Cathode Synthesis and Voltage Fade: Designed Solutions Based on Theory

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Project ID: ES190

Overview

Timeline

- Start – Mar. 2012
- Finish – Sep. 2015
- Percent complete: 30%

Budget

- Total project funding in FY2013: $335K
- 100% DOE

Barriers

- Loss in energy density with cycling (voltage fade or VF)
- Cost
- Rate capability
- Low temperature performance

Partners

- Lead P.I. – C. S. Johnson
- Collaborators (Argonne):
  - E. Lee, M. Slater (CSE Argonne)
  - R. Benedek (CSE Argonne), H. Iddir (MSD Argonne)
  - Ali Abouimrane, Ilias Belharouak, Ira Bloom, Jason Croy (all CSE Argonne)
  - M. Balasubramanian (APS Argonne)
  - S. Hackney (Michigan Technological University (MTU))

Relevance

- New cathode materials are required to improve the energy density of Li-ion cells for transportation technologies.
- LMR-NMC suffers from a voltage drop, thus lowering the overall energy density during long-term cycling. This impedes its effectiveness as a new high-energy cathode material for PHEVs, and Evs.
- Synthesis of new materials with slight composition perturbations will assess effectiveness for improvements.
- In this work, we are comparing our synthesis results to theoretical predictions from First principles calculations. This will tie in theory to experiment.

Objectives

Synthesize Voltage Fade corrected cathode materials possessing high capacity and high-energy cathode materials that are **low cost, with high-thermal stability** for PHEVs & EVs

- The implementation of layered transition metal oxides to Li batteries is well established, but this task must meld theory & modeling to guide synthesis.
- Demonstrate viability of syntheses routes to make VF-free cathode materials
  - Effectively dope or substitute elements into $Li_2MnO_3 \cdot LiMO_2$ without changing the composite components such that high energy is lost.
- Perform both physical property and electrochemical property measurements
  - Cycle the material in Li half cells and show at least 40 cycles above 200 mAh/g
  - Conduct power rate tests and demonstrate a capacity of 200 mAh/g at C/1 rate
  - Evaluate the phase type of the material using microscopy methods
  - Measure the phase purity by XRD after multiple cycles to evaluate stability
  - Measure oxygen loss and oxygen content in materials

Milestones of FY13

- Evaluation of link between synthesis and theory/modeling — Completed
- Multiple synthesis routes to VF-free materials — On target
- Conduct synthesis of materials — On-going
- Investigation of physical and electrochemical properties — On-going
- Oxygen analysis of synthesized materials during first charge and subsequent cycling — Initiated

Approach: Synthesis Team – problem solving

$$xLi_2M'O_3 \bullet (1-x)LiMO_2$$

THE TEAMS and OUR THEMES:

A. Ilias – precursor synthesis and processing

• domain size and component segregation/integration

B. Chris – structure, doping and substitution, layer stacking sequence

• stop spinel formation, maximize pre-plateau capacity

C. Ali – surface events/coatings & doping

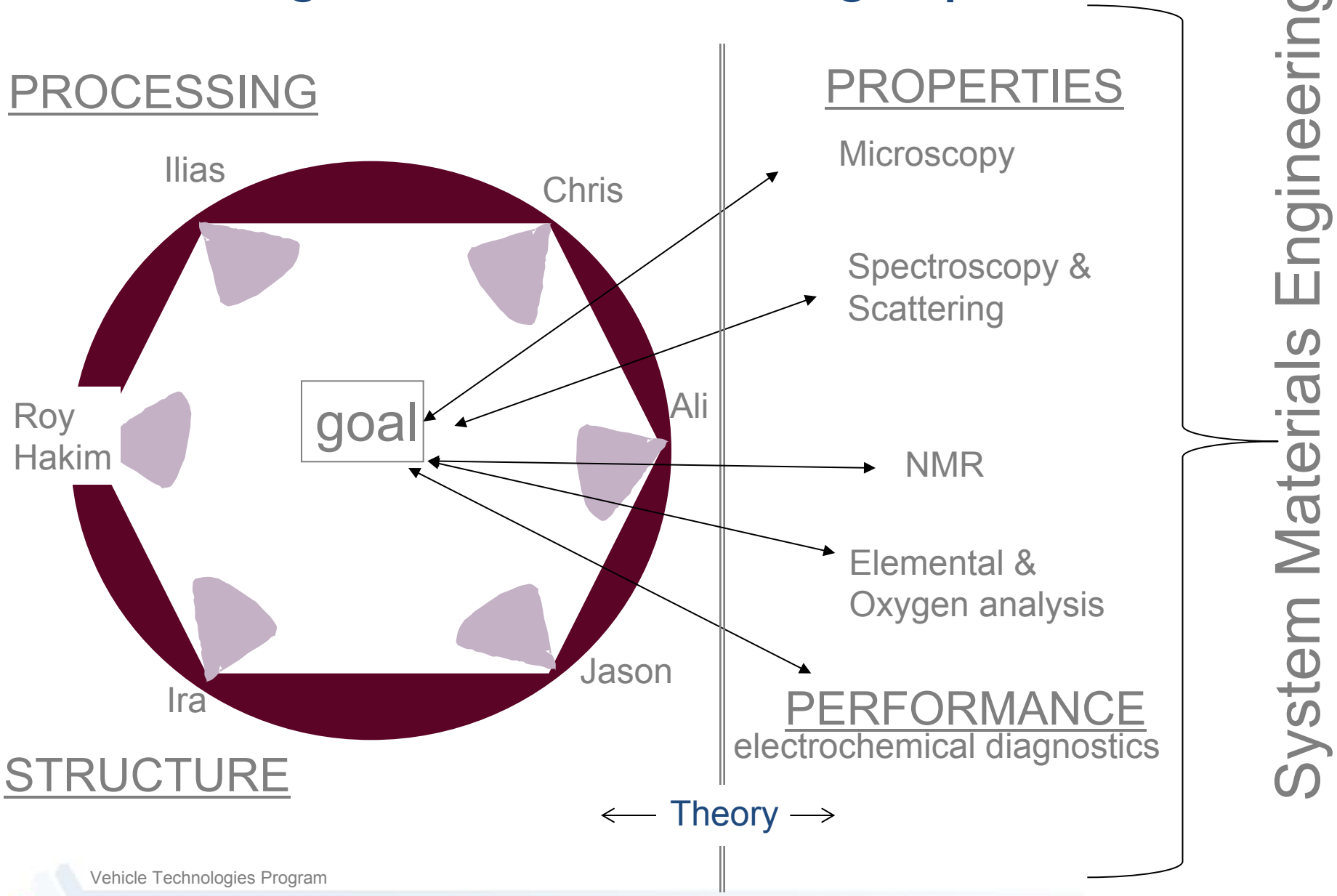
• control reactions initiated at surface; surface doping

