Examining Hysteresis in Li- and Mn-Rich Composite Cathode Materials

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Project ID# ES189

Overview

Timeline

- Start: October 2012
- Finish: September 2013

Barriers

- Development of a safe cost-effective PHEV battery with a 40 mile all electric range that meets or exceeds all performance goals
  - Interpreting complex cell electrochemical phenomena
  - Identification of cell degradation mechanisms

Budget

- Total project funding
  - 100% DOE
- FY2013: $290K

Partners (Collaborators)

- ANL Voltage Fade Team

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

- Characterization of hysteresis and path dependence in OCV curve (Dec 2012) **complete**
- Determination of mechanism of hysteresis phenomenon in LMR-NMC (Sept 2013) **on target**
- Initiate OCV numerical model for LMR-NMC (Sept 2013) **on target**

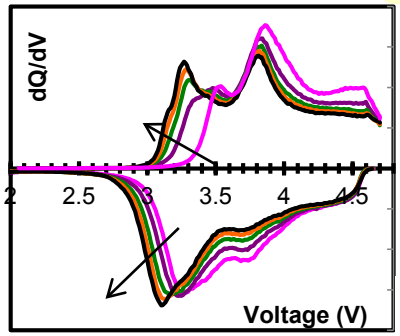
Approach

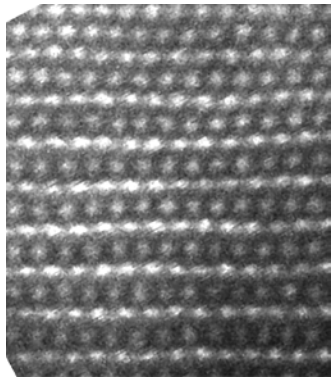
- Multi-institution effort to identify factors that contribute to voltage fade in lithium– and manganese– rich NMC oxides (LMR-NMC)

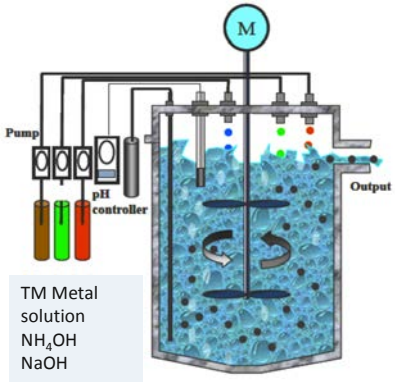
Electrochemical Characterization & Modeling

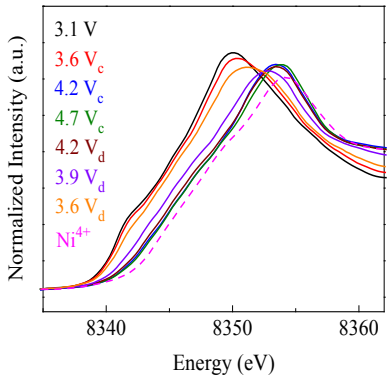
Physicochemical Characterization & Atomistic Modeling

Oxide Synthesis & Surface Modification





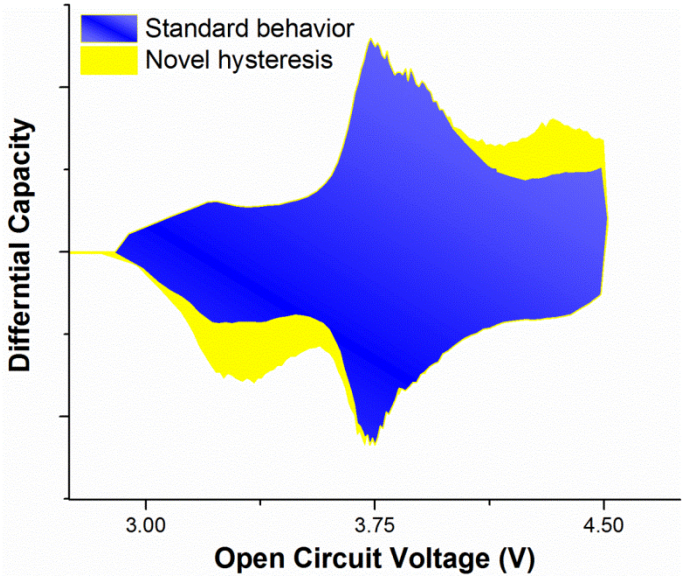


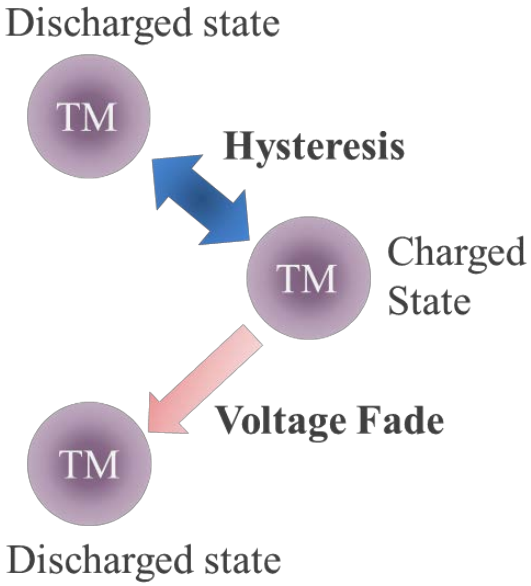


Suggest/implement approaches to mitigate voltage fade

Major Accomplishments and Technical Progress

- Identified that hysteresis in LMR-NMC is actually a 1 V hysteresis in 10-15% of the lithium content
- Correlated this hysteresis behavior to the voltage fade phenomenon
- Proposed overall mechanism for electrochemical observations: reversible and irreversible transition metal ion (TM) migration

