Solid State NMR Studies of Li-Rich NMC Cathodes: Investigating Structure Change and Its Effect on Voltage Fade Phenomenon

Project ID: ES 187

Baris Key

Voltage Fade Team

Annual Merit Review

Washington DC, June 16-20, 2014

Overview

Timeline

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

Budget

- Voltage Fade project

Barriers

Development of a 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 on calendar–life and cycle–life aging

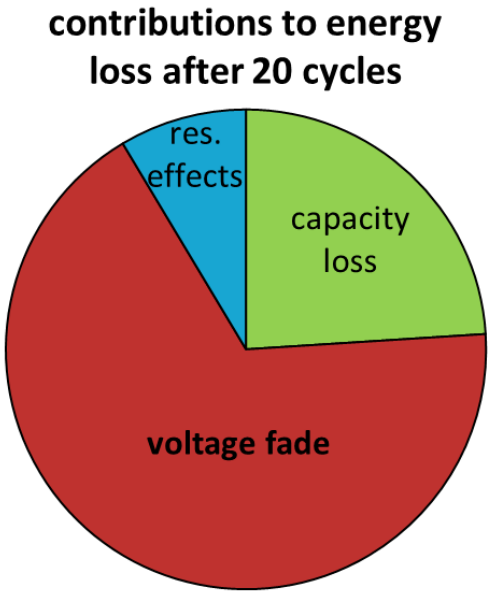
- Mitigating voltage fade will enable the use of these high–energy NMC composite oxides {$xLi_2MnO_3 \bullet (1-x)LiMO_2$ (M=Ni, Mn, Co)} for PHEV and EV applications

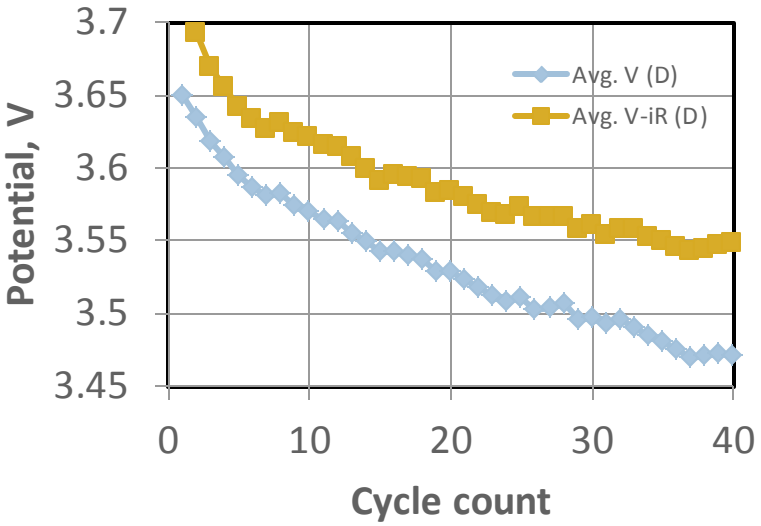
Milestones

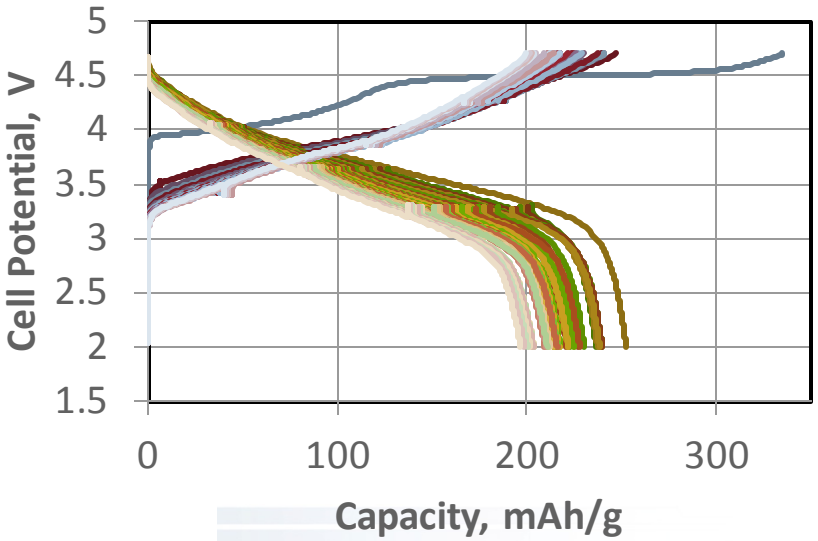
- Elimination of proton insertion as a structural cause for voltage fade (complete)
- Electrochemical characterization of LMR-NMC cathode materials with fully lithium-6 enriched cells (enriched electrolyte, Li-metal and cathode) and quantitative high resolution ^{6}Li MAS NMR experiments on the enriched pristine and cycled materials (complete)
- Correlation of local structure changes with electrochemical hysteresis (data collection complete, analysis near completion)
- Quantitative correlation of structural changes with voltage fade (complete)
- Full realization of voltage fade mechanism (near completion)

Approach: Investigation of possible structural causes for the fade in voltage using NMR spectroscopy

- Loss of local ordering/Formation of new ordering in Li and TM layers for Li and transition metals
  - TM migration
- Oxygen loss mechanism and formation of defect sites
- Materials loss of the ability of hosting Li in TM layer octahedral sites, *i.e.* occupancy in tetrahedral Li sites
  - Defects/Vacancies ?
- Tied to all points above: Formation of a spinel-like structure ?
- Effect of domains and domain size ?
- H^+ insertion into the lattice ?







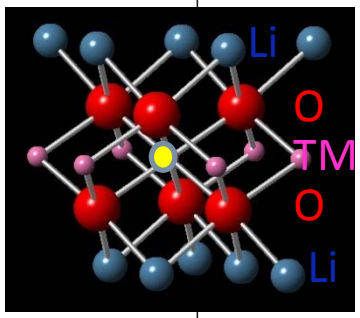
Progress and Major Technical Accomplishments

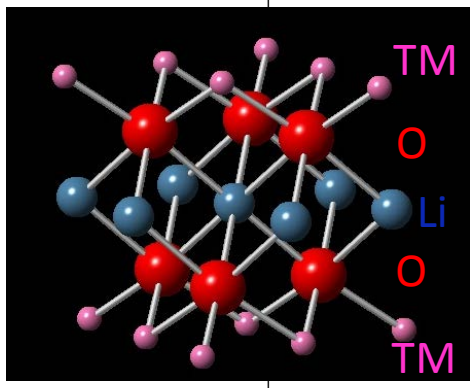
- Elimination of proton insertion hypothesis as a structural cause for voltage fade
- Electrochemical characterization of LMR-NMC cathode materials with fully lithium-6 enriched cells (enriched electrolyte, enriched Li-metal and enriched cathode)
  - Quantitative high resolution ^{6}Li MAS NMR experiments on the enriched pristine and cycled materials at states of charge of interest over multiple cycles and compositions
  - Resolution and detail in detected Li-local structures by this NMR methodology is unprecedented in literature. Such work is only possible due to collaborative effort of the Voltage Fade Team.
- Correlation of local structure changes with electrochemical hysteresis
- Quantitative correlation of structural changes with voltage fade
- Spectroscopic evidence of transition metal migration
- Quantitative NMR data deconvolutions are in progress…
- Theory assisted NMR shift calculations are in progress…