D. Jason – component composition; new materials

E. Ira – phase space; home in on preferred compositions that show less VF

F. Roy & Hakim – theory

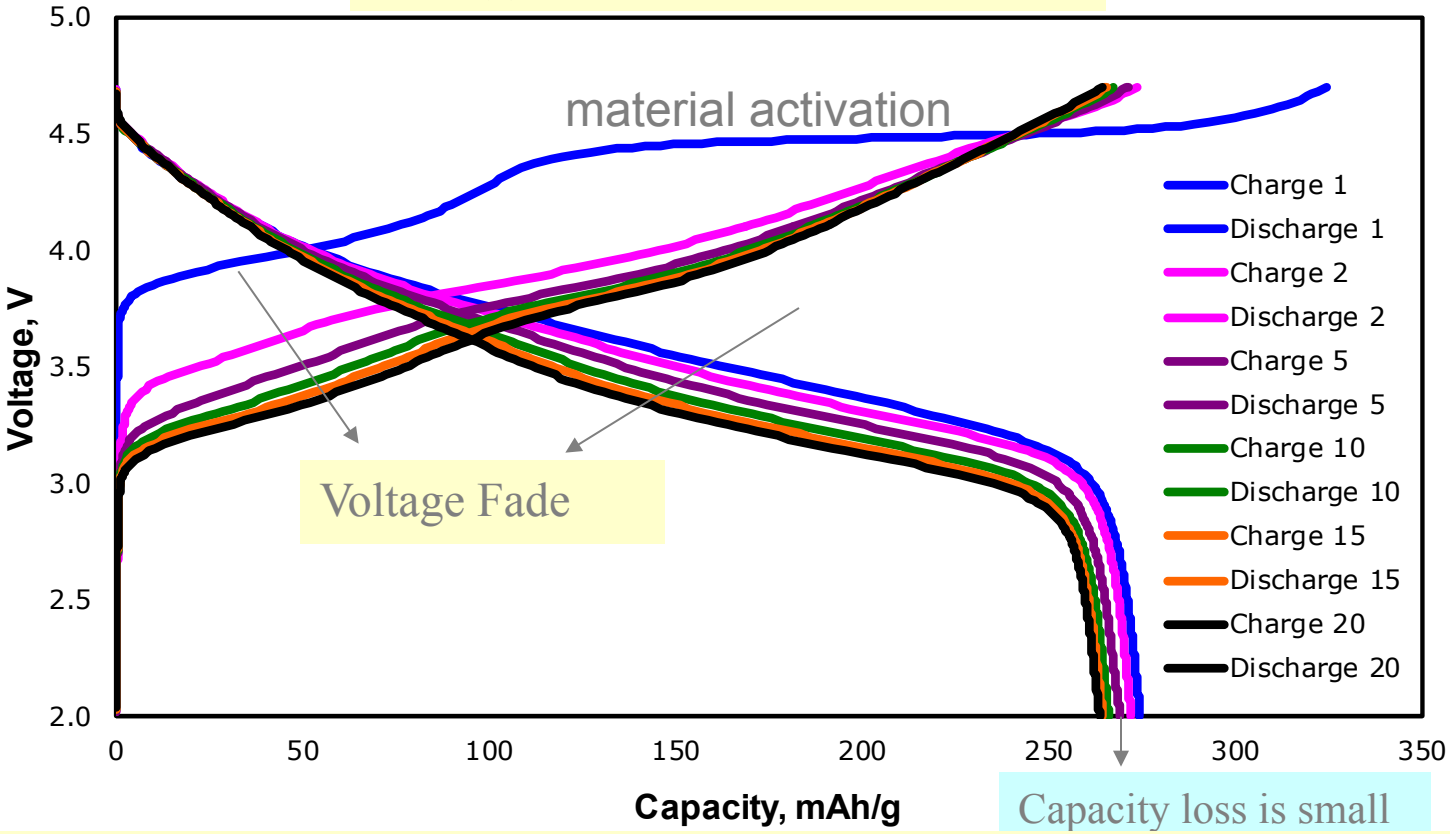
Interfacing & Communication – a group effort



Voltage Fade

$0.5Li_2MnO_3 \bullet 0.5Li[Ni_{0.375}Mn_{0.375}Co_{0.25}]O_2$

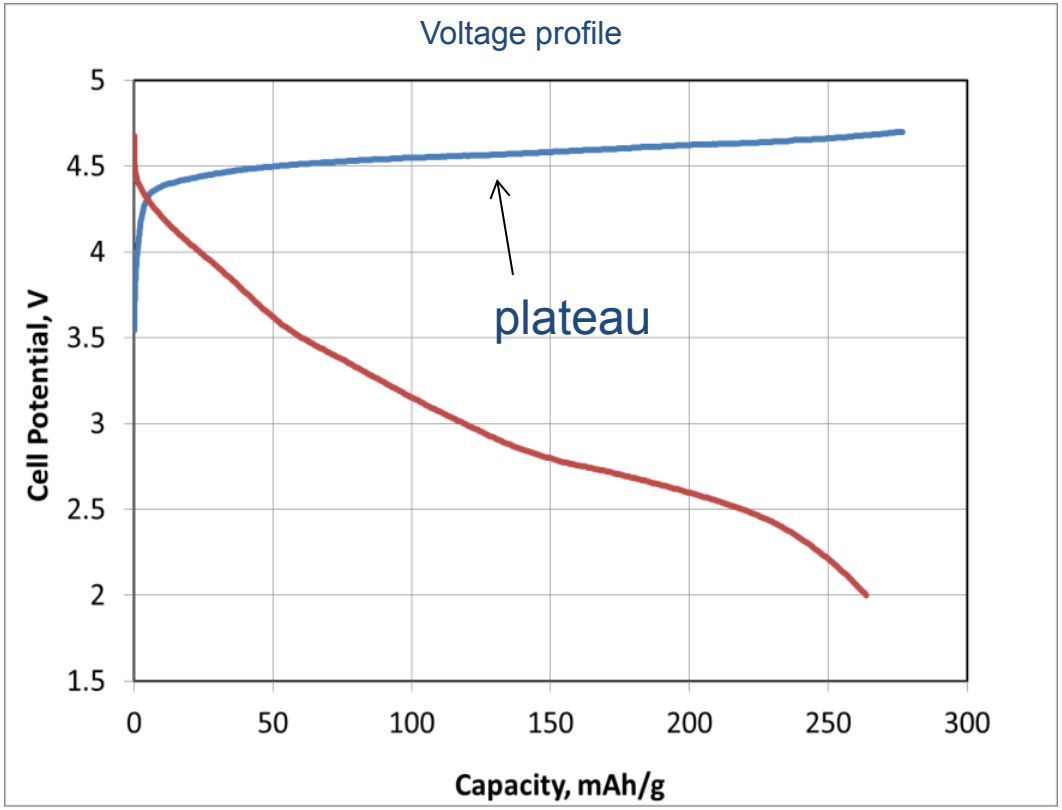
ABR-1(+)/Li; 2 – 4.7V, 30 °C; ~ C/25 Rate

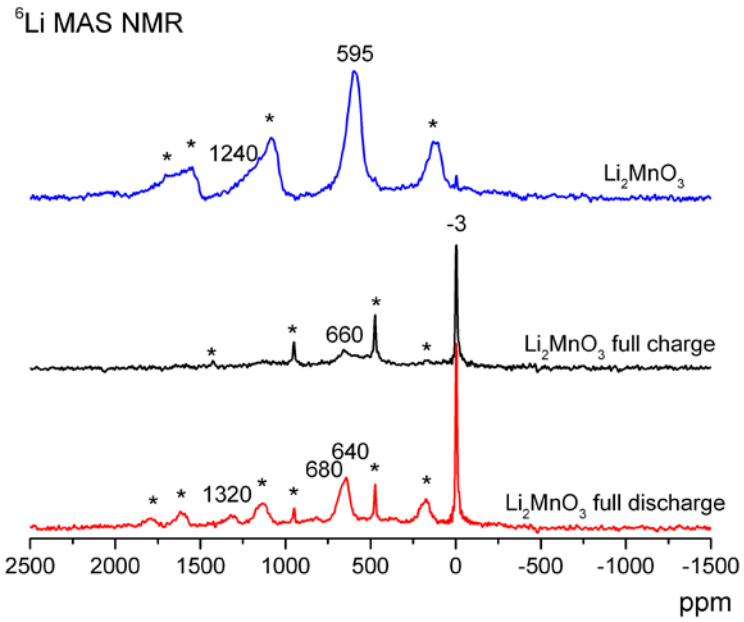


Voltage Fade is significant during the early cycles, and slows with cycle number. Fade is accelerated by higher test temperature and higher upper cutoff voltage.