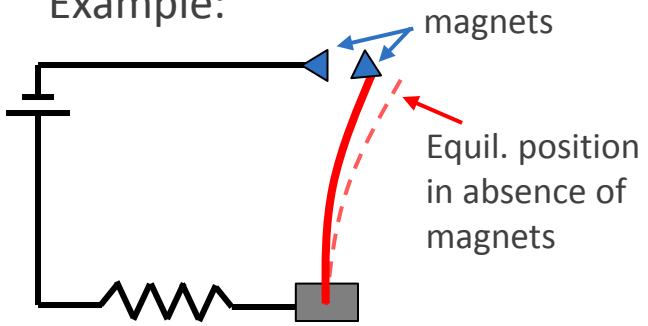




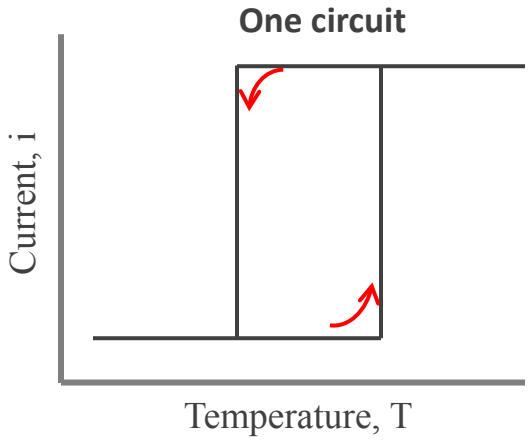
Hysteresis in battery electrode materials

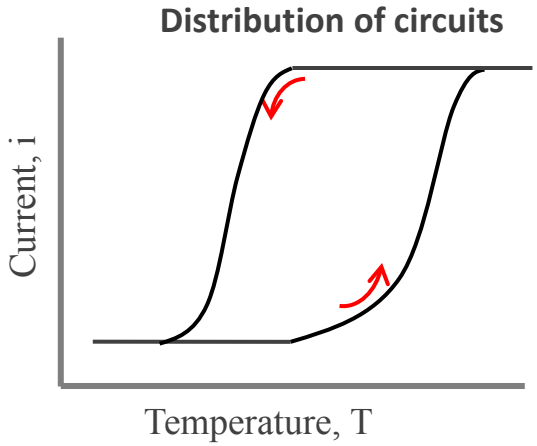
- Exists in many different systems
- Origin often difficult to discern
  - Kinetically driven
  - Metastable states
  - Ensemble of particles
- Consider Everett's General Approach
  - Underlying physics don't matter
  - Independent domains, which at least some can exist in a **metastable state**

Example:



Bimetallic wire opens and closes switch depending on the temperature (T) in room. Hysteresis is observed in measured current between the critical "closed" T and "open "T" due to competition between strain in wire and attraction of magnets





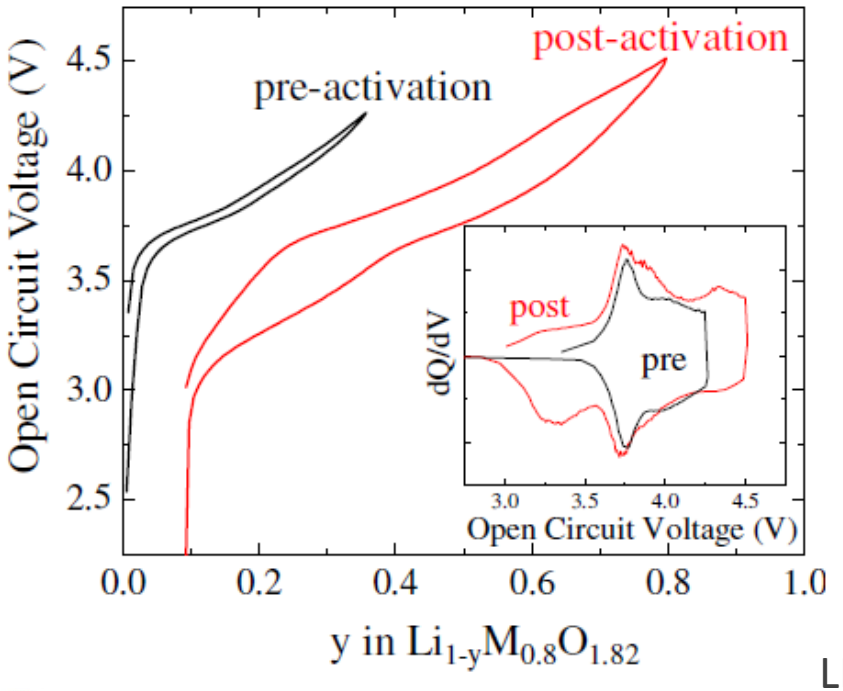
Everett and Whitton *Trans. Faraday Soc.* 179 (1952)

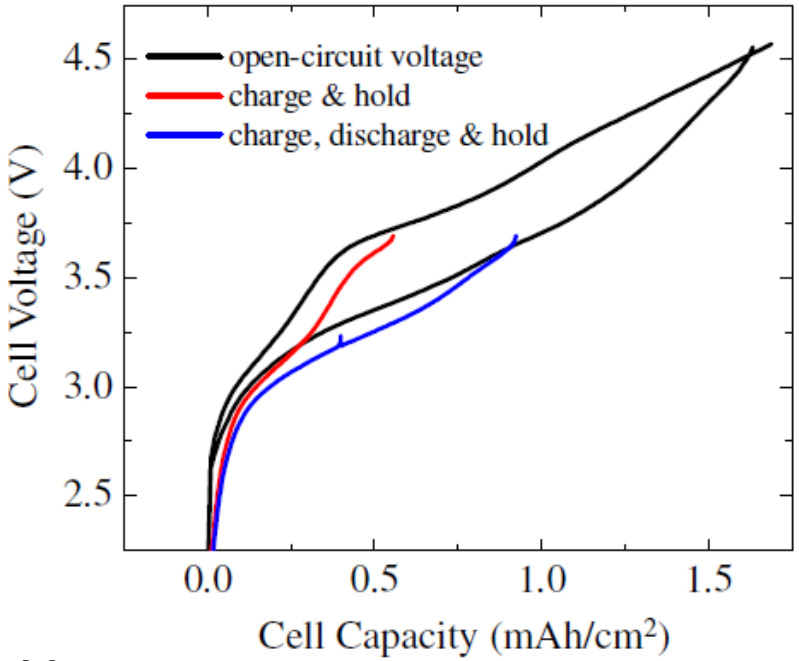
Cathode materials examined

- HE5050 (Toda)
  - $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.10}O_2$ or $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Mn_{0.31}Co_{0.25}O_2$
  - Synthesis: hydroxide co-precipitation, then calcination with Li_2CO_3 (?)
- Li_2MnO_3_Ni (Argonne)
  - $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$ or $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.5}Mn_{0.5}O_2$
  - Synthesis: Li_2MnO_3 treated with $NiNO_3$ in Nitric Acid, then calcination
- LLS_Mg (Argonne)
  - $Li_{1.25}Mn_{0.65}Ni_{0.33}Mg_{0.02}O_{2.28}$ or $0.94\{0.3Li_2MnO_3 \bullet 0.7LiMO_2\} \bullet 0.06Li_{0.5}M'O_2$
  - Synthesis: oxalate co-precipitation, then calcination with Li_2CO_3
- Cell configurations
  - Lithium half cells
  - 1.2 M $LiPF_6$ in EC/EMC (3:7 wt), no additives in 2032 coin cell
  - All cycling data at least in duplicate at room temperature

