First Principles Calculations and NMR Spectroscopy of Electrode Materials

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Stony Brook University

March 20, 2009

Project ID #
es_27_grey

Overview

Timeline

- Start date: May 2006
- End date: February 2010

Budget

- Total project funding: – $1M
- Funding in FY08: – $270K
- Funding in FY09: – $385K

Objectives

- Determine the effect of structure on stability and rate capability of cathodes and anodes.
- Explore relationship between electrochemistry and particle size and shape.
- Understand and predict reactivity of anode and cathode electrode materials with electrolytes.
- Develop new materials

Barriers

- Low rate capabilities
- High cost
- Poor Stability

Partners

- **Gerbrand Ceder (MIT) (co-PI)**

- Collaborators (BATT):
- Prof. M.S. Whittingham, Binghamton
- Dr. M. M. Thackeray, ANL
- Drs. T. Richardson, J. Cabana, LBNL

- Profs. J. –M. Tarascon, C. Masquelier, Amiens

Milestones

- (a) November 1, 2008: Demonstrate the application of the *in situ* NMR technology to investigate nanoparticle deintercalation/intercalation methods. COMPLETE
- Complete studies of structural changes that occur at high voltages in nickel and manganese containing layered materials. COMPLETE
- (b) May 1 2009: Computational results on lithiation of nanomaterials; Produce initial results on broad search for new materials.
- Complete NMR/electrochemical studies of coatings on lithium nickel manganese oxides materials. In progress*
- Complete NMR and pair distribution function (PDF) studies study of silicon, during the 1st cycle; initiate structural and reactivity studies on the effect of cycling Si to different states of (dis)charge. COMPLETE
- Complete investigation of mechanisms for phase transformations in $LiMPO_4$ as a function of shape for M = Fe. Initiate studies for (M = Mn, Ni, Co and solid solutions of Fe and these elements). In progress*

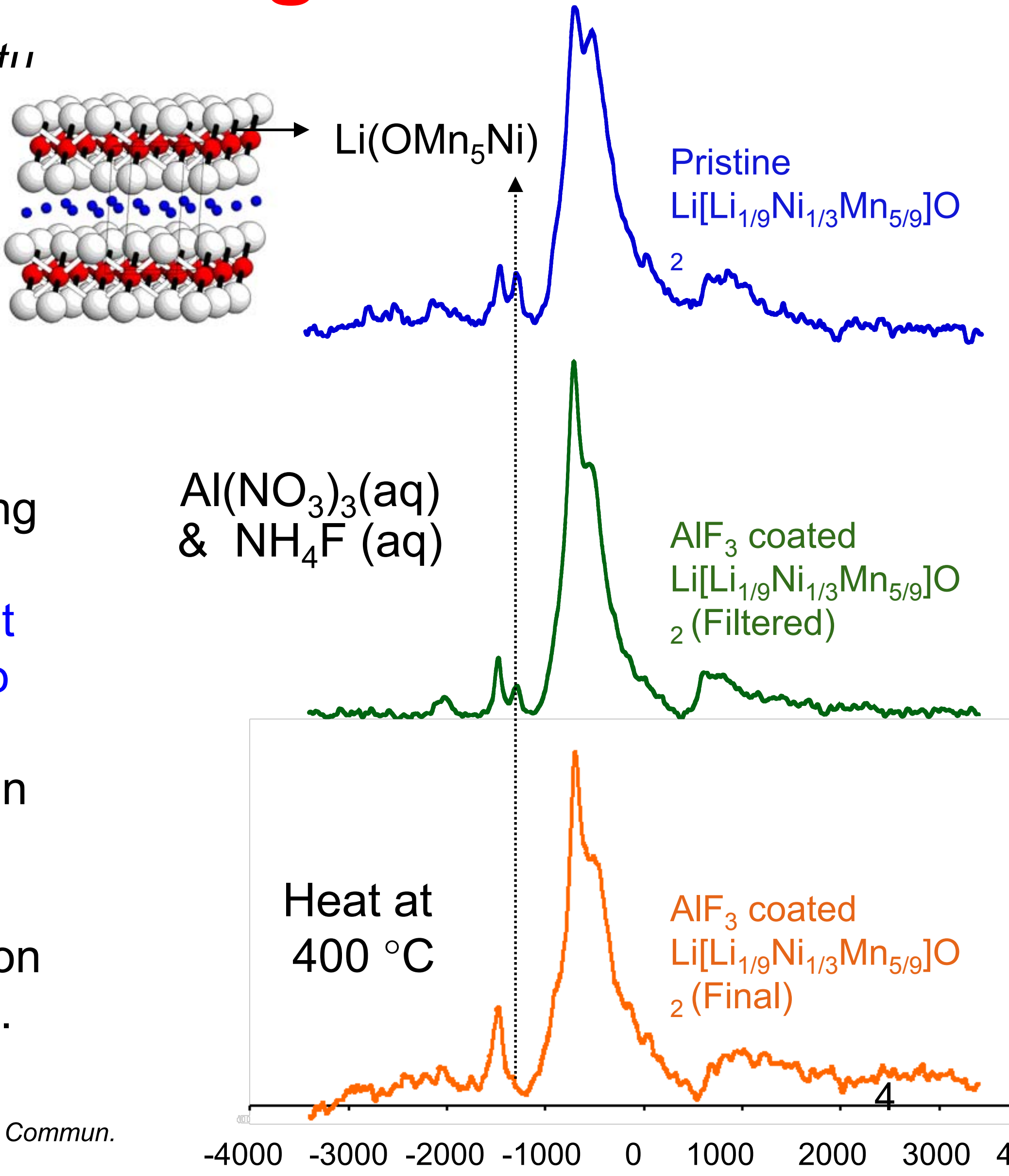
Approach

*As of March 20, 2009

- Use solid state NMR and diffraction/TEM to characterize local and long range structure as a function of particle size, sample preparation method, state of charge and number of charge cycles (cathodes).
- Use electrochemistry to correlate particle size with rate performance.
- Continue to develop the use of *in-situ NMR* methods to identify structural changes and reactivity in oxides and intermetallics.

Technical Accomplishments/Progress/Results

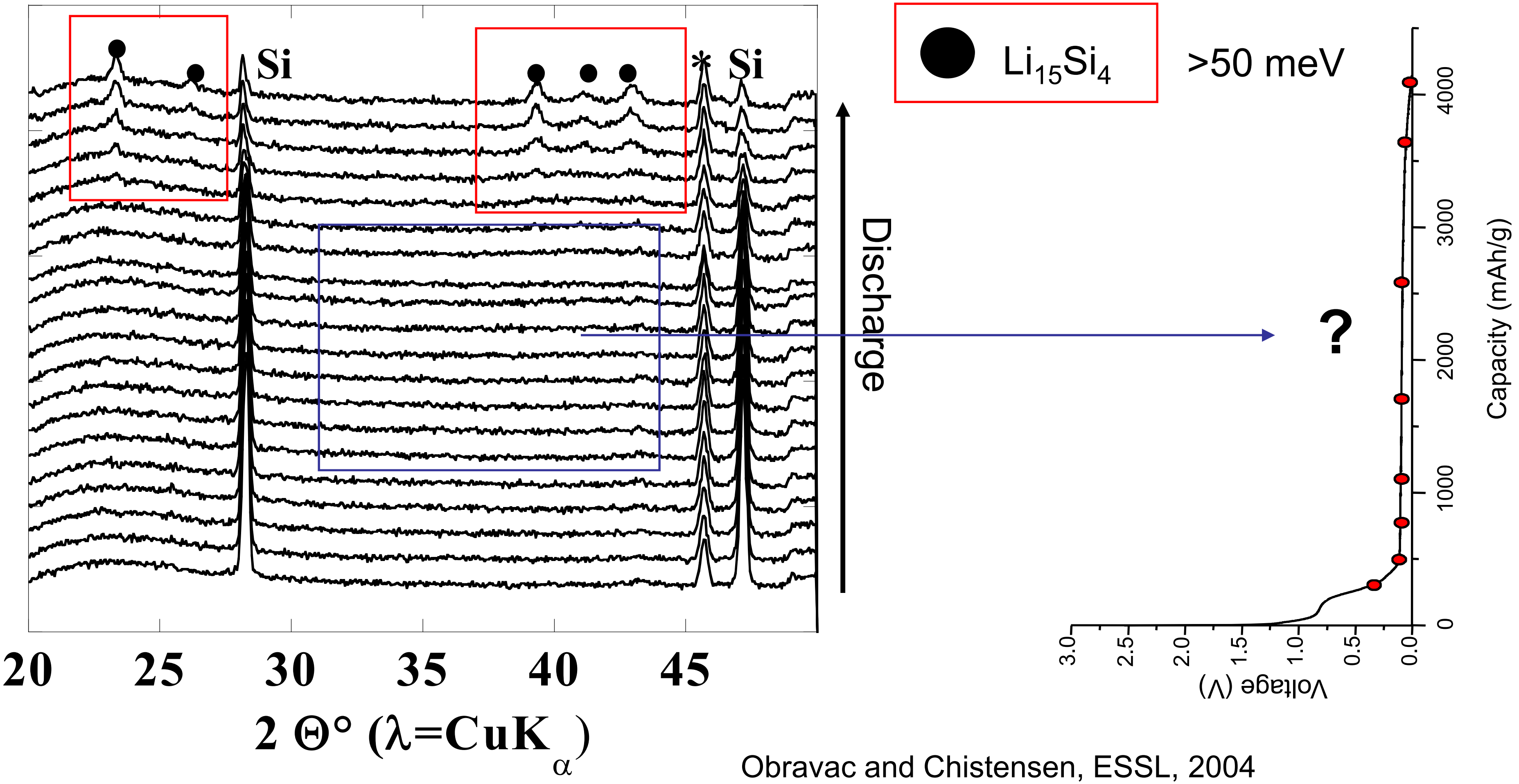
1. Development and application of *in situ* NMR methodology: Application Si – potential replacement for graphite (10 x larger volumetric and gravimetric capacity)
2. Size effects in intercalation chemistry rate, reactivity and dislocation investigation
3. Structures of coatings: effect of coating method on pristine materials: e.g., AlF_3 "coating"*: Significant effects on bulk structure due to coating method
4. 2-phase reactions: Effect of doping in phosphates. NMR/Calcs-> structure
5. New electrode chemistries: Conversion reactions, organics, MOFS etc.
6. BATT collaborations



* K. Amine, *Electrochem. Commun.* **8** (2006) 821

What are the structures of the different lithiated silicides formed on cycling?

