First Principles Calculations and NMR Spectroscopy of Electrode Materials

Project ID ES054

G. Ceder
Massachusetts Institute of technology
and C. P Grey
Cambridge University and Stony Brook University

Peer Review, Washington May 11, 2011

Overview

Timeline

- Project start date: May 2006
- Project end date: Jan 2012
- Percent complete: 30% (FY 2011)

Budget

- Total project funding: $1,351,370
- Funding for FY10: $351k (GC) $351k (CPG)
- Funding for FY11: $385k (GC) $385k (CPG

Barriers Addressed

- Low rates
- High cost
- Poor stability
- Low specific energy and cycle life

Partners/Collaborations

BATT program:

- J. Cabana, T. Richardson, G Chen, M.M.Thackeray, M. S. Whittingham , K. Persson, R. Kostecki, V. Srinevasan

Others:

- J. M. Tarascon, M. Morcrette, C. Masquelier (Amiens)
- A. S. Best, A. F. Hollenkamp (CSIRO)
- V. Chevrier
- Companies: Bosch , Umicore

Objectives

- Determine the effect of structure on stability and **rate** capability of cathodes and anodes. Use this information to improve performance
- Apply ***in situ* NMR spectroscopy** to working lithium-ion cells
- Explore relationship between electrochemistry and **particle size** and shape.
- Develop **new, stable, cathode materials** with high energy-density.

Milestones

Milestones 2010

Obtain size effect on Li mobility in olivines. (Sep. 10) - **COMPLETE**

Li mobility calculations in other materials (graphite and spinel). (Sep. 10)) - **COMPLETE**

Identify potential new electrode materials for synthesis experiments. (Sep. 10)) - **COMPLETE**

Complete Si PDF data. Initiate *in situ* NMR studies of multicomponent electrodes (Mar. 10)

Complete analysis of Si nanoparticles. (Sep. 10) **COMPLETE**

Milestones 2011

Initiate Na calculations. (Mar. 11)) - **COMPLETE**

Initiate electrochemical testing of one new material in sidorenkite class. (Mar. 11) - **COMPLETE**

Initiate surface characterization. (Mar. 11) **- ONGOING**

Investigate two new cathode materials and structurally characterize. (Sep. 11) **- ONGOING**

Explore Li dendrite formation on a series of ionic liquids. (Sep. 11) **- ONGOING**

Investigate local structure in various $Li(Ni_{0.5}Mn_{1.5})O_4$ spinels and compare with rate performance. (Sep. 11) **- ONGOING**

Approach

Kinetics

- Use **first principles modeling** to determine Li migration barriers
- Apply **phase transformation theory** to understand rate of first order transitions
- **Electrochemical rate testing** in cells/electrodes optimized to evaluate rate

New Materials

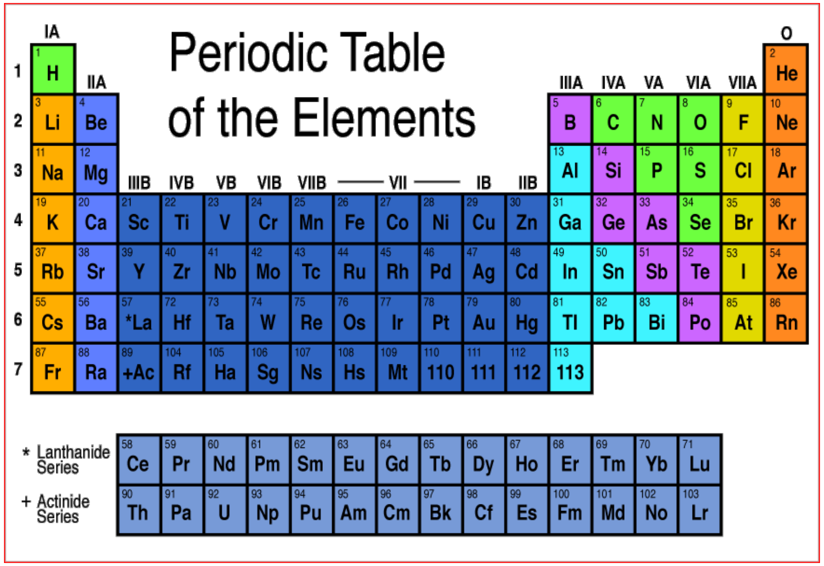
- **High-throughput computational screening** of candidate materials on voltage, capacity, stability, Li mobility, and oxygen release (safety)
- **Synthesis, characterization** and **electrochemistry** of novel materials

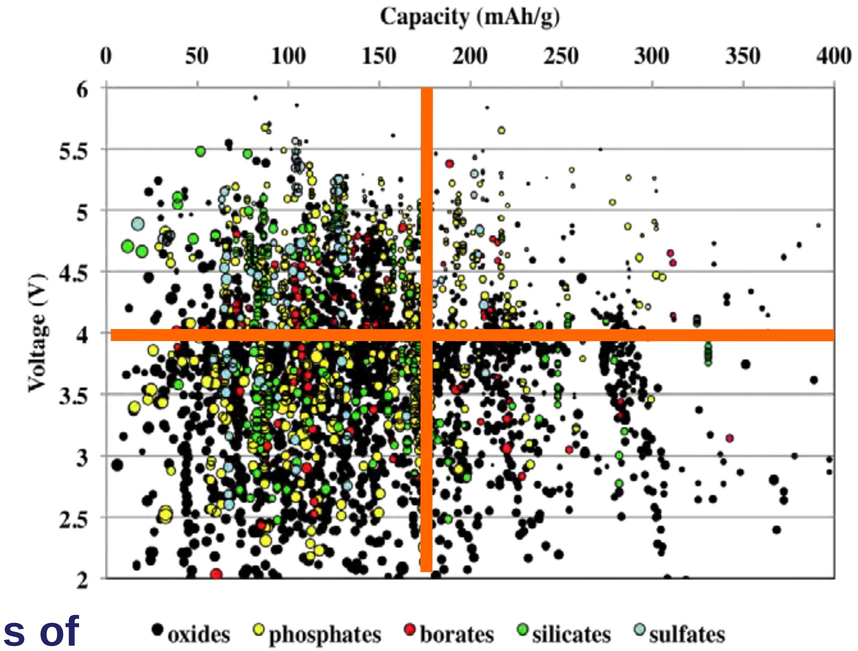
Characterization

- Use **solid-state NM**R and **diffraction** based methods to characterize short, intermediate and longer-range structure as a function of state of charge, and number of cycles
- Continue to develop the use of **in-situ NMR** methods to identify structural changes and reactivity in oxides and intermetallics.
- Use in-situ methods to capture **metastable or reactive intermediates**
- Apply **PDF methods** to examine disordered systems.

Technical Accomplishments

New materials discovery (ongoing)





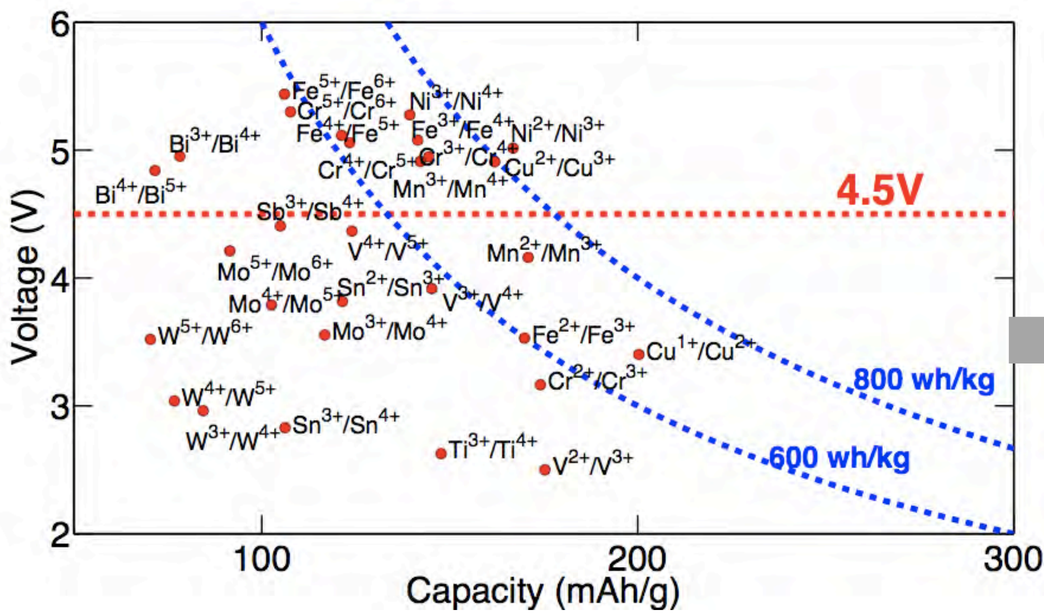
Voltage vs capacity for over 20,000 potential Li-ion cathode compounds calculated by high-throughput ab initio methods.

