First-Principles Models of Properties of LMR-NMC Materials

Project Id: ES193

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DOE Vehicle Technologies Program Annual Merit Review

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Overview

Timeline

- Start: October 1, 2012
- End: Sept. 30, 2013
- Percent complete: 30%

Budget

- FY13: part of $4M

Barriers

- Poorly understood atomic-scale structures and mechanisms of Voltage Fade

Partners

- Voltage Fade Team at Argonne
- J. Bhattacharya, C. Wolverton, NU

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

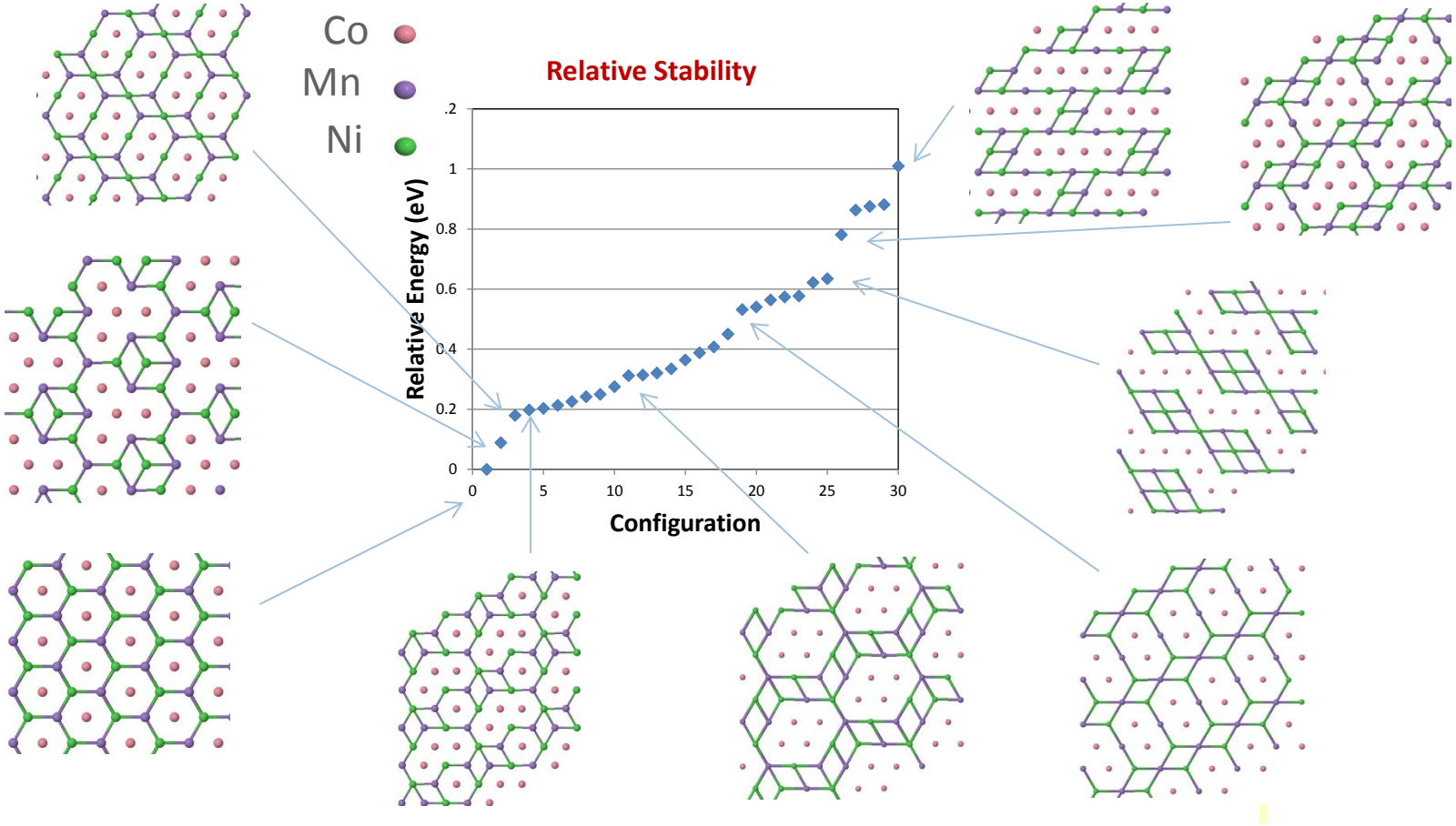
- First-principles modeling can yield insights into the mechanism of VF, suggest directions for materials synthesis, and assist in interpretation of spectroscopies (e.g., NMR, XAS) for characterization of LMR-NMC composites

