

Solid State NMR Studies and Local Structure of Voltage Fade Materials

Project Id: ES187

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Overview

Timeline

- Start: October 1, 2012
- End: Sept. 30, 2015
- Percent complete: 20%

Budget

- FY13: \$120K

Barriers

- Structural complexity of Lithium Rich Transition Metal Oxides
- Lack of understanding of the activation process
- Lack of local structure information

Partners

- Voltage Fade Team at Argonne



Project Objectives - Relevance

Voltage fade phenomena 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 $\{x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2 \text{ (M=Ni, Mn, Co)}\}$ for PHEV and EV applications

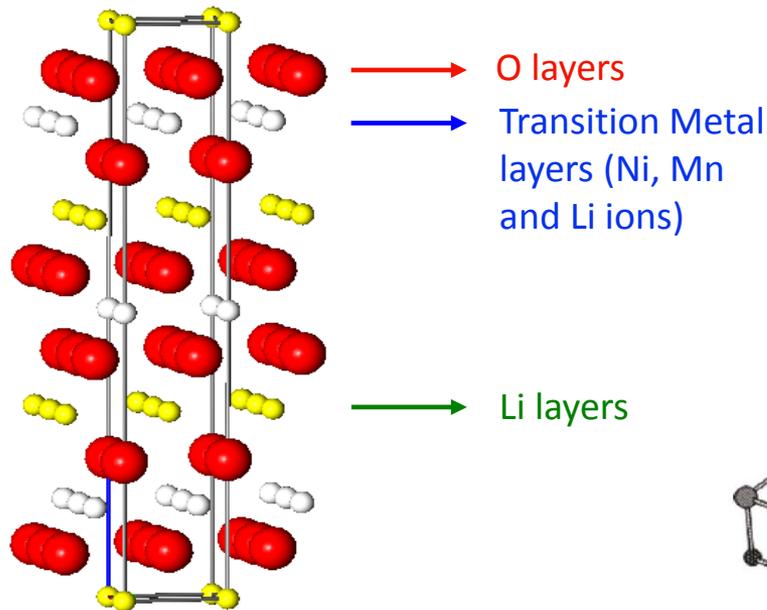
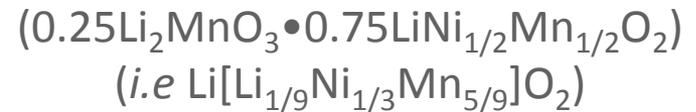
Milestones

- Establish high resolution solid state NMR capabilities to investigate local structure changes in cathode materials **Completed** April 2013
- Obtain ^2H NMR data to investigate the effect of proton insertion as a secondary intercalation phenomenon on voltage fade
Completed March 2013
- Obtain NMR data to determine the structure of the activated material and the difference between structure of the pristine vs. cycled (voltage faded) materials
September 2014

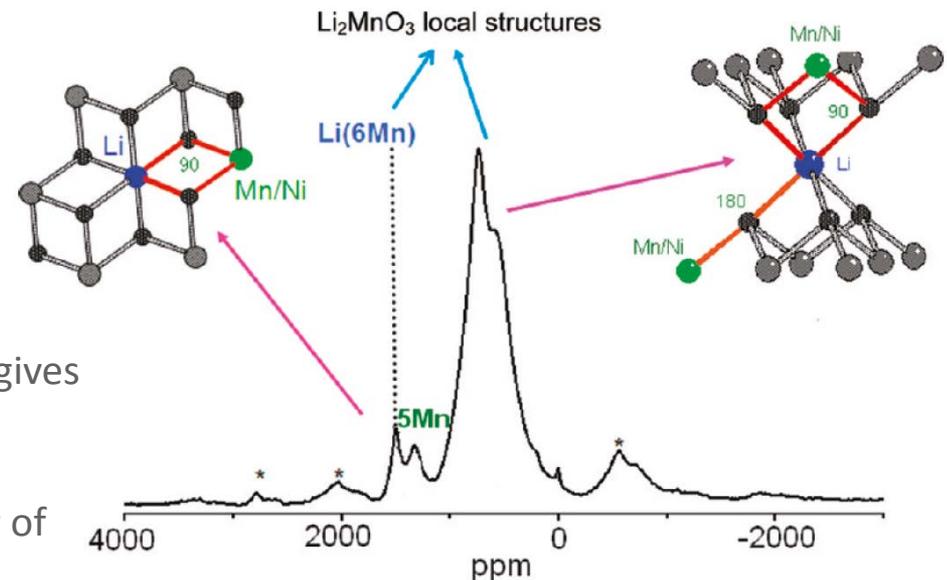


Approach: A fundamental study

- Fundamentally understand and study the structural (both long and short range) factors that contribute to voltage fade in lithium- and manganese-rich NMC oxides (LMR-NMC)



Li ordering in TM layers Li ordering in Li layers



Local coordination of Li vs. Li, Mn and Ni gives rise to resonances at different shifts

The amount of shift is due to the number of Fermi-contact shift via O p-orbitals

* indicates spinning sidebands due to MAS

M. Jiang, B. Key, Y. S. Meng, C. P. Grey, *Chem. Mater.*, 2009

Technical Accomplishments and Progress

- Selected $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ ($0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiNi}_{0.375}\text{Mn}_{0.375}\text{Co}_{0.25}\text{O}_2$) as the baseline oxide to study voltage fade
- Established on-site solid state NMR capabilities to investigate the types short and long range of changes for paramagnetic materials (*milestone completed*)
- Established solid state NMR characterization support for the synthesis and electrochemistry groups within the voltage fade group
- Concluded that the effect of proton insertion is not a contributing factor to the voltage fade phenomenon (*milestone completed*)
- Determined the local structure of the pristine baseline oxide and confirmed the profound loss of order upon cycling as a potential primary cause of voltage fade.
- Confirmed complete lithium removal from disordered Li_2MnO_3 and electrochemical activity by quantitative ^6Li NMR



Cathode materials examined

- HE5050 (Toda)
 - $(0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiNi}_{0.375}\text{Mn}_{0.375}\text{Co}_{0.25}\text{O}_2)$ or $\text{Li}_{1.0}[\text{Li}_{0.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.10}]\text{O}_2$
 - Synthesis: hydroxide co-precipitation
- Li_2MnO_3
 - Synthesis: Li_2MnO_3 calcined at 850°C
- Electrochemically active Li_2MnO_3
 - Synthesis: Li_2MnO_3 calcined at 450°C
- Cell configurations
 - 1.2 M LiPF_6 in EC/EMC (3:7 wt.) and 1.0 M LiPF_6 in Deuterated EC/DMC (1:1 wt.) in 2032 coin cells
 - All cycling data using voltage fade protocol (2.0V – 4.7V) and reproducible
- **NMR Characterization**
 - Magic Angle Spinning (spinning speeds up to 35kHz @ 11.7 Tesla)
 - ^2H and ^6Li



^6Li NMR study on LMRNMCs

Typically 35 KHz

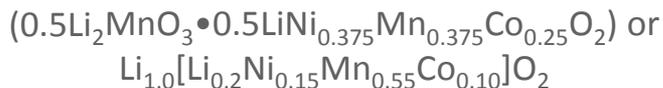
- Distinct local ordering in the synthesized pristine material for Li and transition metals
- Ni, Mn and Co rich domains detected