- Bettge/ Abraham

Electrochemical Activity of Li_2MnO_3 ($Li_2M'O_3$)





Lithium is fully removed from Li_2MnO_3 material as measured by ^{6}Li NMR

Li_2MnO_3 is useful as a surrogate for $Li_2MnO_3 \cdot LiMO_2$ composites

- Fulya/Baris

First charge of $Li_2M'O_3$ component: predicted voltage for hypothetical reactions

Reaction	Voltage (DFT)
$2/3Li_2MnO_3\text{-}Li\ \text{-}1/4O_2 \rightarrow 1/6\ Li_2Mn_4O_9$	4.1
$5/6Li_2MnO_3\text{-}Li\text{-}1/2O_2 \rightarrow 1/6Li_4Mn_5O_{12}$	4.2
$Li_2MnO_3\ \text{-}Li_x \rightarrow\ Li_{2-x}MnO_3$	4.5 (Okamoto,'12)
$Li_2RuO_3\ \text{-}\ Li_x \rightarrow\ Li_{2-x}RuO_3$	<4.5
$2Li_2MnO_3\text{-}\ Li \rightarrow Li_3MnO_4 + MnO_2$	4.6

Theory predicts that spinel formation occurs first at the surface of the composite material.

- Roy/Hakim

Model capacity Q_{tot} of layered-layered composites

phase		$[LiMO_2]$		$[Li_2M'O_3]$
Q_{tot}	=	$(1-x)\, f_1/m$	+	$2x\, f_2/m$
f_1, f_2	:	$f_1 \sim 0.5 - 1.0$ (empirical)		$f_2 = f_2(M') + f_2(O)$ preplateau 4.5 V plat.

- possible strategy: Maximize Q_{tot} by optimization of $\{M,M',x, f_2\}$
- but, $f_2(O) > 0 \rightarrow$ hysteresis and fade, so optimize only $\{M,M',x, f_2(M')\}$

Theory predicts that one should avoid oxygen loss on the first cycle to maintain the composite 'layered-layered' structure.

- Roy/Hakim

Materials approach: Selection of M'

Criteria for M'

(1)Strong bonding with oxygen
(2)Oxidation state higher than 4+ is stable
(3)Preferencially substitute for the Mn in Li_2MnO_3 domain
(4)Should form reversible dumbbell configuration with Li_{tet} during deep charge in order to maintain structural stability

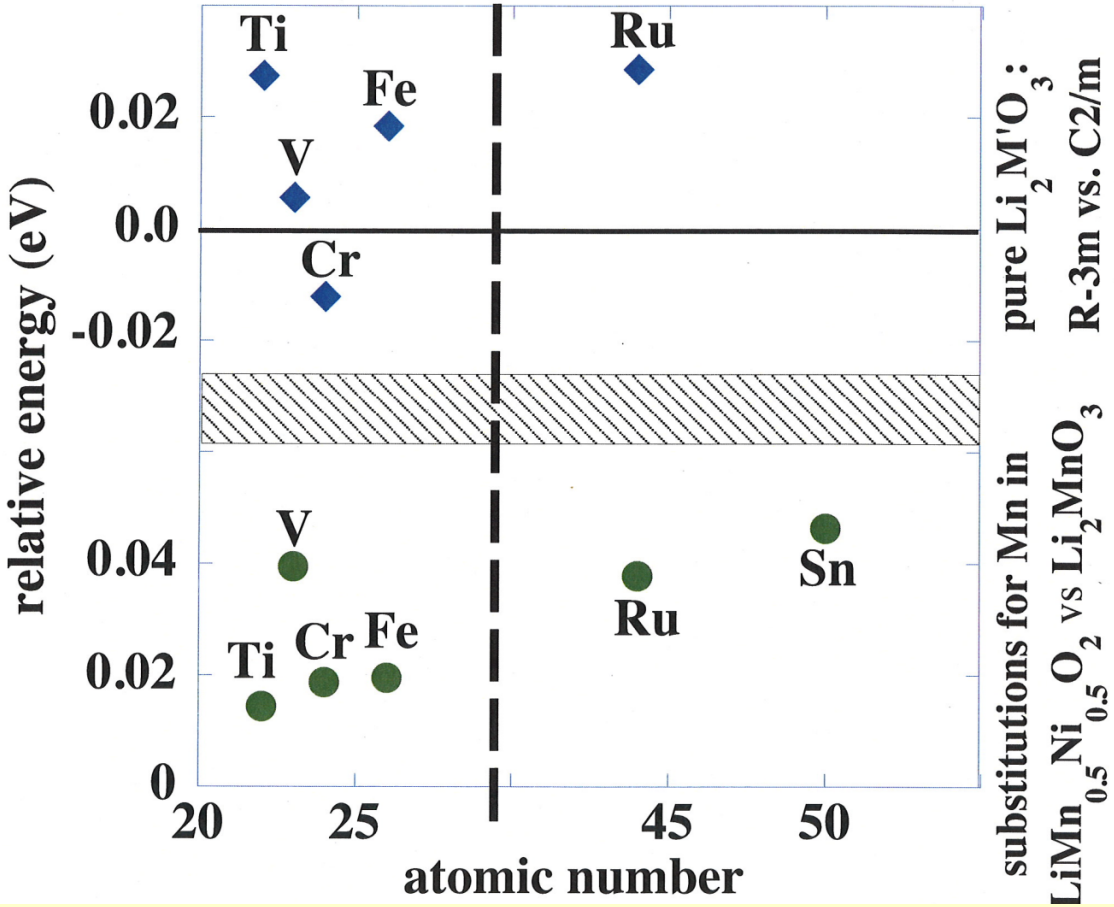
Candidates for M'

V: **5**,4,3,2+ stable
Mo: 2,3,4,5,**6**+ stable
Ru: 2,**3**,**4**,6,8+ stable
Cr: 2,**3**,6+ stable
Sn: 2,4+ stable

Ti, **Zr**: strong bonding with oxygen, but not stable higher than 4+ oxidation state. Can be used for control system

Prediction from modeling calculations: doping or substitution should be made on Li_2MnO_3 component to be effective in countering voltage fade.

Relative energies of substitution and doping



First principles DFT calculations are used to predict stability of dopants and substitutions into either $LiMO_2$ (layered) or Li_2MnO_3 (monoclinic) components. Many cases the $LiMO_2$ substitution is favorable. Prediction: it will be difficult to dope or substitute into Li_2MnO_3 and voltage fade will be hard to control.

- Roy/Hakim

Materials approach

Target systems

(1)$Li_2M_{1-x}M''O_3$ (M'' = Ti^{4+}, Zr^{4+}, **Ru^{4+}**, **$V^{?}$**, **$Mo^{?}$**…)
- high temperature synthesized well crystalline form is good for structural study. However electrochemically not active at room temperature.
- low temperature synthesized poorly crystalline form is electrochemically active at room temperature, but not good for structural study.

→ Electrochemical test of well crystalline $Li_2Mn_{1-x}M''_xO_3$ at elevated temperature.