- Use scalability of computing to evaluate thousands of possible new cathode materials.
- Screen on voltage, capacity, density, stability, thermal stability in charged state. Interesting compounds further studied for Li diffusion and electron mobility.
- Search covers existing compounds as well as completely new materials
- Many existing battery compounds found back in search, as well as novel intercalation compounds

Collaboration with Dr Persson (LBNL)

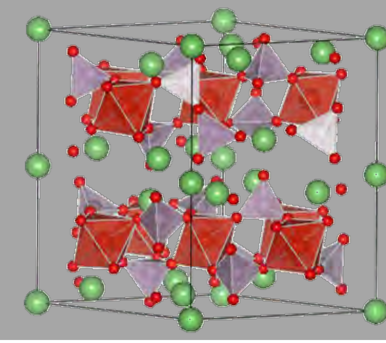
Technical Accomplishments

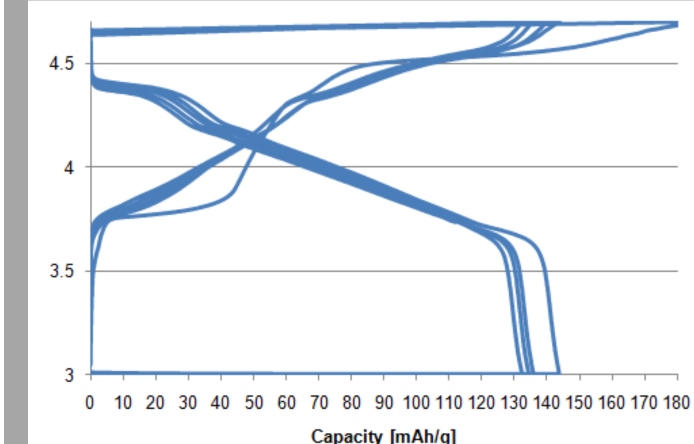
New materials discovery (phosphates)



- Voltage versus theoretical capacity in phosphates obtained from calculations on several hundred compounds
- Leads to focus on Mn, (Cu ?) , V and Mo

New material developed: $Li_9V_3(P_2O_7)_3(PO_4)_2$



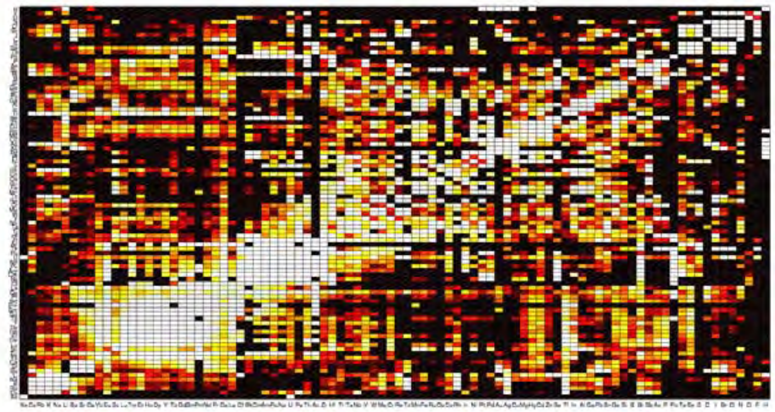


Technical Accomplishments

New materials discovery

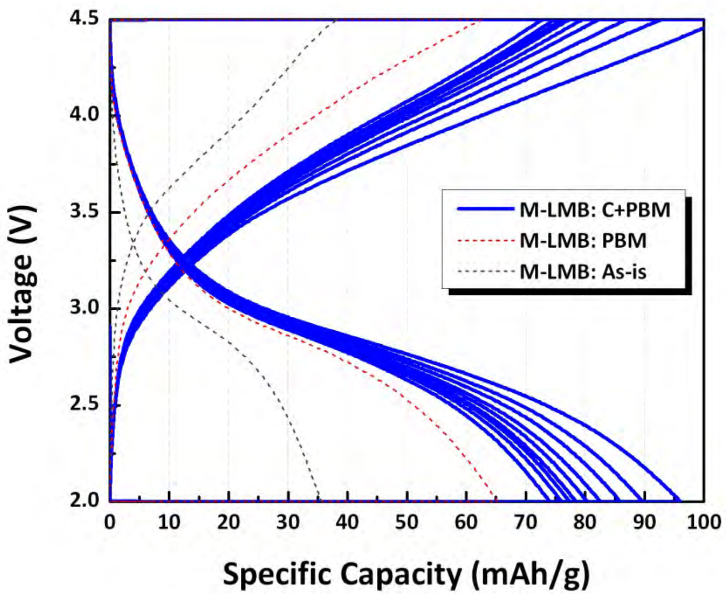
Search **known compounds**

Materials Substitution Information



Novel Compounds

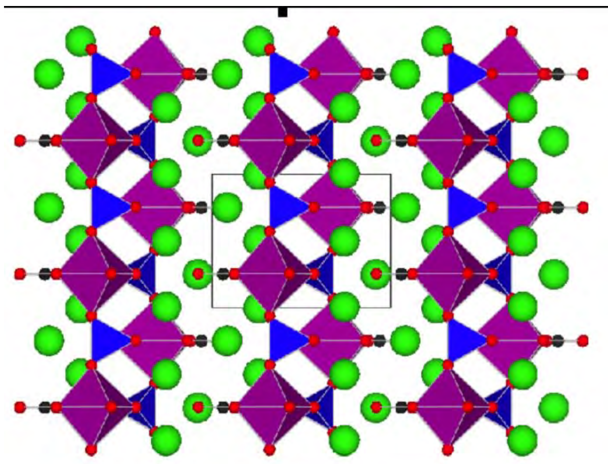
Identification of monoclinic **$LiMnBO_3$**