Cathode materials examined

- HE5050 (Toda) and Li rich NM
  - $(0.5Li_2MnO_3 \bullet 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2)$ or $Li_{1.2}[Ni_{0.15}Mn_{0.55}Co_{0.10}]O_2$
  - $Li_{1.2}Mn_{0.4}Co_{0.4}O_2$
  - Synthesis: hydroxide co-precipitation and oxalate precursor co-precipitation
- Li_2MnO_3
  - Synthesis: Li_2MnO_3 calcined at 850°C
- Half-cell configurations vs. 95% enriched ^6Li metal
  - 1.0 M (95% enriched) $^6LiPF_6$ in EC/DMC (1:1wt.) and 1.0 M $LiPF_6$ in 95% Deuterated EC/DMC (1:1 wt.) in 2032 coin cells
  - All cycling data using "voltage fade protocol" (2.0V – 4.7V, 10mA/g 1st cycle then 20mA/g subsequent cycles with current interrupts to measure impedance contribution and calculate Avg. V – iR corrected)
- NMR Characterization
  - 1.3mm Magic Angle Spinning Bruker probes with Avance III spectrometers (spinning speeds up to 67kHz using 11.7 and 7.02 Tesla fields)
  - ^2H and ^6Li nuclei of interest

Li local structures in LMR-NMCs





^{6}Li MAS NMR 67 kHz at 7.02 T

Li in Li layers (*262* integral total)

Li in TM layers (*47.4* integral total)

1505 1470 1396

7.4 *25* *15*

Shift in ppm → 807

Integral value → *39.2*

735

100

Li_2MnO_3-like domains

Li_2MnO_3-like domains

5Mn1Ni+5Mn1Co

Li in domain boundaries

594

11

551

17

1500 1000 500 [ppm]

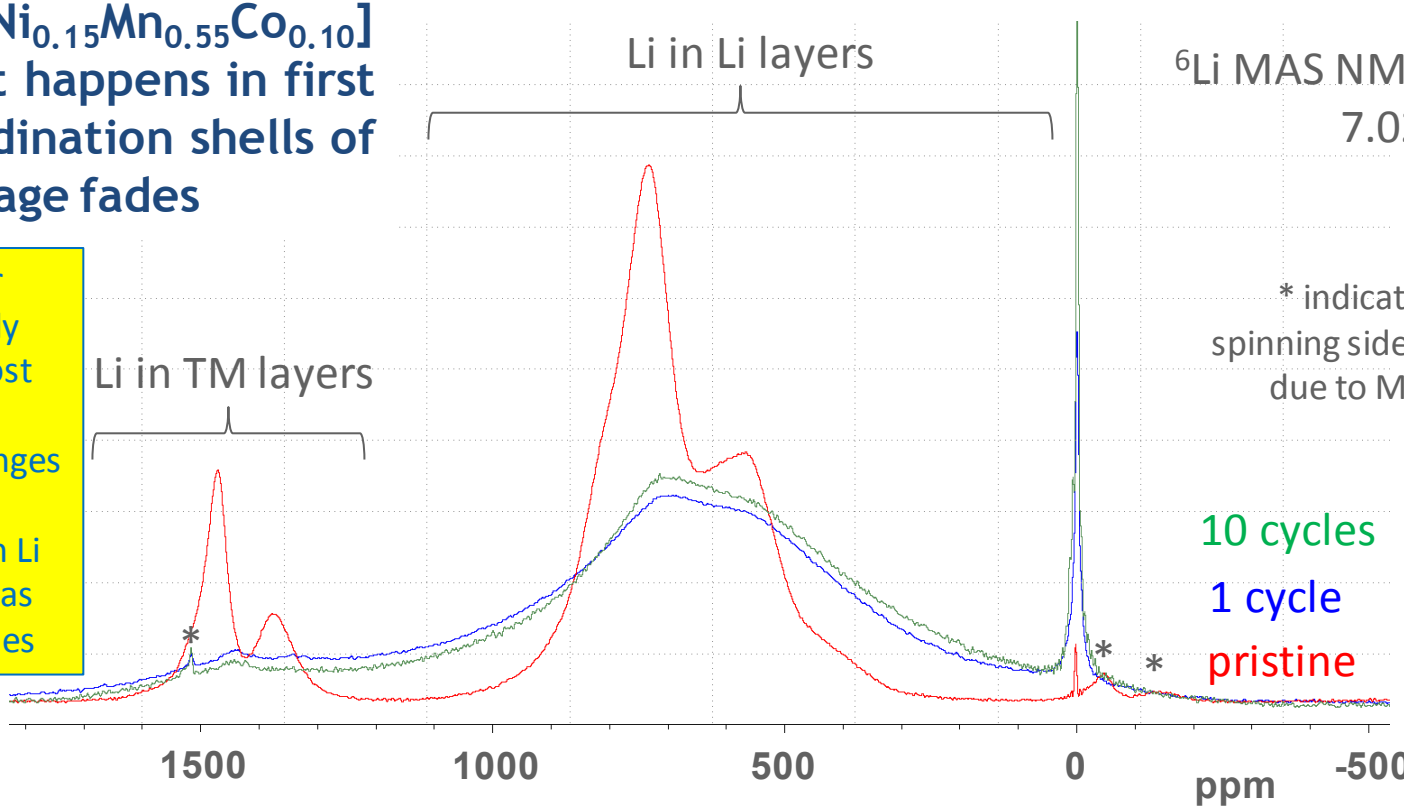
- Li in Li layers and transition metal layers quantified
- Individual domains and domain boundaries quantified

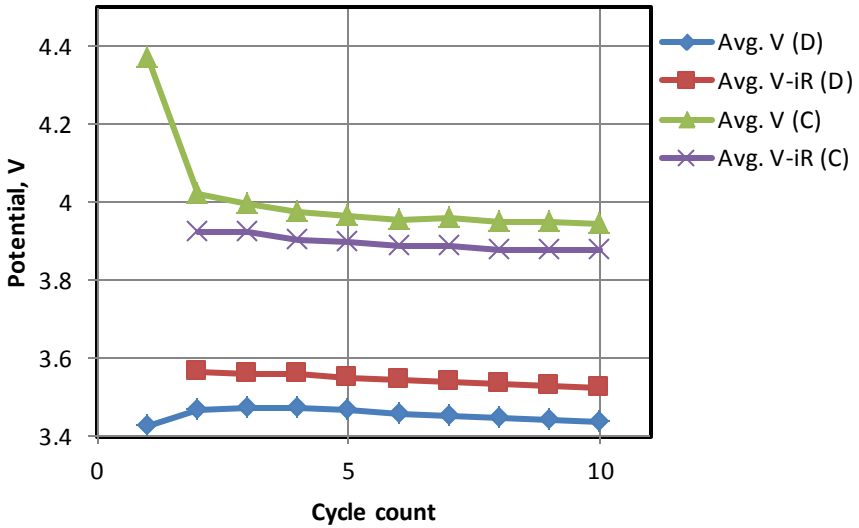
^{6}Li Enriched $Li_{1.0}[Li_{0.2}Ni_{0.15}Mn_{0.55}Co_{0.10}]O_2$ Toda HE5050 composition pristine

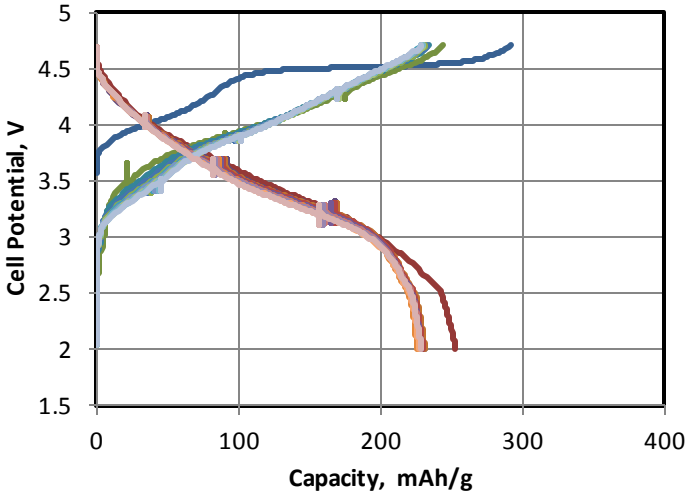
Fulya Dogan, Jason Croy, Mahalingam Balasubramanian, Michael Slater, Hakim Iddir, Christopher Johnson, John Vaughey, Baris Key, *submitted to Chemistry of Materials*, 2014