(2)$Li_{1.2}Ni_{0.2}Mn_{0.6-x}M''_xO_2$ (M'' = Ti, Zr, **Ru**, V, Mo)
- 50/50 composition
- M'' substitute for Mn^{4+} in Li_2MnO_3 domain or in $LiNi_{0.5}Mn_{0.5}O_2$ domain. (control sample of $Li_{1.2}Co_{0.4}Mn_{0.4-x}M''_xO_2$ where M''^{4+} substitutes for Mn^{4+} in Li_2MnO_3 domain).
- Room temperature electrochemical test of well crystalline material.
- Can be extended to $Li_{1.2}Ni_{0.15}Mn_{0.55-x}Co_{0.1}M''_xO_2$

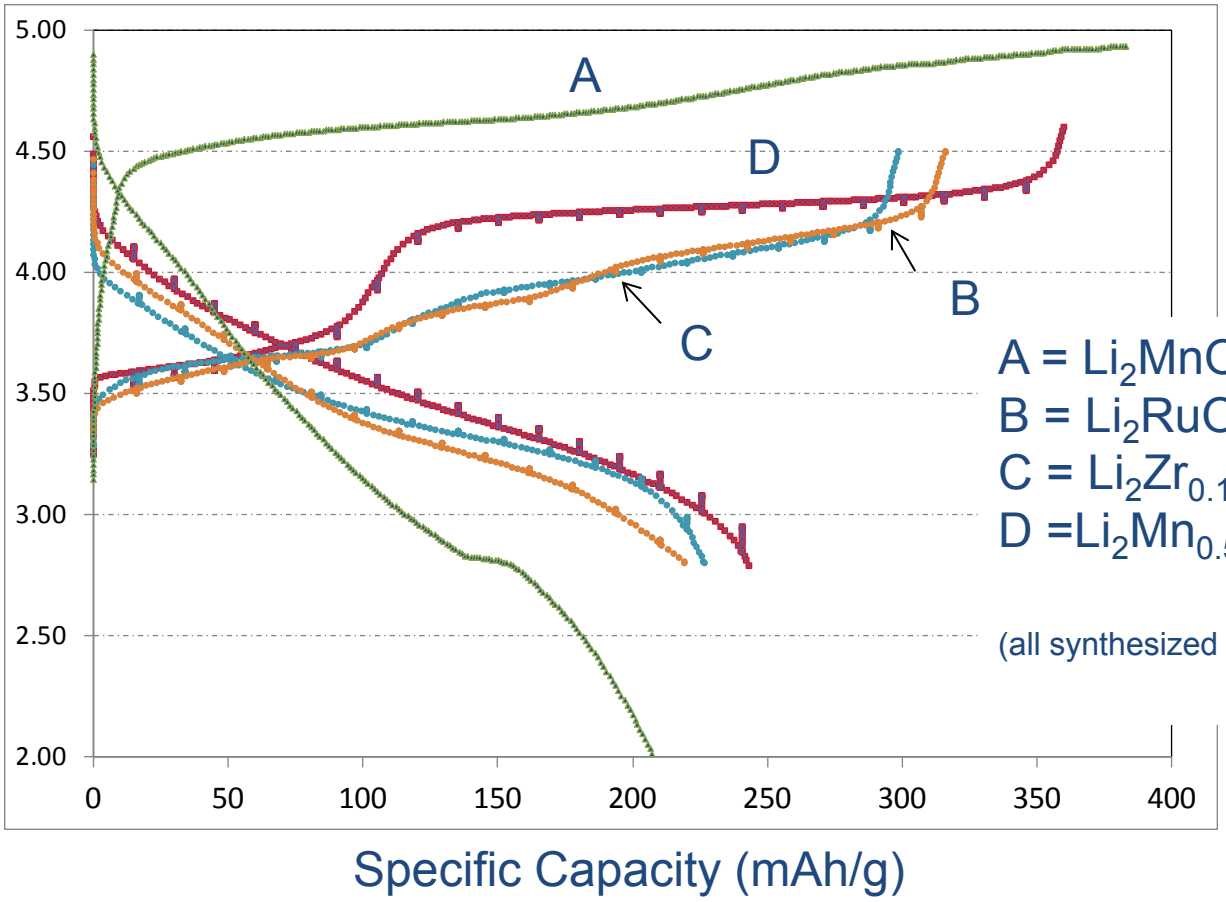
(3)$Li_{1.2}Ni_{0.15-x/2}Mn_{0.55-x/2}M'_xO_2$ (M'=Fe, Co, **Cr**, V, Mo)
- 50/50 composition
- M'^{3+} substitutes for $Ni_{0.5}Mn_{0.5}$ in $LiNi_{0.5}Mn_{0.5}O_2$ domain.
- Effect of Co can be compared.

Applications of capacity model

LiMO2	Li2M'O3	x	f1	f2	Q1	Q2	Qtot
M= Co		0.0	0.85		135		135
Co	M'=Mn	0.5	0.85	0.95	106	236	342
Ni0.5Mn0.5	Mn	0.5	0.85	0.75	107	189	296
(0.375,0.375,025)	Mn	0.5	0.85	0.60	107	151	257
	Ru	1.0		0.91		298	298
	Ru0.9Zr0.1	1.0		0.84		278	278
	Ru0.5Mn0.5	1.0		0.91		305	305
(0.375,0.375,025)	Ru	0.5	0.85	0.50	88	103	191
(0.375,0.375,025)	(V,Cr,…Ru)						?

Capacities model estimates the results of substitution or entirely new $Li_2M'O_3$ materials.