Spinning sidebands are separated from the main resonance by

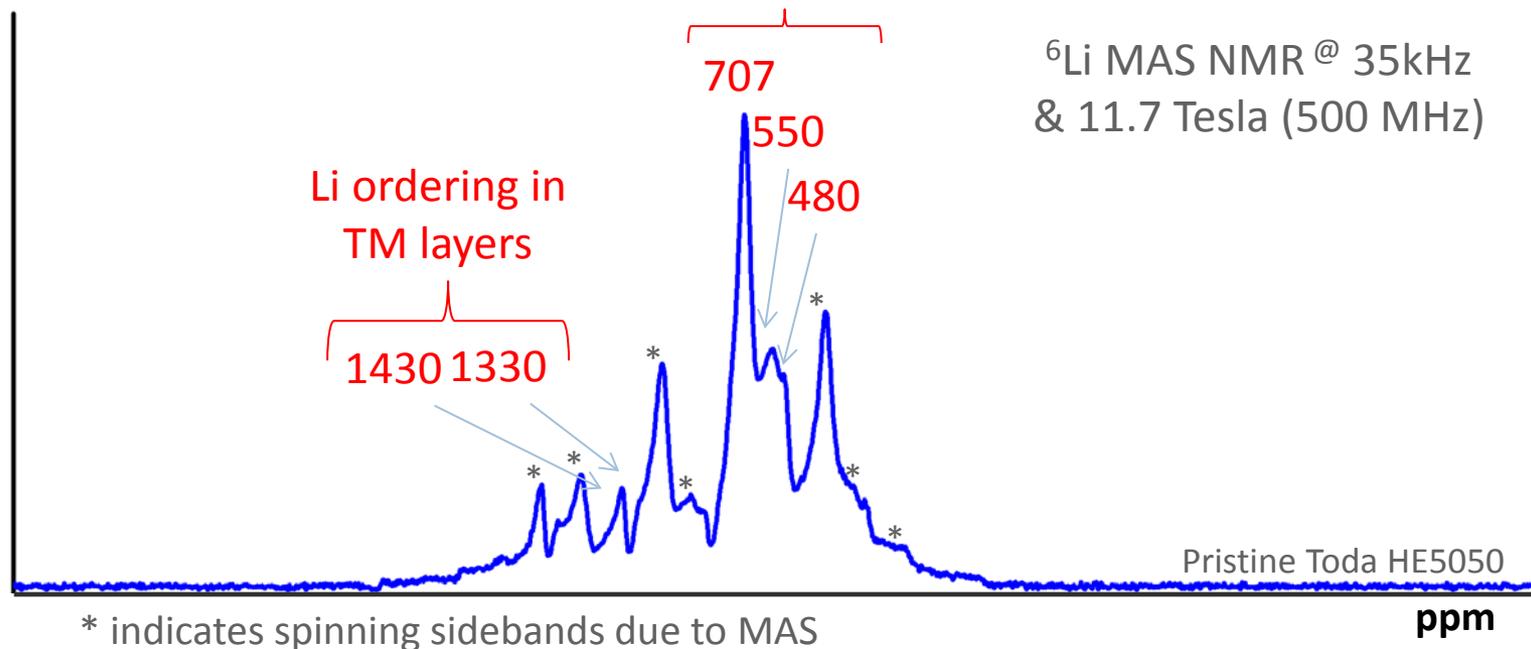
$$\text{Spinning Speed} = \frac{\text{Larmor Frequency}}{\text{Larmor Frequency}}$$