$Li_{1.0}[Li_{0.2}Ni_{0.15}Mn_{0.55}Co_{0.10}]O_2$ - What happens in first few coordination shells of Li as voltage fades

- Local order dramatically changes post activation
- Subtle changes in local structure in Li in Li layers as voltage fades

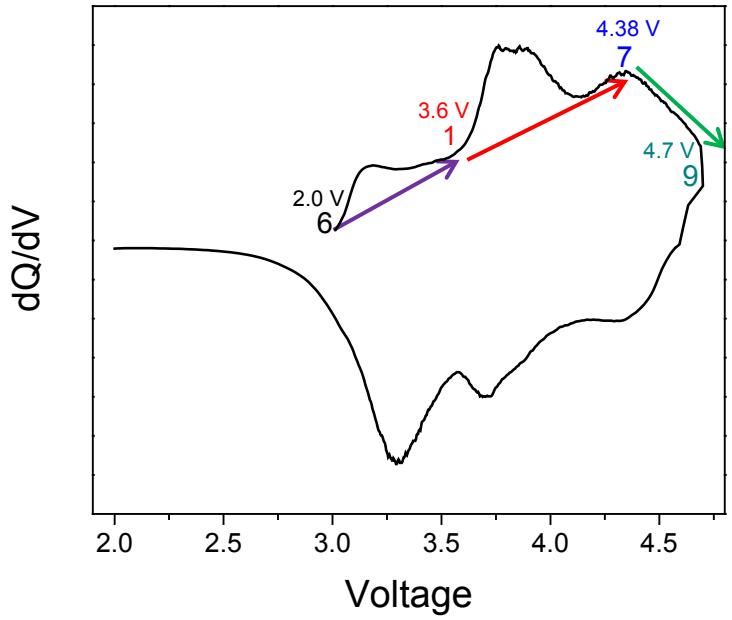






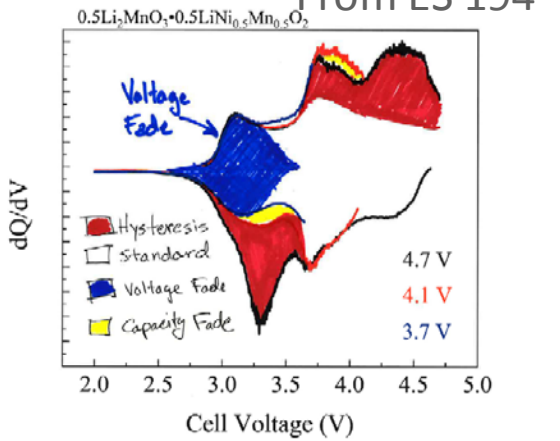
electrochemical profile of the 10 cycle electrode

$Li_{1.0}[Li_{0.2}Ni_{0.4}Mn_{0.4}]O_2$ - Electrochemical Hysteresis and Structure Change



From ES 194

Changes upon delithiation (post-activation)



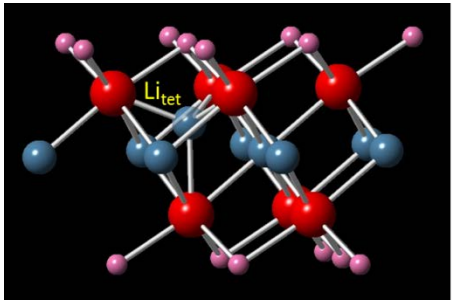
Li layer

Delithiation progresses from Li removal from both layers

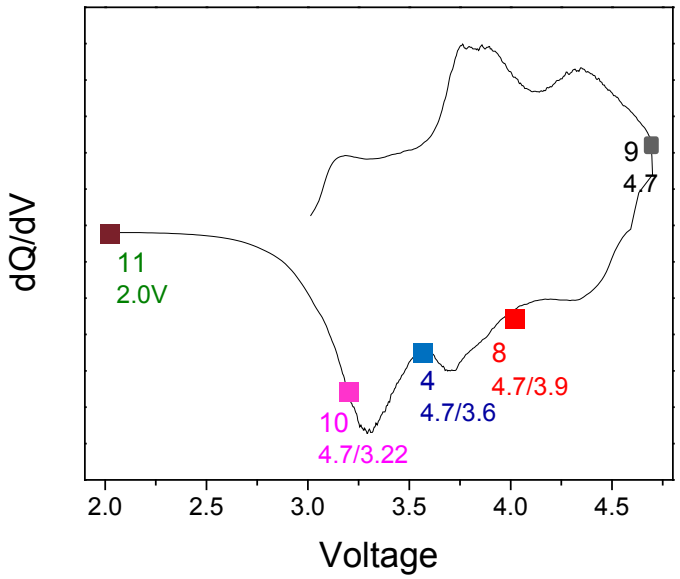
Shifts larger than 1480ppm only possible by an additional TM coordination to $Li(Mn)_6$

TM layer

Transition Metal migration (via tetrahedral sites) detected !



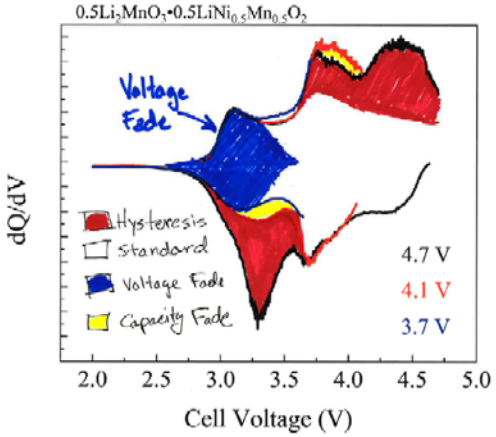
$Li_{1.0}[Li_{0.2}Ni_{0.4}Mn_{0.4}]O_2$ - Electrochemical Hysteresis and Structure Change

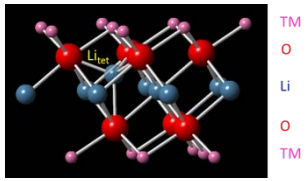


Li layer

Changes upon relithiation (post-activation)

From ES 194



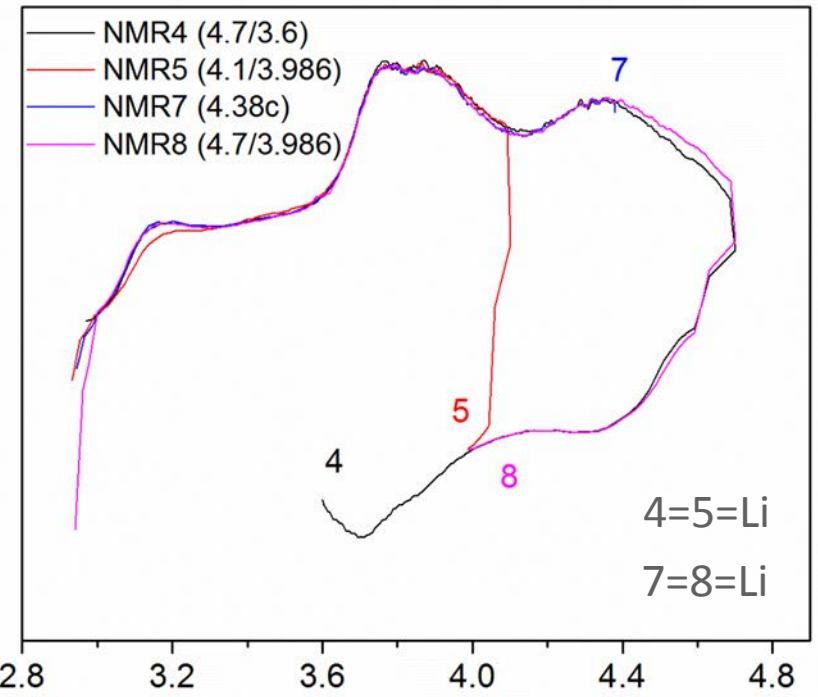


Shifts larger than 1480ppm only possible by an additional TM coordination to $Li(Mn)_6$

Transition Metal migration (via tetrahedral sites) detected !