Plateau variation – Ru effect; C2/m monoclinic

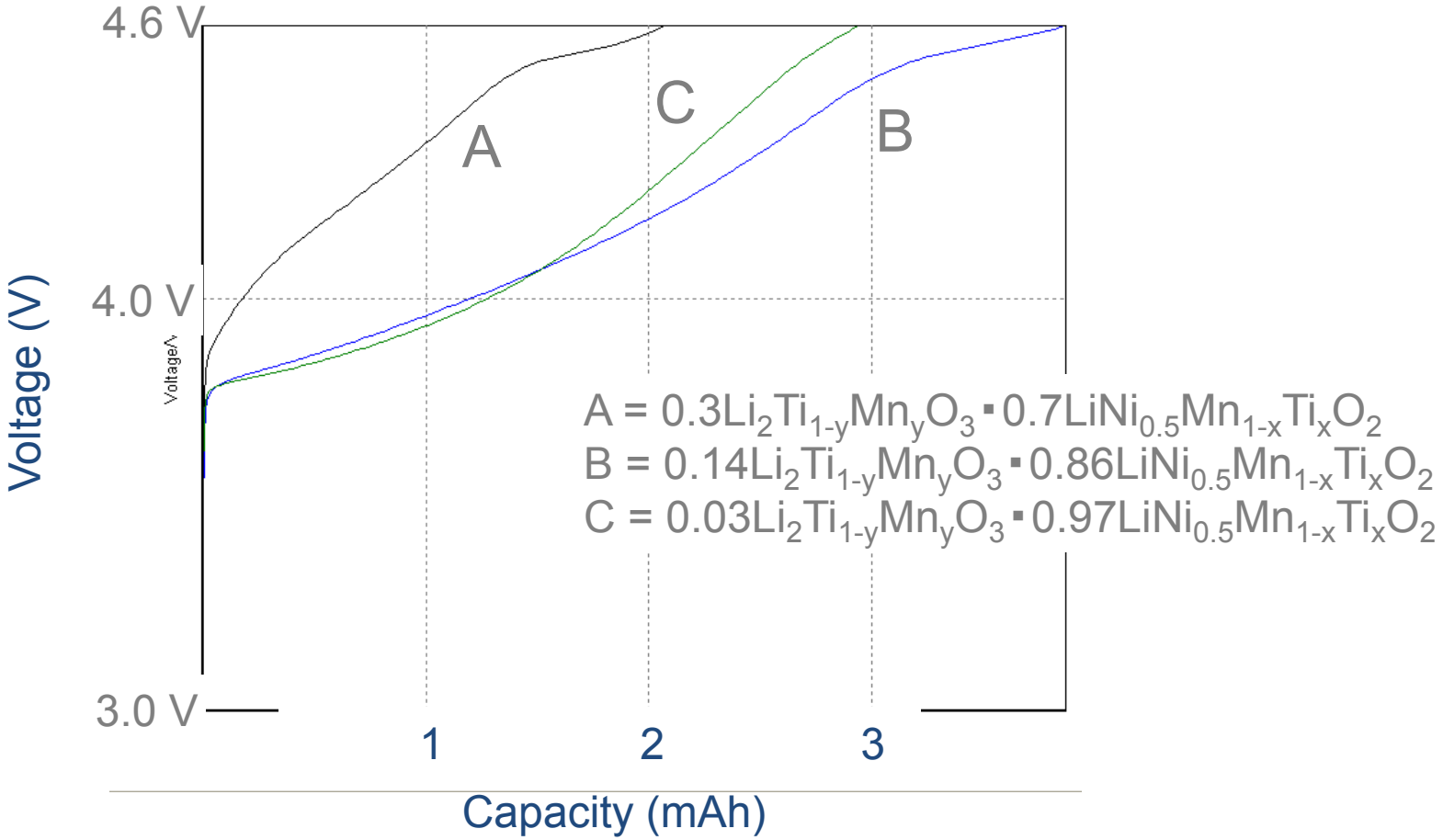


A = Li_2MnO_3
B = Li_2RuO_3
C = $Li_2Zr_{0.1}Ru_{0.9}O_3$
D = $Li_2Mn_{0.5}Ru_{0.5}O_3$

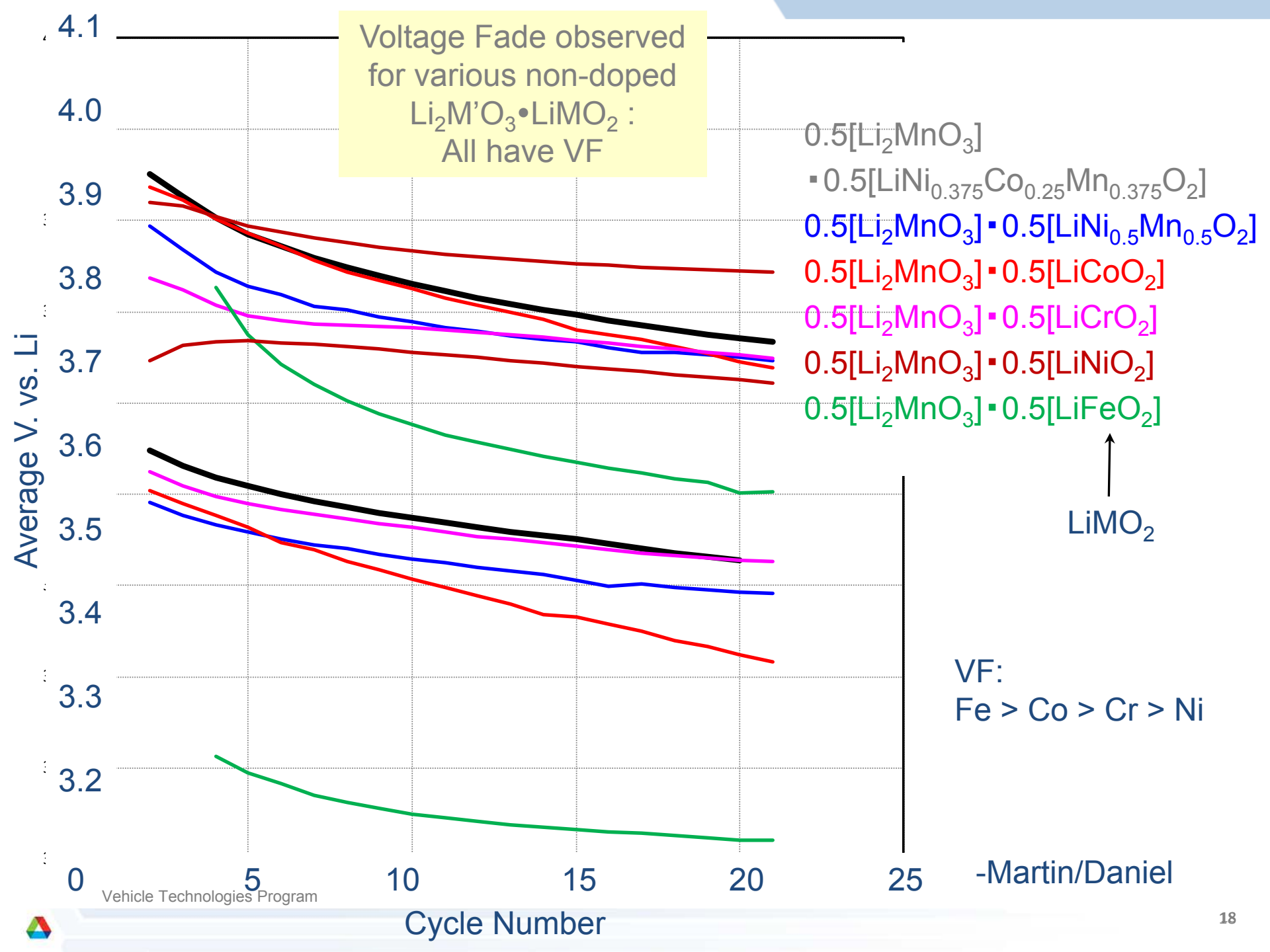
(all synthesized by combustion method)

Materials that theoretically hold onto their oxygen in $Li_2M'O_3$ component were synthesized and run in Li batteries.

$xLi_2Ti/MnO_3 \cdot (1-x)Li(Ni_{0.5}Mn/Ti_{0.5}O_2)$: first charge



Analysis of first charge in Ti-substituted materials suggests that oxygen loss is mitigated, but impedance is higher.