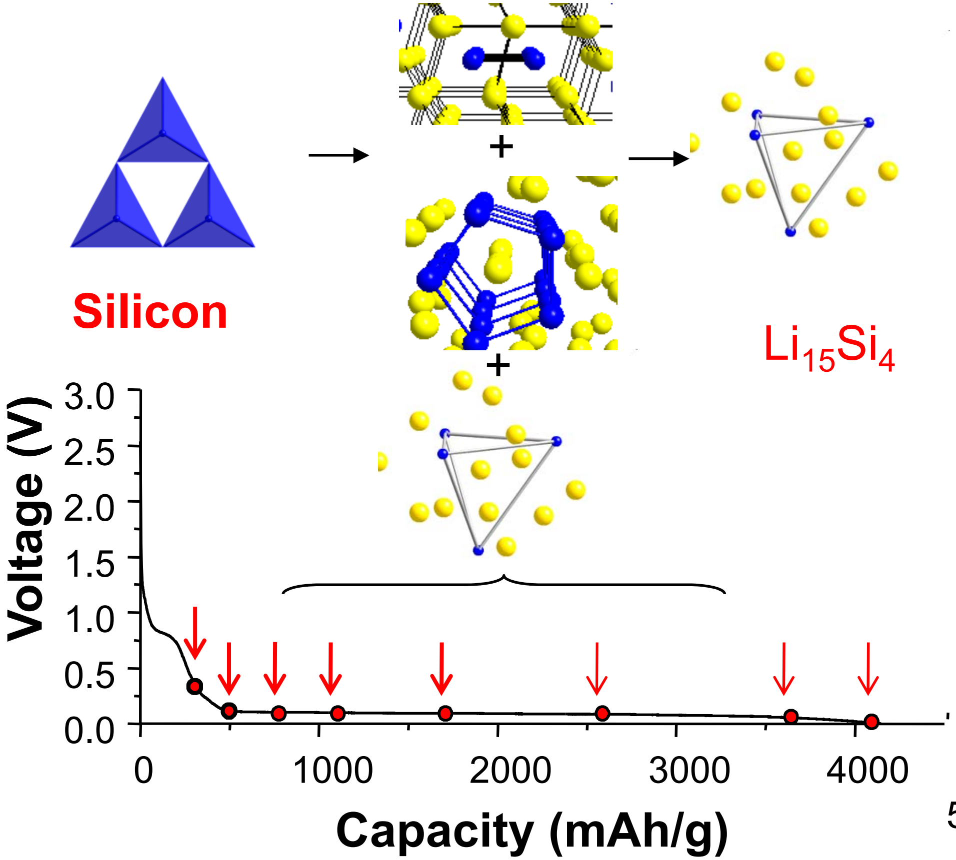
In-situ studies of cycling: Diffraction

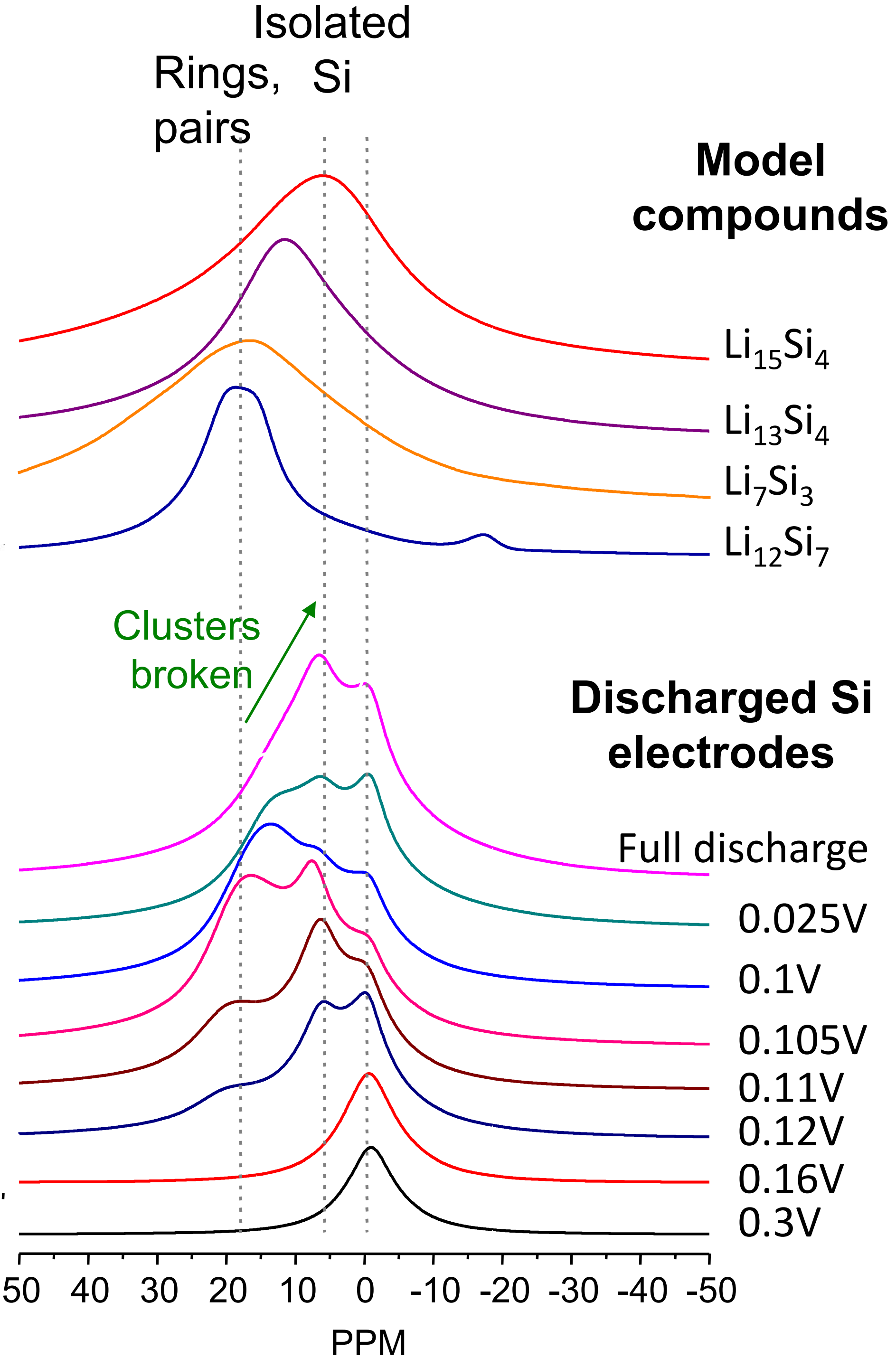


Obravac and Chistensen, ESSL, 2004
Hatchard and Dahn, JES, 2004

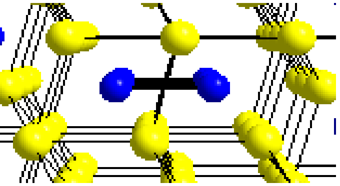
Structure of the amorphous phase?

Ex-Situ NMR: Crystalline phases vs. amorphous phase





X-ray Pair Distribution Function Analysis of Model Compounds

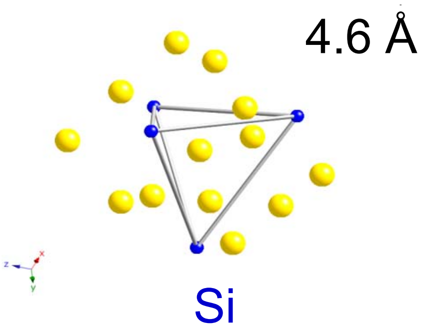


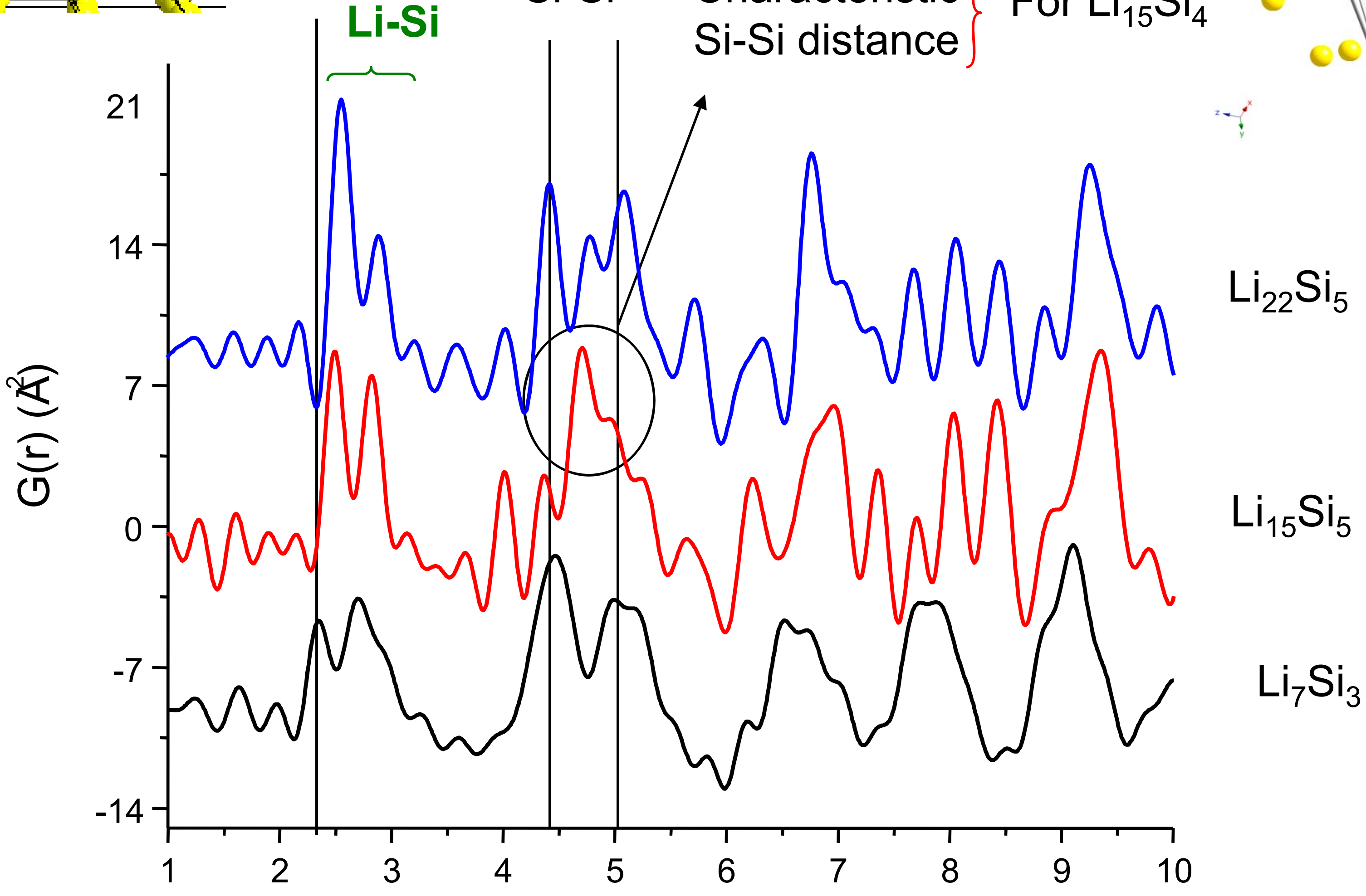
$[Si{=}Si]_2^{4-}$

2.3 Å

Si-Si

Characteristic Si-Si distance } For $Li_{15}Si_4$



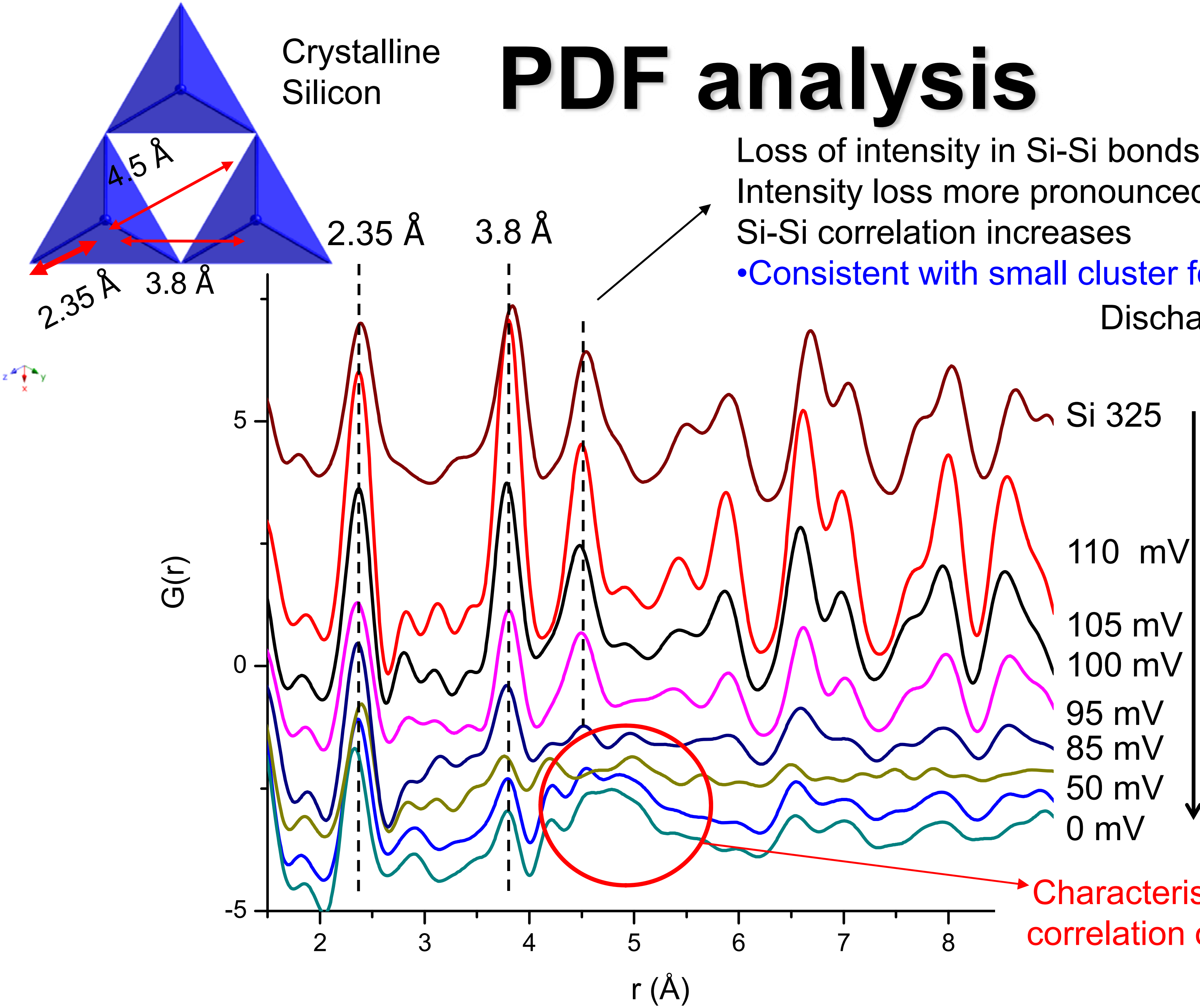


Li-Si: 2.6 – 2.9

Model Compound X-ray PDF 1-10 A. (Q range ~ 22)