Milestones

- First-principles calculations for 30+ low energy configurations of L333 completed, and applied to fit Cluster Expansion coefficients; to be used in MC simulations at synthesis temperatures (Feb. 2013)
- First principles calculations performed for series of Li_2MO_3 compounds (M=Mo, Ru, V, Cr, Fe, Sn, Ti) and related materials (March 2013)
- Develop code for Heuristic-Model analysis of NMR Fermi-contact shift of LMR-NMC materials (April 2013)

Approach

- Apply first principles density functional theory methods to LMR-NMC composites and related materials (example below)
- Employ extensions of first principles methods, e.g., Cluster Expansion methods, to address finite temperatures



Technical Accomplishments and Progress (slides 5-13):

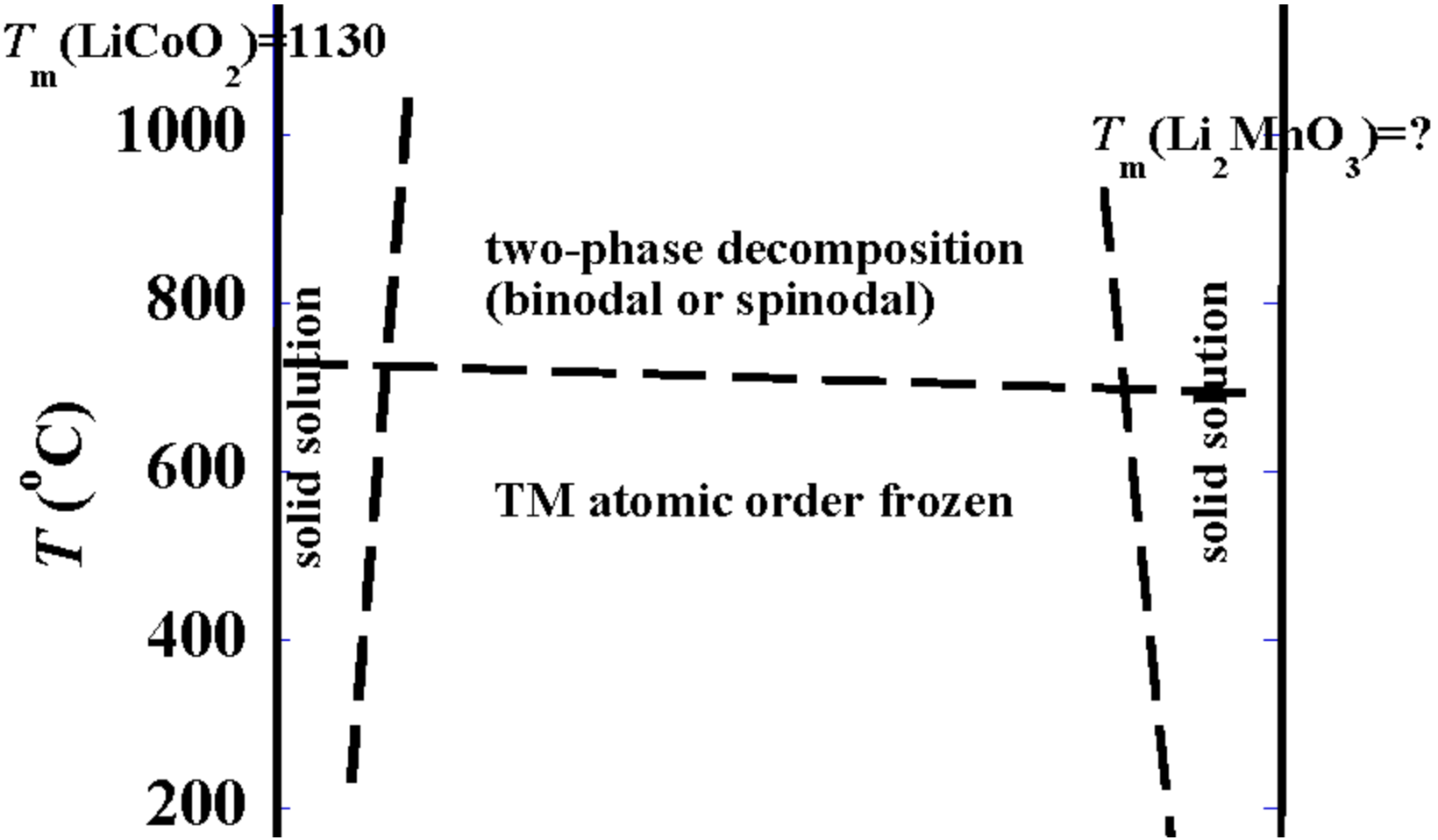
I. Phase composition of LMR-NMC

- Composite $xLi_2MnO_3 \bullet (1-x)LiMO_2$ (where M=Ni,Mn,Co) consists of a mixture of Li_2MnO_3 and $LiMO_2$ domains for most of the range of x ($0<x<1$) [see slide 6]