For ^6Li in a 500 MHz magnet 73.65 MHz

For ^6Li in a 200 MHz magnet 29.46 MHz
So it is favorable for resolution

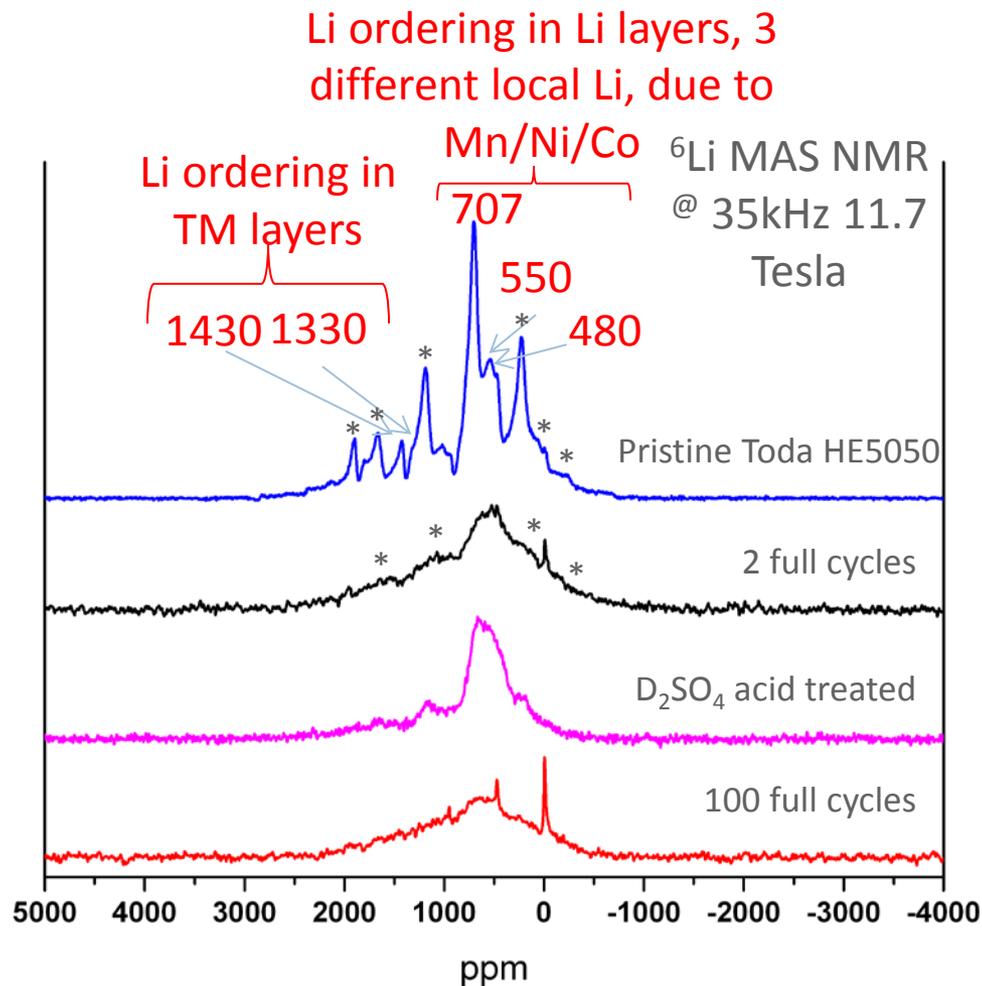


Li ordering in Li layers, 3 different local Li, due to Mn/Ni/Co



^6Li NMR study on LMRNMCs

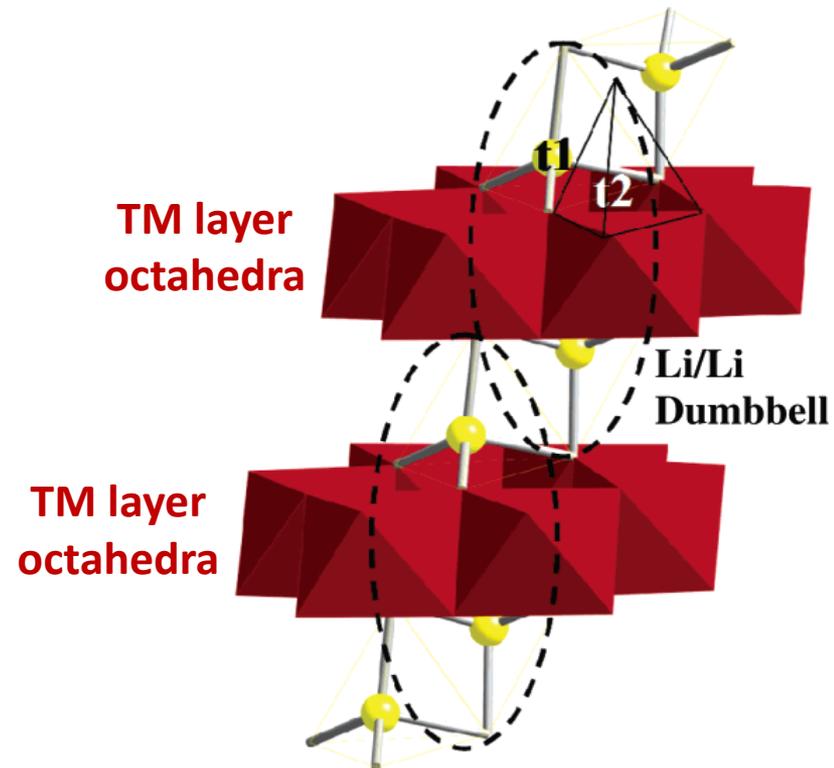
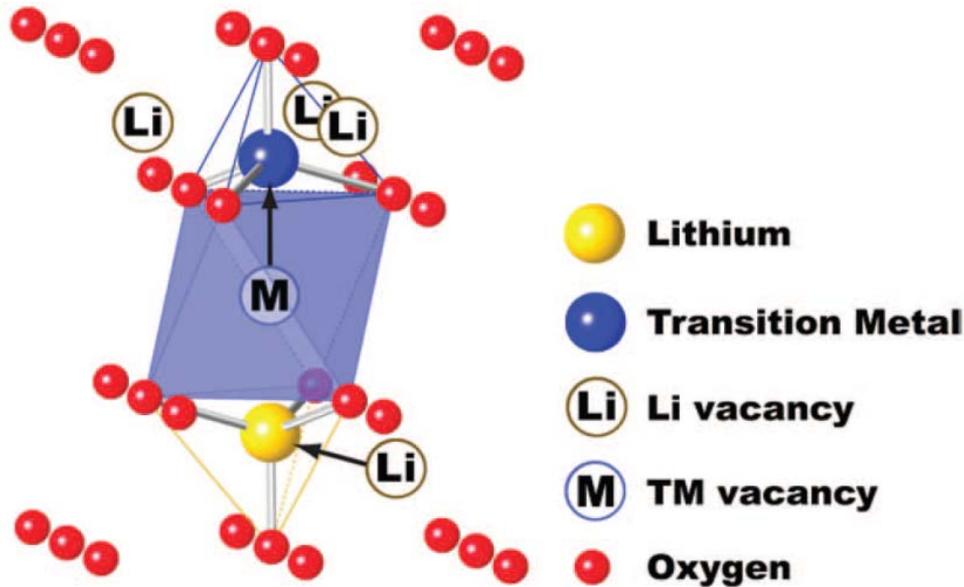
- Profound loss of local ordering observed after cycling
- Loss of ordering due to cycling is analogous to the loss of ordering due to acid treatment (commonly used for coating methods)
- A number of questions need to be answered regarding O_2 loss mechanism, TM migration and tetrahedral site/dumbbell occupancy using ^6Li NMR
- Acquired a low field, high spinning speed capable system to improve resolution (April 2013)



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Structure and Li local ordering

- Role of Li occupancy in subsequent cycles on electrochemistry
- Origin of the excess capacity ?
 - $\text{Li}_{\text{tetrahedral}}$ – dumbbell configuration



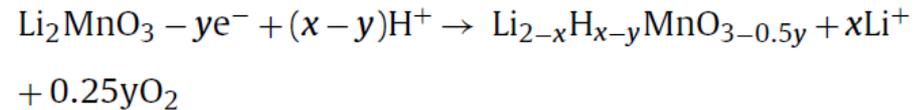
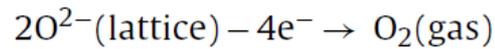
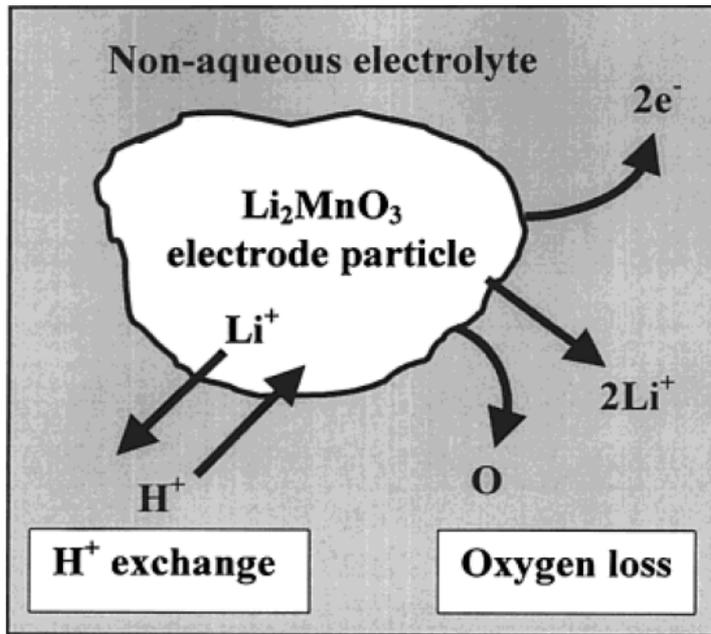
Possible structural causes for the fade in voltage