TM layer

$Li_{1.0}[Li_{0.2}Ni_{0.4}Mn_{0.4}]O_2$ - Pinpointing Hysteresis effect in local structure



Electrochemical hysteresis can be followed directly via NMR by different Li site occupancies at hysteresis points in dQ/dV plot

Li layer

TM layer

ch 4.7, disch. 3.986; NMR8

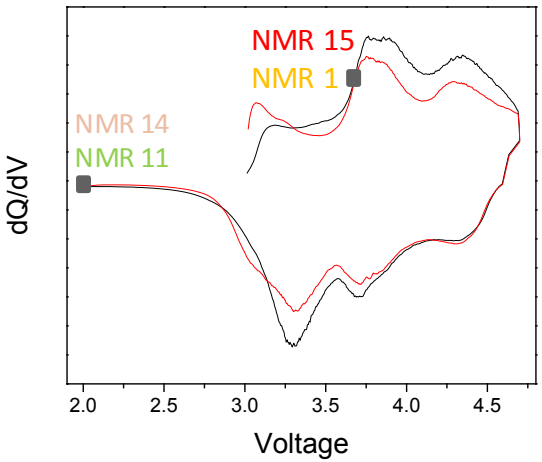
ch 4.38; NMR7

ch. 4.1, disch. 3.986; NMR5

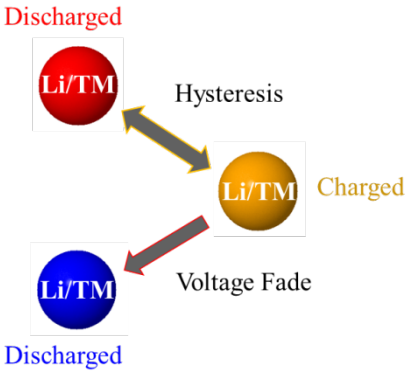
ch. 4.7, disch. 3.6; NMR 4

2000 1500 1000 500 0 ppm -500

$Li_{1.0}[Li_{0.2}Ni_{0.4}Mn_{0.4}]O_2$ - Electrochemical Hysteresis and Structure Change - 2nd cycle vs. 11th cycle

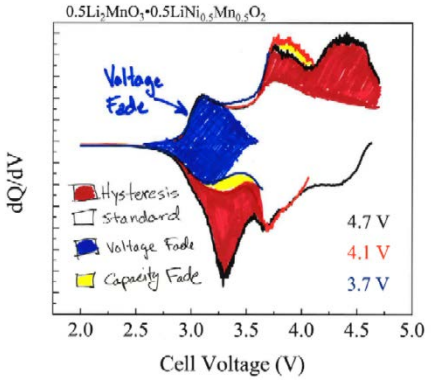


- Transition metal migration slows down after 10 cycles
- Effect of hysteresis continues but as voltage fade configuration appears in dQ/dV plots center of mass of Li shifts in NMR spectra shift to lower frequencies.



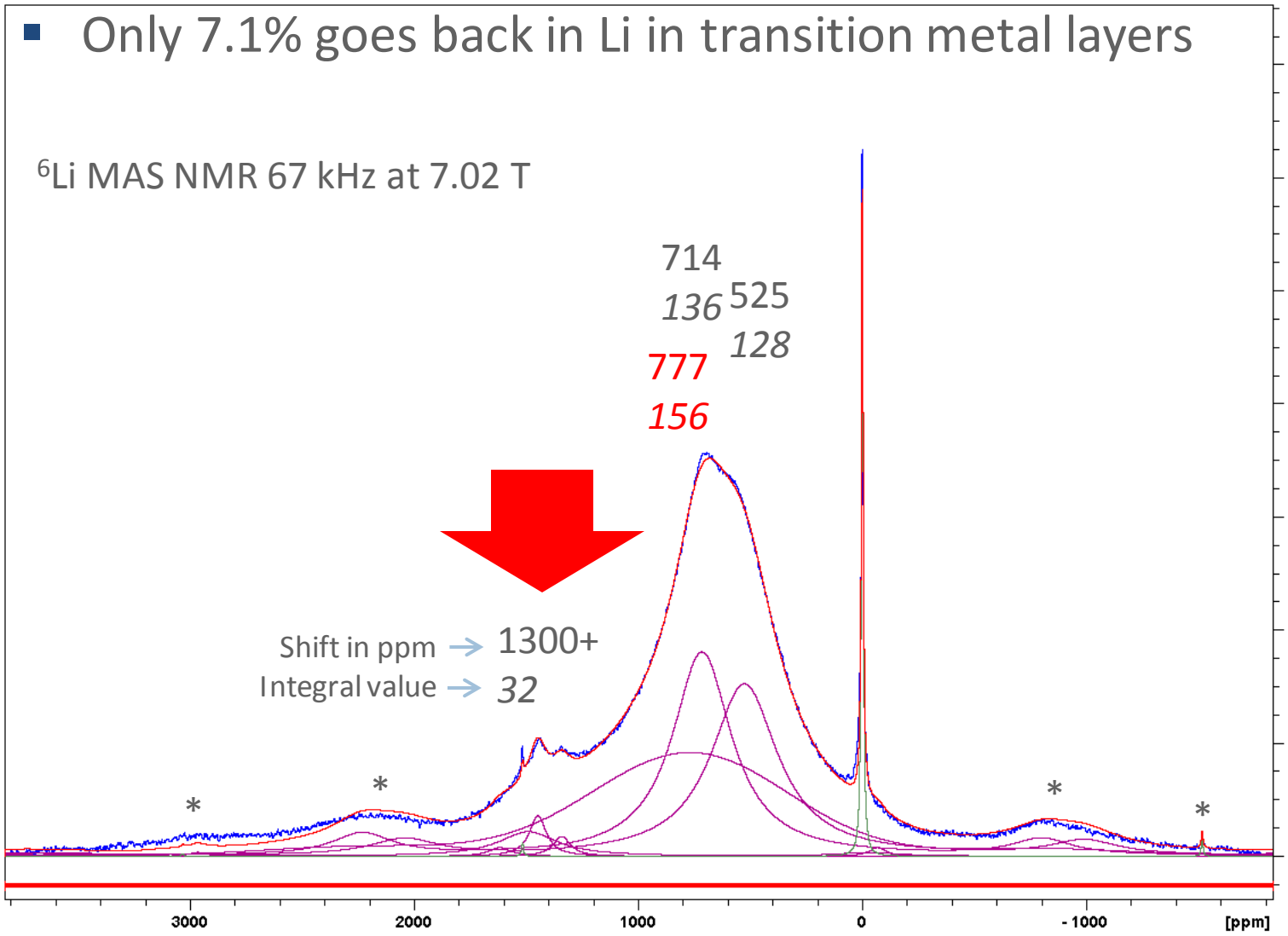
From ES 194

- Transition metal migration slows down by 11th cycle
- Subtle shifts observed for Li layer resonances