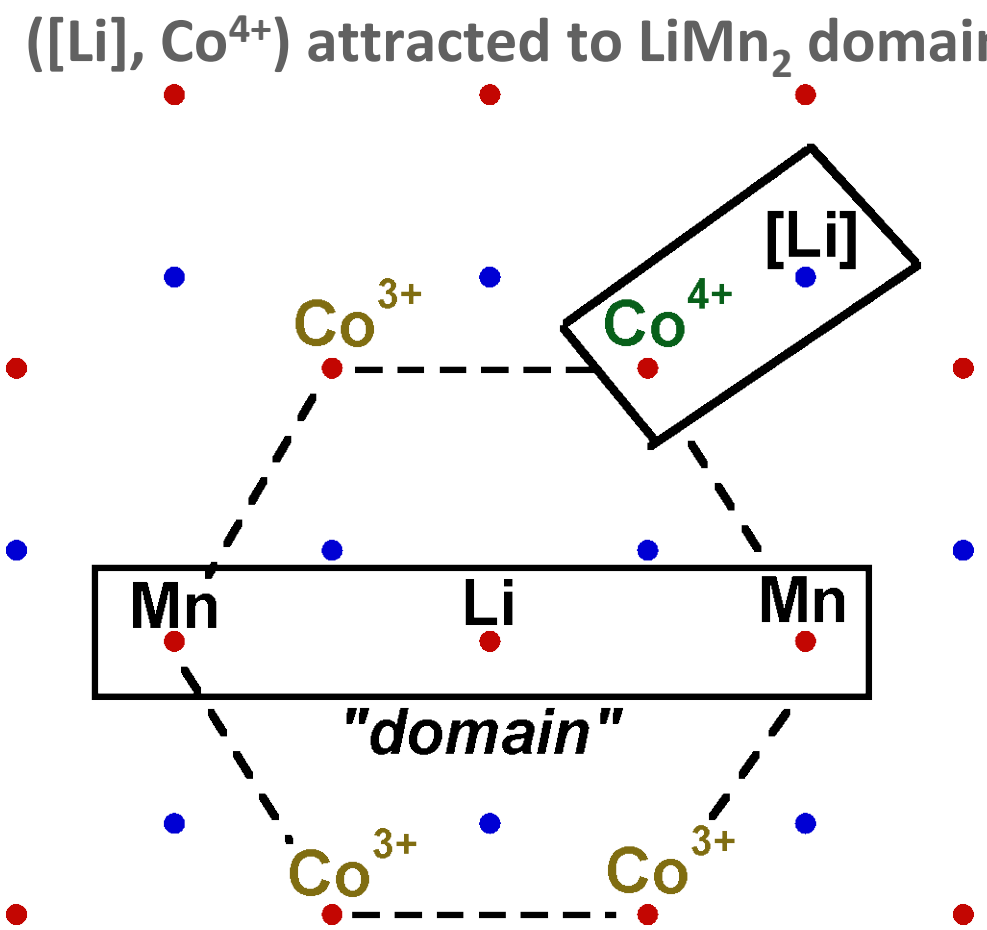
- Zero order model: random mixture of Ni, Mn, Co in $LiMO_2$ and no mixing between Mn (in Li_2MO_3) and M (in $LiMO_2$); applied to predict first-charge reaction energies [see slide 7]

- First order model: allow short range order in M [see slide 8], and mixing between M and Mn [see slide 8]

Technical Accomplishments: Schematic phase diagram of $(1-x)LiMO_2 \bullet xLi_2MnO_3$



Technical accomplishments: Indirect evidence against solid solution behavior; lower predicted (but not observed) initial first charge voltage : $xLi(Li_{1/3}Mn_{2/3})O_2 \cdot (1-x)Li_{1-y}CoO_2$



Technical Accomplishments: Predicted voltage for hypothetical first charge reactions of $Li_2M'O_3$