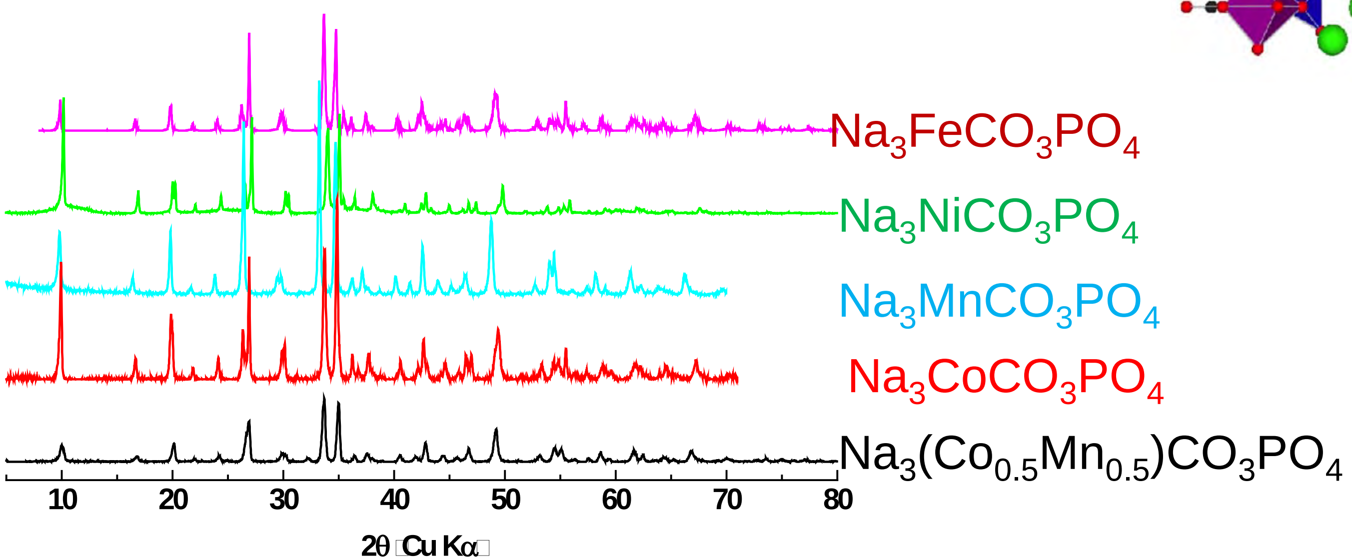


Technical Accomplishments

New materials discovery: Sidorenkite Class

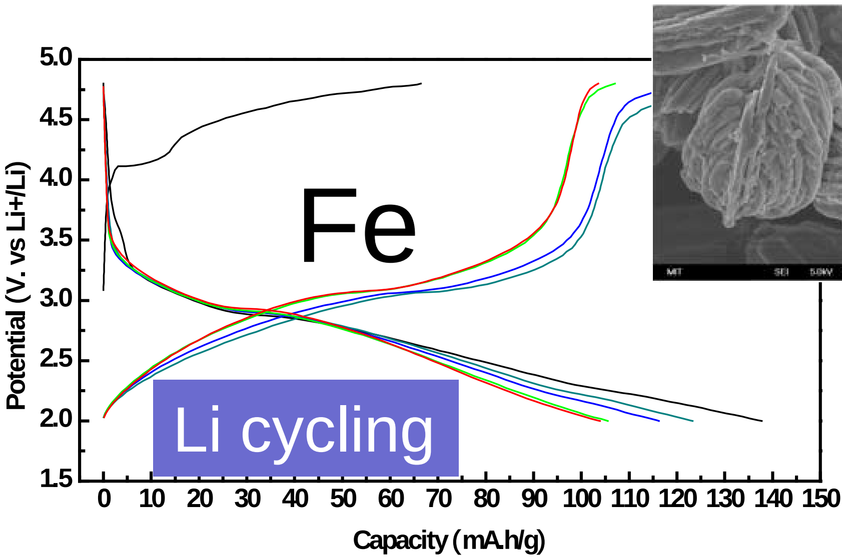
- Sidorenkite $Na_3Mn(CO_3)(PO_4)$ is a rare mineral
- Calculations predict that structures may be good for Li intercalation.
- Made many "synthetic carbono phosphates with Mn replaced by Fe, Co, Ni …
- Created first ever Li-containing carbono phosphates

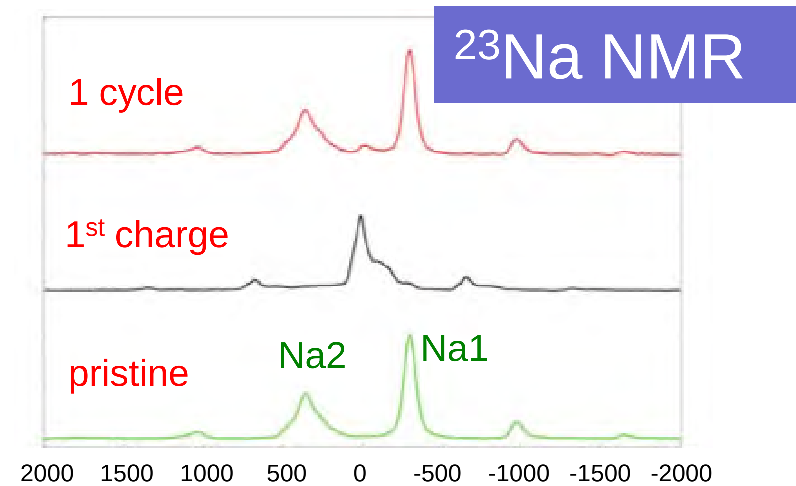




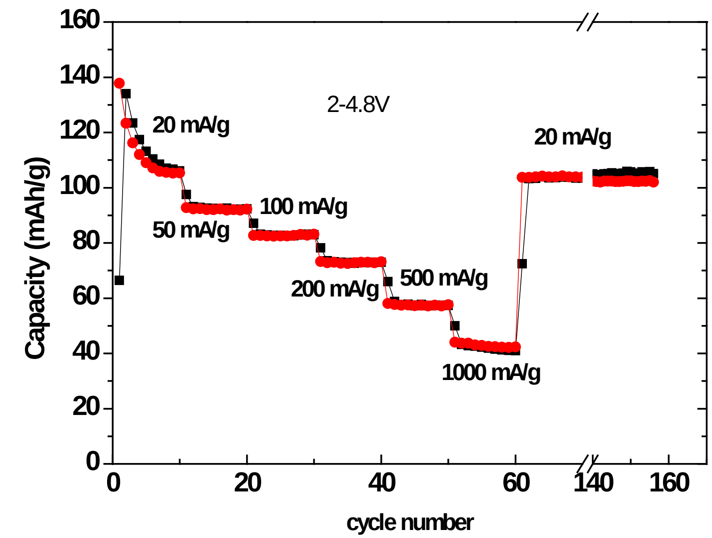
Technical Accomplishments

New materials discovery: Sidorenkite Class





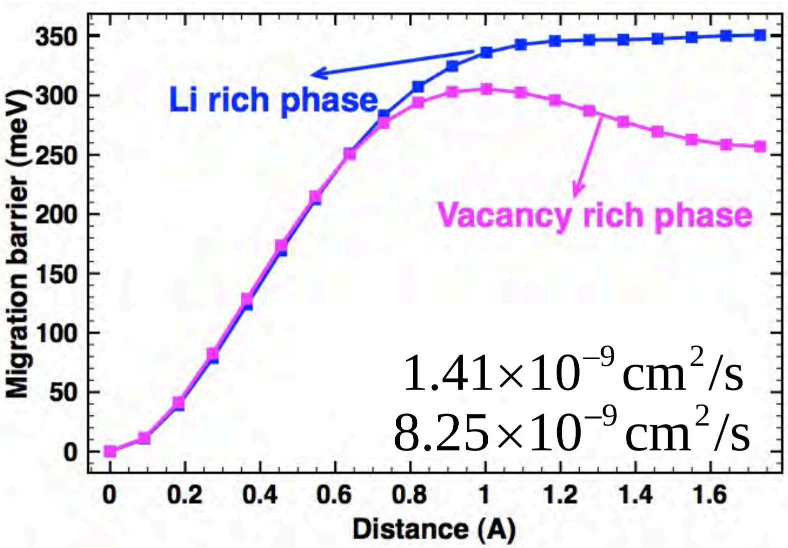
- Established that this structure is very good for Li intercalation
- Mn system has theoretical capacity of 220 mAh/g
- Only release of CO_2 upon thermal decomposition
- ^{7}Li and ^{23}Na NMR used to follow structural changes and Fe oxidation state and to investigate Na materials as Na cathodes.