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



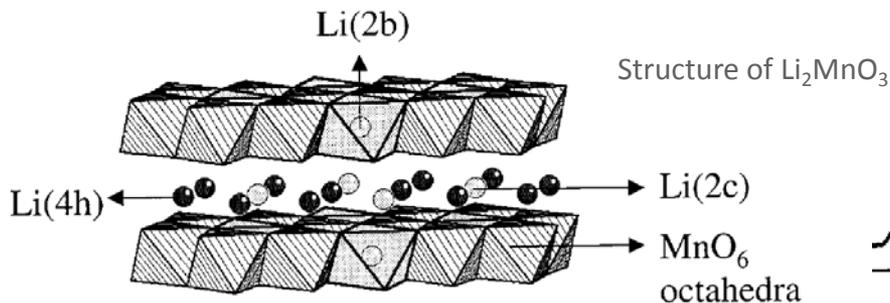
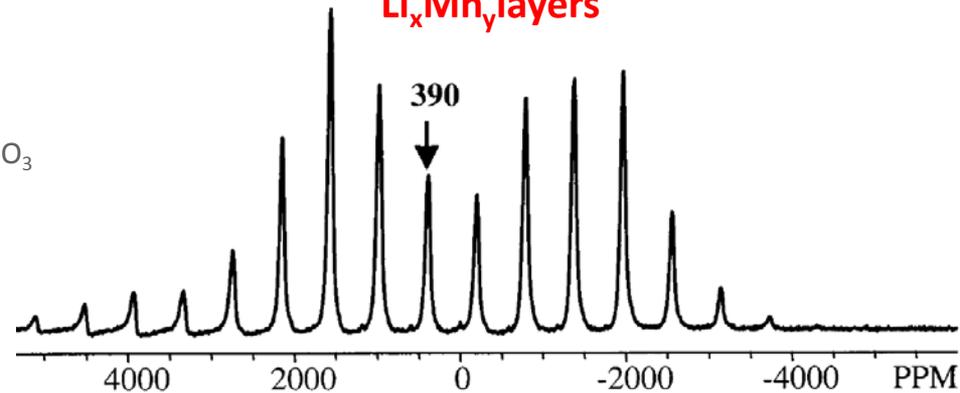
H⁺ insertion

Suggested mechanism for oxygen removal from Li₂MnO₃ structure and the exchange between Li⁺ and H⁺



²H MAS NMR

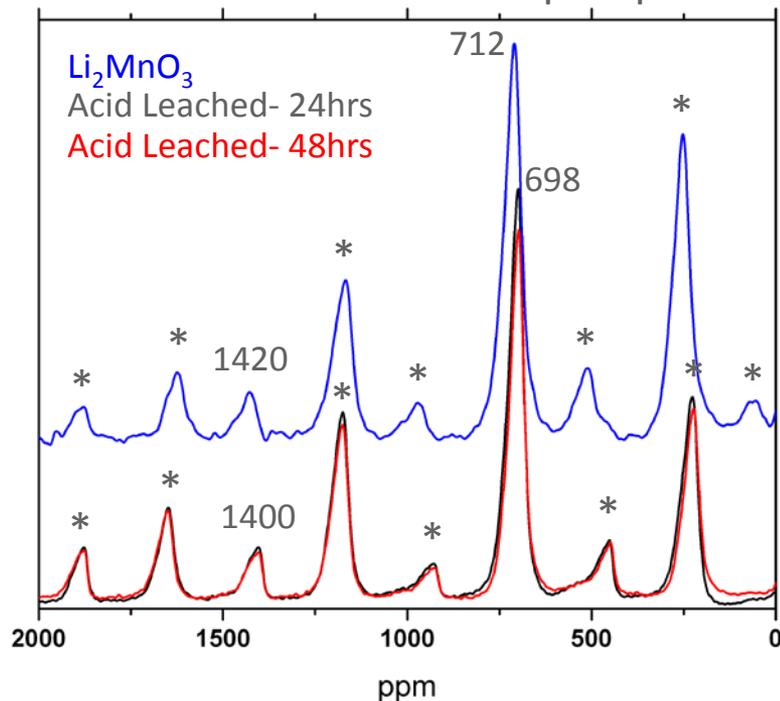
Single deuteron environment bind to intact Li_xMn_y layers



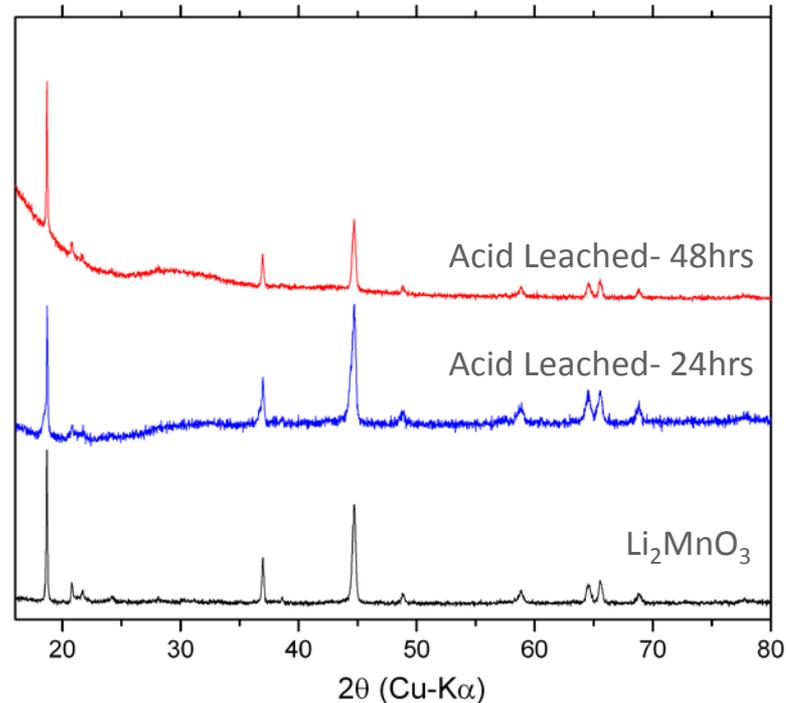
Detection of ^2H in Electrode Materials: Acid Leaching

- Deuterium (proton) insertion into structure (with some removal of Li) is possible for Li_2MnO_3 using DNO_3

^6Li MAS NMR at 35 kHz spin speeds



Lab. XRD

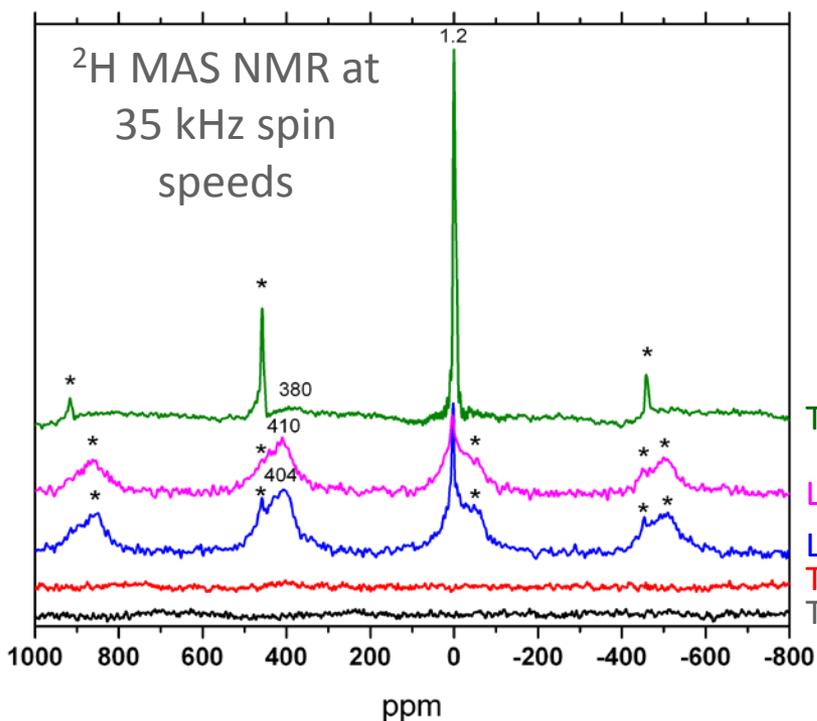


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Detection of ^2H in Electrode Materials: Acid Leaching