PDF analysis

Crystalline Silicon



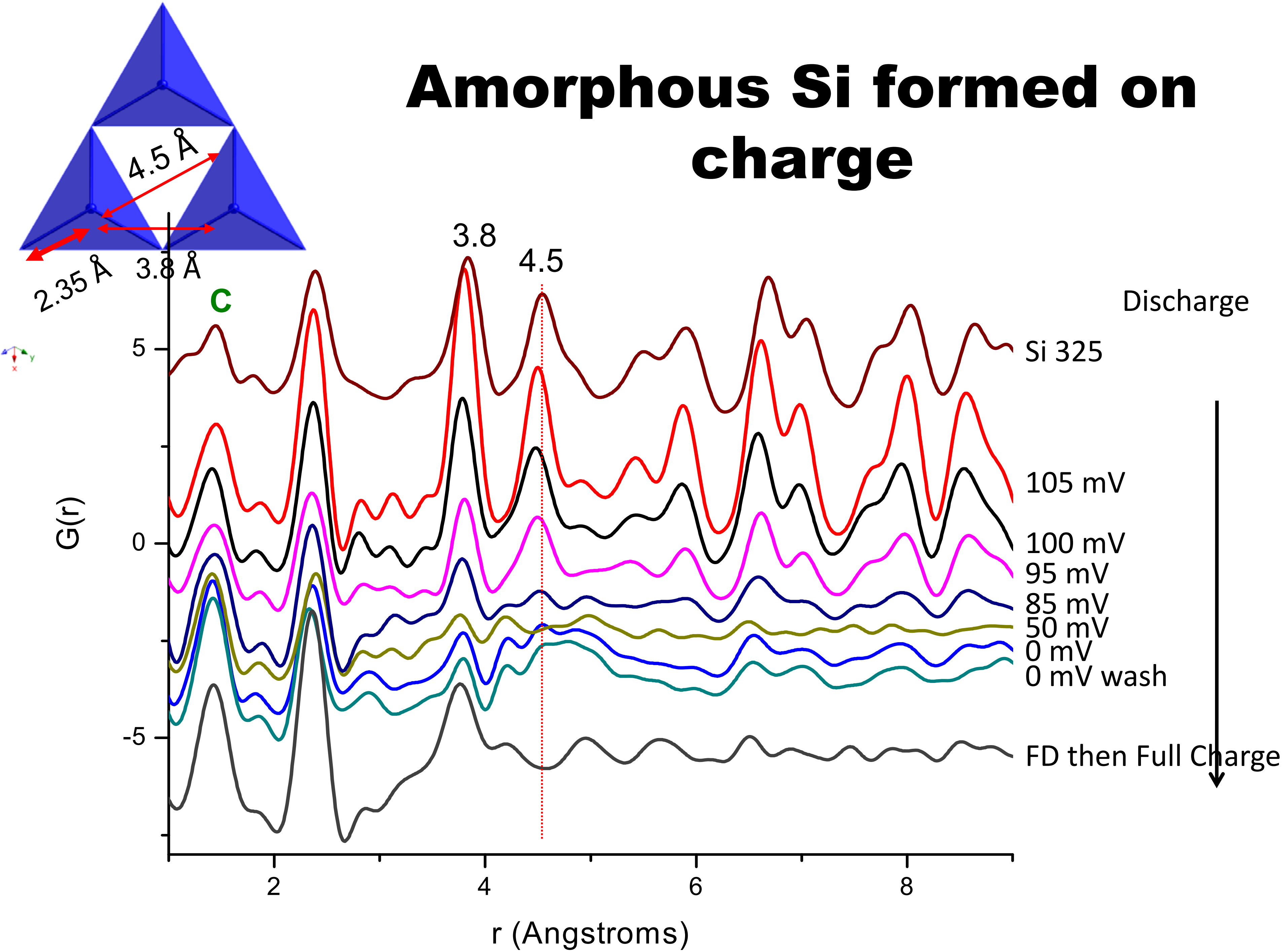
Loss of intensity in Si-Si bonds
Intensity loss more pronounced as Si-Si correlation increases

- Consistent with small cluster formation

Discharge

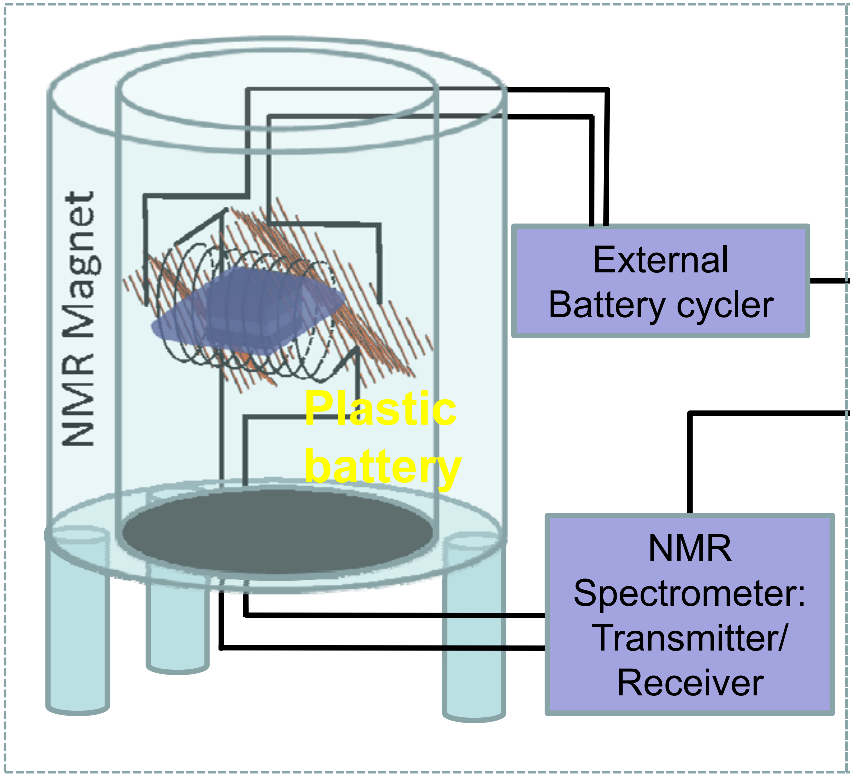
Characteristic Si-Si correlation of $Li_{15}Si_4$

Amorphous Si formed on charge



Following the Li ions in real time, in a working lithium ion battery

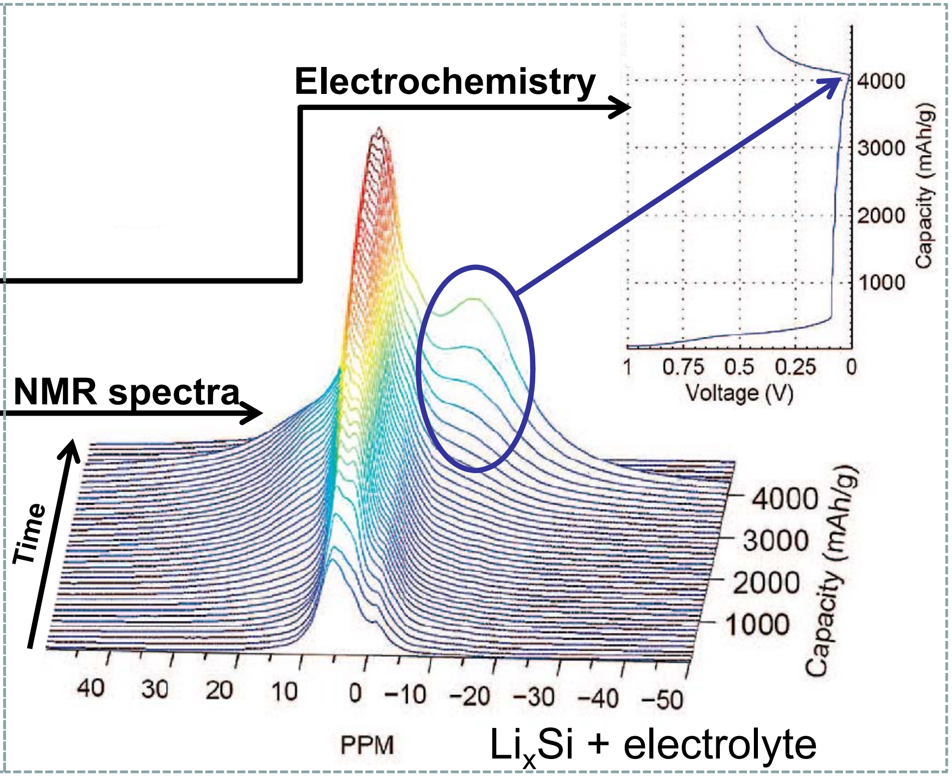
Plastic bag: Si + C (1:1) + PVDF; C/75



External Battery cycler

NMR Spectrometer: Transmitter/ Receiver

NMR spectrometer working in synchrony with the battery cycler.



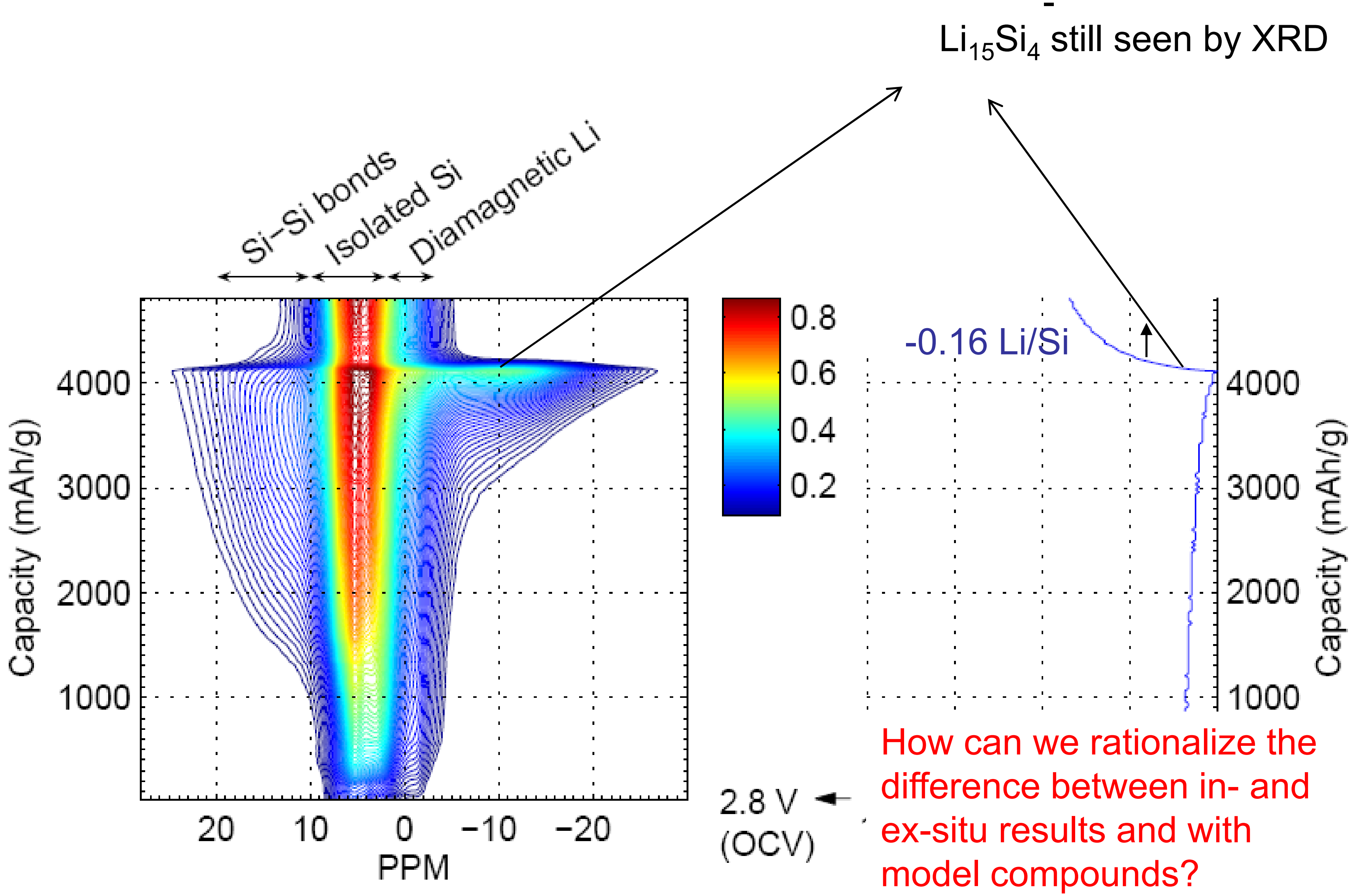
Li_xSi + electrolyte

Li NMR spectra and electrochemistry for Si

(short pulse delay - suppress electrolyte peak)

- On deep discharge, a new Li signal is observed due to the metastable phase $Li_{15+\delta}Si_4$ (blue ellipse).