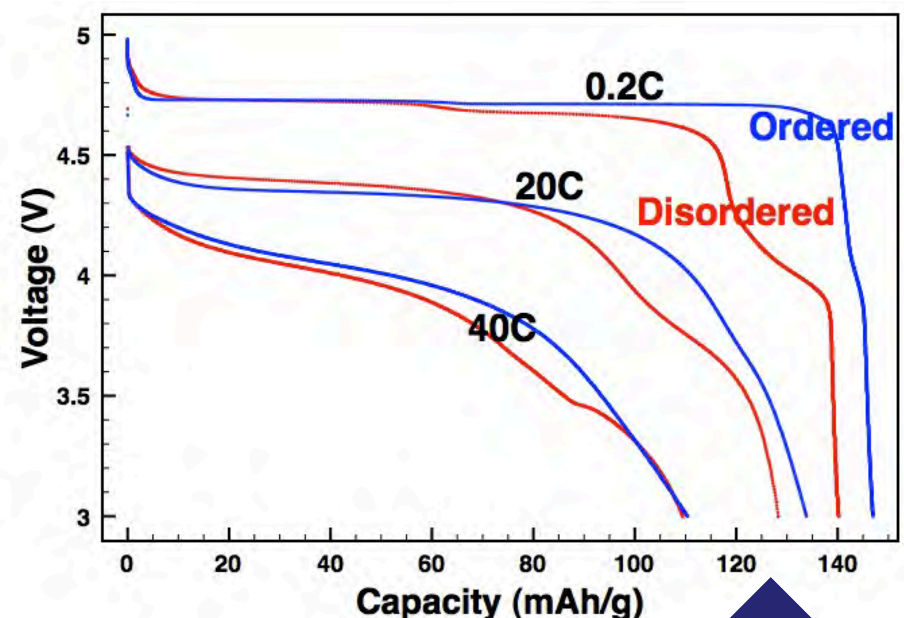


Good capacity retention and rate capability

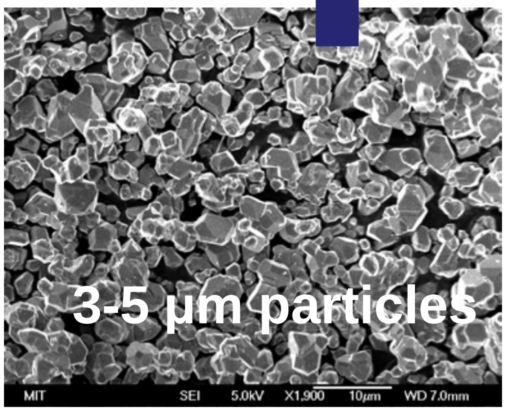
Technical Accomplishments

Rate issues in $Li(Ni_{0.5}Mn_{1.5})O_4$ spinel





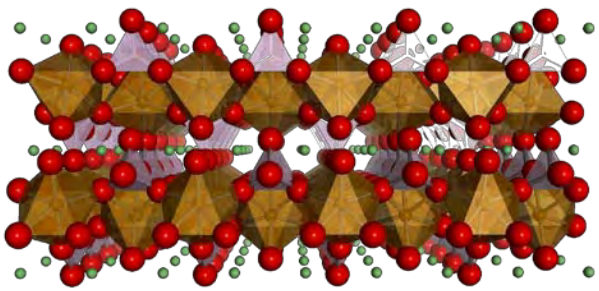
- •Li migration energy calculations indicate high Li mobility
- •No significant difference between ordered and disordered spinel
- •NMR studies of spinels initiated (in collaboration with J. Cabana and G. Chen (LBNL))



XH Ma, B. Kang, G. Ceder, J. Electrochem. Soc., 15), A925-A931 (2010).

Technical Accomplishments

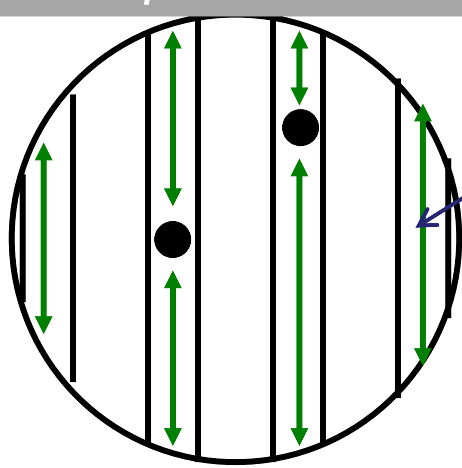
Understanding Dimensionality and Particle Size Effects on Diffusion of Lithium



1D diffusion and very high rate

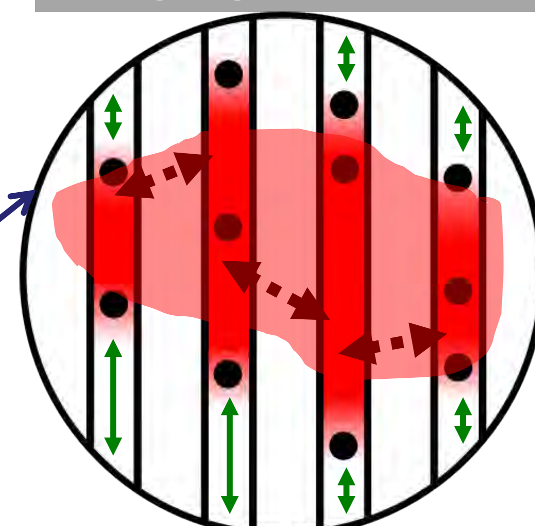
Why no micron sized $LiFePO_4$ with good rate ?

Small particles



In small particles only need motion in channel: $E_a \approx$ 200-300meV

Large particles

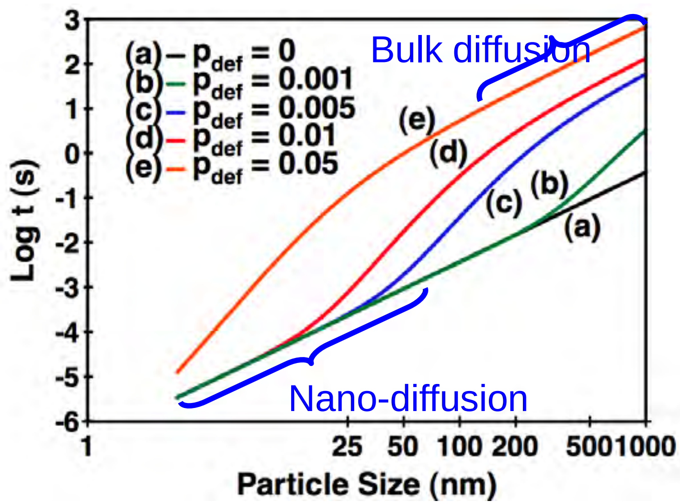


In large particles also need Li transfer between channels: $E_a \approx$ 500 meV

R. Malik et asl., Nano Letters, 10 (10), 4123-4127 (2010).

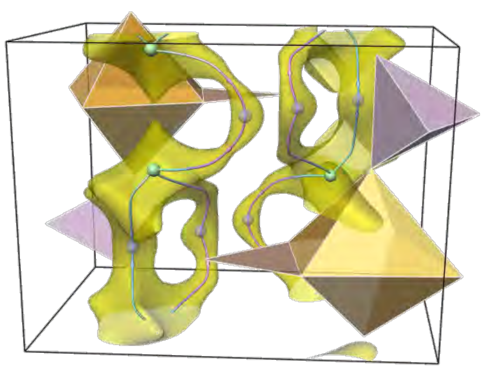
Technical Accomplishments

•Computationally predicted that the anti-site (Fe_{Li} and Li_{Fe}) is lowest energy defect



Time to diffuse into particle shows two distinct behaviors

There are two Li diffusion constants: one for nanomaterials (controlled by in-channel diffusion and one for large crystals (dominated by channel cross over diffusion)



IMPORTANT GENERAL CONCLUSION

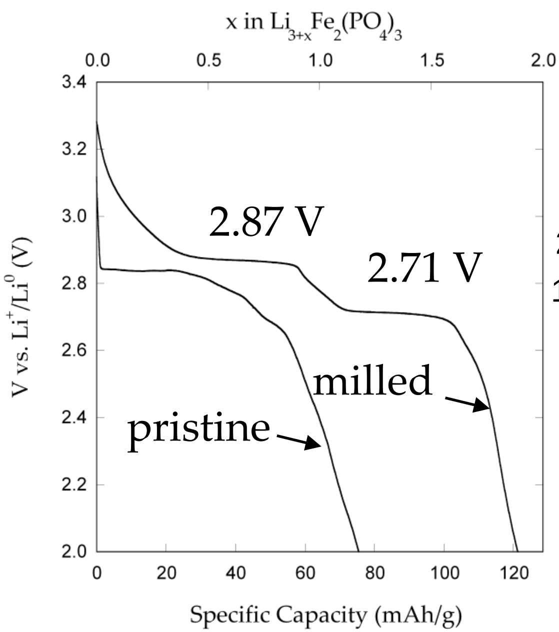
This nano effect will also be seen in other 1D diffusers