- Deuterium (proton) insertion into structure (with some removal of Li) is possible for Li_2MnO_3 using DNO_3
- Toda HE5050 is found to be resistant to acid leaching and deuterium insertion, rather undergoes surface modification/ ^2H bearing species



Toda 48hr D_2SO_4 treated

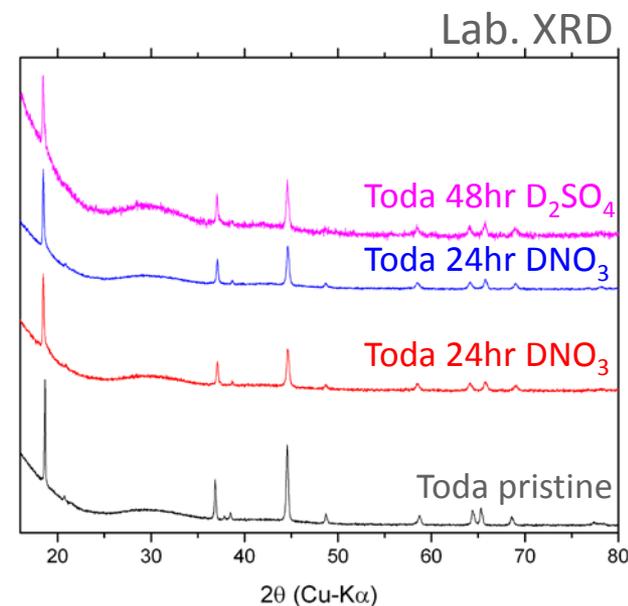
Li_2MnO_3 48hr DNO_3 treated

Li_2MnO_3 24hr DNO_3 treated

Toda 48hr DNO_3 treated

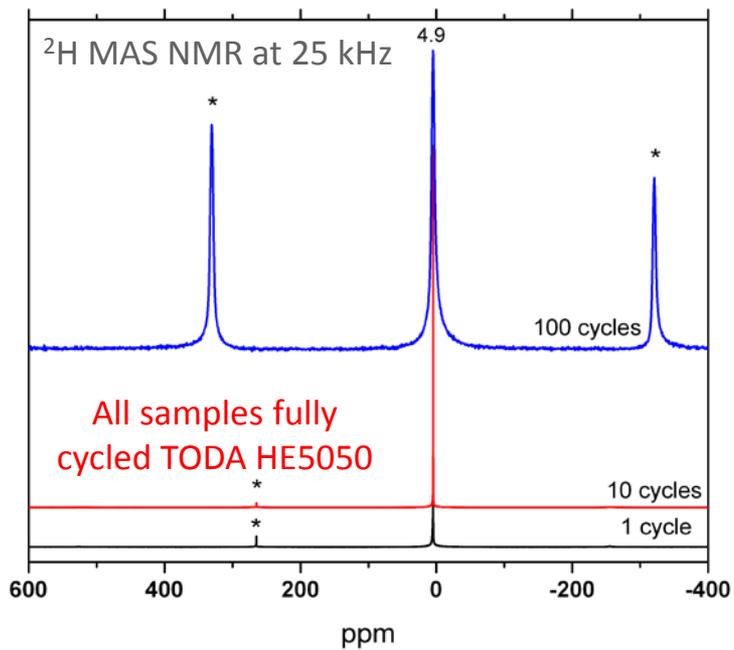
Toda 24hr DNO_3 treated

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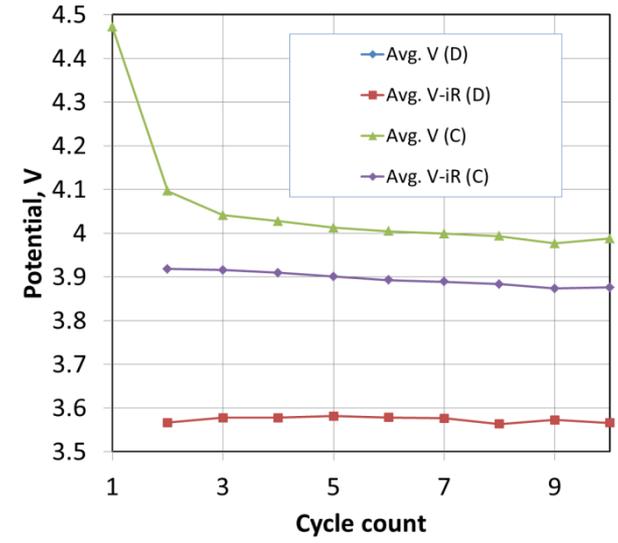


Electrochemical insertion of ^2H ?

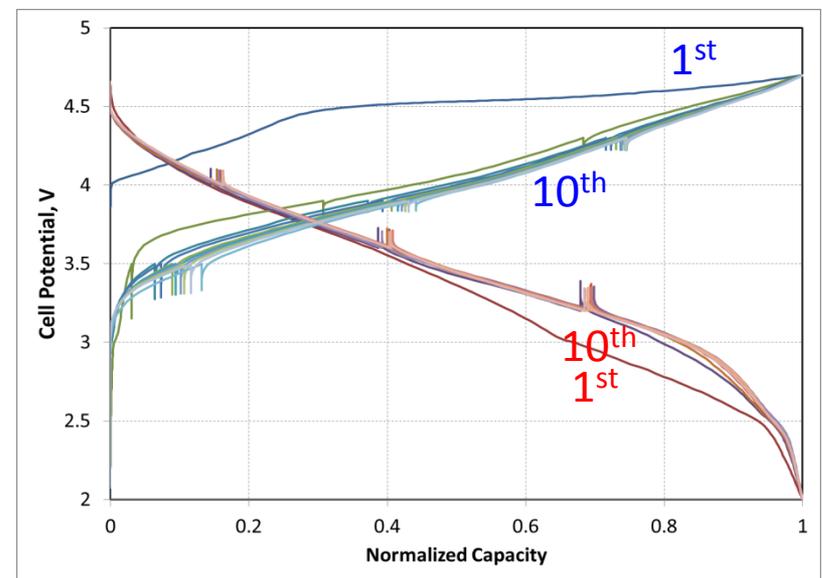
- No structural ^2H detected after cycling for Toda HE5050 (Voltage Fade present)
- Significant accumulation of diamagnetic (surface) deuterium bearing species detected consistent with impedance rise and SEI build-up