Measurement of Open-Circuit Voltage Function

- Use slow cycling or GITT study to determine open-circuit voltage as function of lithium concentration
- Large stable hysteresis observed in LMR-NMC cathodes after activation of Li_2MnO_3 domains in $xLi_2MnO_3(1\text{-}x)LiMO_2$
- Hysteresis loop does not close even after seven day hold at 3.7 V

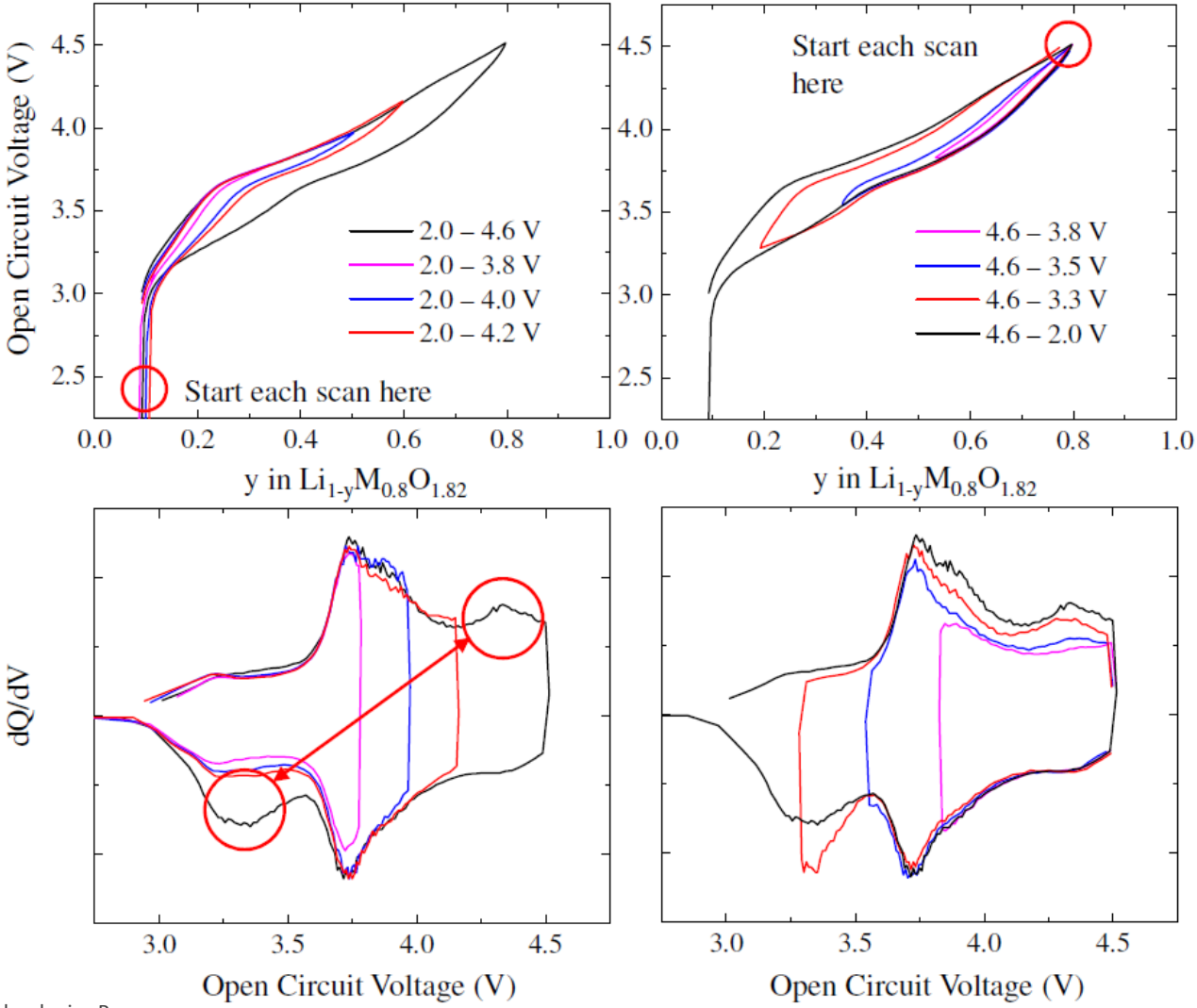




LLS_Mg

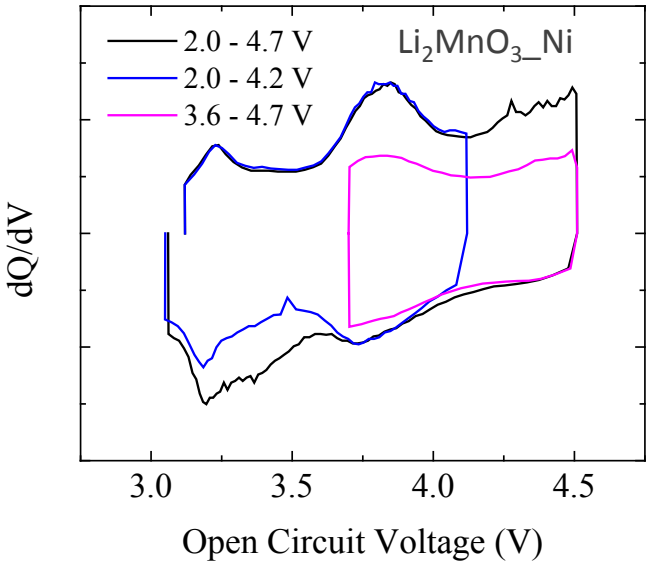
Hysteresis and Path-Dependence in OCV Curve

