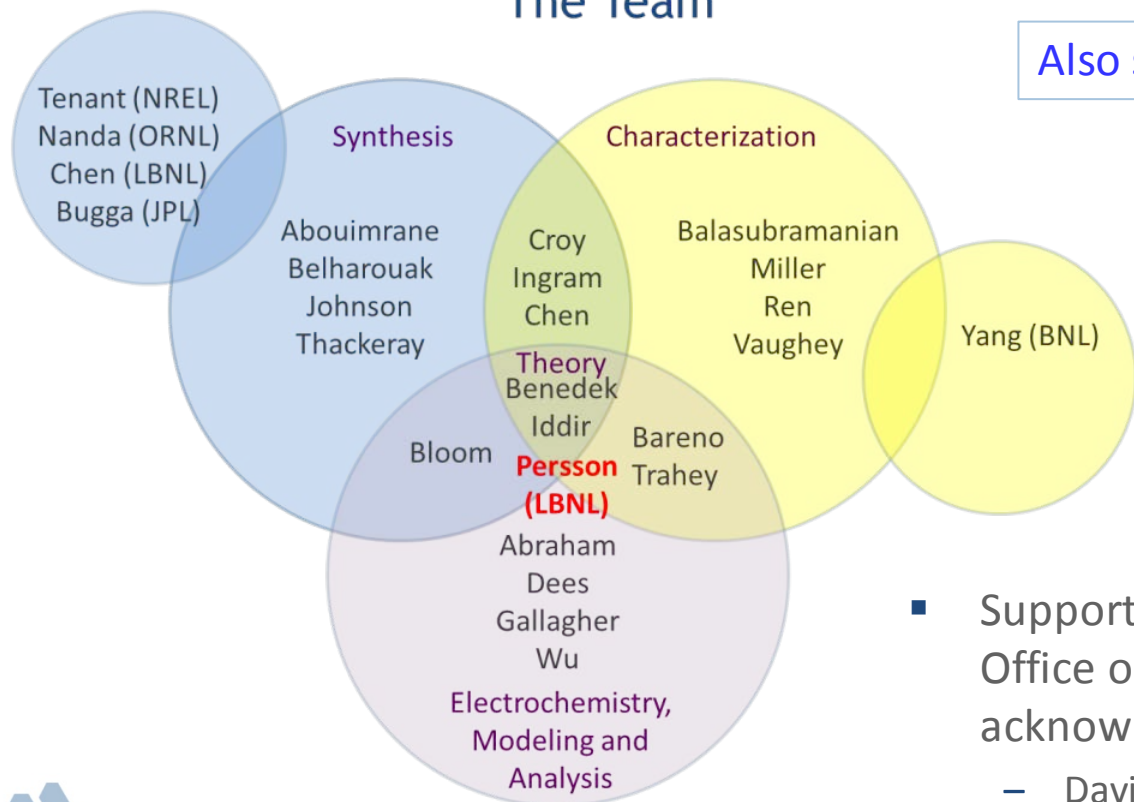
Response – Examined $\text{Li}_{1.2}\text{Ni}_{0.4}\text{Mn}_{0.4}\text{O}_2$, $\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$, $\text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$, $\text{Li}_{1.2}\text{Fe}_{0.4}\text{Mn}_{0.4}\text{O}_2$ and $\text{Li}_{1.04}(\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33})_{0.96}\text{O}_2$, and other oxides. Impedance spectroscopy and GITT protocols applied to better understand voltage fade behavior.



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.