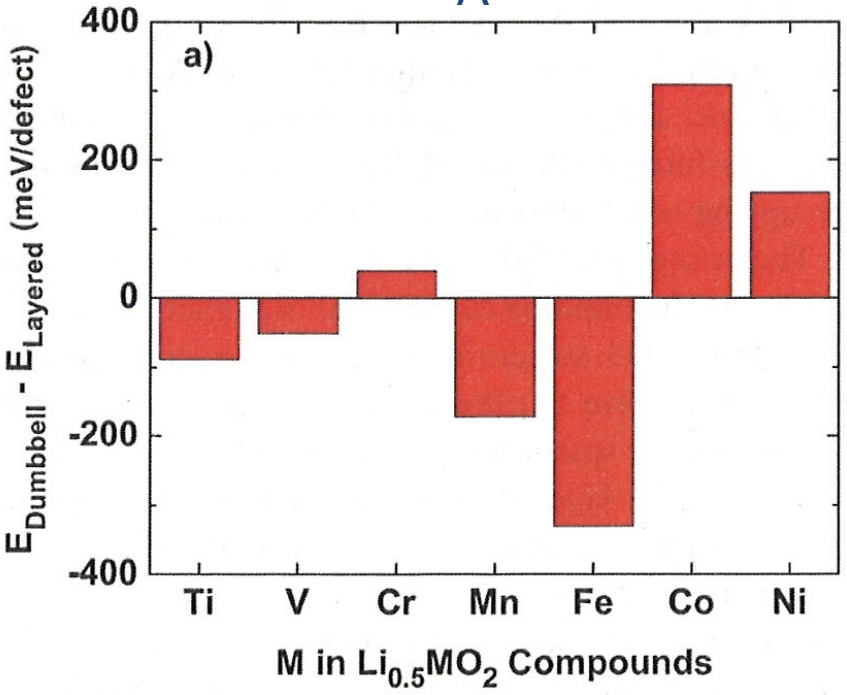

Voltage Fade observed for various non-doped $Li_2M'O_3 \bullet LiMO_2$: All have VF
$0.5[Li_2MnO_3]$
▪ $0.5[LiNi_{0.375}Co_{0.25}Mn_{0.375}O_2]$
$0.5[Li_2MnO_3]$ ▪ $0.5[LiNi_{0.5}Mn_{0.5}O_2]$
$0.5[Li_2MnO_3]$ ▪ $0.5[LiCoO_2]$
$0.5[Li_2MnO_3]$ ▪ $0.5[LiCrO_2]$
$0.5[Li_2MnO_3]$ ▪ $0.5[LiNiO_2]$
$0.5[Li_2MnO_3]$ ▪ $0.5[LiFeO_2]$
$LiMO_2$
VF:
Fe > Co > Cr > Ni
-Martin/Daniel
Average V. vs. Li
Cycle Number
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
0
5
10
15
20
25

Layered O3 $LiMO_2$: M substitution

Formal M oxidation states in $LiMO_2$ = 3+; $Li_{1-x}MO_2$ > 3+

dumbbell defect formation energies

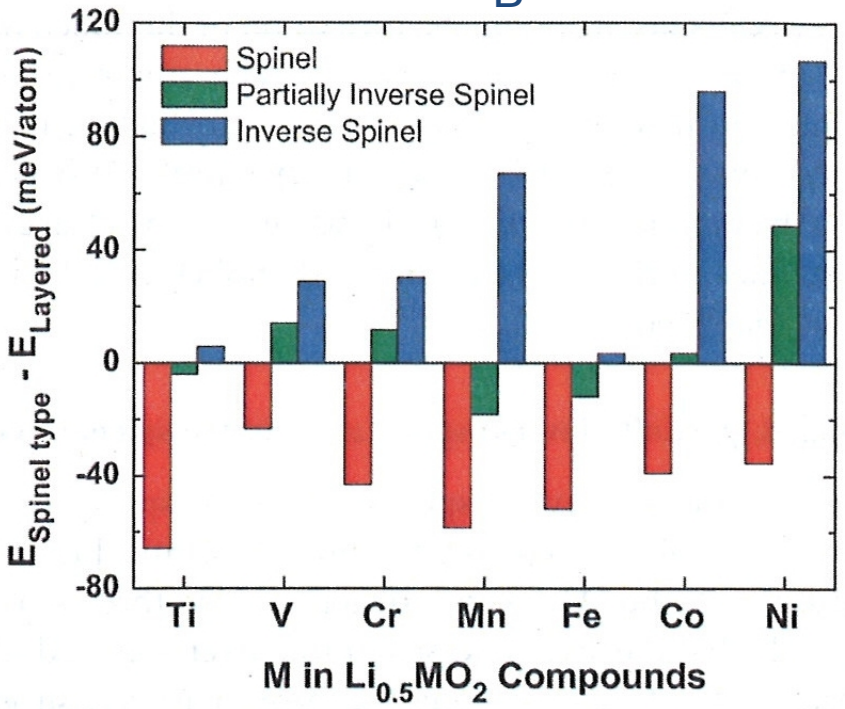
A



dumbbell – Fe and Cr dominates

spinel formation energies

B



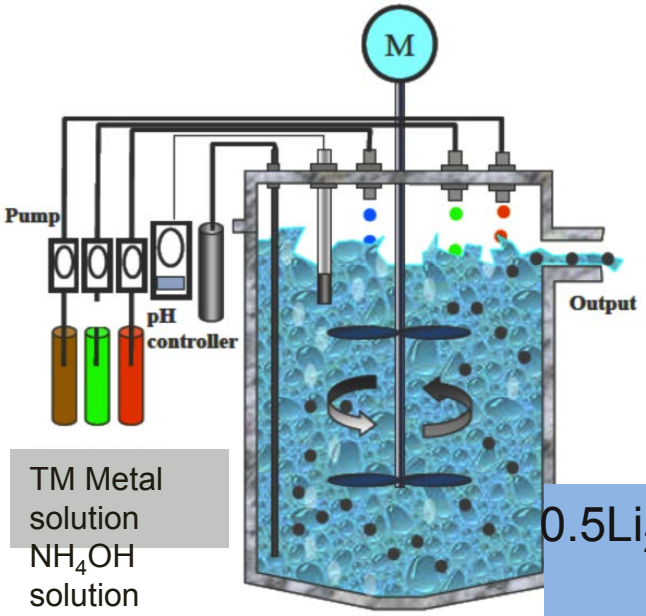
spinel – Co and Ni dominates

These are the energies predicted for structure alterations of composites likely occurring and/or are favored during cycling.

A, B : Kim, Ceder et al. JPPC (2012)

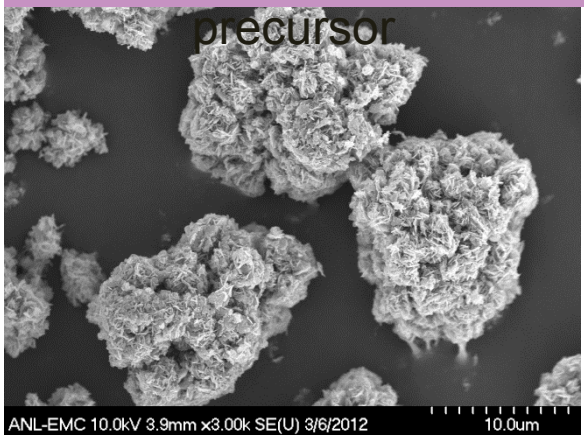
Homogeneity: critical parameter

Production of $Ni_{0.25}Mn_{0.75}(OH)_2$ precursor using our CSTR reactor.
Product – Lithiation
-temperature, time @ temp.