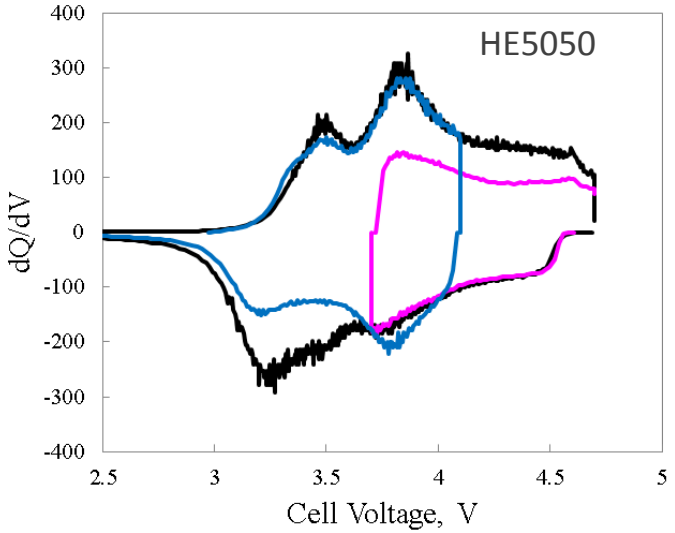
- Scanning curves shift from one boundary to other depends on voltage



Other LMR-NMC materials exhibit 1 V hysteresis

- Increasing Li_2MnO_3 content and adding Cobalt both add complexity to the open-circuit voltage vs SOC function.

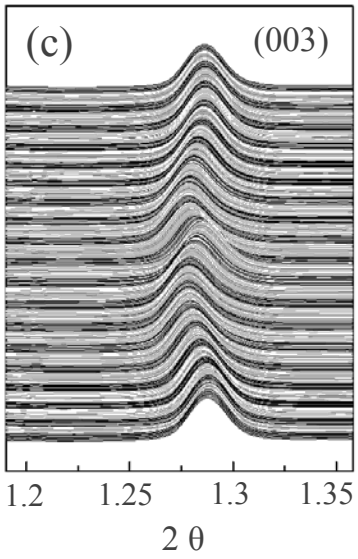


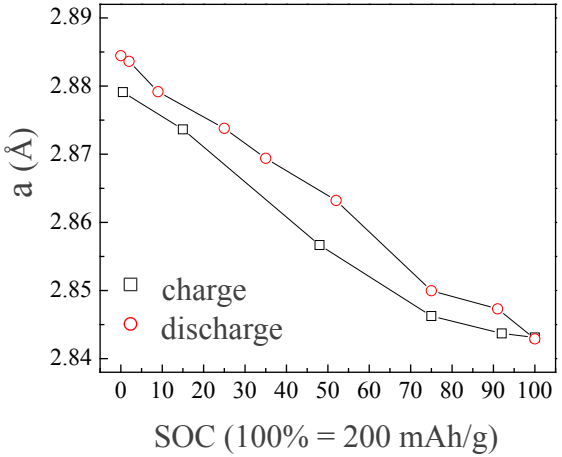


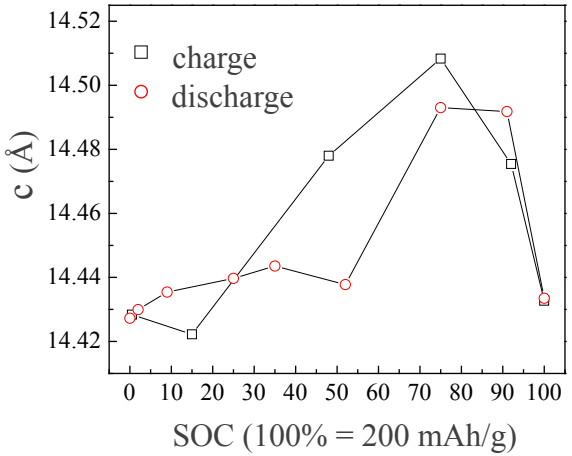
- Post-activated dQ/dV suggests lithium removed above 4.3 V but does not fill these sites until 3.3 V on discharge
- Not an impedance issue as still exists at 85 °C (and 7 day hold data)
- Capacity associated with hysteresis around 10-15% of total lithium content
- Could vacant sites be blocked by migrating TMs?

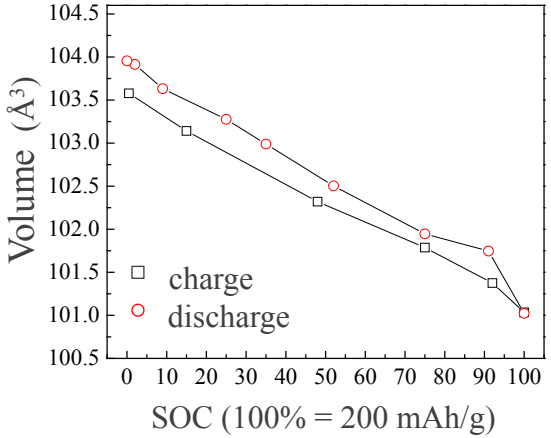
In situ and Ex situ (APS) Synchrotron X-ray Diffraction

- Behavior appears similar to $LiNi_{0.5}Mn_{0.5}O_2$
  - No strong evidence observed for ~1 V electrochemical hysteresis