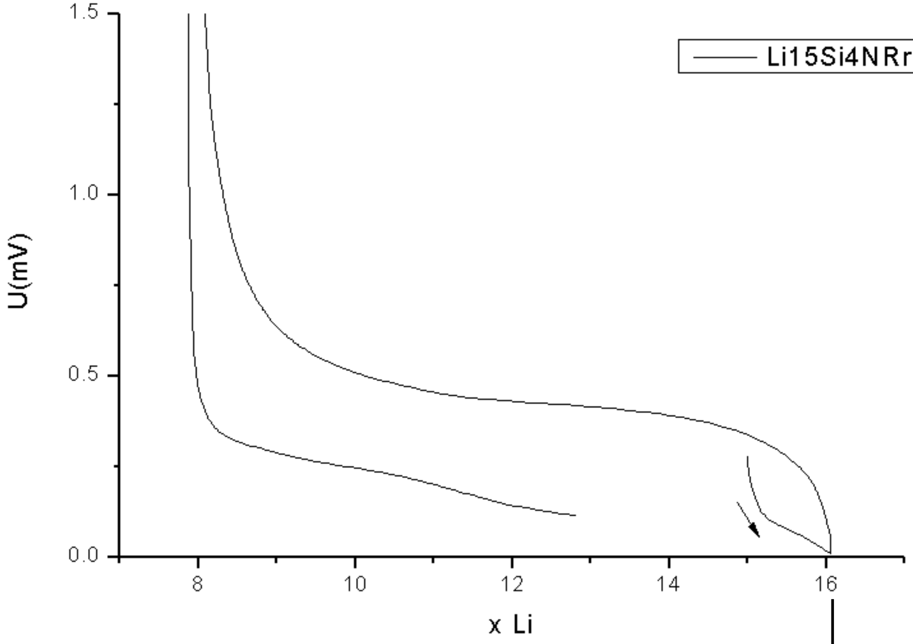
The New Environment Disappears V. Rapidly on Charge

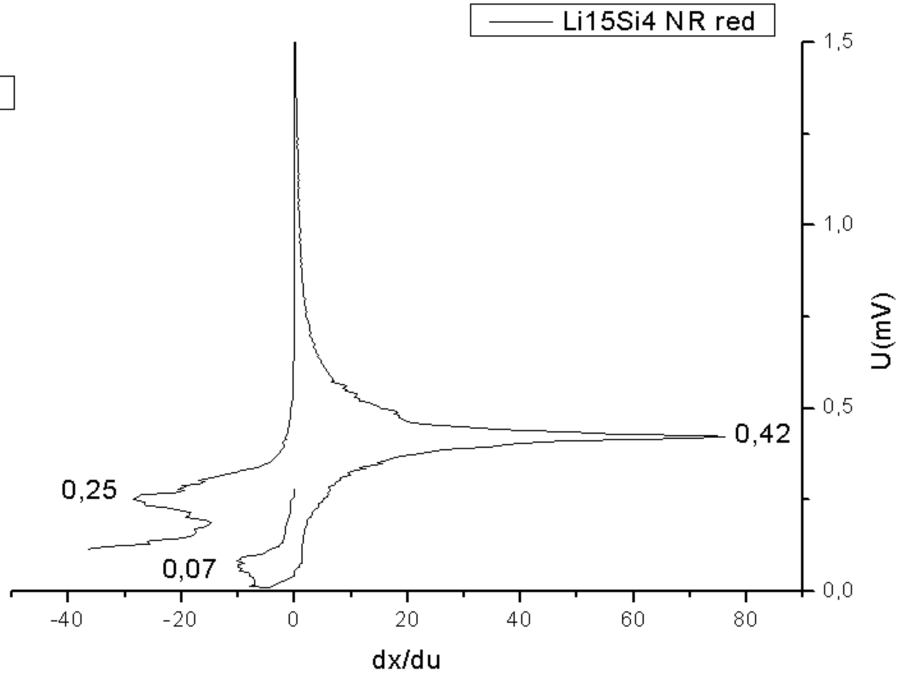


$Li_{15}Si_4$ still seen by XRD

How can we rationalize the difference between in- and ex-situ results and with model compounds?

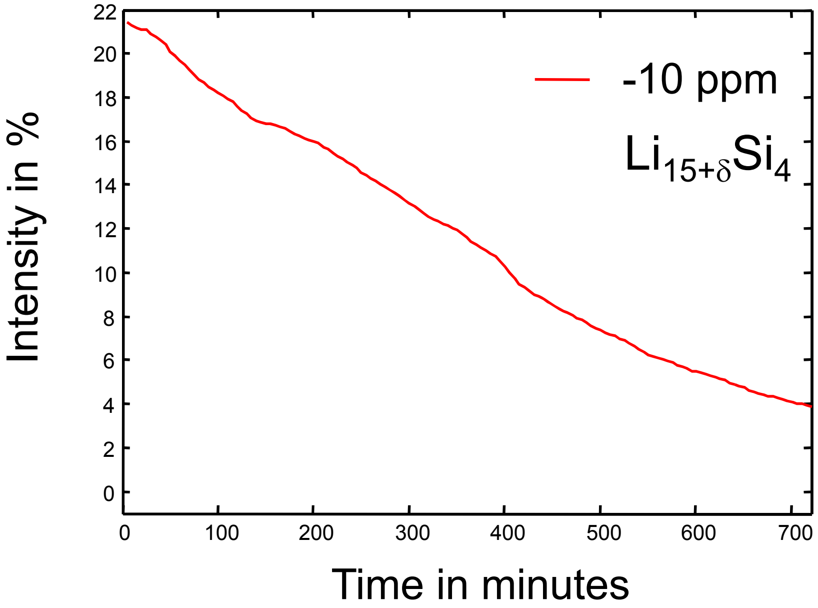
$Li_{15}Si_4$ does not appear to be a line phase – can tolerate more Li

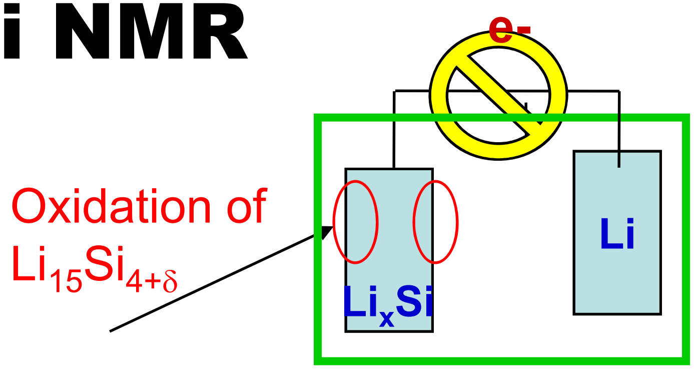




- ^{7}Li peak of $Li_{15}Si_4$ shifts from 6 to 2ppm at full discharge – capacity not just due to rxn with C
- $Li_{15}Si_4$ ($Li_{3.75}^{3.75+}$ $Si^{3.75-}$) is an electron deficient phase – different from all other Li_xSi phases which are “electron excess” (e.g. $Li_{21}Si_5$ Li:Si ratio greater than 4)
- $Li_{14}MgSi_4$ exists, which is a perfect Zintl phase

Following the self-discharge process in real time with ^{7}Li NMR



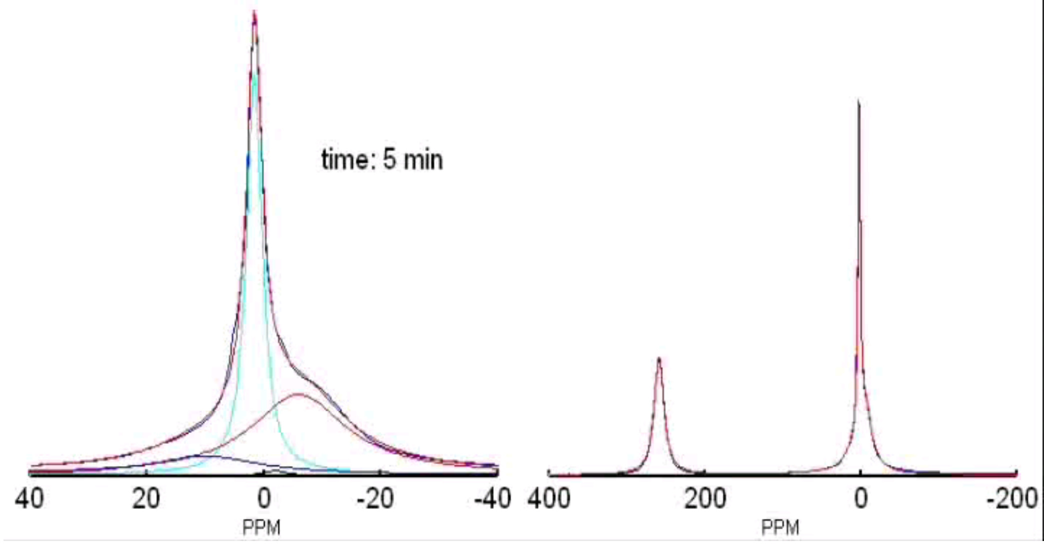


$Li_{15+\delta}Si_4 \rightarrow Li_{15}Si_4 + Li^+ + e^-$

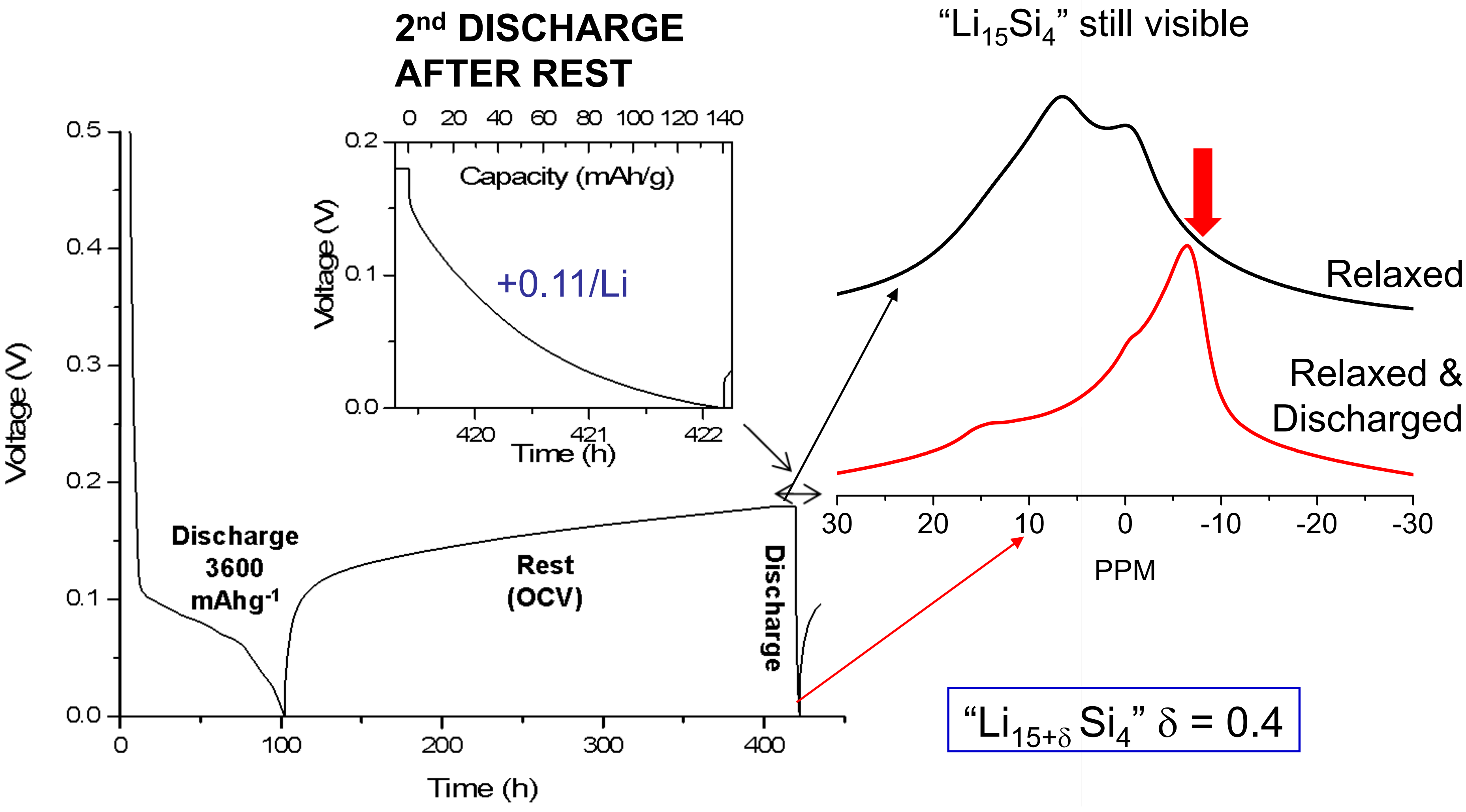
Accompanied by reduction of organics in electrolyte (carbonates (e.g. DMC/EC)))

- -10 ppm peak due to $Li_{15+\delta}Si_4$ disappears in about 6 hours, in absence of a binder

The –ve (shielded Li) environment can be seen in ex-situ studies of cells are shorted, washed and NMR run asap