After 1 cycle - Deconvolution of Li Local Structures

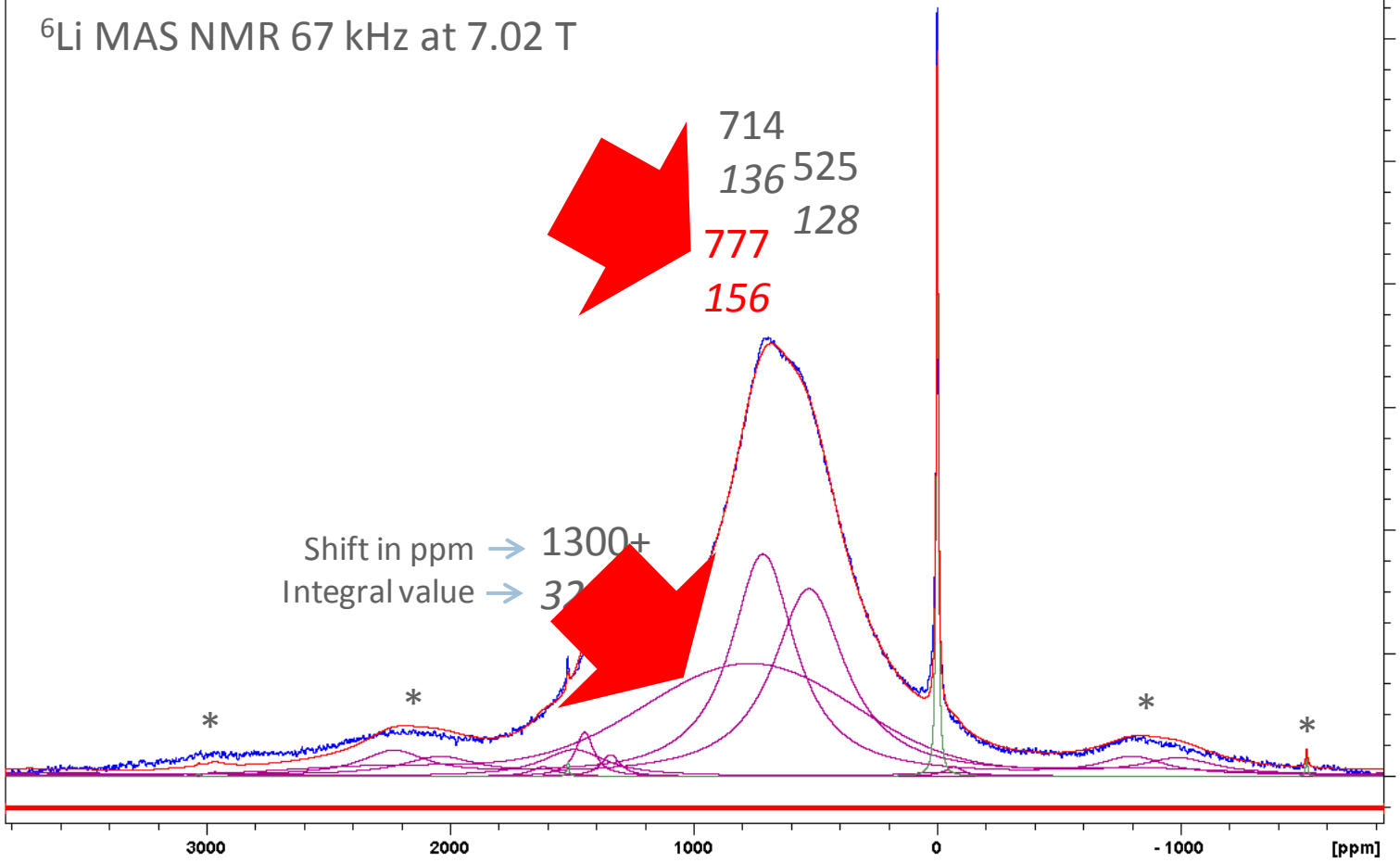
- Only 7.1% goes back in Li in transition metal layers



* indicates spinning sidebands due to MAS

After 1 cycle - Deconvolution of Li Local Structures

- Only 7.1% goes back in Li in transition metal layers
- 34.5% of Li appears to be in a new disordered environment(s)



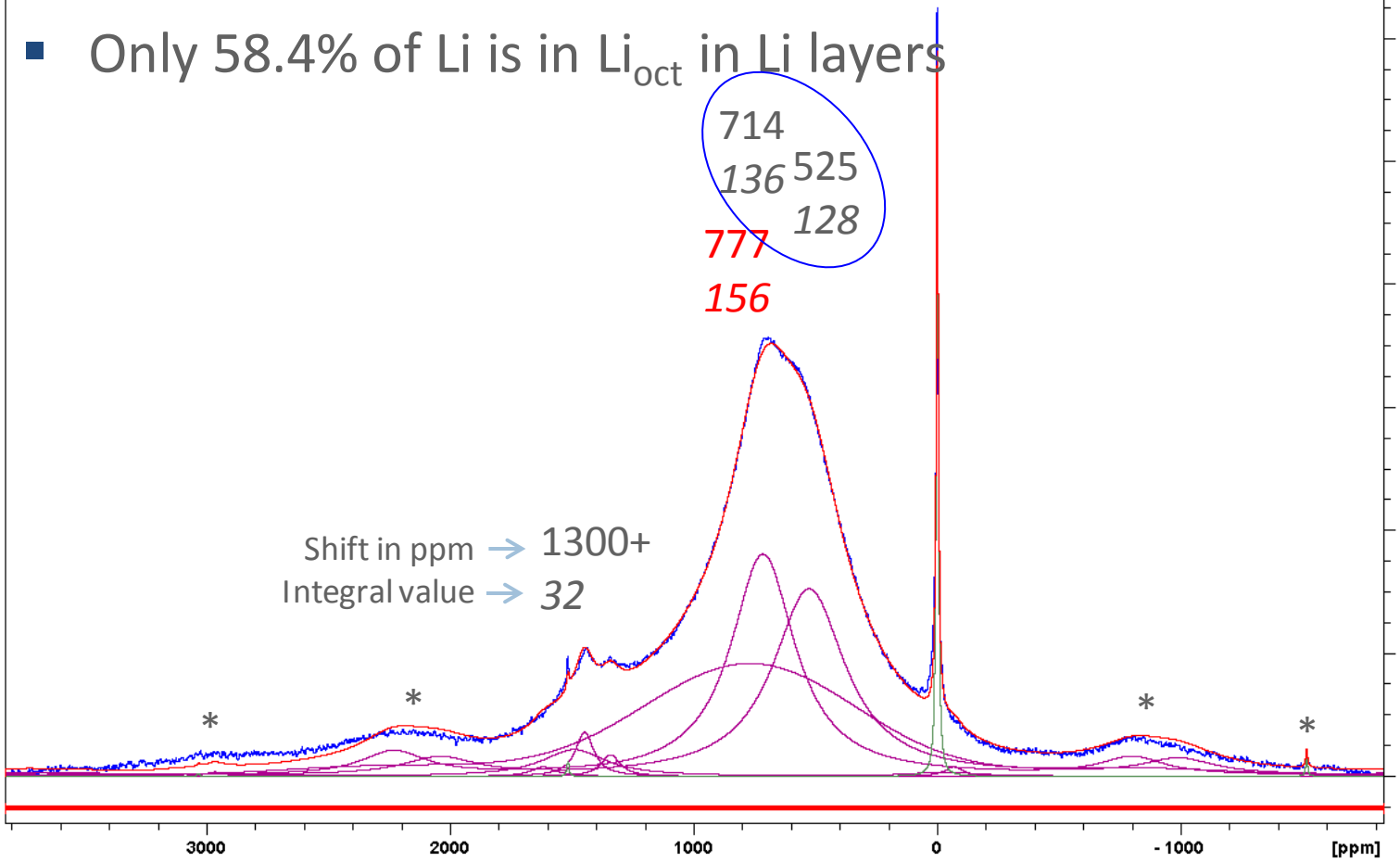
* indicates spinning sidebands due to MAS

^{6}Li Enriched $Li_{1.0}[Li_{0.2}Ni_{0.15}Mn_{0.55}Co_{0.10}]O_2$

Fulya Dogan, Brandon Long, Jason Croy, Michael Slater, Hakim Iddir, Roy Benedek, Martin Bettge, John Vaughey, Baris Key, *in preparation*, 2014

After 1 cycle - Deconvolution of Li Local Structures

- Only 7.1% goes back in Li in transition metal layers
- 34.5% of Li appears to be in a new disordered environment(s)
- Only 58.4% of Li is in Li_{oct} in Li layers