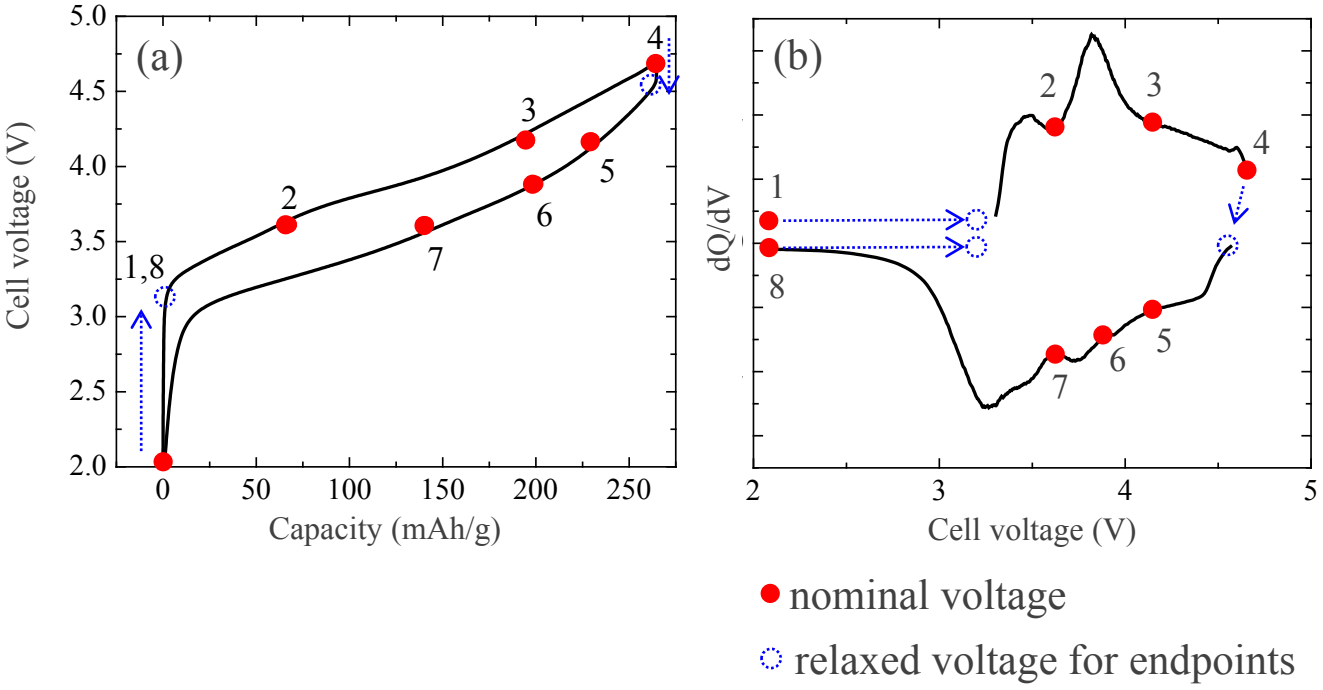






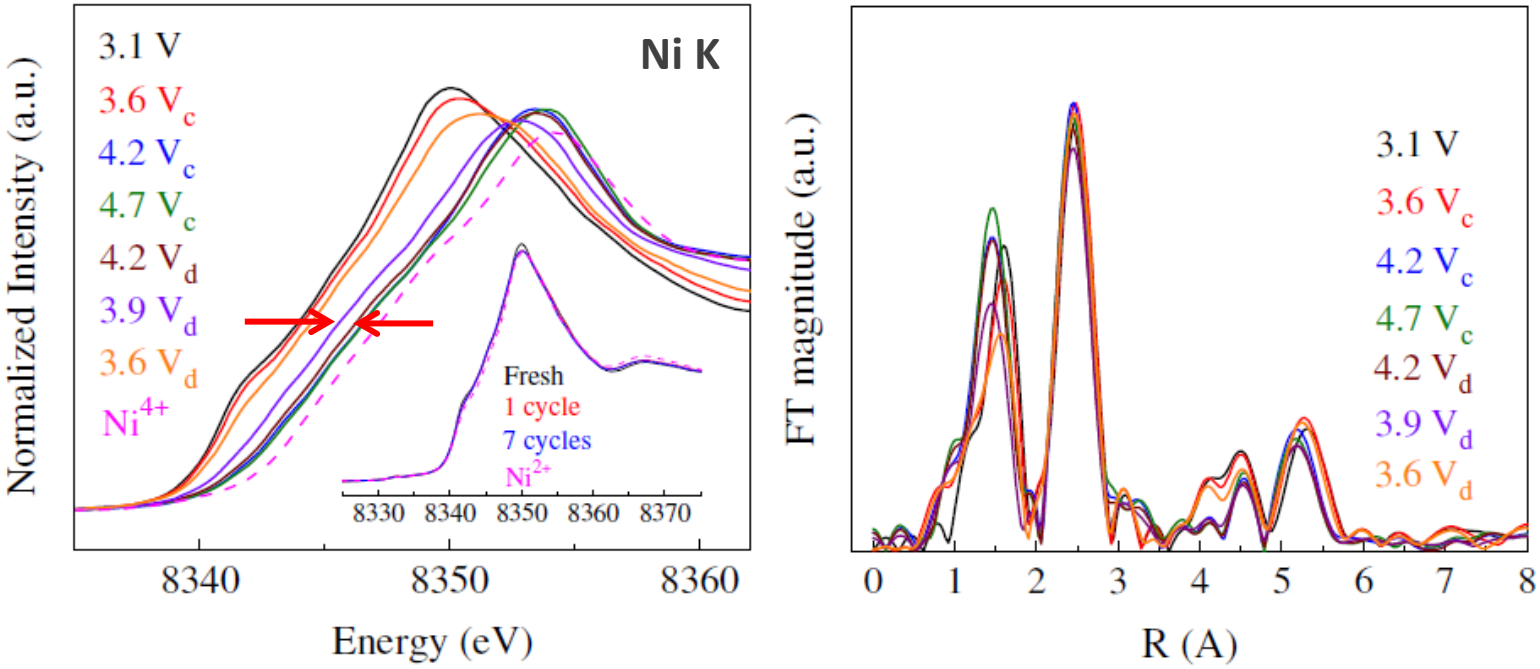
X-ray Absorption Spectroscopy: HE5050

- Examine oxidation and coordination at different states of lithiation
  - HE5050 for 7th cycle 2-4.7 V vs Li at 22 °C
- Ex-situ measurements completed at Advanced Photon Source



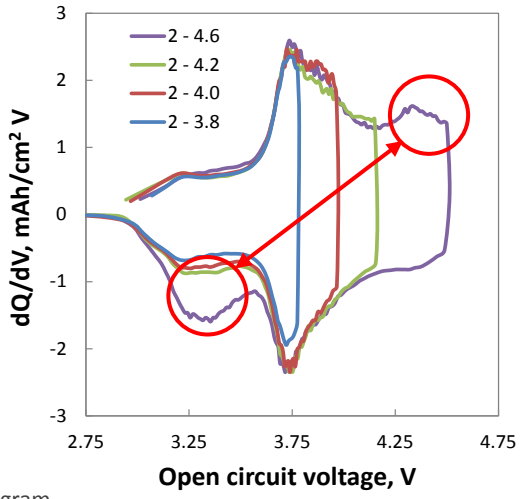
Spectroscopic Verification of Hysteresis