The Li non-stoichiometry can be estimated by electrochemistry…



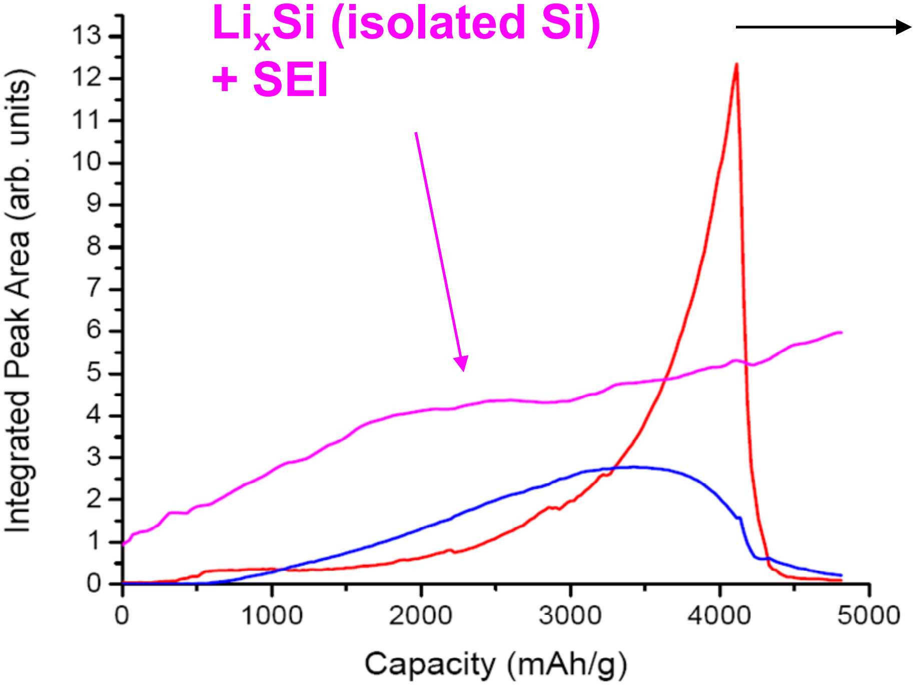
"$Li_{15+\delta}Si_4$" $\delta = 0.4$

A similar Li content is obtained from the charge curve

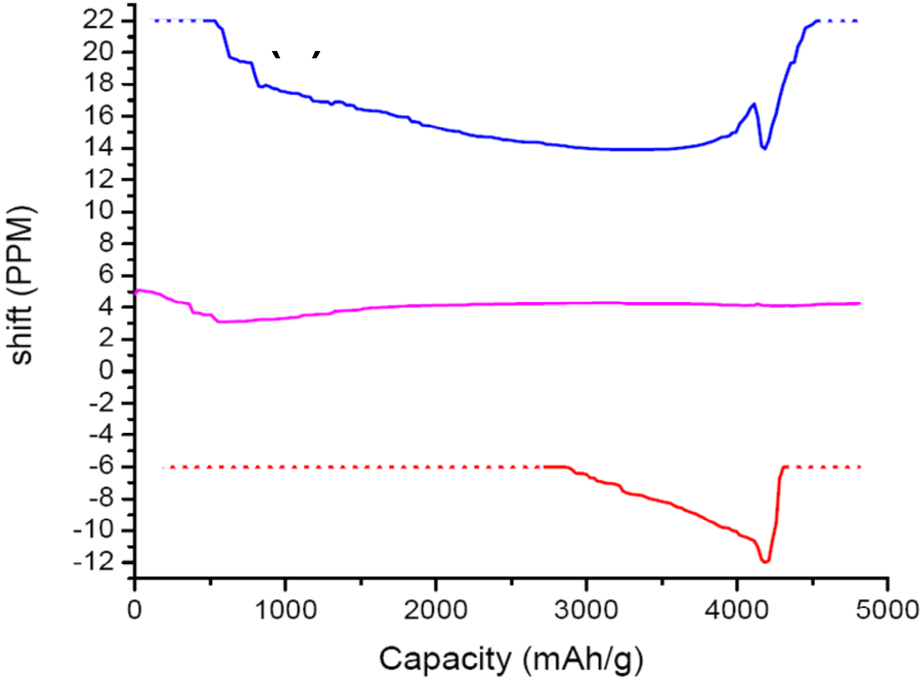
Analysis of peak intensities in insitu NMR: Li_xSi is reactive, even at higher voltages

Intensity

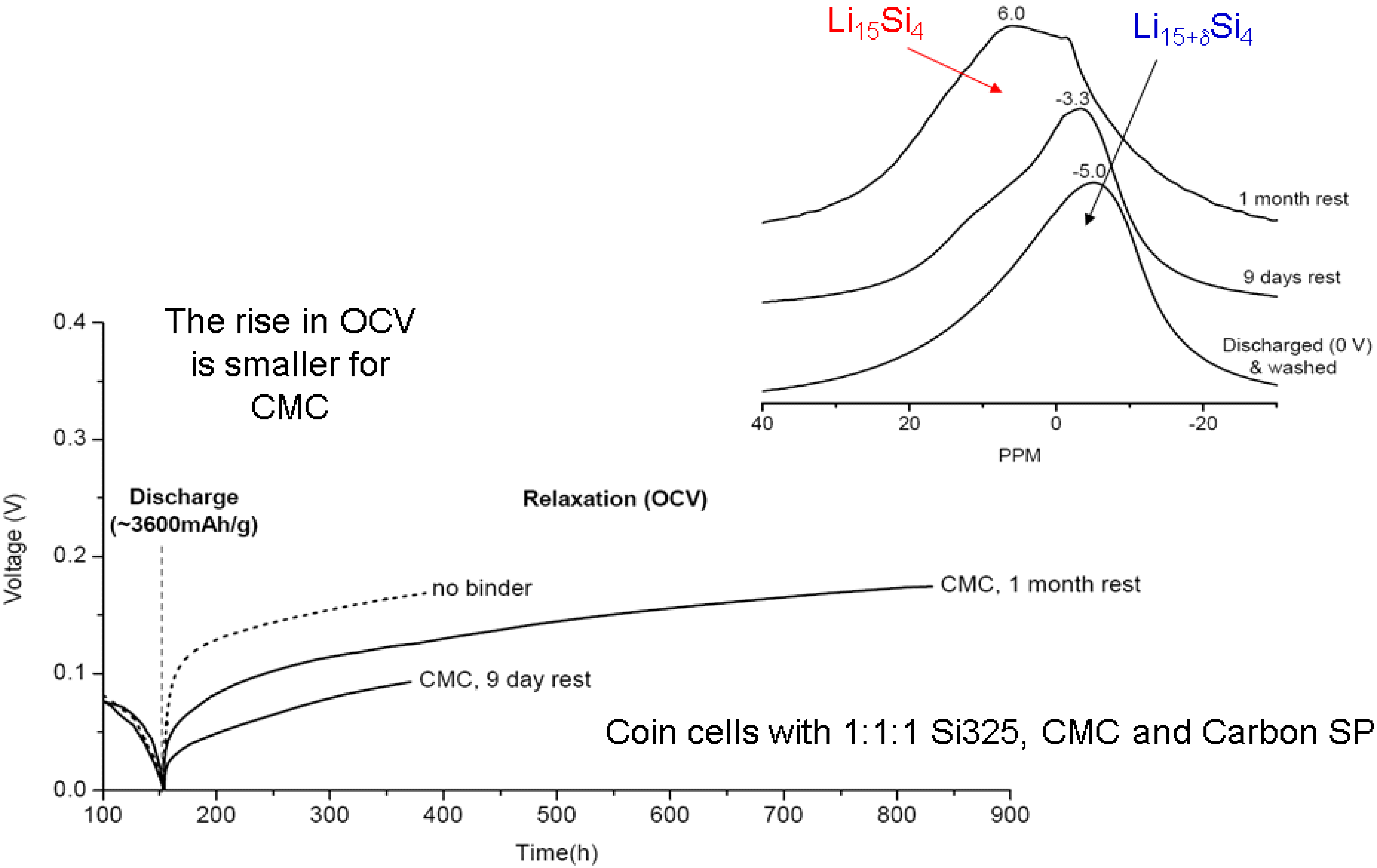
charge



Shifts



Use of CMC binder inhibits self discharge



The rise in OCV
is smaller for
CMC

Coin cells with 1:1:1 Si325, CMC and Carbon SP

Conversion Reactions

- Utilize multiple electron processes => can be very high capacity systems
- Optimization requires control of diffusion processes at atomic level
- Difficult to characterize because a series of nanostructure/poorly crystalline phases are formed.

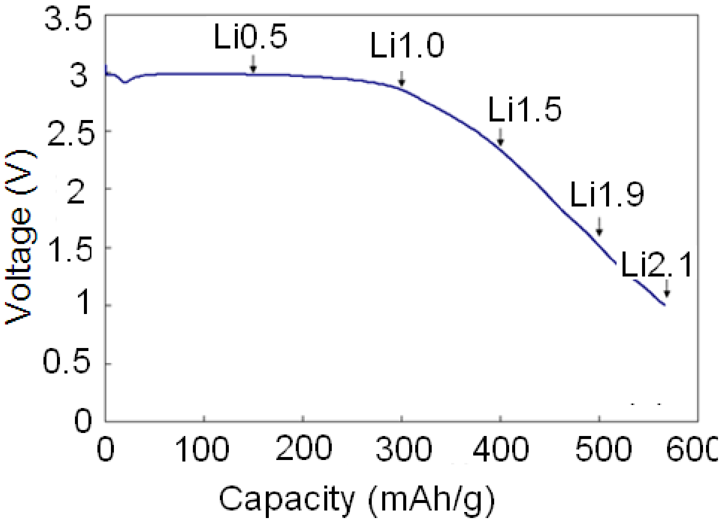
APPROACH: Li, F, (Cu), NMR and PDF studies of structure

Calculations to identify metastable phases and possible reaction pathways

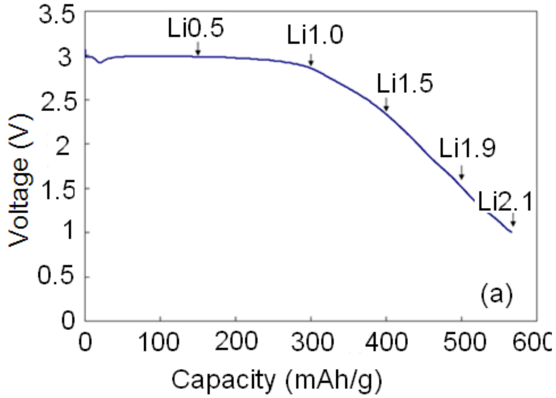
SYSTEMS: Fe fluorides (cheap), Copper systems (CuF_2, CuO, CuS) – systematic understanding of mechanism

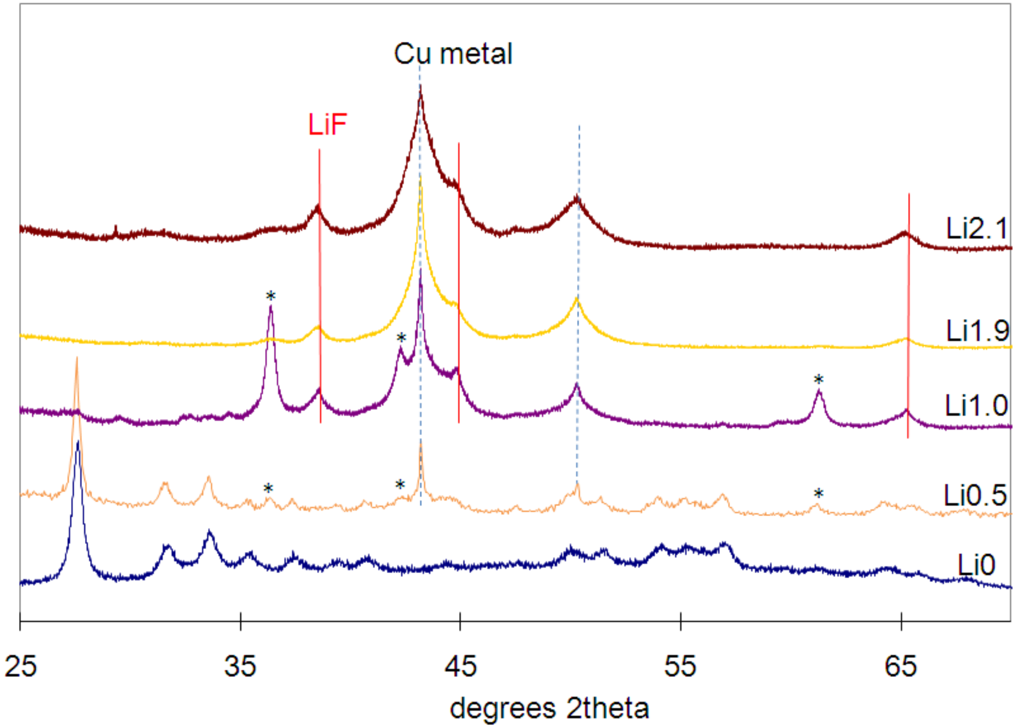
E.g., $CuF_2 + 2Li \rightarrow 2LiF + Cu$