The Team



Also see Publications and Presentations

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

Publications and Presentations

1. M. Bettge, Y. Li, K. Gallagher, Y. Zhu, Q. Wu, W. Lu, I. Bloom, D.P. Abraham, J. Electrochemical Society 160 (2013) A2046-2055.
Title: Voltage Fade of Layered Oxides: Its Measurement and Impact on Energy Density
Link: <http://jes.ecsdl.org/content/160/11/A2046.full>
2. D. Mohanty, A.S. Sefat, J. Li, R.A. Meisner, A.J. Rondinone, E.A. Payzant, D.P. Abraham, D.L. Wood, III, C. Daniel, Physical Chemistry Chemical Physics 15 (2013) 19496–19509. *(With Oak Ridge National Laboratory)*
Title: Correlating Cation Ordering and Voltage Fade in a Lithium- Manganese-Rich Lithium-Ion Battery Cathode Oxide: a Joint Magnetic Susceptibility and TEM Study.
Link: <http://pubs.rsc.org/en/content/articlehtml/2013/cp/c3cp53658k>
3. I. Bloom, L. Trahey, A. Abouimrane, I. Belharouak, H. Wu, Q. Wu, W. Lu, D.P. Abraham, M. Bettge, J. Elam, X. Meng, A. Burrell, J. Power Sources 249 (2013) 509-514.
Title: Effect of Interface Modifications on Voltage Fade in $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiNi}_{0.375}\text{Mn}_{0.375}\text{Co}_{0.25}\text{O}_{0.2}$ Cathode Materials
Link: <http://www.sciencedirect.com/science/article/pii/S0378775313016881>
4. D. Mohanty, A. Huq, E.A. Payzant, A.S. Sefat, J. Li, D.P. Abraham, D.L. Wood, III, C. Daniel, Chem. Mater. 25 (2013), pp 4064–4070. *(With Oak Ridge National Laboratory)*
Title: Neutron Diffraction and Magnetic Susceptibility Studies on a High-Voltage $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ lithium-ion Battery Cathode; an Insight to the Crystal Structure
Link: <http://pubs.acs.org/doi/full/10.1021/cm402278q>
5. K.G. Gallagher, J.R. Croy, M. Balasubramanian, M. Bettge, D.P. Abraham, A.K. Burrell, M.M. Thackeray, Electrochemistry Communications 33 (2013) 96–98.
Title: Correlating hysteresis and voltage fade in lithium- and manganese-rich layered transition-metal oxide electrodes
Link: <http://www.sciencedirect.com/science/article/pii/S138824811300163X>
6. D. Mohanty, A.S. Safat, S. Kalnaus, J. Li, R.A. Meisner, E.A. Payzant, D.P. Abraham, D.L. Wood, C. Daniel, J. Mater. Chem. A 1 (2013) 6249. *(With Oak Ridge National Laboratory)*
Title: Investigating Phase Transformations in $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ lithium-ion battery cathodes during high-voltage hold (4.5V) via magnetic, X-ray diffraction and electron microscopy studies.
Link: <http://pubs.rsc.org/en/content/articlehtml/2013/ta/c3ta10304h>



Future Work - FY 2014

- Initial electrochemistry experiments have indicated that gradual voltage fade during cycling is also observed in layered oxides that are not “activated”, i.e., in oxides cycled below the oxygen evolution plateau
 - Diffraction, spectroscopy, microscopy and atomistic modeling data from $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ and $\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$ samples are being obtained and analyzed to determine reasons for this behavior
- Various electrochemistry experiments suggest that the high (>320 mAh/g) discharge capacities reported for LMR-NMC oxides are a consequence of testing in Li-metal counter electrode cells
 - LMR-NMC charge compensation mechanisms will be re-examined because tests in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ counter electrode cells show discharge capacities less than 275 mAh/g
- “Wrap up” studies exclusively associated with voltage fade
 - Document data in reports and share information with the battery community to enable development of advanced high-energy and high-power PEV and EV battery chemistries



Summary

- Investigated Voltage Fade in various lithium– and manganese– rich, and lithium–stoichiometric oxides, with the iR-corrected voltage protocol
 - All Li- and Mn-rich layered oxides display voltage fade and voltage hysteresis
 - Li–stoichiometric oxides, cycled to 4.7V, also show fade but at a much lower rate
 - In general, voltage fade rate is greater at higher temperatures, at higher upper cutoff voltages and at longer aging periods
- Voltage Fade is not mitigated by surface coatings and additives that form passivation films on the oxide particles
 - This fade arises from crystal structure changes in the oxide
- AC impedance data are strongly affected by voltage hysteresis
 - For the same oxide potential and/or Li-content, observed differences indicate that Li atoms occupy different sites during the charge and discharge cycles
- Extended cycling data from $\text{Li}_4\text{Ti}_5\text{O}_{12}$ counter electrode cells indicate that the voltage profile stabilizes around 400 cycles
 - Voltage hysteresis decreases but persists even after 1000 cycles
 - High-resolution electron microscopy of oxides from aged cells show co-existence of multiple crystal structures including areas with spinel-ordering
 - Neutron diffraction and magnetic property data are also consistent with presence of spinel structures



Technical Back-Up Slides



Advantages & disadvantages of tracking the iR-corrected avg. voltage

+ Advantages of this methodology

- Eases comparison between similar materials under similar testing conditions
- Good & reasonably fast tracking of an “average quasi-OCV” during cycling
- Tracking of other materials-related properties: capacities, and energy densities
- Measurement of the average cell resistance
- *This protocol allows us to evaluate strategies that tackle voltage fade*