* indicates spinning sidebands due to MAS

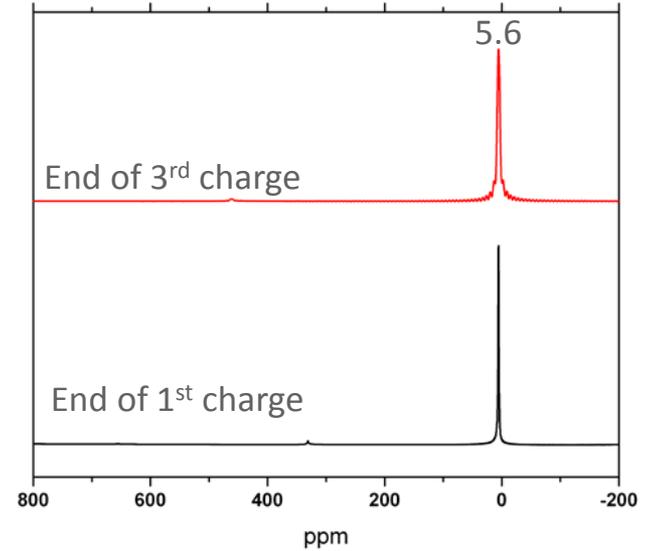
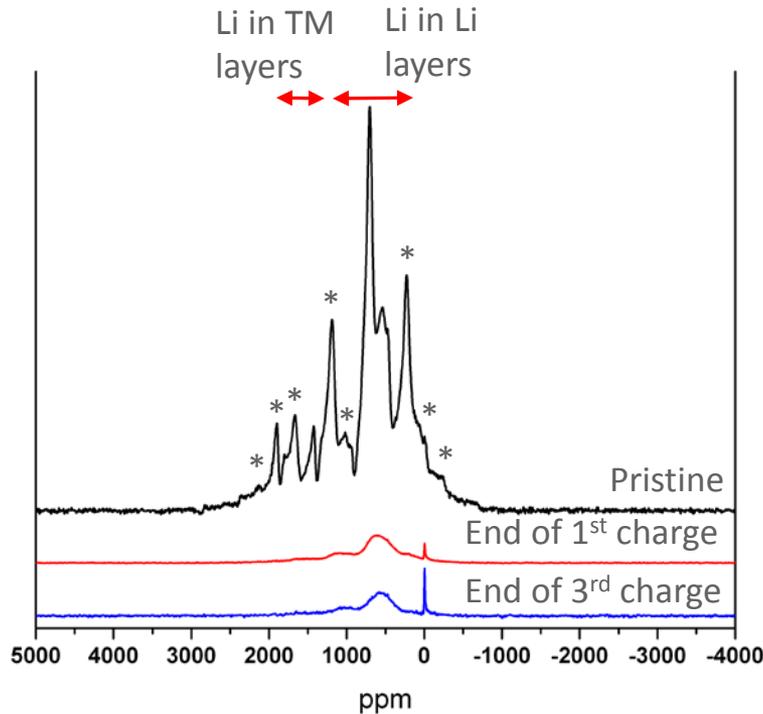


Voltage profile of TODA HE5050 after 10 cycles

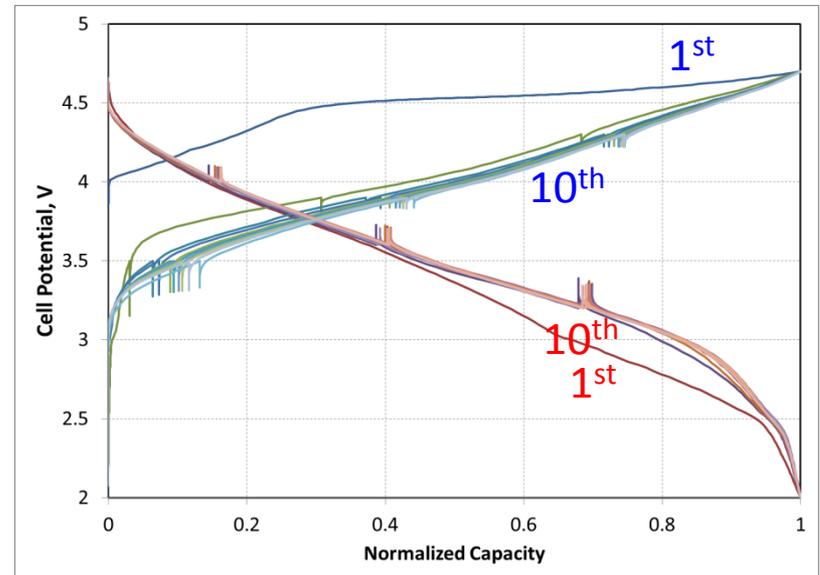


Electrochemical insertion of ^2H ?

- No structural ^2H detected after cycling for Toda HE5050 (Voltage Fade present)
- At fully charged states > %90 of Li removed with no structural ^2H accumulation