$FeF_3 + 3Li \rightarrow 3LiF + Fe$

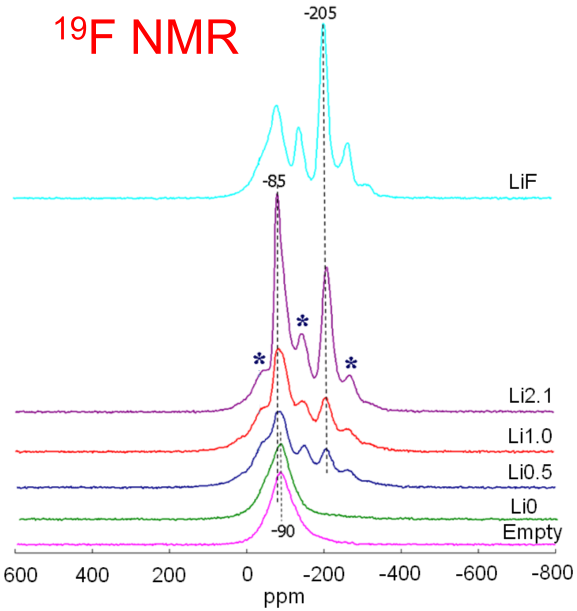


CuF$_2$: Even a simple reaction follows a complex mechanism





^{19}F NMR

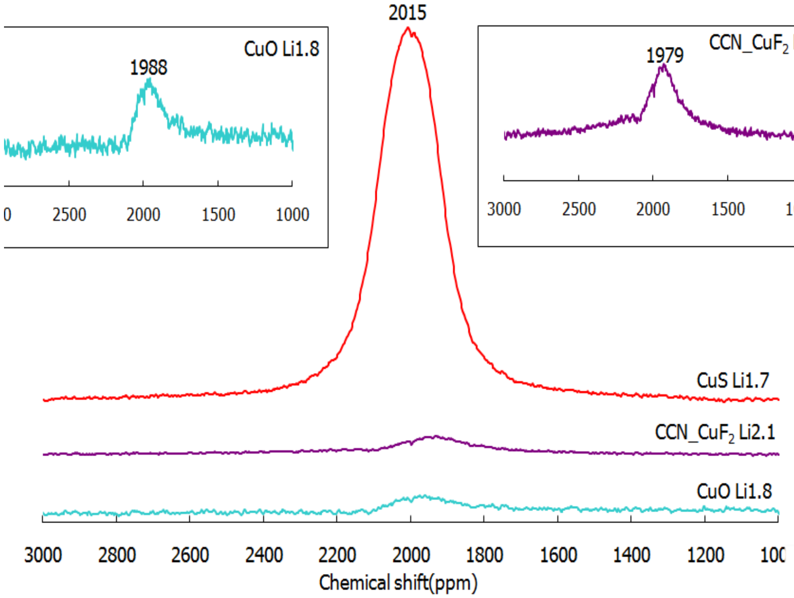


LiF grows steadily, SEI seen for Li >1.0

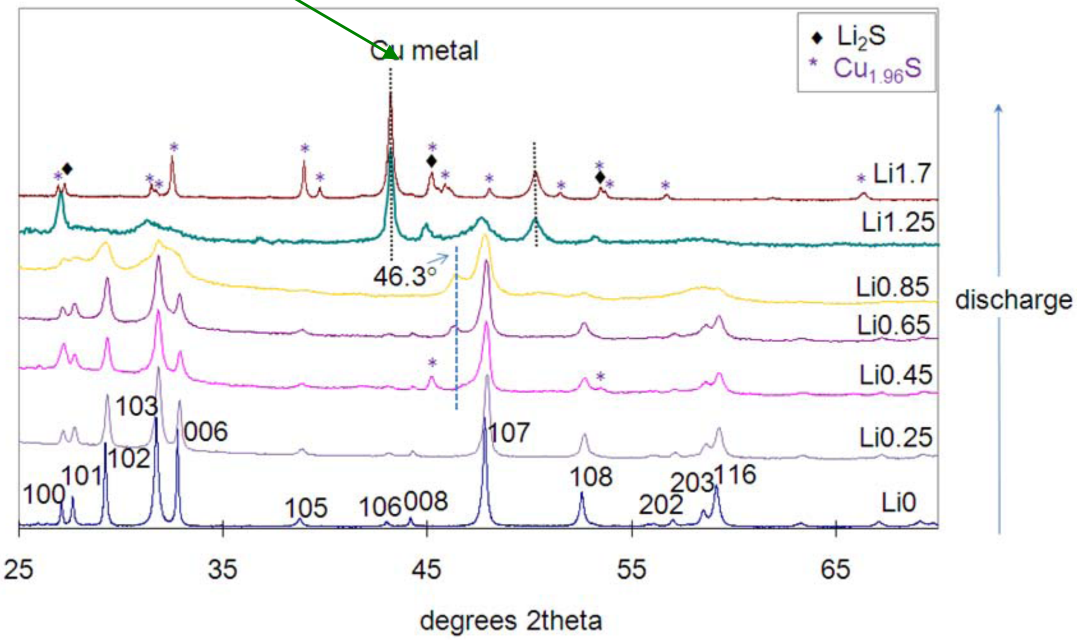
Intensity of Cu reflections increases *but* particle size decreases

CuF$_2$ XRD pattern disappears by Li = 1.0

Sizes of particles depend on diffusivity in different components

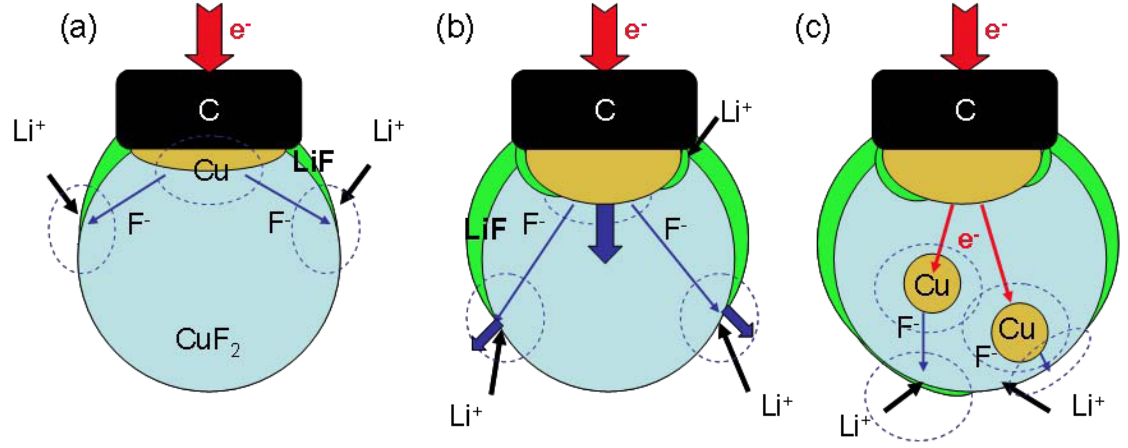


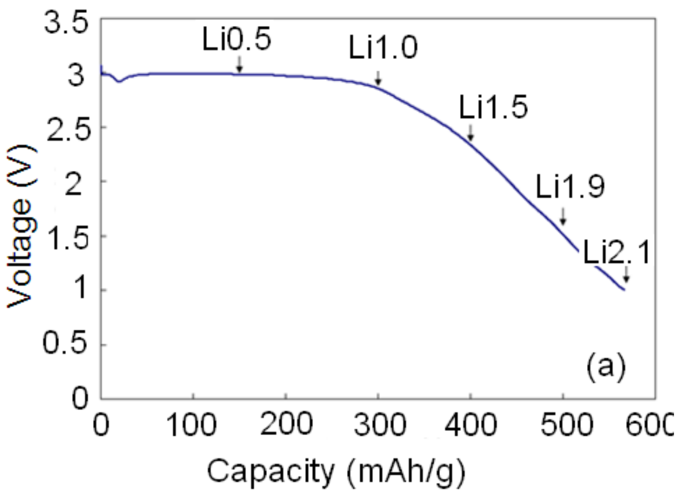
Cu NMR – only large Cu particles are observed

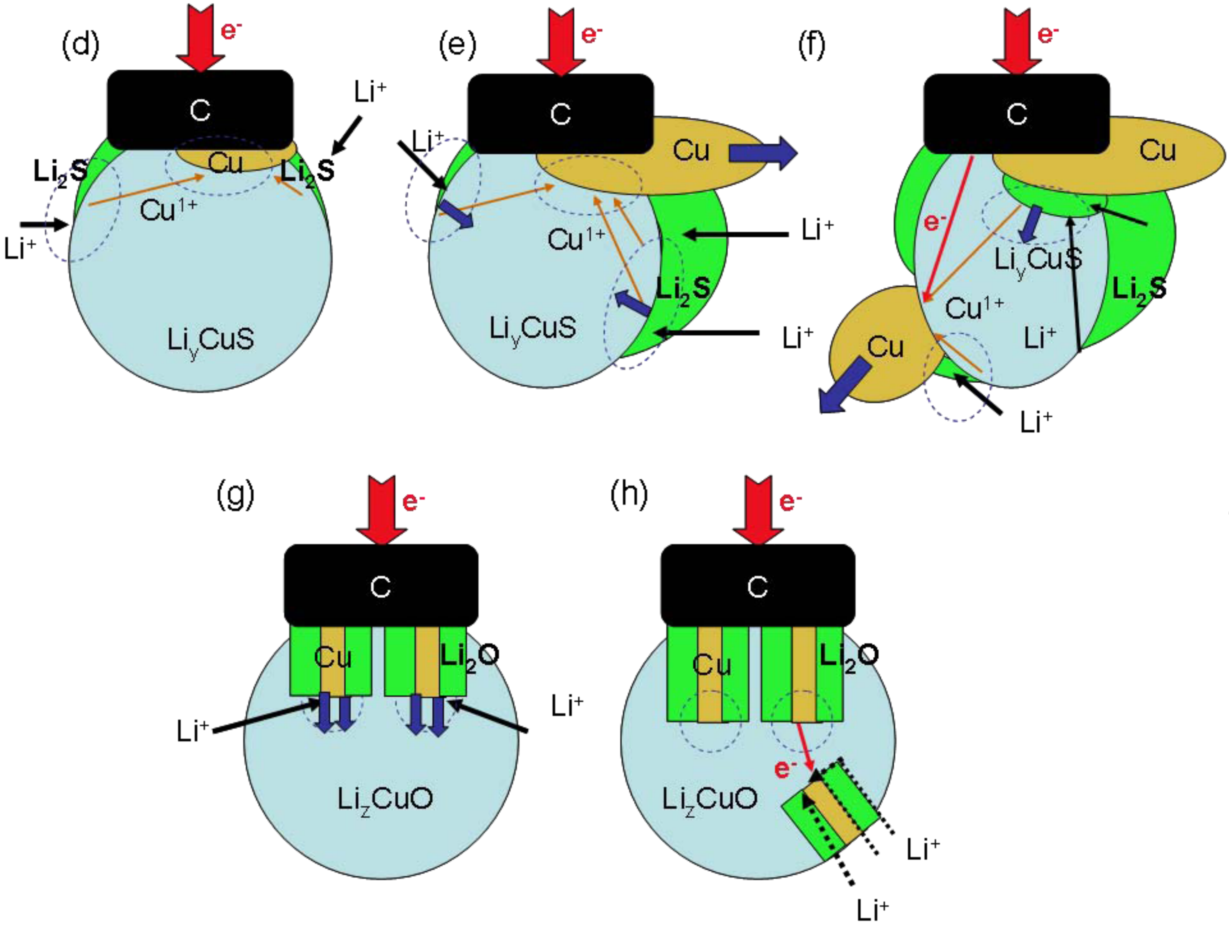


$LiCuS + Li \rightarrow Li_2S + Cu$

$Li + CuS \rightarrow Li_xCuS$

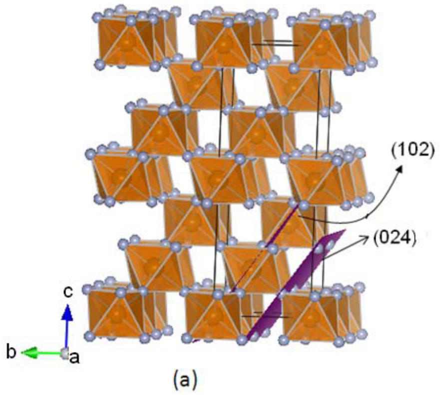


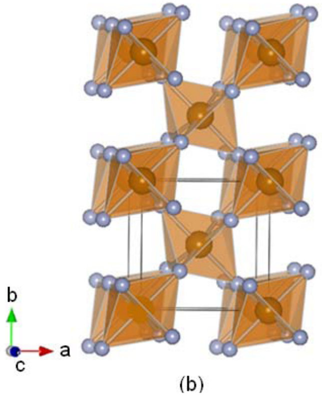




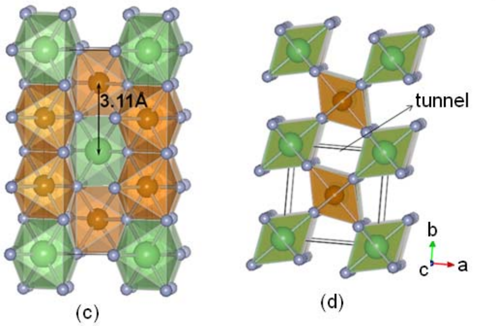
Depending on diffusivity, reactions can occur at either 2 or 3 interfaces leading to very different nanostructures

FeF_3: Metastable phases, Phase Transformations

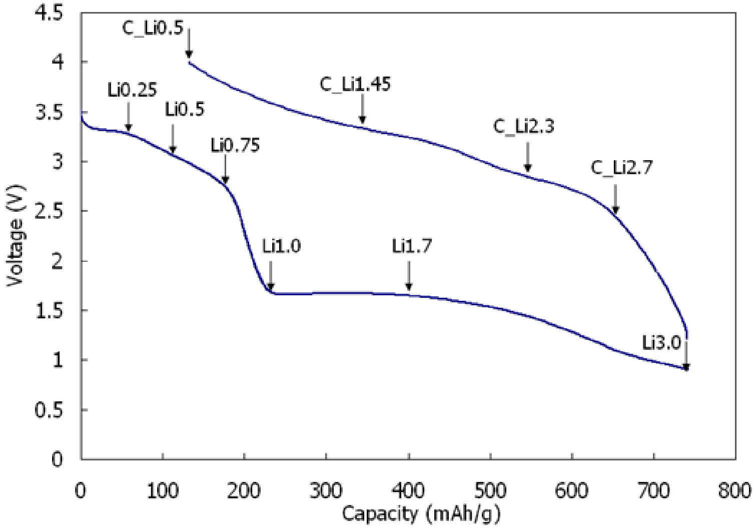


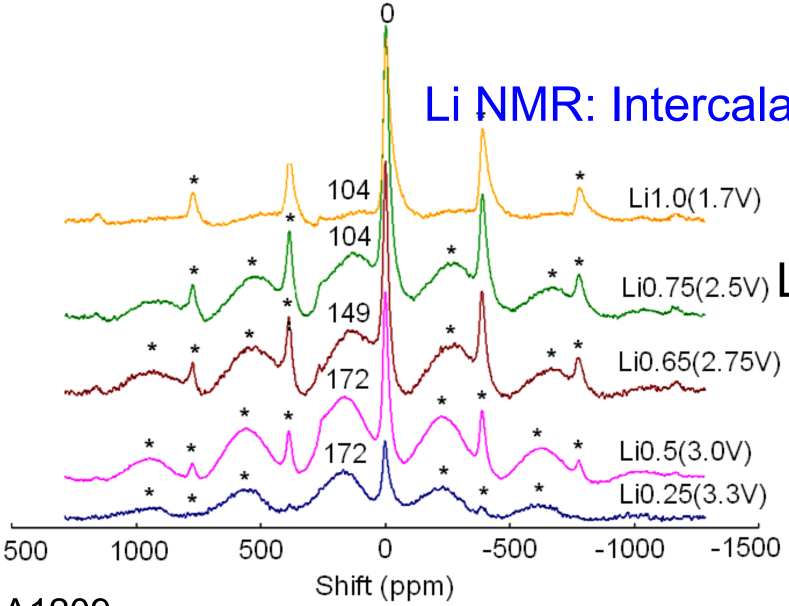


ReO_3 -> Rutile (on charge)*



Trirutile: $LiFe_2F_3$: Stable intermediate
From DFT Calcs
Doe and Ceder, Chem Mat 08.