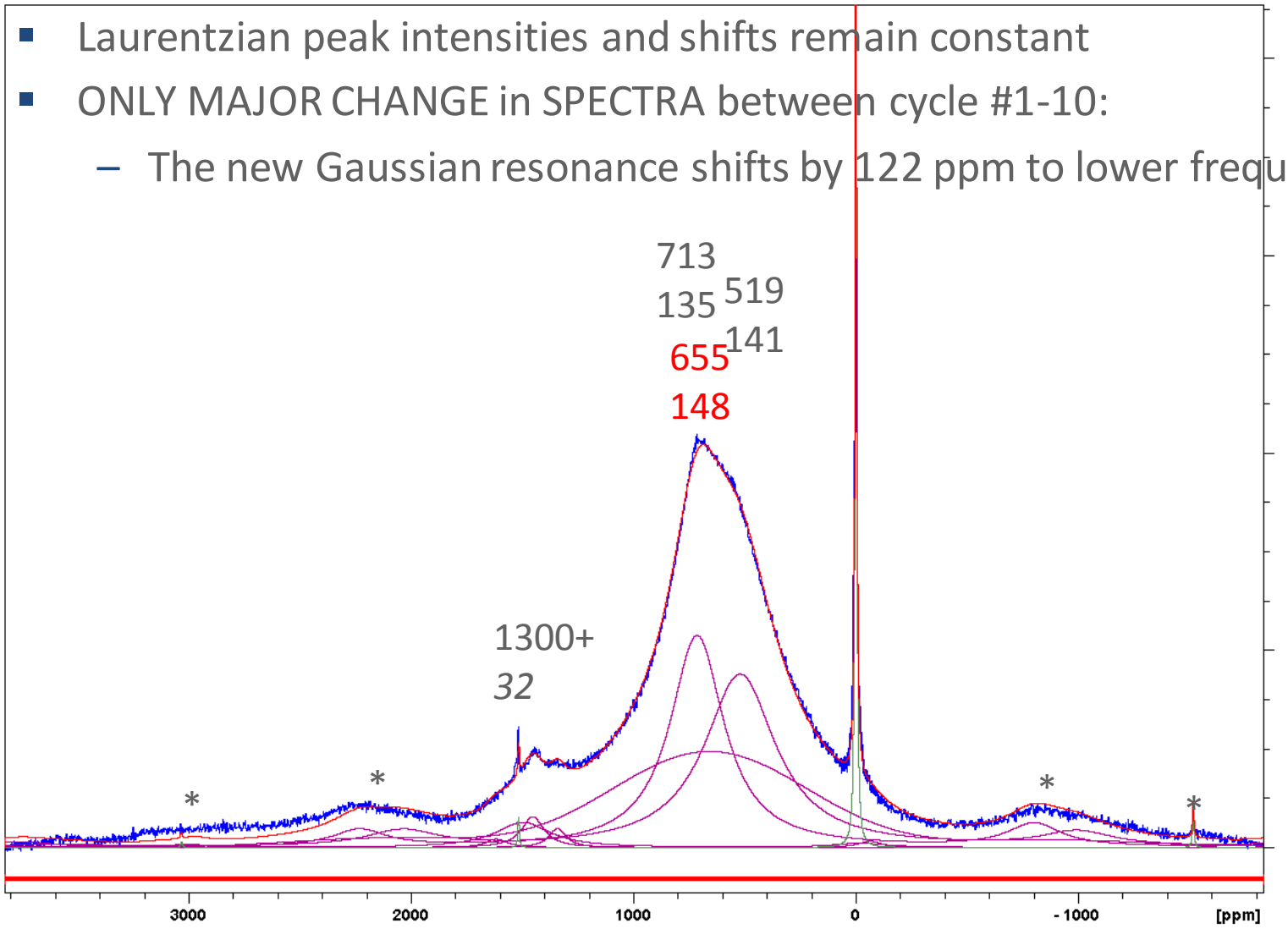


* indicates spinning sidebands due to MAS

^{6}Li Enriched $Li_{1.0}[Li_{0.2}Ni_{0.15}Mn_{0.55}Co_{0.10}]O_2$

After 10 cycles - Deconvolution of Li Local Structures

- Laurentzian peak intensities and shifts remain constant
- ONLY MAJOR CHANGE in SPECTRA between cycle #1-10:
  - The new Gaussian resonance shifts by 122 ppm to lower frequency !

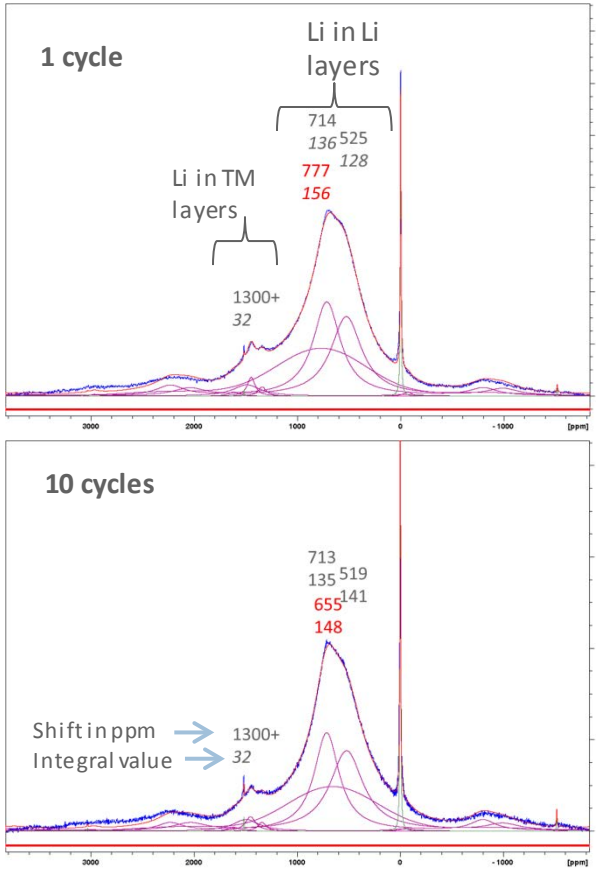


* indicates spinning sidebands due to MAS

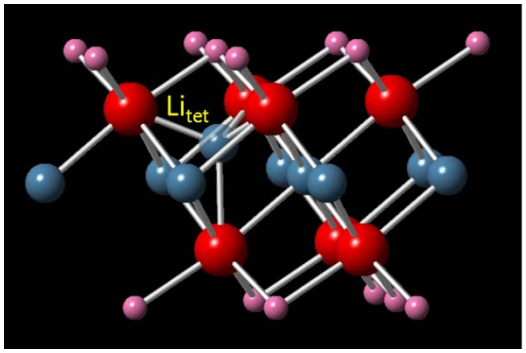
^{6}Li Enriched $Li_{1.0}[Li_{0.2}Ni_{0.15}Mn_{0.55}Co_{0.10}]O_2$

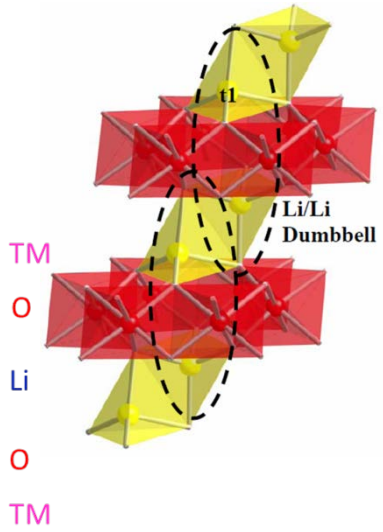
Fulya Dogan, Brandon Long, Jason Croy, Michael Slater, Hakim Iddir, Roy Benedek, Martin Bettge, John Vaughey, Baris Key, *in preparation*, 2014