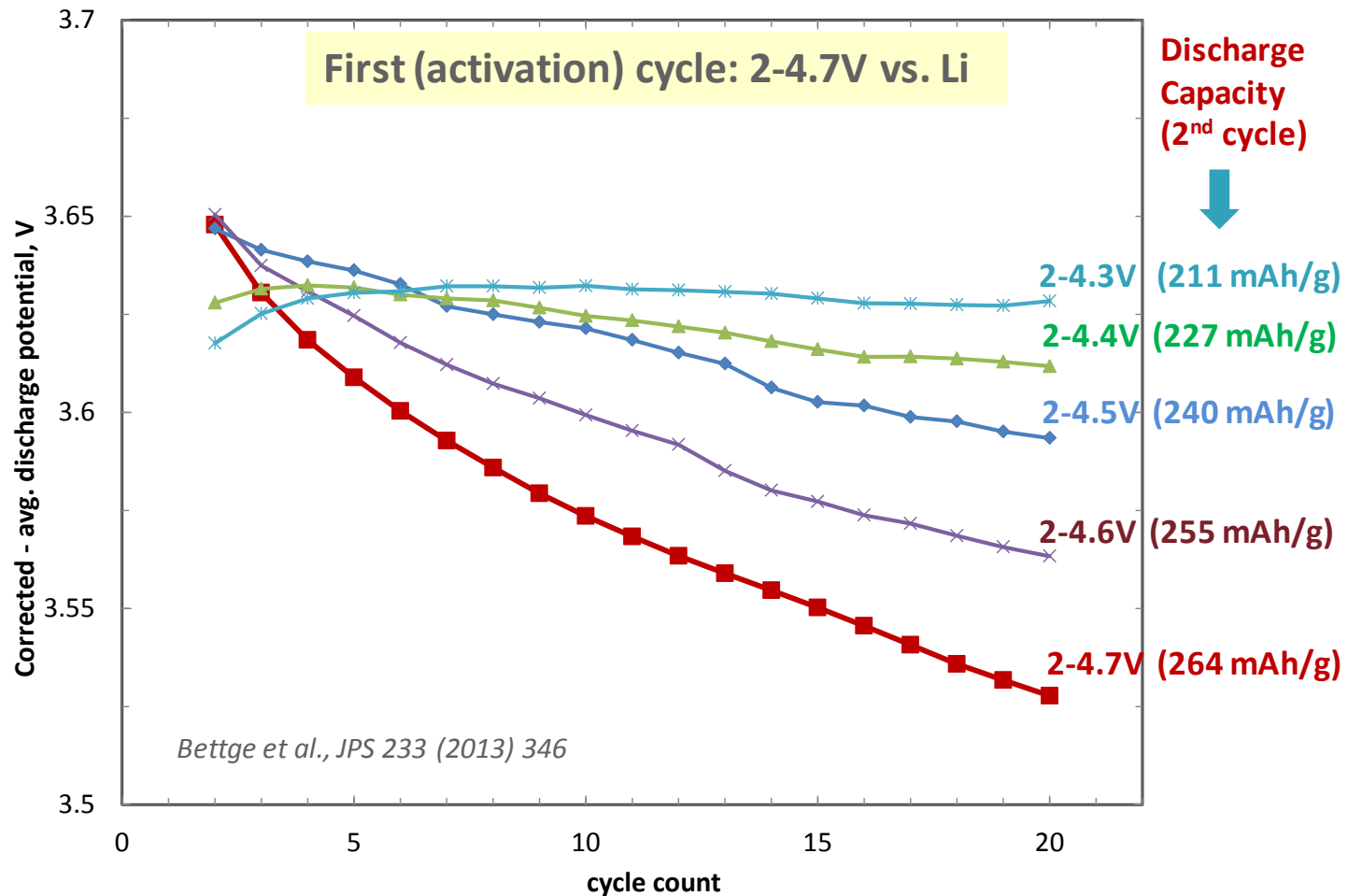
- Limitations of this methodology

- Only approximation of the “true” average voltage (averaging effects, changes in SOC, long relaxation times)
- Exp. conditions need to be carefully adjusted depending on material & cycling conditions (interrupts & window & rate & holds)
- Sensitive to temperature effects
- *Tracking average voltage does not capture mechanistic details*



Voltage fade decreases as upper cut-off voltage is lowered

But there is a corresponding reduction in capacity/energy density



No discernible voltage fade for cells cycled between 2 and 4.25V vs. Li