Li NMR: Intercalation phases

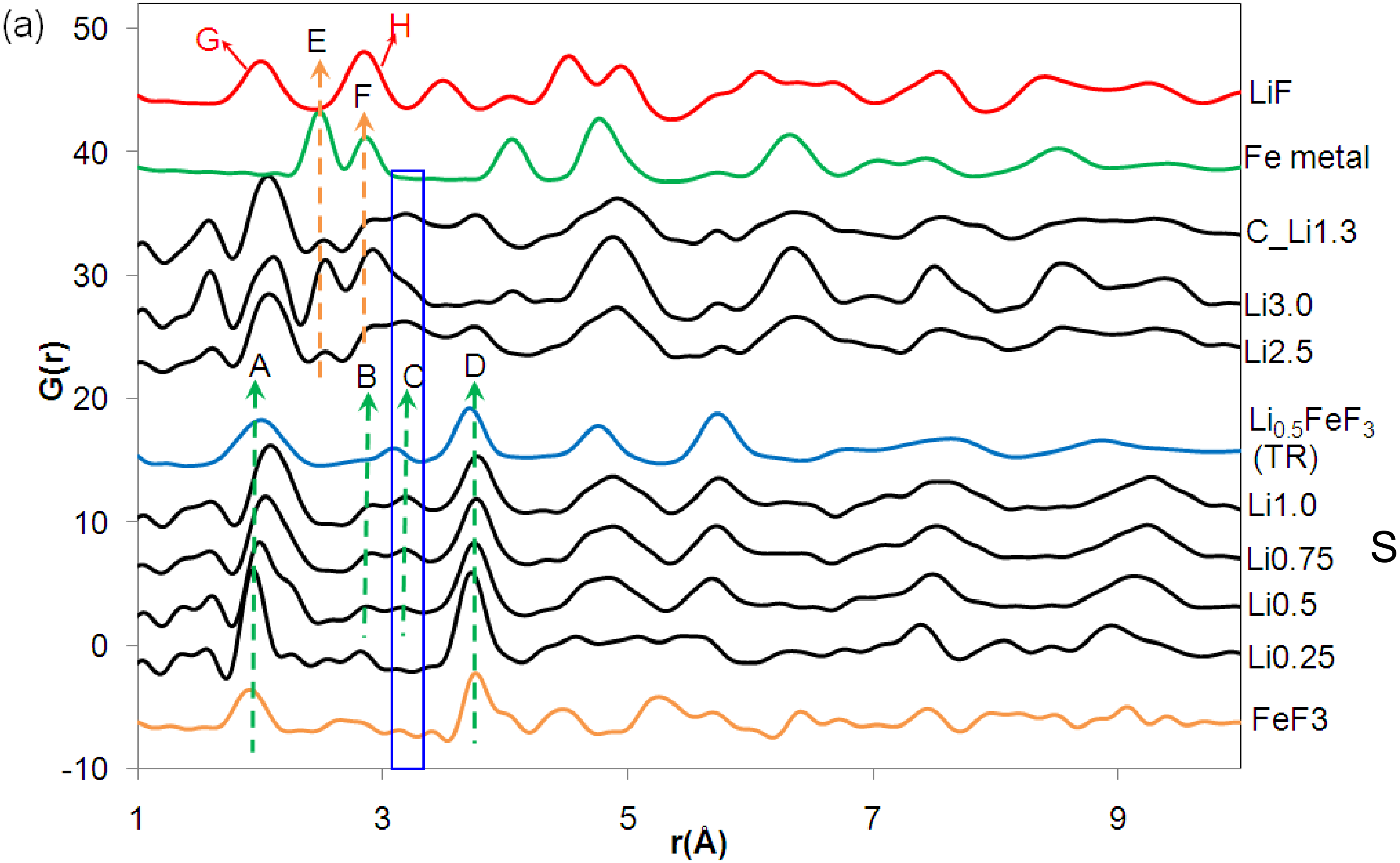
$Li_{0.5-x}Fe_{1+y}F_3$

$Li_{0.5}FeF_3$

*G. Badway et al. *J. Electrochem. Soc.* **2003**, *150*, A1209

FeF_3: Path followed on discharge is not the same as on charge - NMR; PDF

PDF – evidence for Rutile Formation

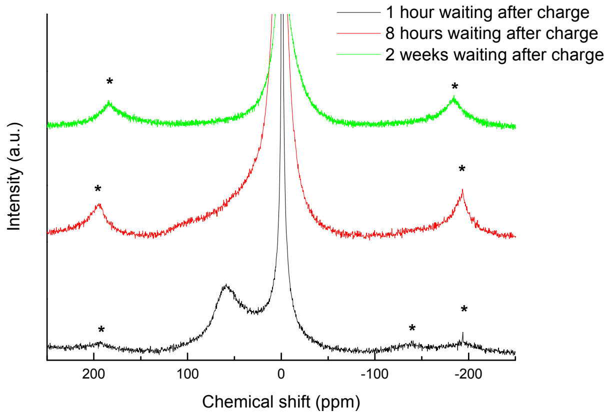


Rutile

Short Fe-Fe contacts

A:Fe^{3+}-F B:F-F (TR) C:Li(Fe)-F (TR) D:Fe-Fe (Fluorides) E&F:Fe-Fe(Fe metal)
G:Li-F (LiF) F:Li-Li or F-F (LiF)

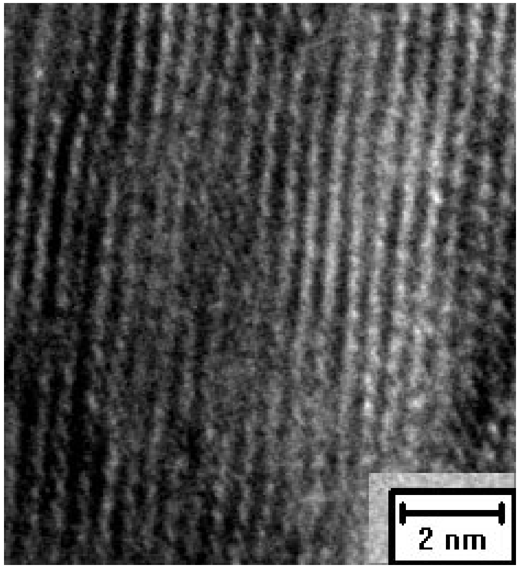
Size Effects on Cycling: Layered Phases

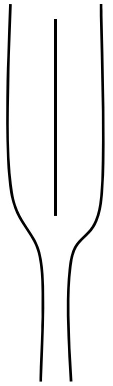


Self discharge of nano-Lii$_{0.5}$CoO$_2$ by in and ex situ NMR

- Synthesis of different nano-particle morphologies with range of sizes
- Investigation of cycling with in and ex-situ XRD, NMR and TEM

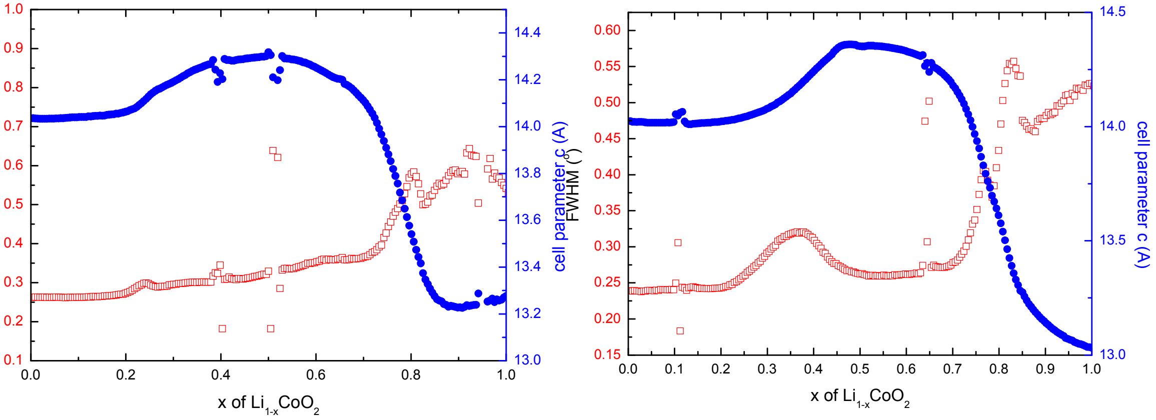
Dislocations formed during the O3 – O1 transition





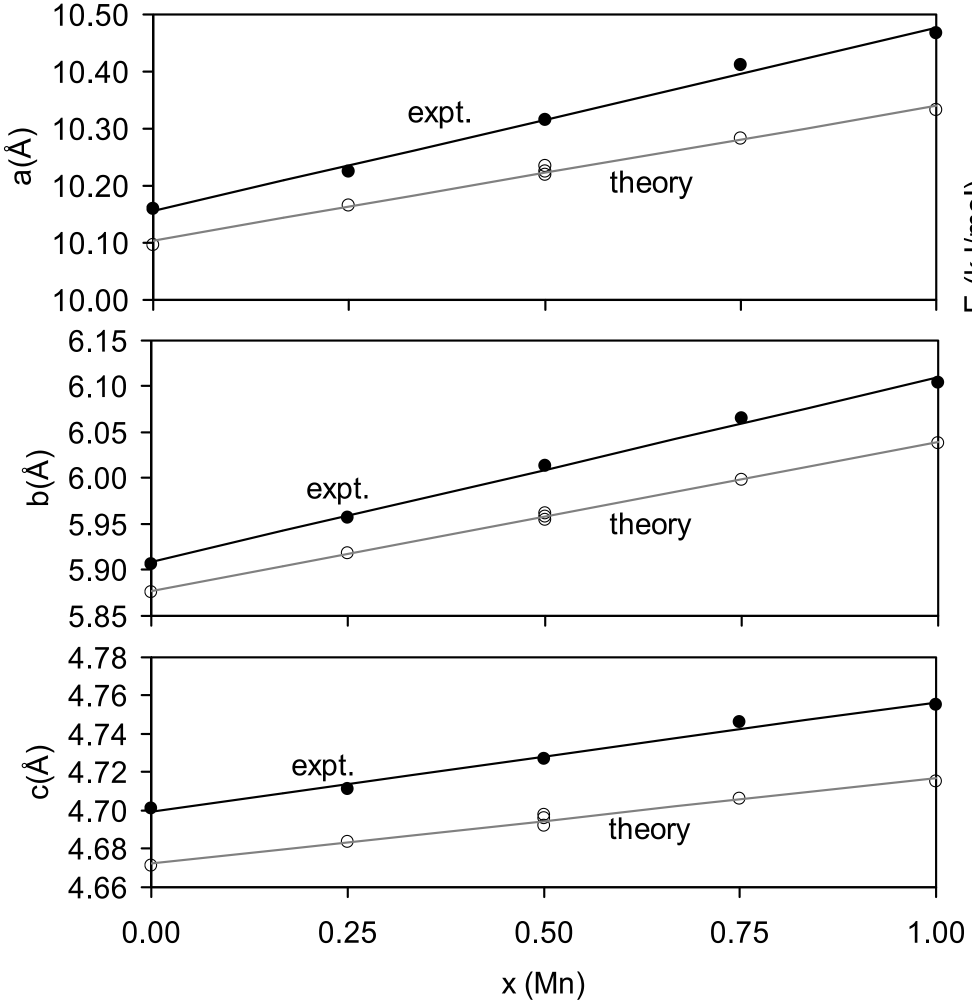
C-parameter and FWHH of 003 reflection

100 300 nm

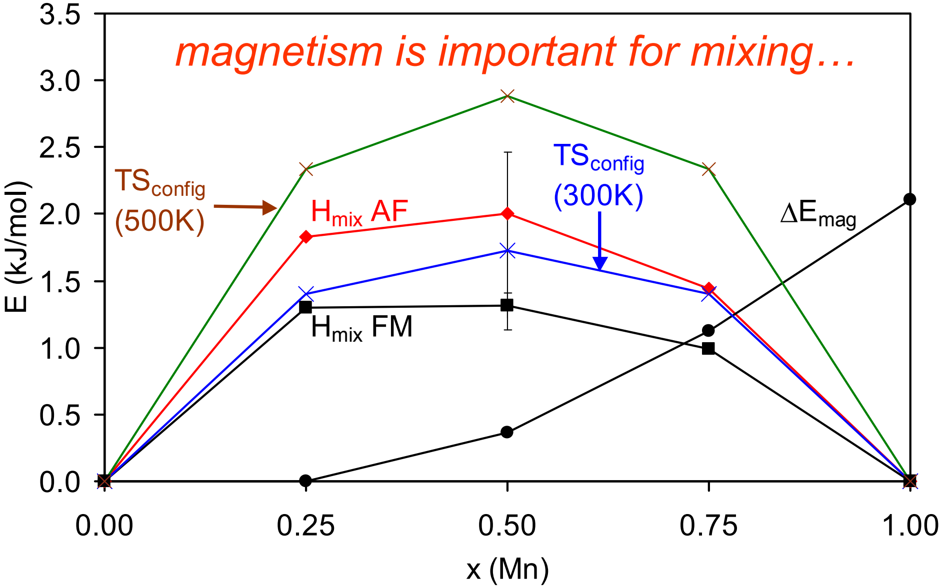


With J. Hanson, Q. Yang and W. Yoon (BNL)