Basis of new Li environment assignments

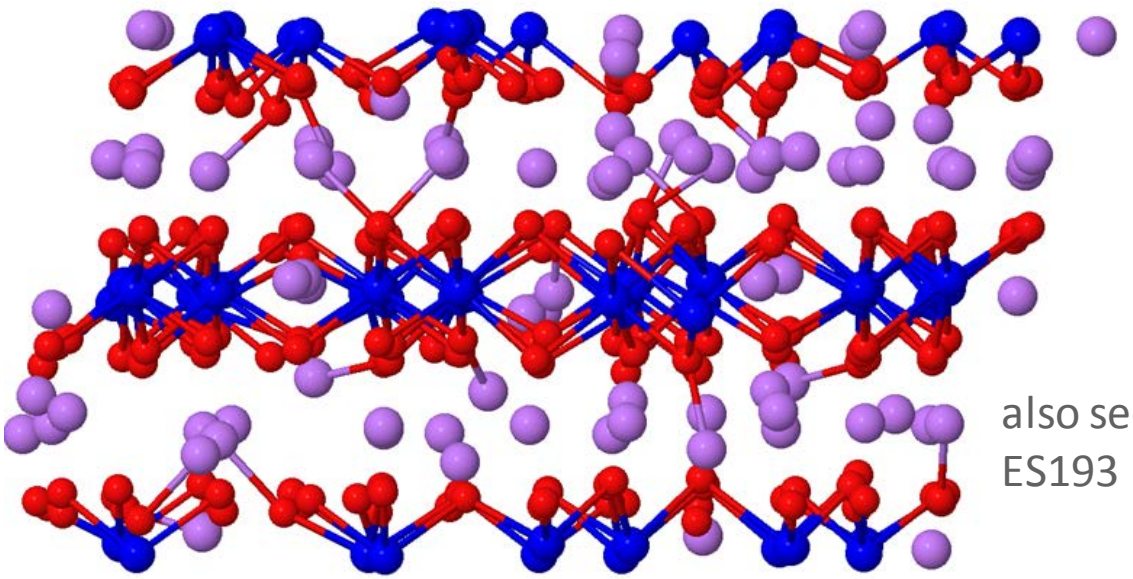


M. Jiang, B. Key, Y.S. Meng, C. Grey., 2009





Similar Li ordering was associated to a combination of Li sites including tetrahedral Li, although it was not quantified or monitored in detail before

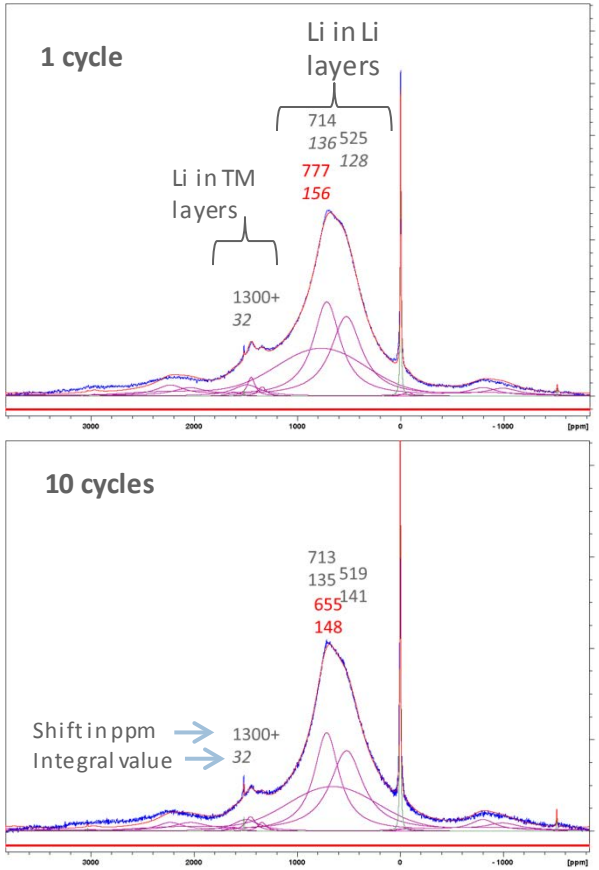


also see ES193

Ab initio Molecular Dynamics calculations on 50% delithiated Li_2MnO_3 show ~40% of Li from TM layers migrate to the Li layers and ~ 34% of Li's occupy tetrahedral sites in Li layers. Additional Li inserted into such a lattice (i.e. fully discharged stage post activation) is expected to have lower average voltage.

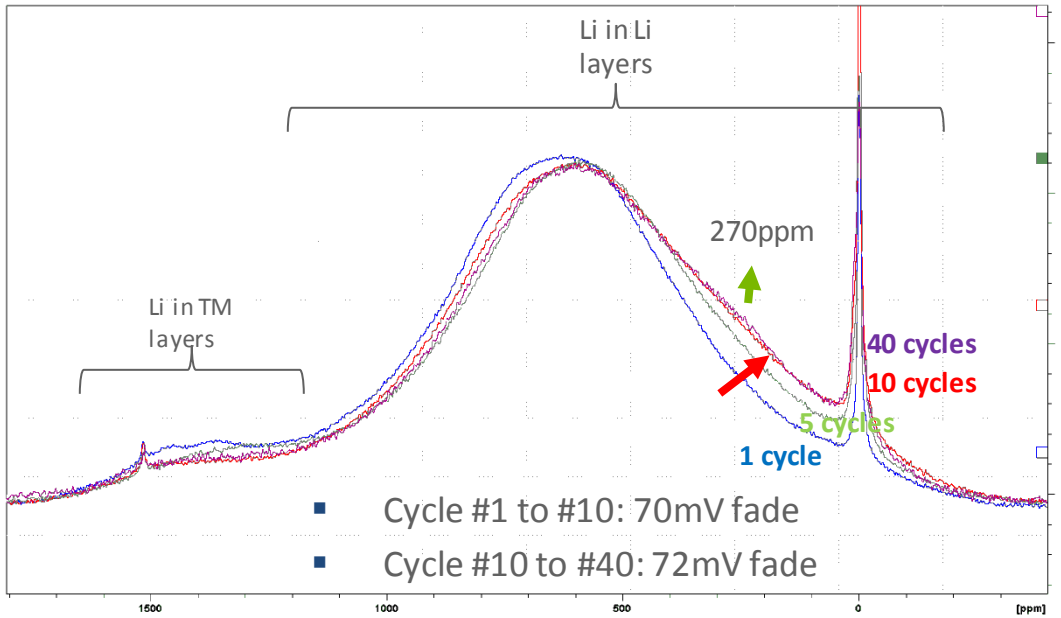
Fulya Dogan, Brandon Long, Jason Croy, Michael Slater, Hakim Iddir, Roy Benedek, Martin Bettge, John Vaughey, Baris Key, *in preparation*, 2014

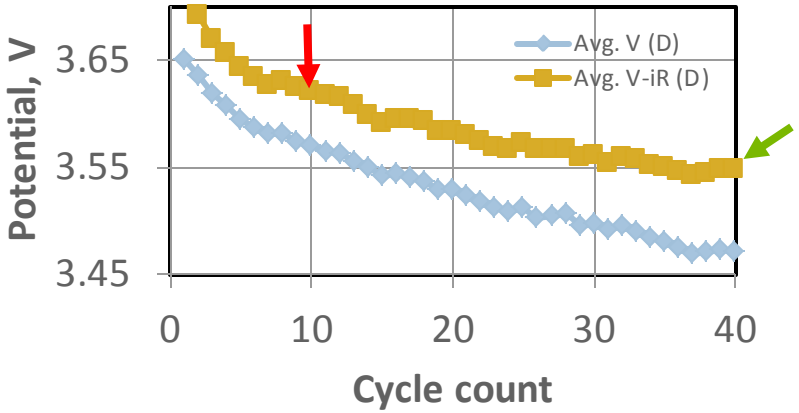
Changes in Li environment and correlation to Voltage Fade rates



- Fastest fade region (cycles 1-10) exhibit large shift in resonance of new Li-site
- Slower fade region (cycles 10-40) exhibit minimal shift in resonance of new site but formation of new order (270ppm)