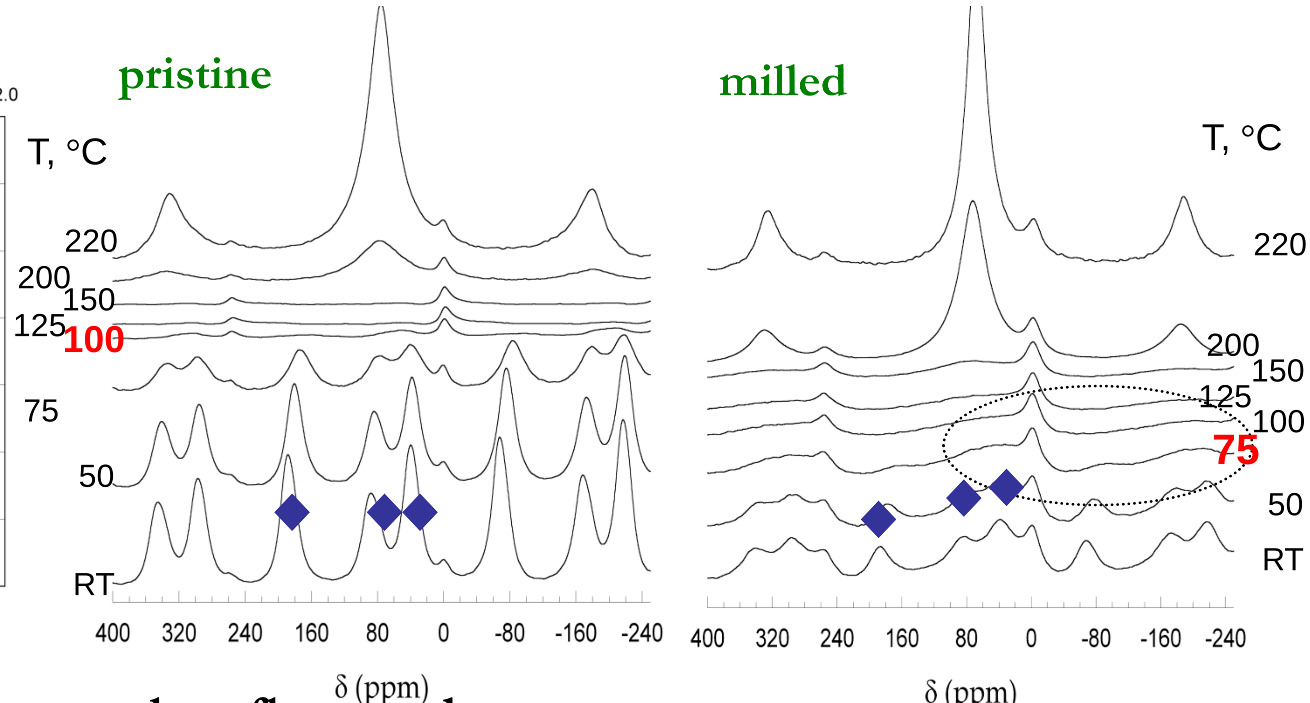
$LiMnBO_3$, $LFeBO_3$, Tavorites: $LiVO(PO_4)$, $LiV(PO_4)F$, and $LiFe(SO_4)F$

Experimental Studies of Particle Size/Shape and Defects

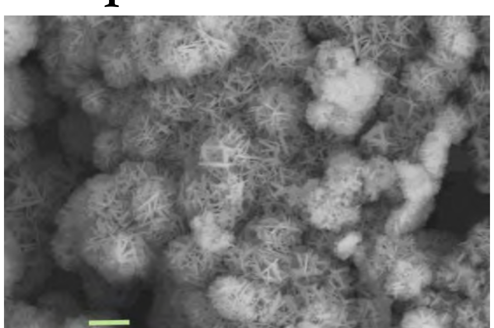
A-type (Monoclinic) Nasicon – milling introduce reduces particle size and introduces defects, increasing mobility

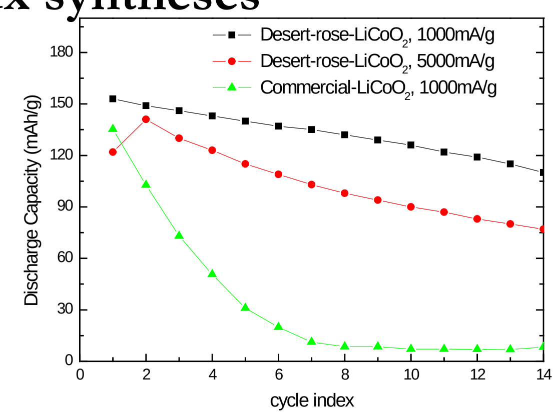
With J. Cabana, J. Shirakawa and M. Wakihara

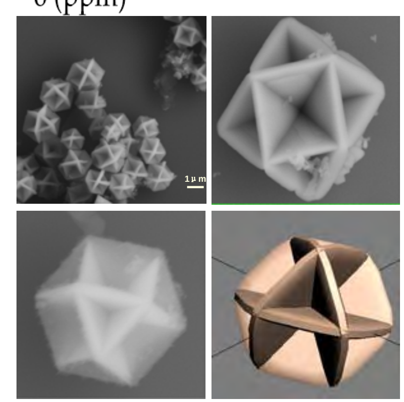




$LiCoO_2$ – low temperature molten flux syntheses

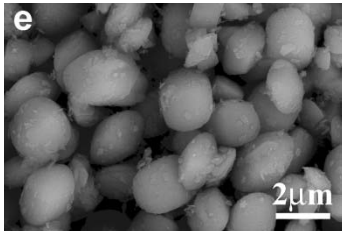




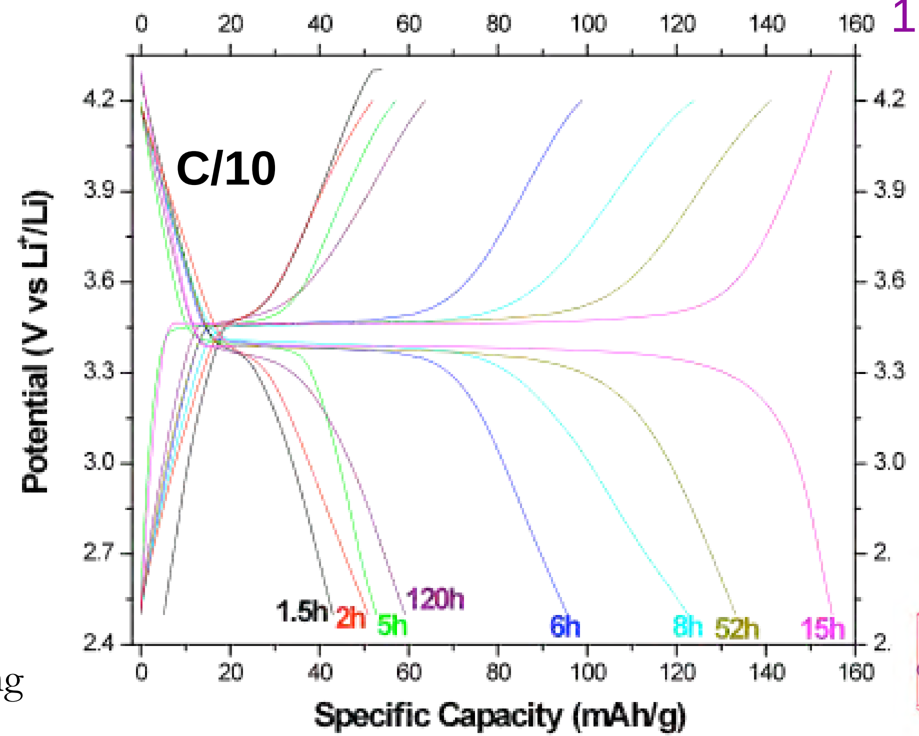


Experimental Studies of Particle Size/Shape and Defects

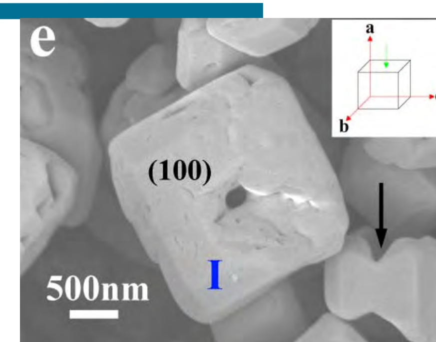
Synthesis of $LiFePO_4$ with citric acid and $(NH_4)H_2PO_4$