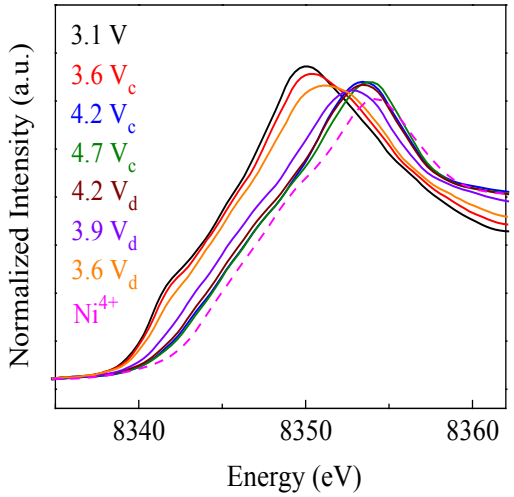
- Samples charged and discharged to 4.2 V have similar XAS
- Samples charged and discharged to same **SOC** are different
  - 65 mAh/g Li remaining = 75% SOC = 4.2 V charge or ~3.9 V discharge
  - Nickel XANES clearly shows lower oxidation state for 3.9 V on discharge



Summary of observations from characterization

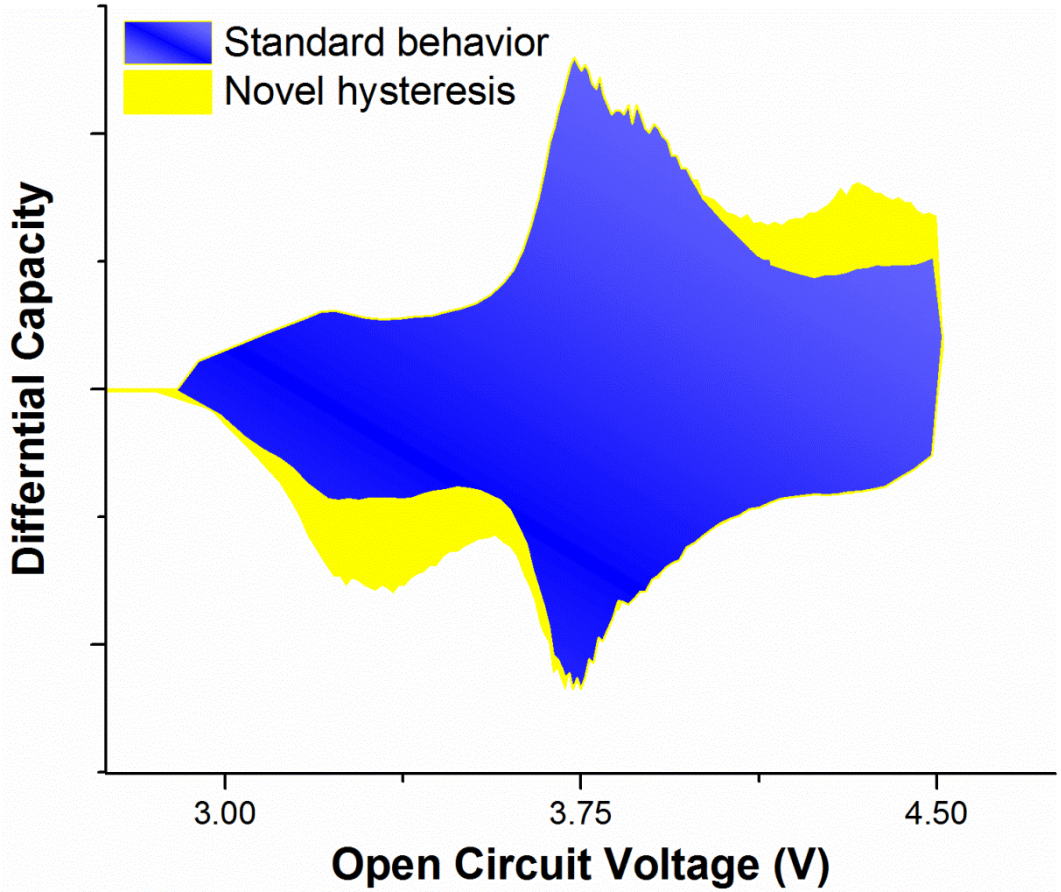
- 1 V hysteresis for 10-15% of lithium content
- No obvious structural changes from XRD
- XAS shows hysteresis in Nickel oxidation state
  - Nickel more reduced during discharge than charge at 75% SOC
- Remaining questions (only a few listed here)
  - Where is the additional capacity originating? (Mn(V) etc)
  - Spectroscopic detection of reversible TM migration (Neutrons)