Voltage profile of TODA HE5050 after 10 cycles

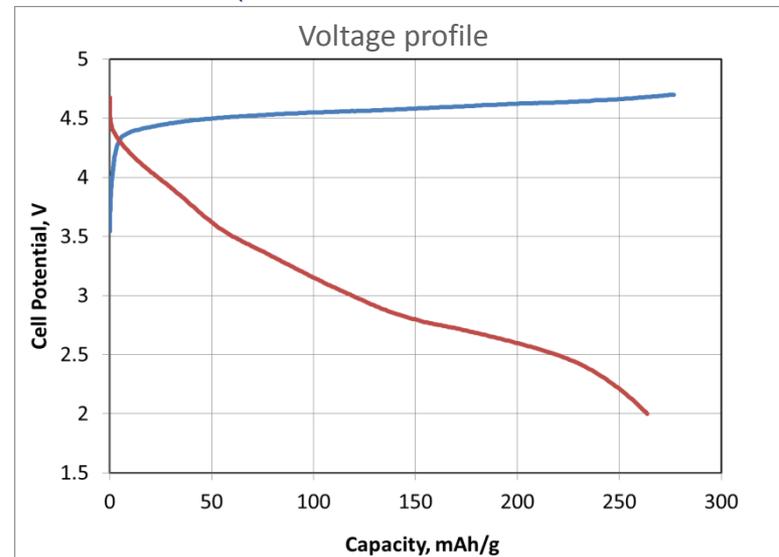


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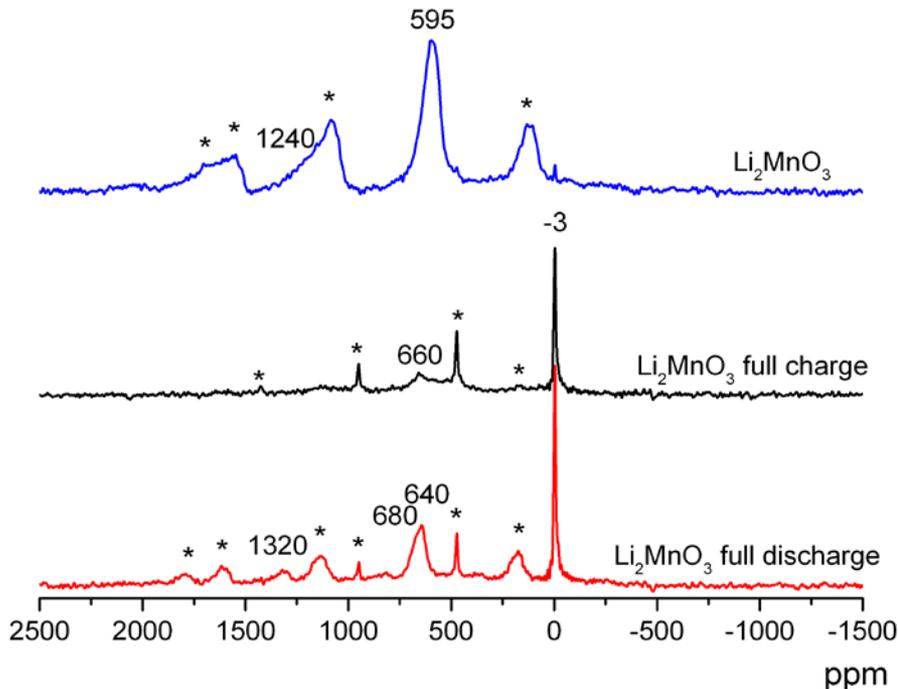


Electrochemical Activity of Disordered (low T synthesized) Li_2MnO_3 ?

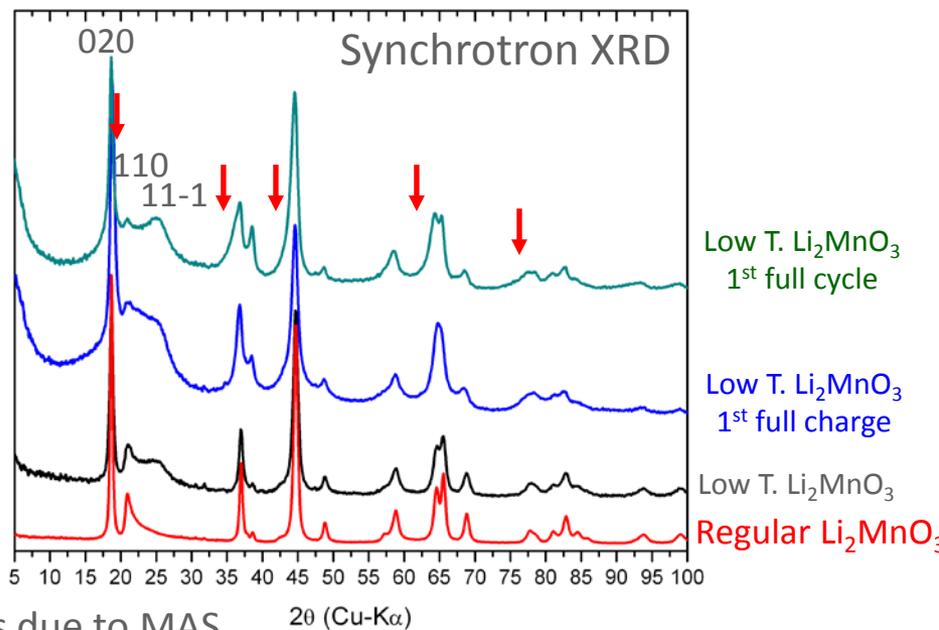
- Where does 1st cycle capacity coming from ?
 - NMR shows 95% "real" Li removal !!!
- Partially reversible (%45, for 1 cycle only) ^6Li extraction detected via NMR
- Electrochemistry: 1st cycle is %95 reversible



^6Li MAS NMR

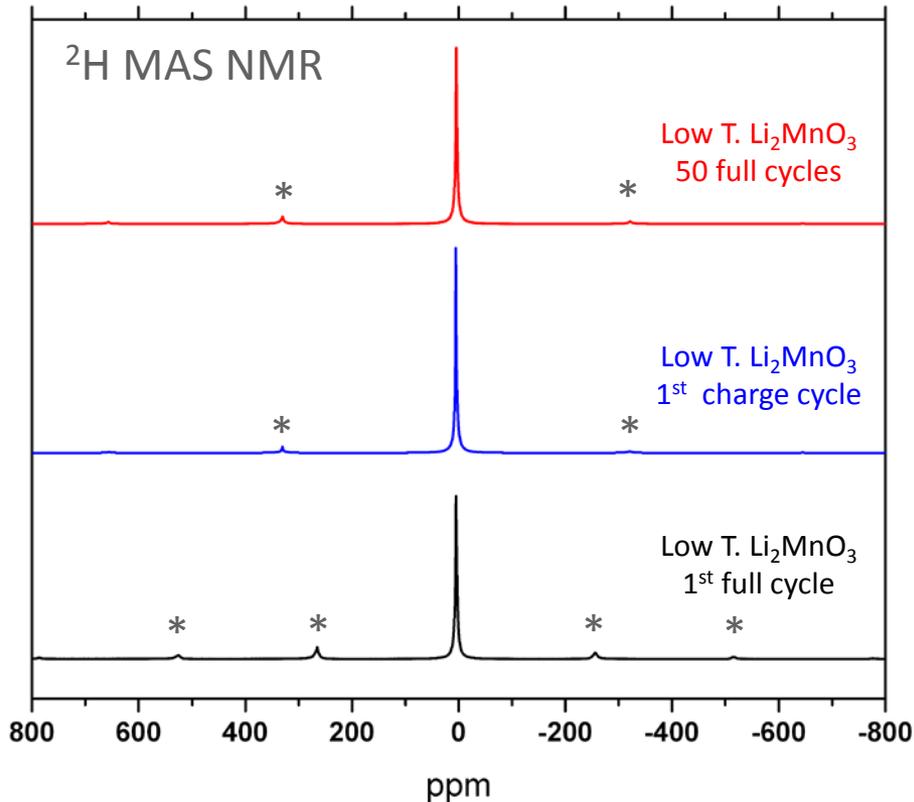


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Protons involved in the so called capacity ?

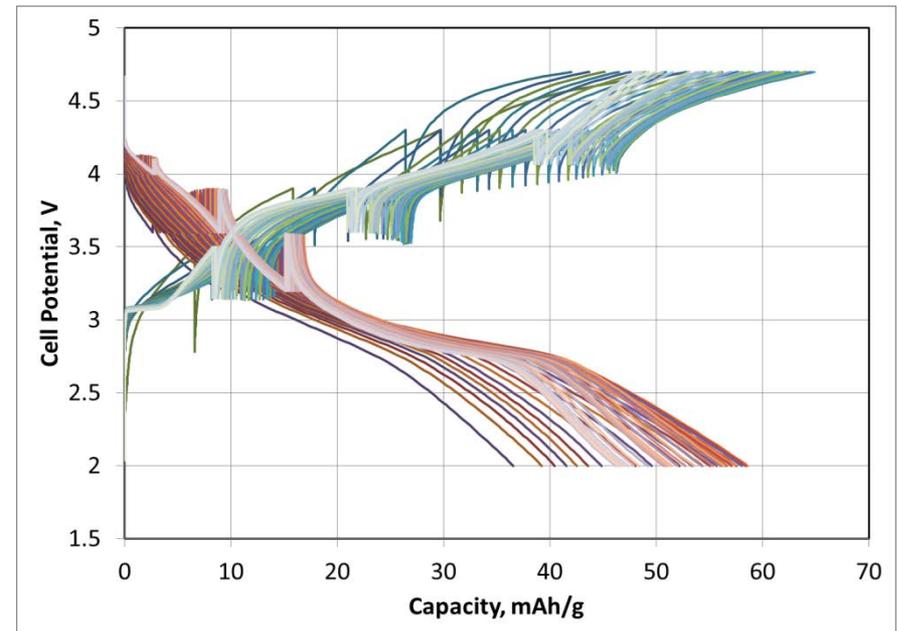
- No structural ^2H detected in cycled samples