Combining Theory & NMR to Explore Mg-Doping in $LiMnPO_4$



Rietveld refinements: Chen *et al*, Solid State Ionics **178**, 1676 (2008)



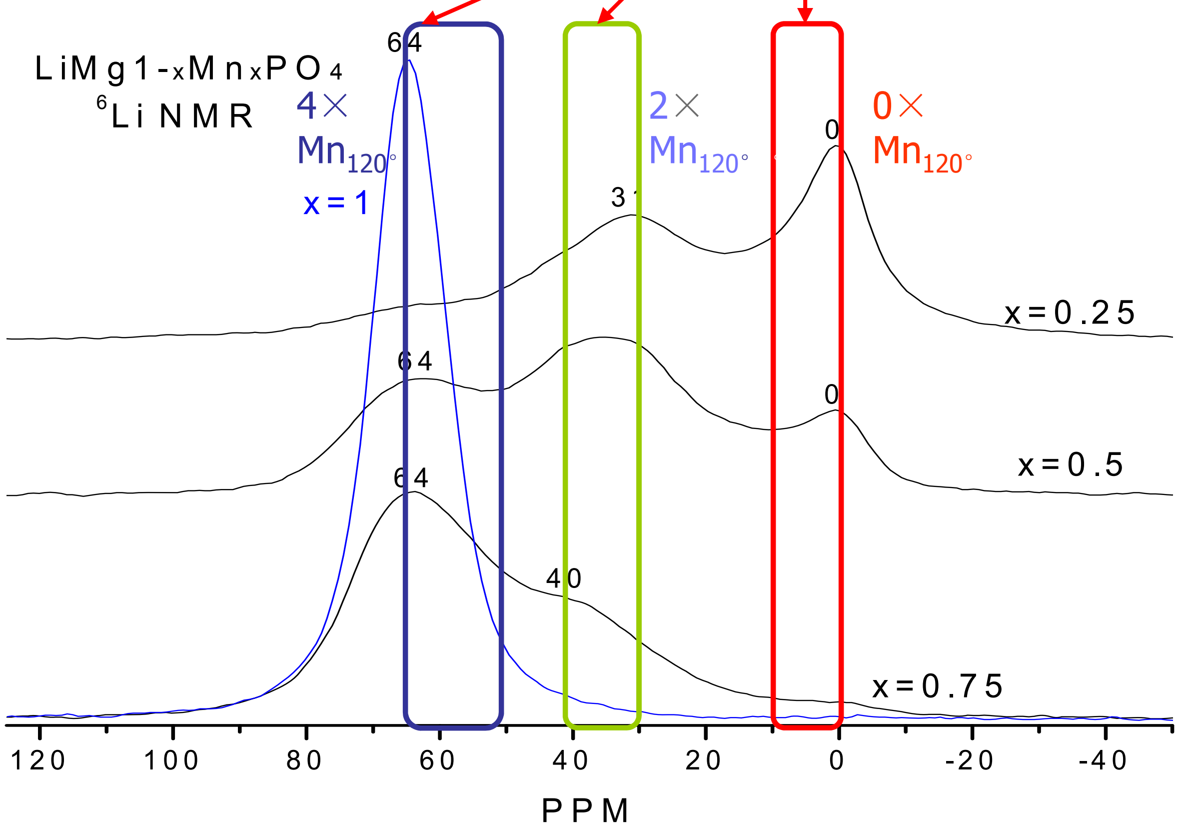
- Solid–state hybrid DFT calculations.
- Weak driving force for mixing: synthesis at approx. 500K, applications around RT.
- Theoretical cell parameters track experimental values.
- Can solid–state calculations add to our understanding of the NMR spectra?

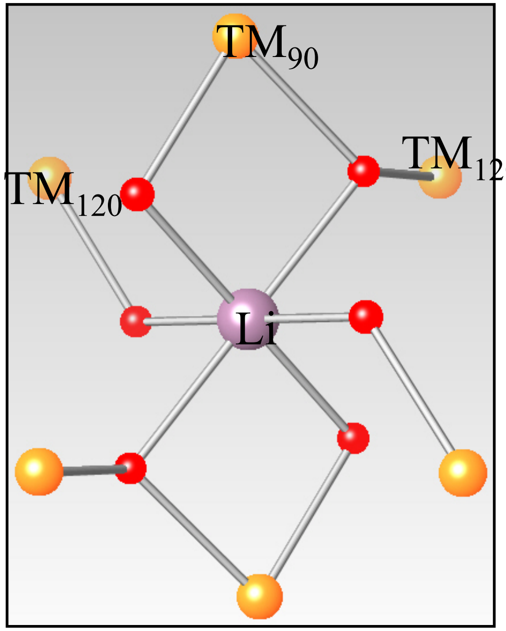
With M. S. Whittingham, N. Chernova

Spin density (ρ_{nuc}) at nuclei of interest from solid–state hybrid DFT.

Fermi contact shift ranges predicted from ρ_{nuc} by scaling of expt. x=1 shifts.

Assign environments to experimental spectra.





Apply to study $Li_{0.6}FePO_4$ phases (Richardson, Cabana)

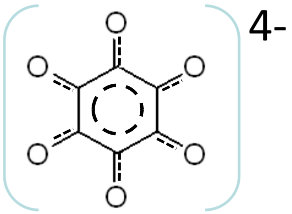
Theory tells us each 120º Li–O–Mn path contributes 4–times more to Li ρ_{nuc} than 90º paths.

- An approach combining solid–state theory & NMR highlights the local magnetic site coordination of the Li ions. Similar techniques are applied to ^{31}P spectra.

Summary

- Developed unique *in situ* NMR capability in BATT program. Utilized this to:
  - Follow structural changes on lithiating Si
  - Identify self-discharge reactions at low voltages in Si
  - Identify self-discharge reactions at high voltages in nanoparticles of layered materials
- Conversion reactions.
  - Utilize a combination of NMR and diffraction to determine reaction mechanism and identify structures in nanocomposites
- Size effects on cycling
  - Examine size effects on structural transformations. Identify dislocations that form at high voltages
- Coating mechanisms
  - Identify structural changes that occur during the coating process
- Develop theoretical approaches to calculate NMR spectra – use to investigate local structure in phosphates
- Extensions to new materials
  - Use NMR methods to determine structure and mechanism in new cathode materials – metal organic frameworks (MIL-53), organics, nanophosphates, oxysulfides

E.g., $Li_4C_6O_6 + 2Li \rightarrow Li_6C_6O_6$
Li salt of tetrahydroxybenzoquinone

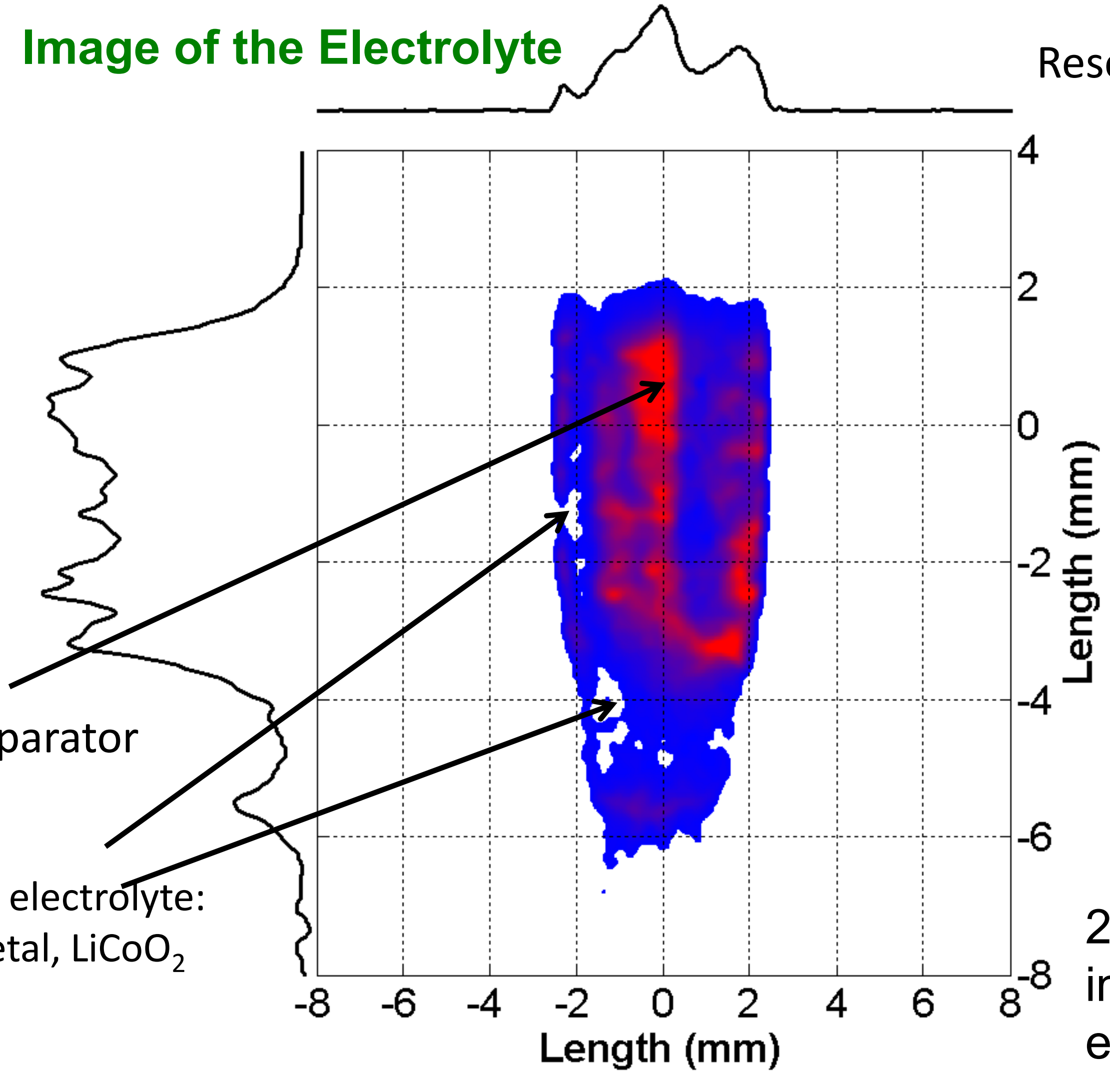


P. Poizot,
J. –M Tarascon

FUTURE WORK

1. Imaging of LiBs (Li metal versus $LiCoO_2$)

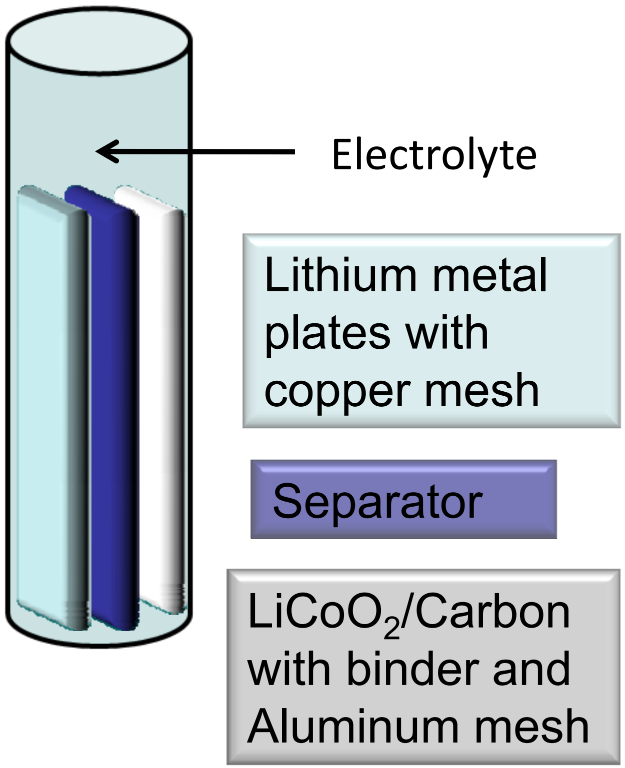
Image of the Electrolyte



Separator

No electrolyte: Metal, $LiCoO_2$

Resolution: 0.05 mm (target: 1-2 µm)



Lithium metal plates with copper mesh

Separator

$LiCoO_2$/Carbon with binder and Aluminum mesh

2. Insitu NMR: Effect of high rates; investigation of composite electrodes (cathode mixtures etc.)
3. Si, conversion reactions
4. $LiM_{1-x}M'PO_4$

With A. Jershow, NYU, S. Harris, GM