^{6}Li MAS NMR 67 kHz at 7.02 T

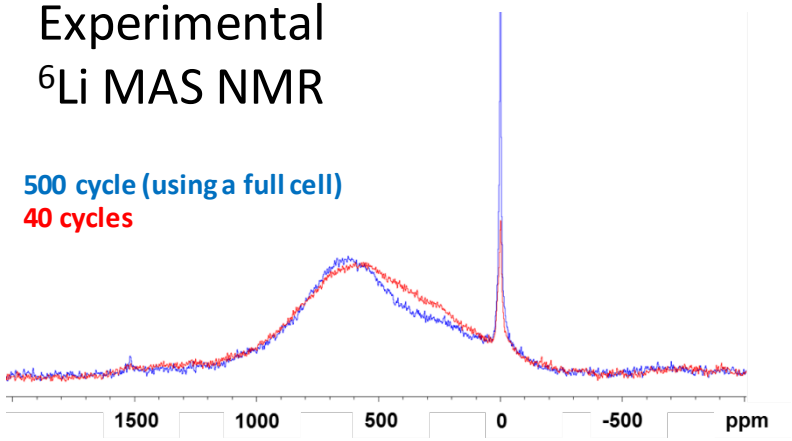




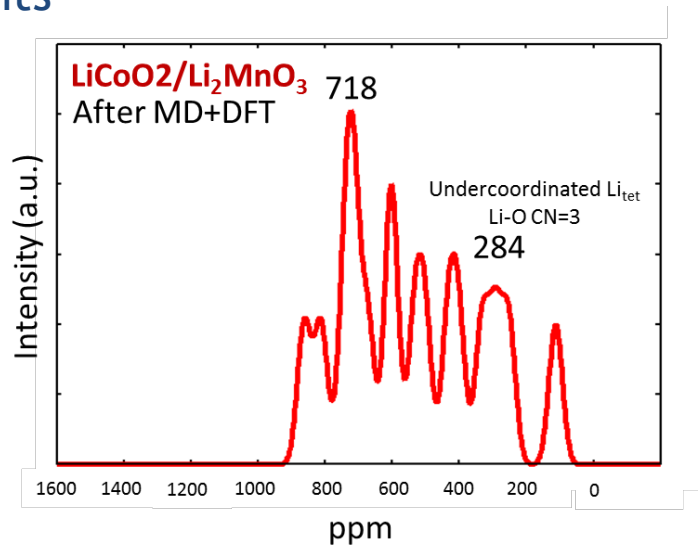
Fulya Dogan, Brandon Long, Jason Croy, Michael Slater, Hakim Iddir, Roy Benedek, Martin Bettge, John Vaughey, Baris Key, *in preparation*, 2014

Insights into extended cycle structure - Li environments

Experimental
^{6}Li MAS NMR

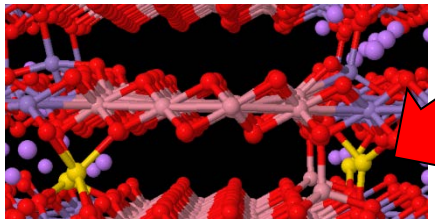


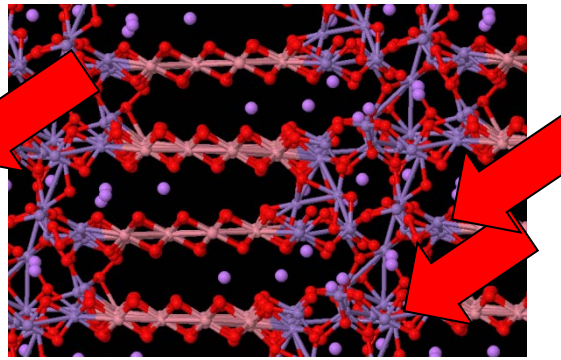
Predicted NMR shifts from simulated local structures



- Beyond 40th cycle, local structure gets locked in place and becomes more order when 500 cycles are reached
- Peaks do not show resemblance of full conversion to typical spinel phases
- Complementary XRD data (500 cycles) suggests retention of layered composite lattice and did not indicate any long range spinel peaks

Oxygen vacancy containing Li-rich Mn-Co composite delithiated MD+DFT simulations suggest lower frequency shifts (~270ppm) are due to undercoordinated Li_{tet} (CN<4)





also see ES193

Fulya Dogan, Brandon Long, Jason Croy, Michael Slater, Hakim Iddir, Roy Benedek, Martin Bettge, John Vaughey, Baris Key, *in preparation*, 2014

Summary of NMR analysis

- Proposed hysteresis and voltage fade configurations are directly correlated with (de)lithiation phenomena from specific local Li arrangements
  - Hysteresis configuration is associated with Li_{tet} activity or lack thereof (high voltages)
  - Voltage fade configuration is associated with TM activity (3.0-3.3V)
- Post activation, Li content in formal sites in TM layers is 7.1% (down from 16.7%)
- %34.5 of Li is now in new sites (tentatively assigned to extensive Li_{tet} and defect sites in TM layers) and remaining %58.4 is in Li_{oct} sites in Li layers. Material is less Li-rich and closer to $Li_{1.0}$ (estimated $Li_{1.1}$ from e-chem)
- Disordered peak shifts to lower frequency by 122ppm ! This coordination must be changing from cycles 1-5-10 where change slows down from 10-40. Possible causes under investigation:
  - TM migration, Voltage Fade configuration: Role of Mn in the shift change
  - Vacancies (oxygen and TM) within the 1^{st} and 2^{nd} coordination shell of these Li
- Excess Li hosted in this new environment, when followed carefully by dQ/dV plots, is the environment that changes incrementally every time Li is being removed. The effect seen in electrochemistry is voltage fade. The structural change is synchronous to hysteresis phenomenon (see ES194 and ES 188)
- A new Li local structure starts to emerge at 270ppm beyond 40 cycles (*i.e.* indicating new order resembling a new tetrahedral motif, possibly due to undercoordinated Li_{tet}) Does not appear to gain long range order
- These local structure changes correlate quantitatively with the amount of voltage fade and require further detailed analyses to narrow down the specific phenomena.

Fulya Dogan, Brandon Long, Jason Croy, Michael Slater, Hakim Iddir, Roy Benedek, Martin Bettge, John Vaughey, Baris Key, *in preparation*, 2014

Future work planned

- Study activation and 1st discharge processes
- EPR studies to monitor tetrahedral paramagnetic transition metals directly (ongoing…)
- Deconvolutions and further analysis of NMR datasets for realization of complete VF mechanism
- Provide local structural probe support to synthetic team led by C. Johnson (ES190) to help mitigate or delay VF mechanism

Related Publications and Presentations

- Fulya Dogan, Jason Croy, Mahalingam Balasubramanian, Michael Slater, Hakim Iddir, Christopher Johnson, John Vaughey, Baris Key, *submitted to Chemistry of Materials*, 2014
- Fulya Dogan* and Brandon Long*, Baris Key, Mahalingam Balasubramanian, Kevin Gallagher, Jason Croy, *in preparation*, 2014
- Fulya Dogan, Brandon Long, Jason Croy, Michael Slater, Hakim Iddir, Roy Benedek, Martin Bettge, John Vaughey, Baris Key, *in preparation*, 2014
- Long, Brandon; Croy, Jason; Dogan, Fulya; Suchomel, Matthew; Key, Baris; Wen, Jianguo; Miller, Dean; Thackeray, Michael; Balasubramanian, Mahalingam, *submitted to Chemistry of Materials*, 2014
- Baris Key et al. 224th Electrochemical Society Meeting, CA, 2013, Oral presentation

Acknowledgements

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

- Collaborators at Argonne National Laboratory
  - Key contributors: Fulya Dogan, Brandon R. Long, Jason R. Croy, Mahalingam Balasubramanian, Michael D. Slater, Hakim Iddir, Roy Benedek, Martin Bettge, Kevin Gallagher, Christopher Johnson, John T. Vaughey
  - Tony Burrell
  - Daniel Abraham