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
$Li_2MnO_3 - Li_x \rightarrow Li_{2-x}MnO_3$	4.5 (Okamoto,'12)
$Li_2RuO_3 - Li_x \rightarrow Li_{2-x}RuO_3$	<4.5
$2Li_2MnO_3 - Li \rightarrow Li_3MnO_4 + MnO_2$	4.6

Technical Accomplishments: Ordering (in $LiMO_2$) and Mixing (between $LiMO_2$ and Li_2MnO_3)

Ordering:

Total energy calc. (slide 4) indicate Ni, Mn, Co prefer unlike neighbors

Mixing:

Calc. form. energy E_f(M-Mn exch.) = $E_f(M_{Mn}) + E_f(Mn_M)$

result: E_f(M-Mn exch.) = 0.8 eV, M=Co

E_f(M-Mn exch.) = 2.0 eV, M=Ni

Implication: Co_{LiMO2}-$Mn_{Li2MnO3}$ exchange more likely than Ni_{LiMO2} - $Mn_{Li2MnO3}$ exchange

Technical Accomplishments: Atomic-scale mechanism of VF?

I. Oxygen-release model

- 1st chg. O-release from Li_2MnO_3 domains

  → form defect spinel at surfaces
- Cycling grows spinel-like phase at expense of high-V "phase"

II. M_{oct}-M_{tet} migration model

- migration of M to Li layer

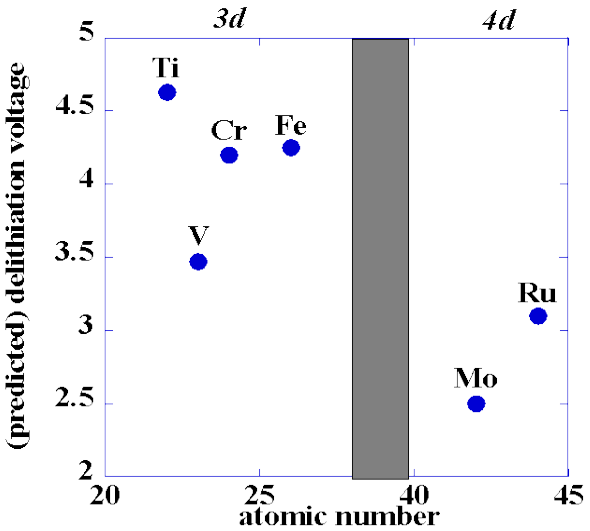
  → spinel-like structures

Technical Accomplishments: Evaluate VF-suppression strategy of shifting redox away from O

- Substitute higher-valent M for Mn in Li_2MnO_3
- Capacity $Q_{tot} = (1-x)\, f_1/m + 2x\, f_2/m$
- Do any substitutions other than Ru work?

Technical Accomplishments: Substitutions for Mn in manganite

- Second row: Mo, Ru
- First row: V, Cr, Fe



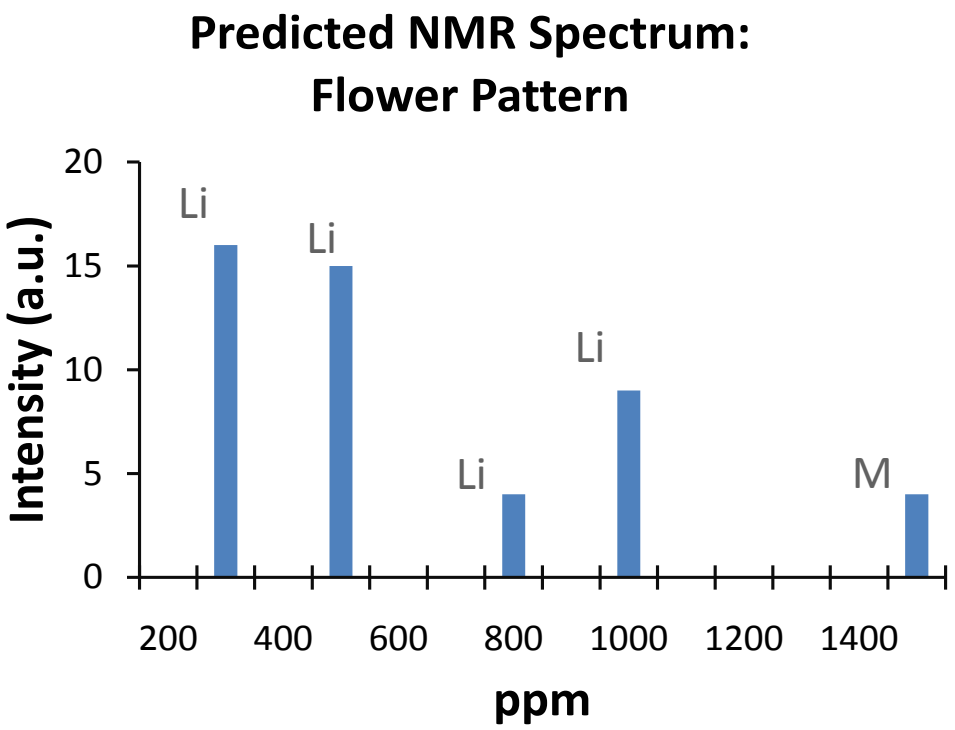
Issues:

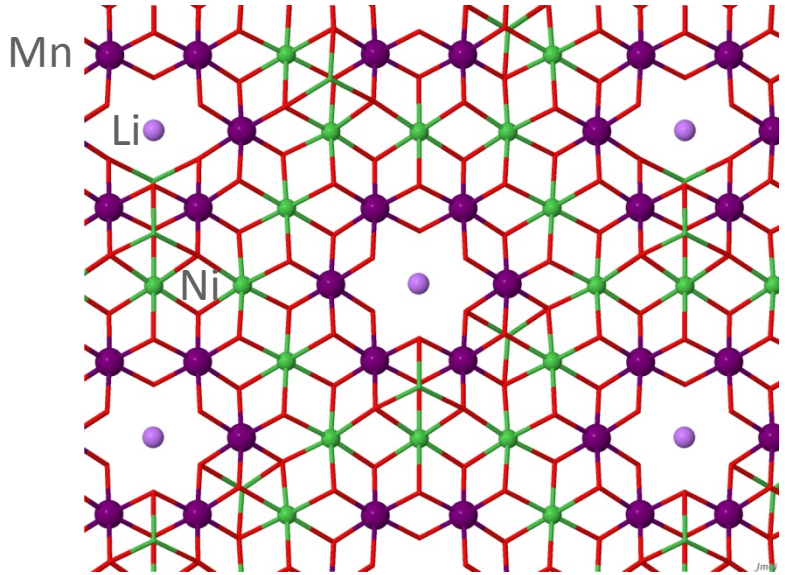
Will they form $LiMO_2$-$Li_2M'O_3$ composites?

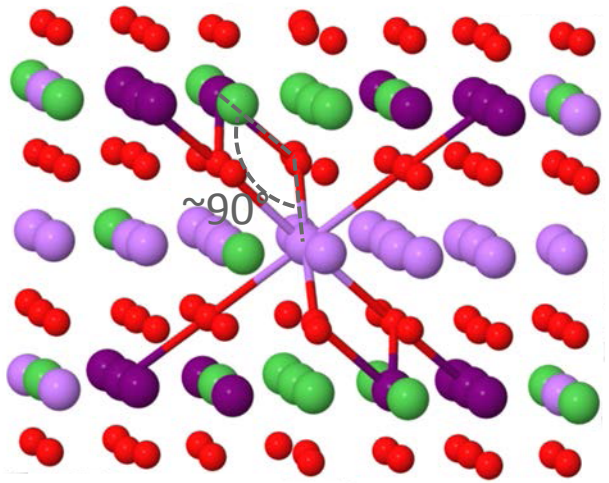
energies for delithiation of $Li_{2(1-f_2)}M'O_3$?

Maximum f_2 ?

Technical Accomplishments: NMR shift prediction







heuristic rules [C. P. Grey and N. Dupré, Chem. Rev. 104, 4493 (2004)] applied to $LiMn_{0.5}Ni_{0.5}O_2$ flower pattern

Work in Progress/Future Work

- Cluster expansion analysis of NMC ordering in $LiMO_2$ domains
- Application of heuristic model to analysis of Li NMR Fermi-contact shift to finger-print Li environments in LMR-NMC materials
- Model properties of materials, e.g., with *O2* stacking, that are targeted for synthesis
- Identify local environments of Mn that make migration between M and Li layers energetically favorable

Summary

- Properties of LMR-NMC materials calculated with First Principles Density Functional Theory methods, within the framework of zeroth order and first order models
- Calculations performed on Li_2MO_3 in C2/m and R-3m structures for various M, to support possible synthesis efforts
- Heuristic model analysis applied to predict NMR Fermi-contact shifts to identify local Li atomic environments in LMR-NMC materials