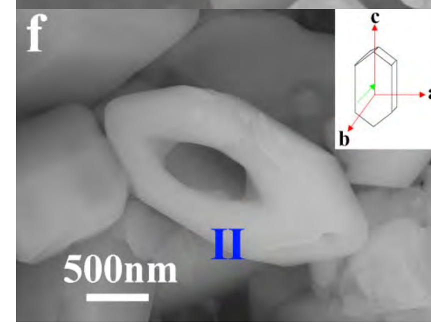


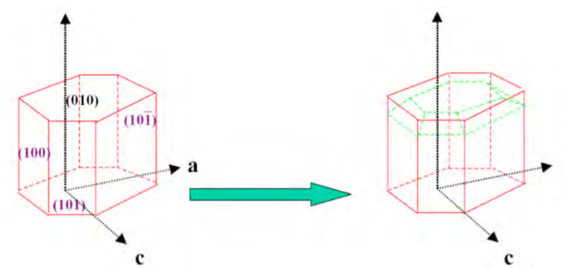
1.5 hours



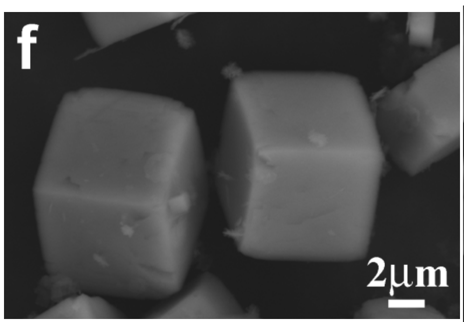
15 hours

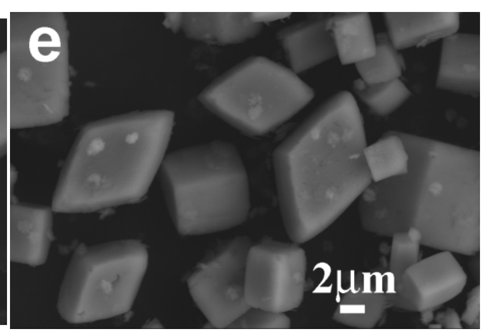




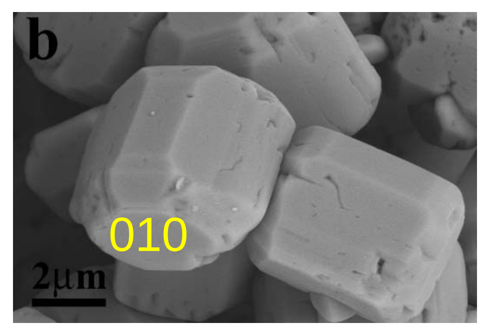


With Z. Lu (Hongkong/SBU, L. Wu (BNL) and Jonathan C.Y. Chung (Hongkong)



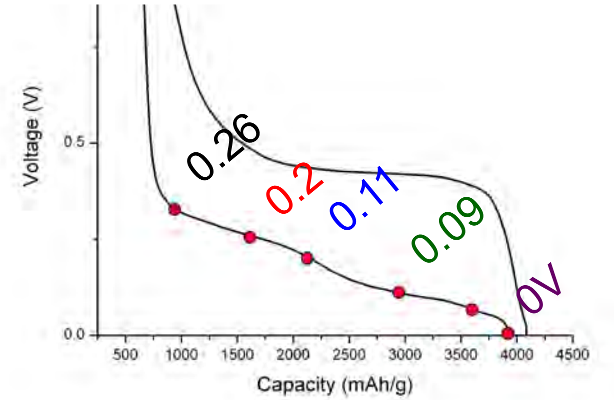


5 hours



52 hours

Anodes: NMR and PDF Studies of Silicon



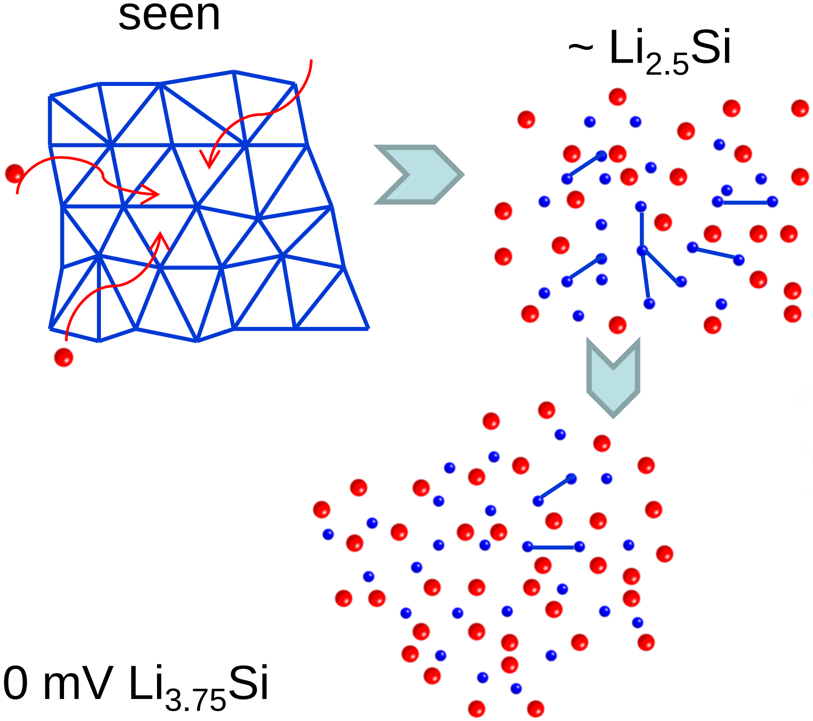
Relevance to goals: Very high capacity (>3700 mAh/g)

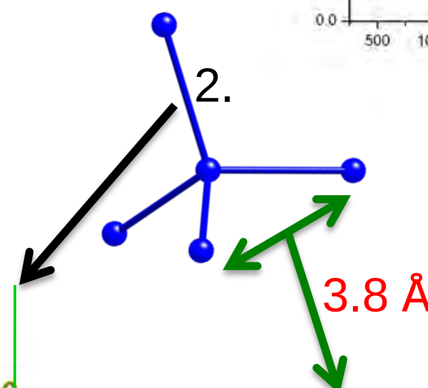
Barriers: Large hysteresis; poor rate performance; reactivity of Si with electrolyte

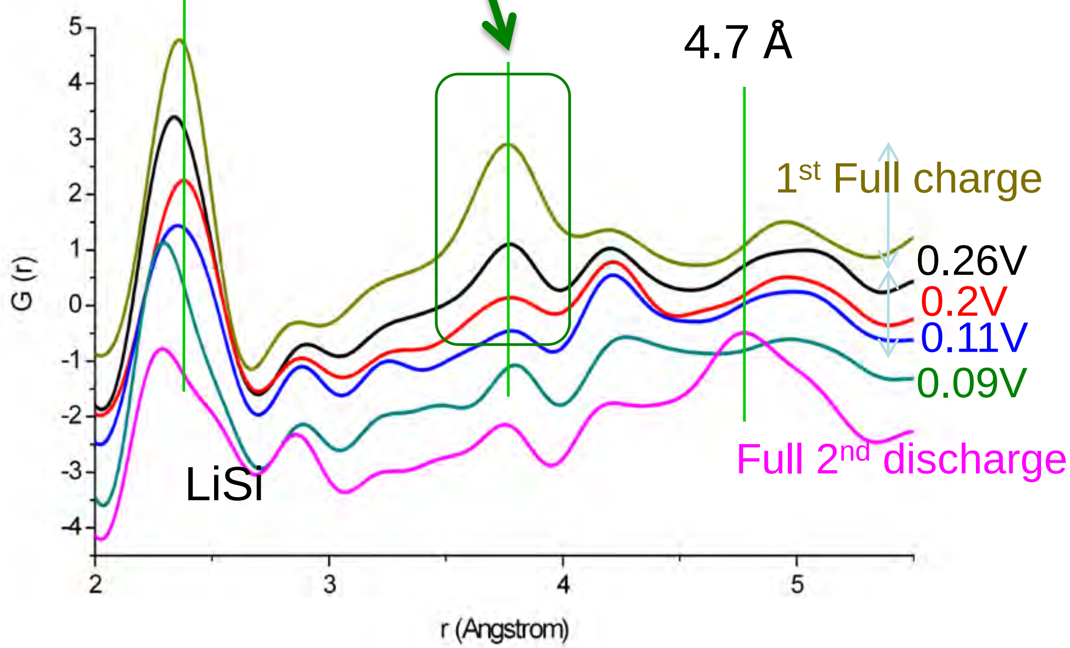
Status March 2011:

1. Determined the structural basis of the electrochemical profile
2. Helps explain why only the xstalline phase(s) containing isolated Si ions are seen

With M. Morcrette and J.-M. Tarascon



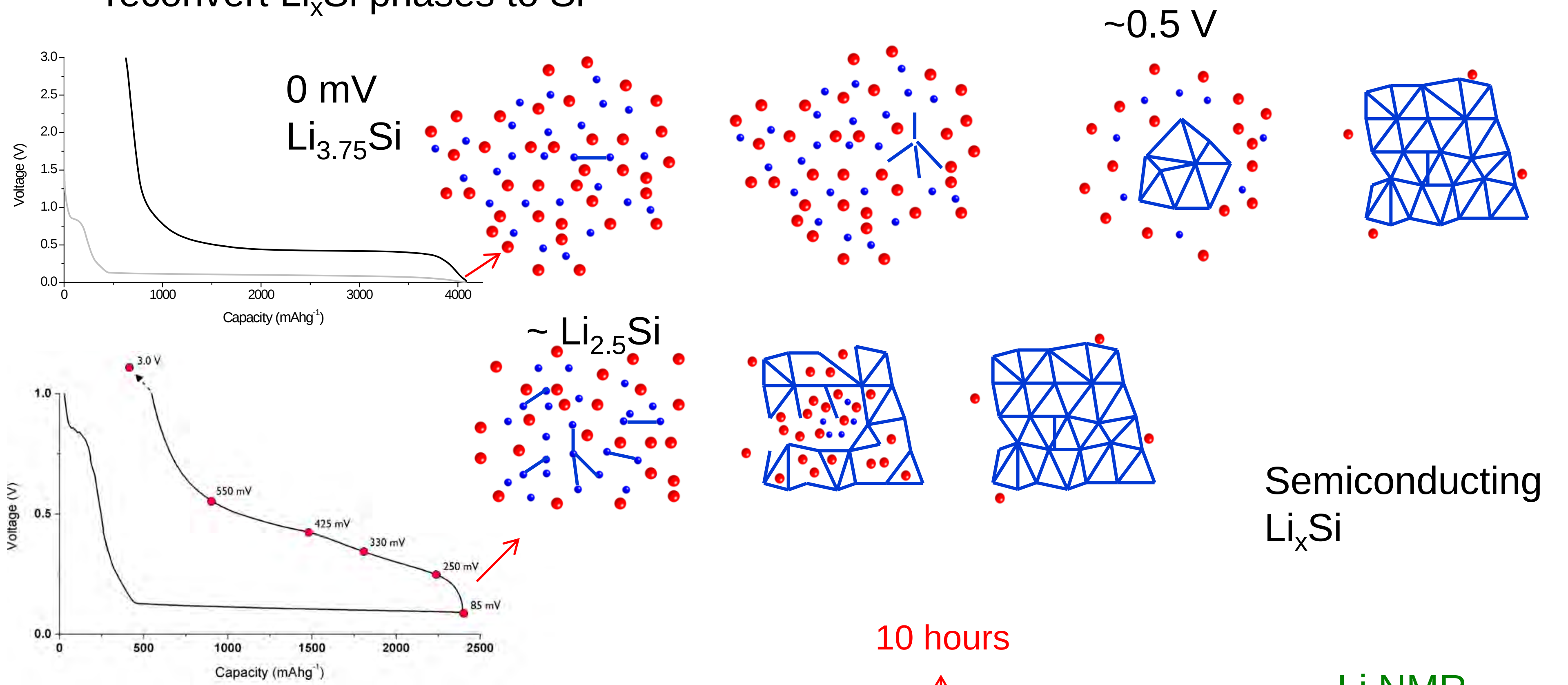




Anodes: NMR and PDF Studies of Silicon

Status March 2011 (cont.):

3. Residual clusters act as nuclei to reconvert Li_xSi phases to Si

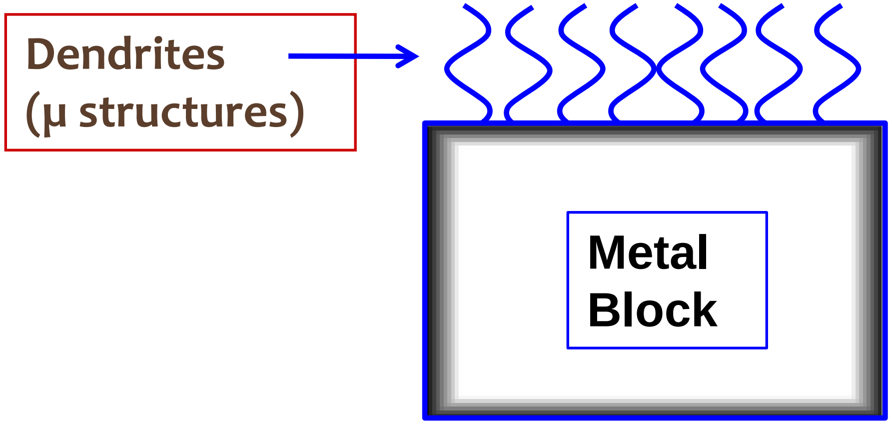


4. Nanostructured Si is more reactive – its electronic properties on full discharge are different

In Situ NMR: Detection of Li Dendrites and Mossy Li

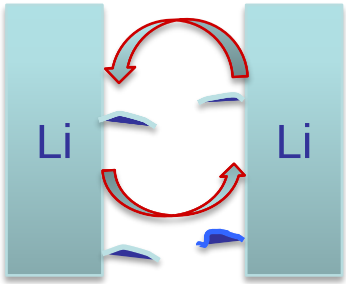
Relevance to goals:
Dendrites and short-circuits are a serious safety issue that:
•Prevents use of (high capacity) Li-metal anode
•Has been implicated in failure of LIBs in PHEV's when charged at high rates (e.g., during regenerative braking)

Status 2011:
•Devised simple, non-destructive method for monitoring and *quantifying* dendrite formation in Li cells and for readily determining the conditions under which these dendrites form.