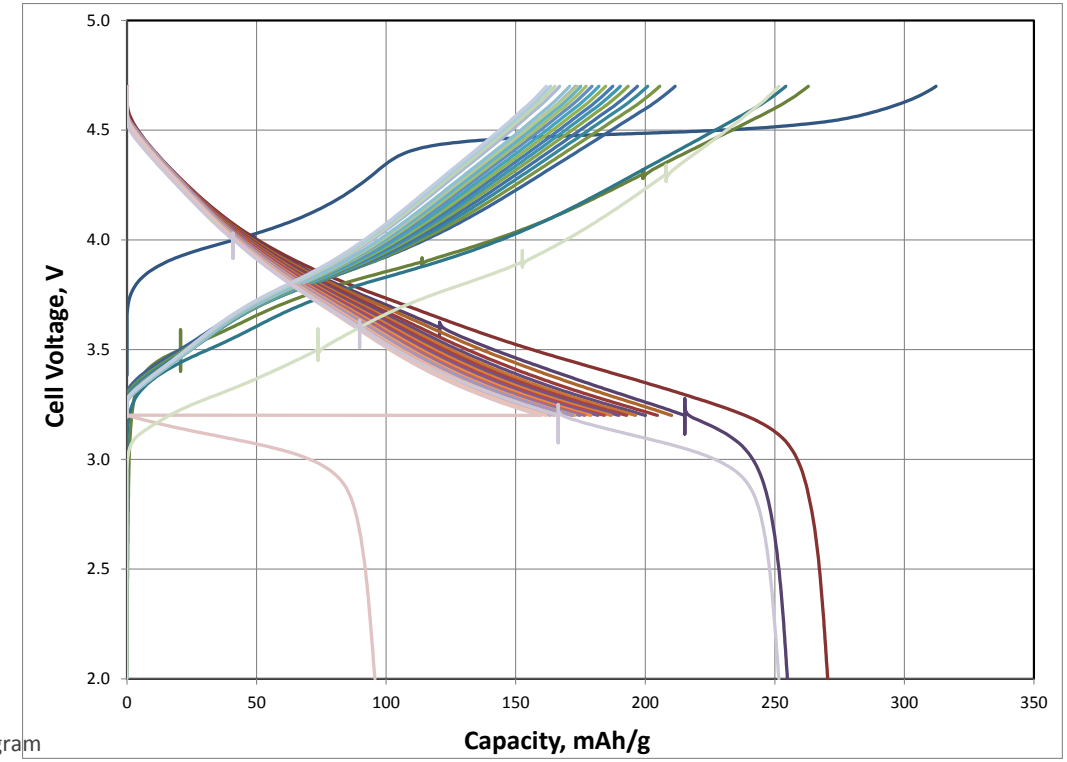
Proposed hysteresis model in LMR-NMC electrodes

- Majority of intercalation similar to traditional materials
- 10-15% of the lithium exhibits a ~1 V hysteresis



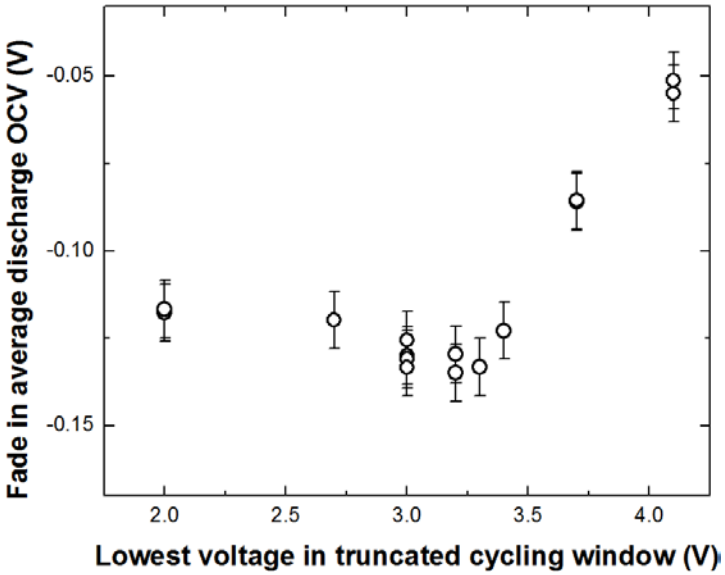
Is hysteresis related to voltage fade?

- Examine by cycling HE5050 in different voltage windows
  - One activation cycle, then one average voltage measurement
  - 20 cycles in truncated window, all have 4.7 V upper potential
  - Measure average voltage in full voltage window
  - 30°C, 10 mA/g 1st cycle, 20 mA/g for all others

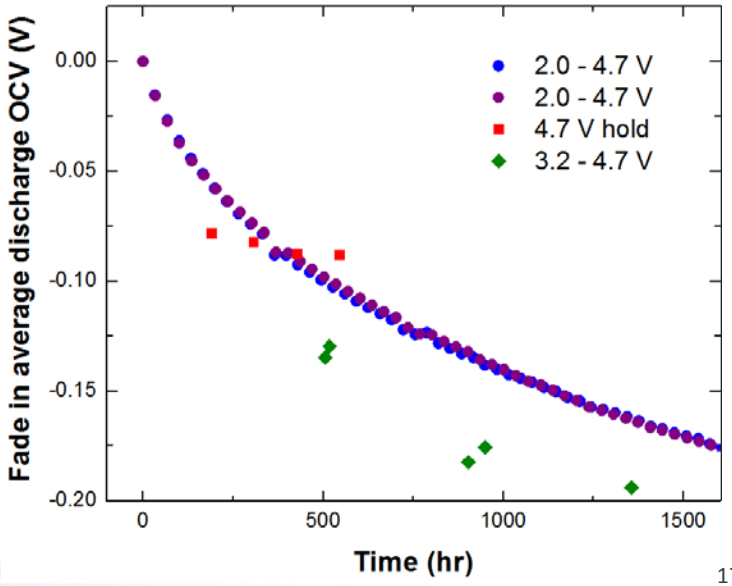


Cycling accelerates fade compared to calendar hold

- Cycling up to 4.7 V with varying lower cutoff voltage
- Maximum voltage fade occurs with lower cutoff around 3.0-3.3 V
  - Does that mean calendar time is everything? (see bottom right)
- Slight improvement when cycled to less than 3.0 V, current hypothesis unproven

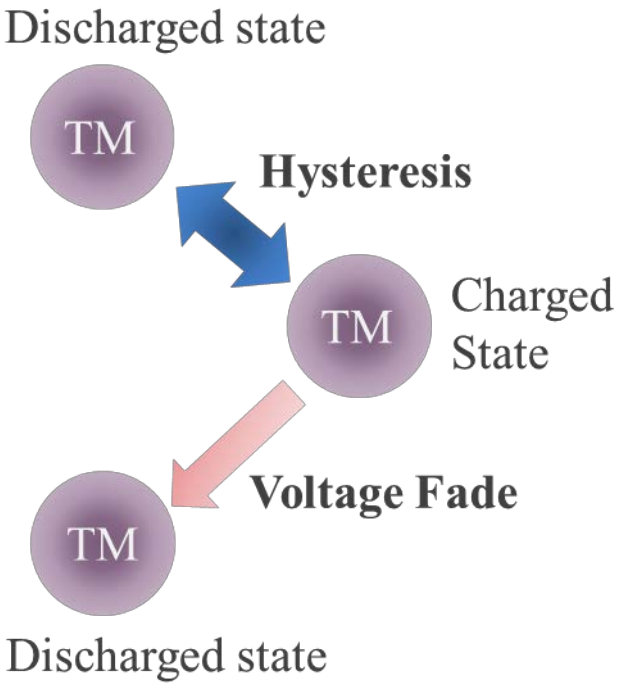


- Calendar induced voltage fade does not match cycling
- Lower cut-off voltage of 3.0 to 3.3 V is worst case