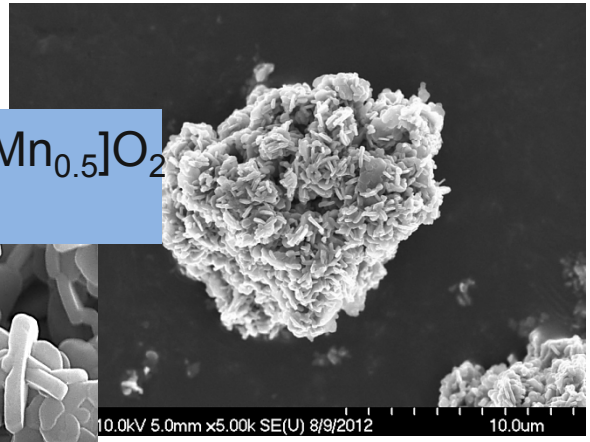
pH = 11
T = 50 °C

$Ni_{0.25}Mn_{0.75}(OH)_2$ precursor



lithiation

$0.5Li_2MnO_3 \bullet 0.5Li[Ni_{0.5}Mn_{0.5}]O_2$ Composite



Primary particles with
Flake-type morphology

- Ilias

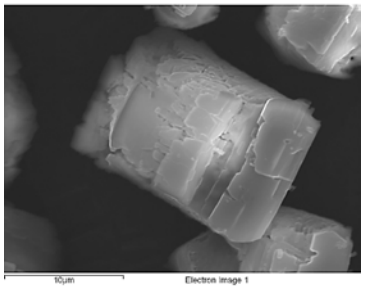
Synthesis Method

Co-precipitation

hydroxide

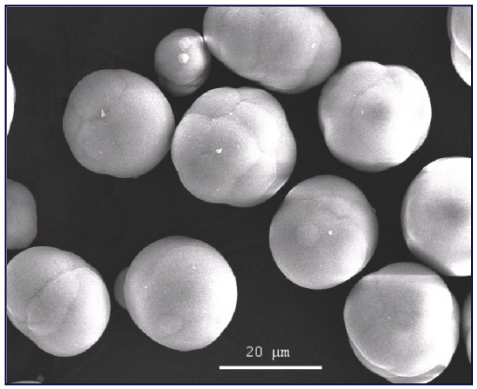
oxalate

carbonate



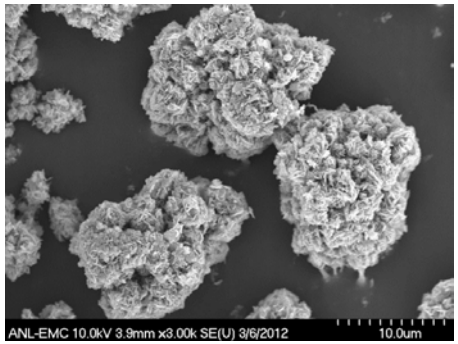
10 µm

lithiation



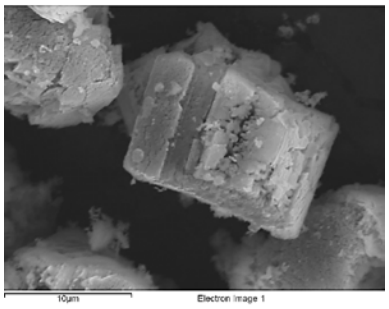
20 µm

lithiation



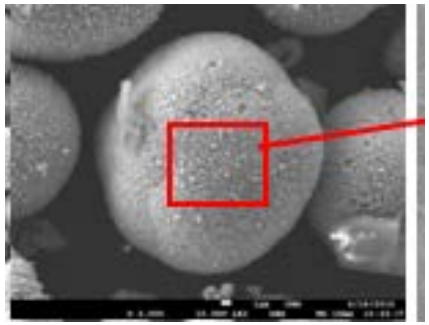
10 µm

lithiation



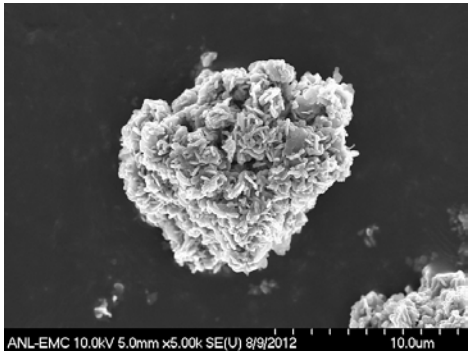
10 µm

oxalate process



10 µm

carbonate process



10 µm

hydroxide process

- I. Belharouak, D. Kim, H. Wu

Synthesis methods to make LMR-NMC TODA HE5050: $0.5Li_2MnO_3 \bullet 0.5Li[Ni_{0.375}Mn_{0.375}Co_{0.25}]O_2$

- Precursors:
  - Direct solid state reaction
  - Sol-gel reaction
  - Combustion synthesis
  - Co-precipitation
    - Hydroxide, oxalate, carbonate
- Direct comparison within typical synthetic processes
- Chemical analysis to confirm stoichiometries

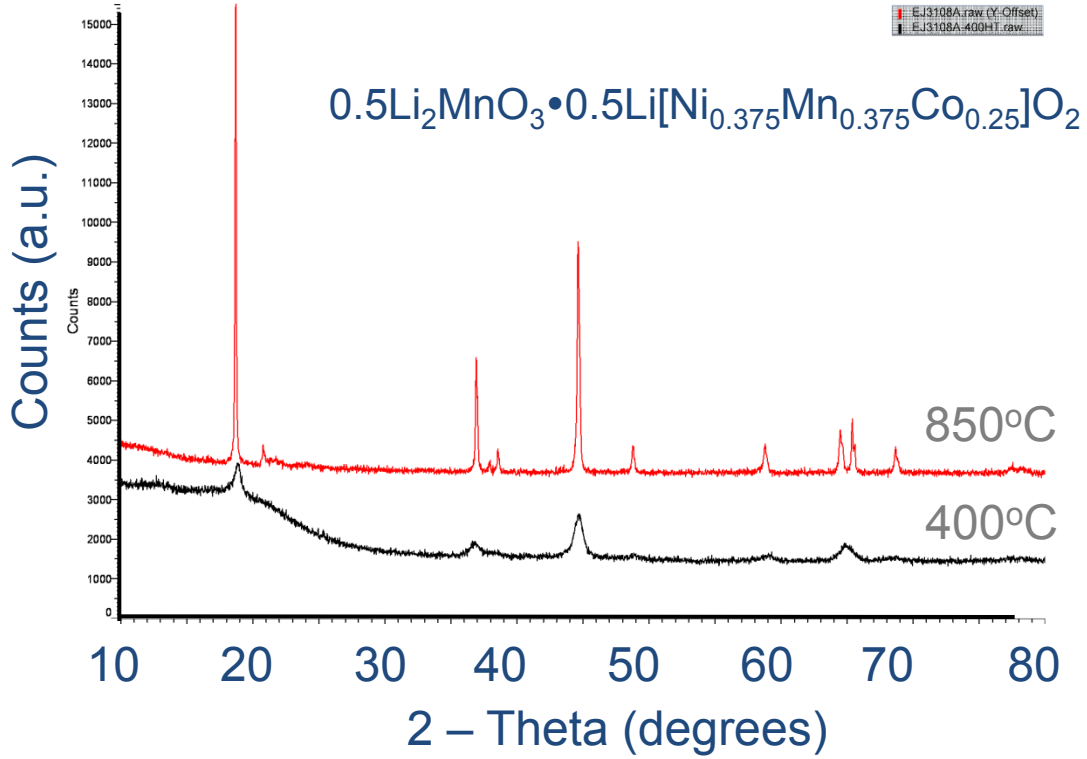
Four routes of synthesis being pursued with confirmed identical stochiometries from ICP elemental analysis. Voltage fade will be assessed per sample and go/no-go decision on synthesis route will be made.