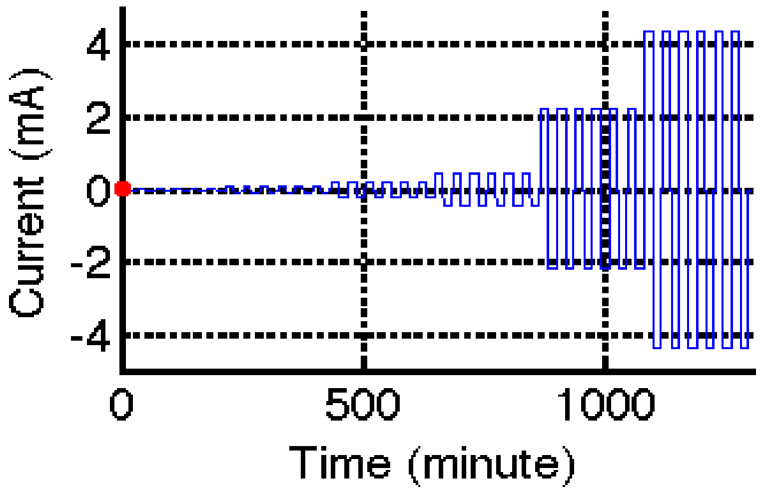
Skin depth, d = 15 μm for Larmor frequency = 77 MHz (Low field ^{7}Li NMR)
i.e., can penetrate the dendrite, not Li foil
(d α $1/f^{1/2}$ => decreases at higher fields

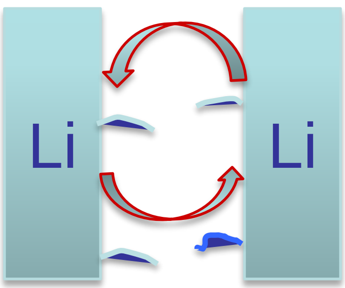
Use to investigate effect of different currents, electrolytes, additives



With A. Best, A. Hollenkamp CSIRO

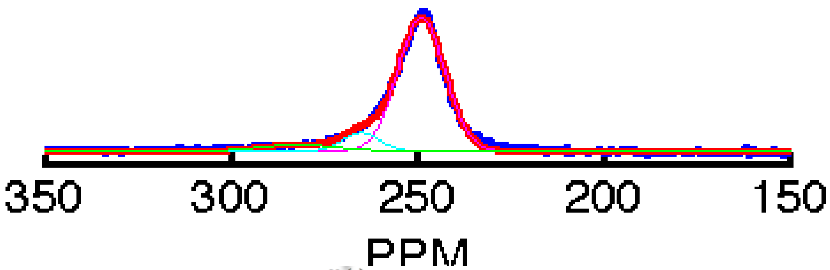
Symmetric Cells (constant Li mass):

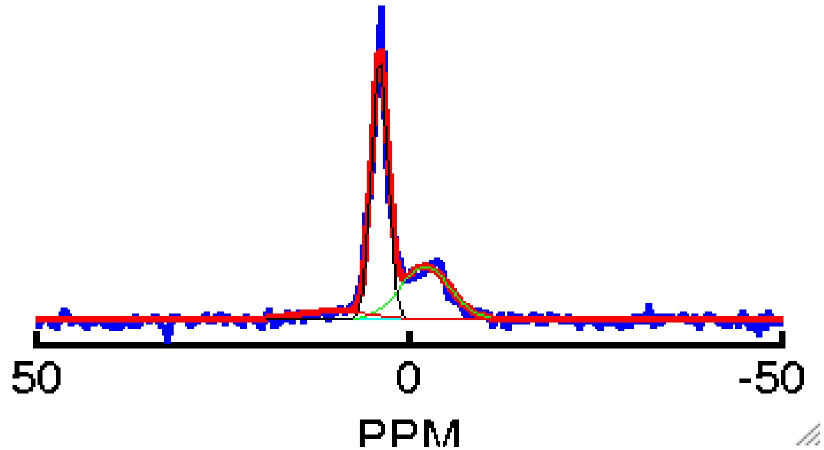




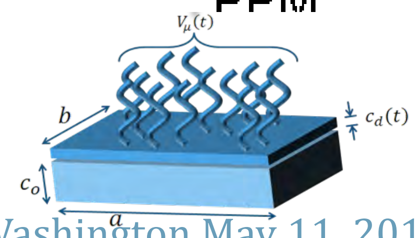
Effect of current on dendrite formation

Electrode size = 0.1mm x 0.4mm
Maximum current 4.4 mA = 11 mA/cm^2





Electrolyte decomposition on Li

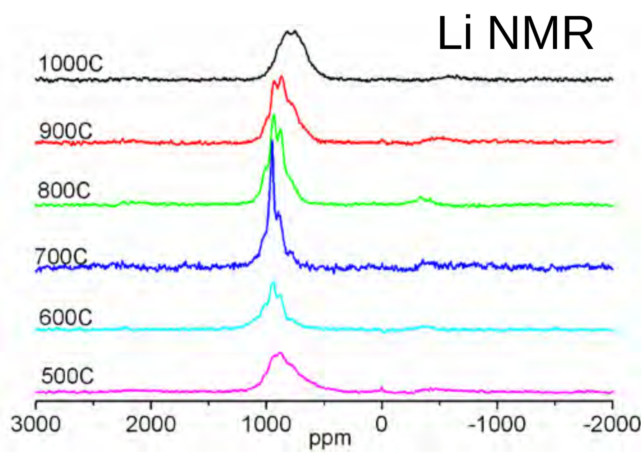


Summary and Future Work

- Understood Li diffusion limits in nano versus micron olivine, and broadened insight to many other 1D intercalation materials.
- Investigated Li diffusion in graphite (with Kostecki and Persson) and Li(Ni0.5Mn1.5)O_4 spinel and established high rate capability of both.
- Investigated shape, size and processing effects on rate in a series of cathode materials
- Several novel intercalation cathodes proposed by high-throughput computing and tested
- Collaborated with Whittingham on novel pyrophosphates
- Developed structure – function correlations in silicon anodes; observed different reactivities of lithiated silicides as a function of size and lithiated state
- Developed new diagnostic method to detect Li dendride formation.

Ongoing and future work

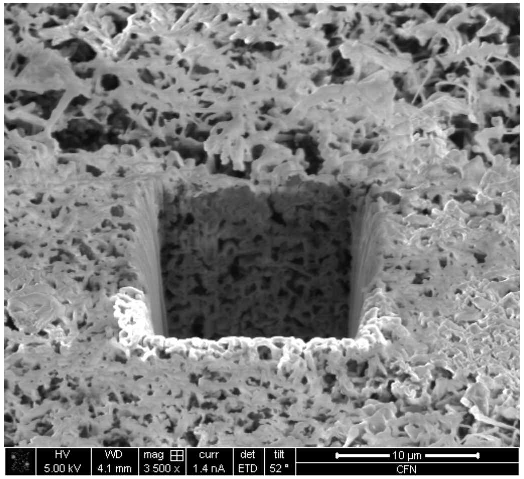
- Local structure – function correlations in the high voltage spinel (BATT collaboration): NMR very sensitive to Ni/Mn ordering
- Develop further structure functions correlations in Si anodes by using ^{29}Si NMR
- Investigate SEI-binder-Si interactions to mitigate side reactions
- Explore Si anodes prepared by A. Dillon (nrel/BATT collab)



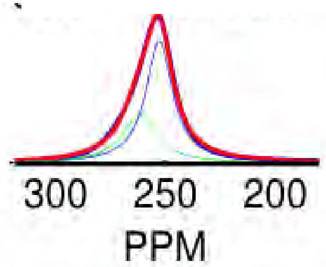
J. Cabana

Ongoing and Future Work continued

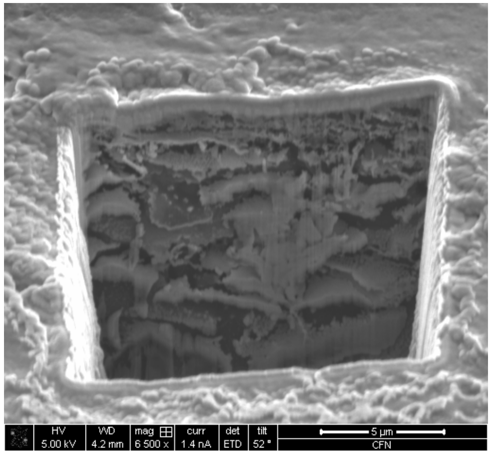
- Investigate relationships between current, temperature, pressure and mossy/dendritic Li by SEM/in-situ NMR and MRI
- Electrode surfaces and degradation mechanisms
- Continue novel compound evaluation. Several other interesting leads to follow up on for new intercalation cathodes
- Carbonophosphates: structural characterization upon delithiation through NMR and in-situ XRD (Brookhaven). Other physical properties
- Evaluate effects on dimensionality in other novel cathode materials
- Support BATT investigation relating $Li(Ni_{0.5}Mn_{1.5})O_4$ structure to performance
- Explore Na batteries: structure, Na mobility, voltage, and structural stability in relation to Li-intercalation compounds



Bag cell vs. coin cell



Li metal signal



D. Zeng, BNL