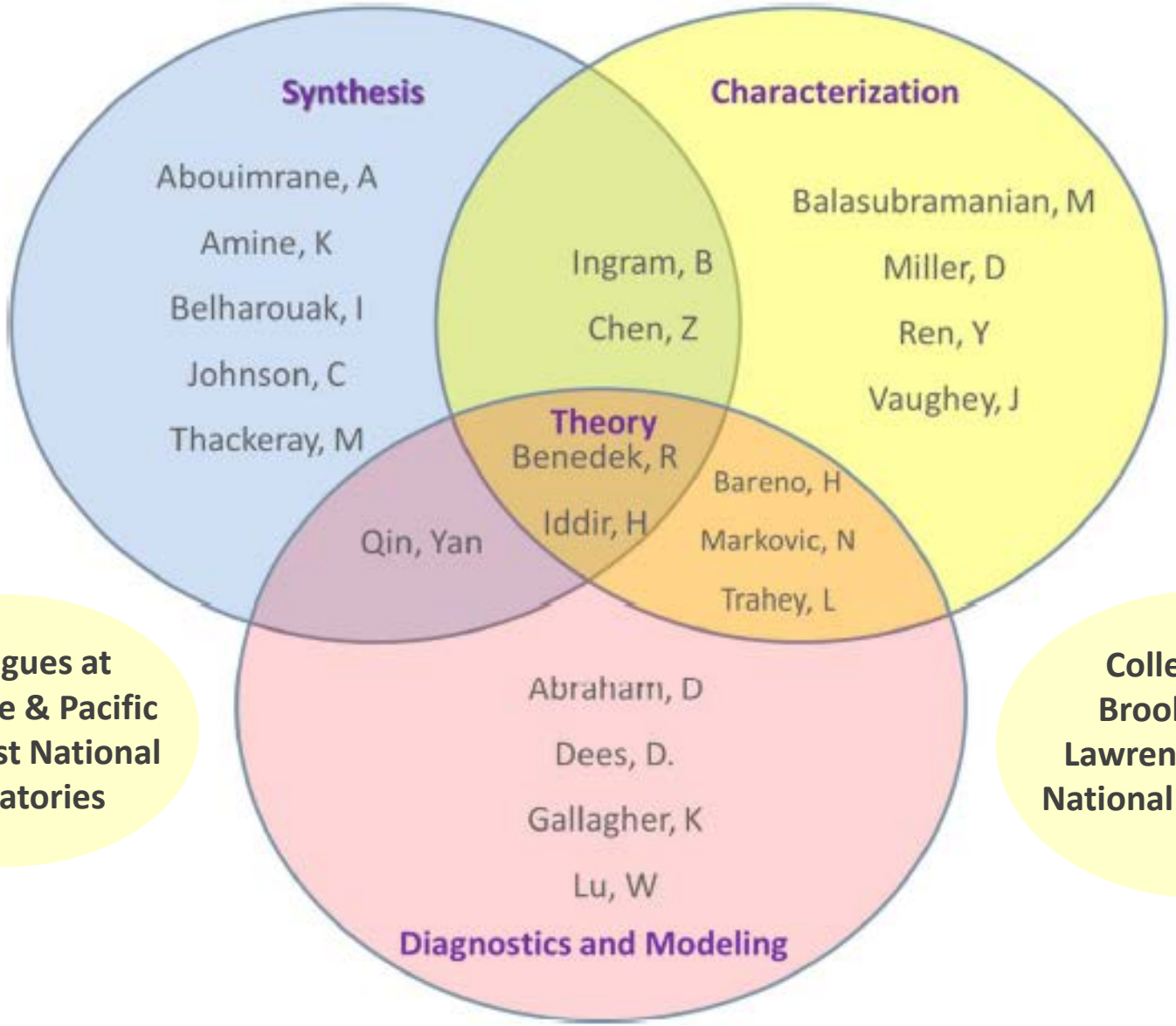
Hysteresis and Voltage Fade Cartoon

- Structural rearrangement of layered lithium metal oxides
  - Transition metal moves in/through tetrahedral site in Li layer
  - Formation of Li^{+}---TM^{z+} dumbbells[1,2] (and possibly Li^{+}---Li^{+})
  - Exact voltage fade state still uncertain – redox near 3.1 V so not pure $LiMn_2O_4$ spinel but rather a different cubic environment with Li in octahedral sites
- Oxidation reaction around 4.2 V
  - Lithium from tetrahedral sites
  - Vacancy ordering
  - Li^{+}---TM^{z+} dumbbell formation?
- Reduction reaction around 3.3V
  - Lithium into octahedral sites
  - Li^{+}---TM^{z+} annihilation?



1. Reed, Ceder, Van der Ven, *Electrochem Solid St. Lett.* **2001**, 4, A78-A81
2. Armstrong et al. *Chem. Mater.* **2004** 16, 3106-3118

Collaborations



Colleagues at Oak Ridge & Pacific Northwest National Laboratories

Colleagues at Brookhaven & Lawrence Berkeley National Laboratories

Future Work

- Determination hysteresis – voltage fade mechanism in LMR-NMC positive electrode materials
  - Collaborate across the entire Voltage Fade inside/outside Argonne
  - Vary Ni to Mn ratio
  - Use solid state NMR
  - Neutron analysis for tetrahedral site occupation
- Initiate OCV numerical model for LMR-NMC
  - Capture OCV behavior in a volume averaged numerical model
  - Model should account for both hysteresis and voltage fade

Hysteresis and Voltage Fade Summary

- 1 V hysteresis in ~10-15% of the lithium content
  - Dumbbell formation > 4.0 V on charge
  - Dumbbell annihilation ~ 3.3 V on discharge
- Cycling accelerates voltage fade faster than calendar testing
- Maximum voltage fade occurs at the lower potential cut-off correlated to hysteresis
- Hypothesis: TM migration involves
  - Fast reversible TM migration between original & metastable state
  - Slow irreversible TM migration from metastable to faded state

Acknowledgements & Collaborators

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Collaborators:

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