Synthesis approach: Sol-gel method

- Atomic mixing

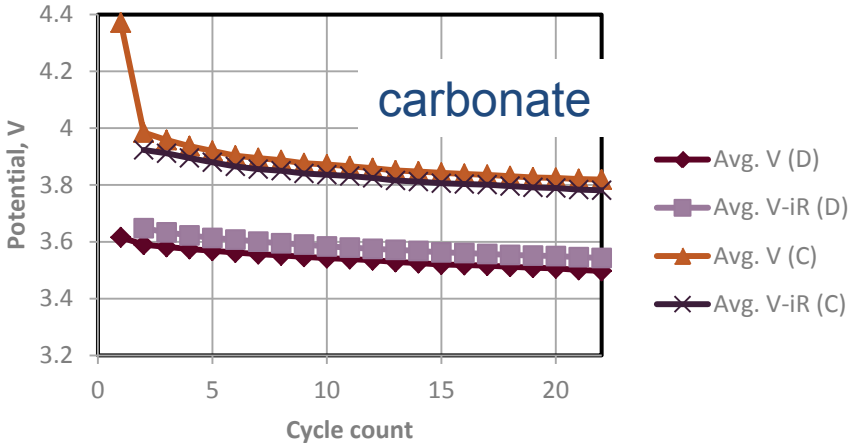
(1) Multi-component system, doped Li(NMCM')O_2 possible

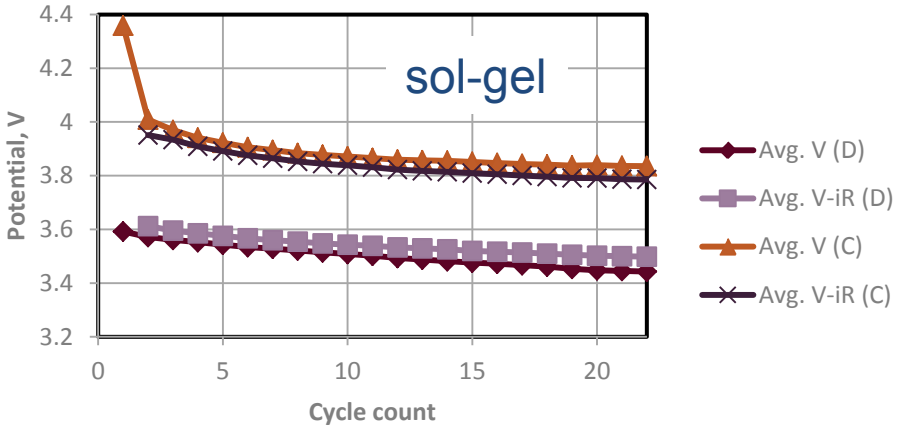
(2) Small primary particle size (nanosize) possible

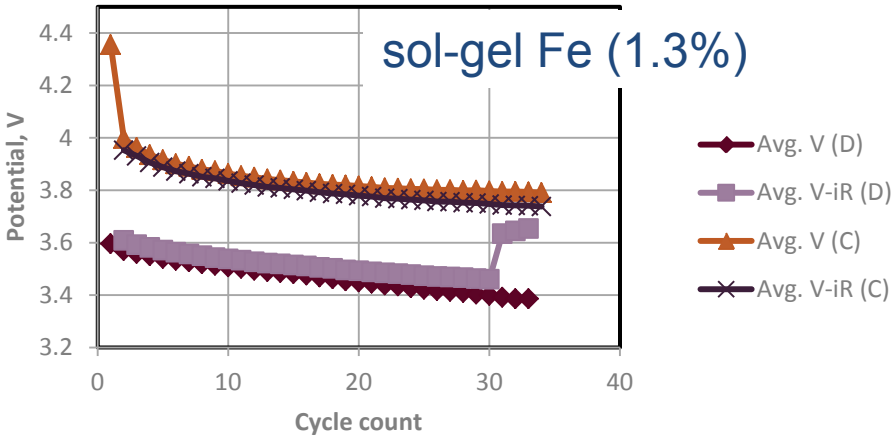


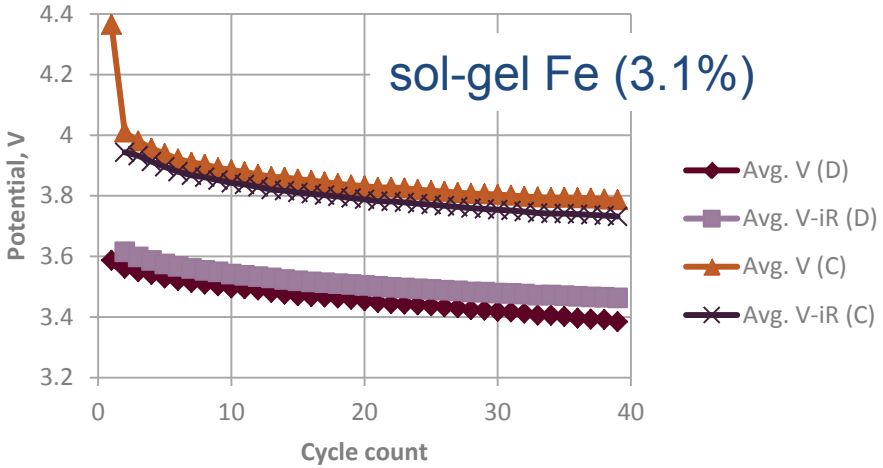
Sol-gel synthesis allows us to make single phase materials as well as control crystallite size by temperature choice.

$0.5Li_2MnO_3 \cdot 0.5Li[Ni_{0.375}Mn_{0.375}Co_{0.25}]O_2$ Carbonate, sol-gel and Fe doped









No change in VF or VF mechanism observed for carbonate precursor versus sol-gel prepared material. No change in VF for Fe-doped samples.

Collaborations

- **Partners:**
  - Academic partner – MTU sub-contract
    - Project titled "Transmisson Electron Microscopy (TEM) Characterization of Battery Materials"
  - Laboratory Partners -
    - ES194 ABR project – "Addressing Voltage Fade: Synthesis and Characterization of Lithium- and Manganese-Rich Electrode Structures" (P.I. Dr. Michael Thackeray)
    - ES191 ABR project – "Impact of Surface Coatings on LMR-NMC Materials: Evaluation and Downselect" (P.I. Dr. Ali Abouimrane)
    - ES193 ABR project – "First-Principles Models of the Atomic Order and Properties of LMR-NMC Materials" (P.I. Drs. Roy Benedek and Hakim Iddir)
    - ES195 ABR project – "Phase Relations and Voltage Fade Response in LMR-NMC Materials" (P.I. Dr. Ira Bloom & team)
    - The Center of Nanoscale Materials (CNM) at Argonne is used to analyze materials.
      - Scientists: Dr. David Gozstola and Dr. Vic Maroni
    - The Advanced Photon Source (APS) at Argonne is used to analyze materials.
      - Scientist: Drs. Mali Balasubramanian (APS Science).

Future work

- Conduct more synthesis focusing on LMR-NMC TodaHE5050 composition.
  - Dopants and substitutions into both Li_2MnO_3 and $LiMO_2$ components
  - Synthetically check/confirm the incorporation of other dopant elements – namely Ti, Cr, V, Mo, Ru and Sn.
- Run batteries, analyze data
  - Feed information to theory group
  - Work together to direct focus or redirect if need be
- Advanced analytical methods (SEM, TEM) and diagnostic tools @APS & CNM (Raman) will be used to characterize new materials and will provide basic science knowledge.
- Glow discharge measurements on samples will be initiated to measure oxygen content in the as-prepared and cycled materials.
- DEMS work will be initiated.
- Collaborations with other ABR teams will continue, and others will be initiated.

Summary & Conclusions

- Strong interface with other Argonne VF groups
  - Would like to work with others
- Li-rich Mn-rich cathodes have a VF
  - Theory focuses on thermodynamics of structures and components
  - Mechanism likely driven by the kinetics
    - Can we slow the transformation that occurs
    - Can we contain the oxygen loss, and mitigate spinel formation at the surface
  - Synthetic solutions are possible
- Synthesis project underway to solve VF
  - Looking at optimized M': Ti, Ru, and Cr; next V & Mo
  - Concept – delay plateau onset, and evaluate both dopants and substitutions
  - Stacking sequence – suppress spinel formation
  - Processing – homogeneous samples critical for best performance