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- Non-structural (i.e. surface) protons is the most likely the source of D. Aurbach findings

Voltage profile of Li_2MnO_3 (50 cycles)
1st cycle not shown



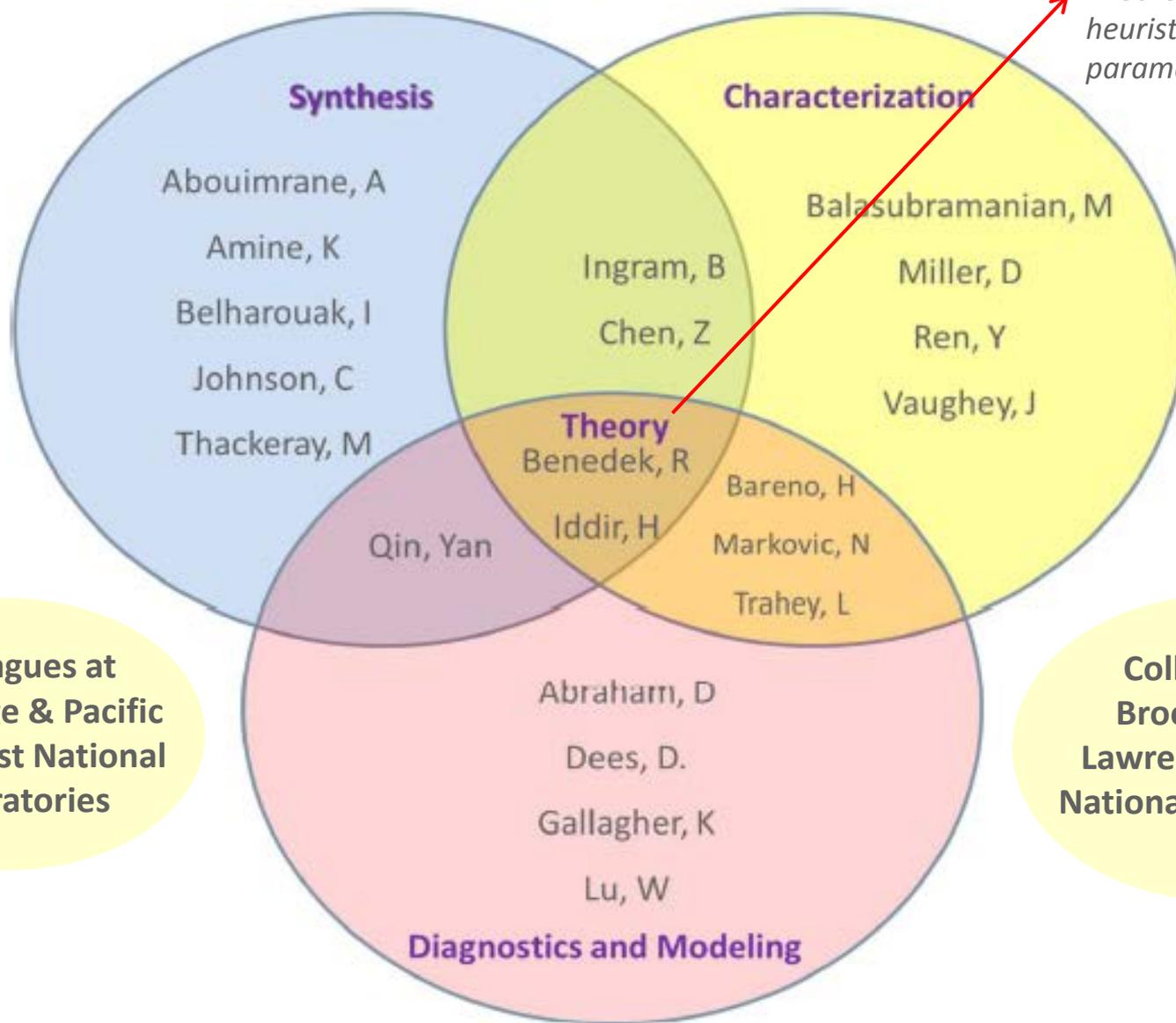
Future work

- Use quantitative ^6Li NMR data along with complimentary Neutron Diffraction/PDF and high resolution EPR (electron paramagnetic resonance) to directly answer the following fundamental questions:
 - What are the Li-TM orderings, clusters ? Domain sizes ?
 - What is the short/long range structure of the charged electrode ?
 - What is the nature of the TM re(dis)ordering upon cycling ? How does these correlate with voltage fade ?
- Details on the quantitative NMR study: State of charge and discharge NMR on cycled electrodes using fully enriched cells (^6Li metal, ^6Li enriched cathodes and $^6\text{LiPF}_6$ electrolyte; all components acquired and electrochemistry currently ongoing) using a 300 MHz 65kHz spinning speed capable NMR system.



Collaborations

With Roy Benedek and Hakim Iddir :
Theoretical input and heuristic calculations of paramagnetic NMR shifts



Colleagues at
Oak Ridge & Pacific
Northwest National
Laboratories

Colleagues at
Brookhaven &
Lawrence Berkeley
National Laboratories



Characterization Effort Summary

- Evidence found for deposition of non-structural deuterium bearing (presumably surface) species. Deposit accumulation with extensive cycling
- Structural ^2H insertion is not a significant process, evidence suggests a catalytic role (i.e. Feng/Ammundsen/P. Bruce mechanism) rather than an electrochemically active one, and likely has minimum effect in voltage fade phenomenon.
- 1 cycle electrochemical activity of disordered Li_2MnO_3 is real (via Li removal/insertion) could be analogous to Li_2MnO_3 component in voltage fade composites (LMRNMCs).
- Significant Li-TM disordering observed for LMRNMC, which is synchronous to hysteresis and voltage fade. Study in preliminary stages, and ongoing.
- A manuscript is currently being prepared summarizing these results:
 - B. Key, F. Dogan, J. Croy, M. Slater, C. Johnson, J. T. Vaughey, *manuscript in preparation*, 2013

Acknowledgements

- Support for this work from DOE-EERE, Office of Vehicle Technologies is gratefully acknowledged
 - David Howell, Peter Faguy and Tien Duong
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 - Tony Burrell and Mali Balasubramanian
 - Roy Benedek and Hakim Iddir for the new collaboration started:
Theoretical input and heuristic calculations of paramagnetic NMR shifts