First Principles Calculations and NMR Spectroscopy of Electrode Materials: NMR

Clare P. Grey

Stony Brook University

April 9, 2010

Project ID #
ES055

Overview

Timeline

- Project start date: May 2006
- Project end date: Jan 2011
- Percent complete: 70%

Budget

- Total project funding: $1,351,370
- Funding for FY09: $375k
- Funding for FY10: $351k

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

Barriers

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

Partners

Gerbrand Ceder (MIT) – co PI

BATT collaborators:

- J. Cabana, T. Richardson, G Chen, M. M. Thackeray, M. S. Whittingham.

Other collaborators:

- J. M. Tarascon, M. Morcrette, C. Masquelier (Amiens)
- A. S. Best, A. F. Hollenkamp (CSIRO)

Milestones (Experimental Program)

March 10:

- Complete Si pair distribution function (PDF) data. COMPLETE
- Initiate *in situ* NMR studies of multicomponent electrodes COMPLETE

September 10:

- Complete analysis of Si nanoparticles. On schedule; (PDF and NMR data collected analysis ongoing)

Approach/Strategy

- Use solid-state NMR 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 and Progress in FY10: Overview

Cathodes

1. **Olivines:** Used NMR to investigate cation mobility and electron mobility in metastable Li_xFePO_4 phase (with J. Cabana, T. Richardson, G. Chen). Completed theoretical studies to calculate hyperfine shifts in iron (III) phosphates. Investigated doping.
2. **Composite electrodes:** Initiated in-situ NMR studies of composite electrodes. Established technical solutions to overcome (some) difficulties associated with investigation of paramagnetic materials.
3. **Conversion reactions:** Identified conditions that improve reversibility of a class of metal fluorides.

Anodes: **Investigated local and mid-range and microstructures of Li and Si**

Subsequent slides focus on anode achievements

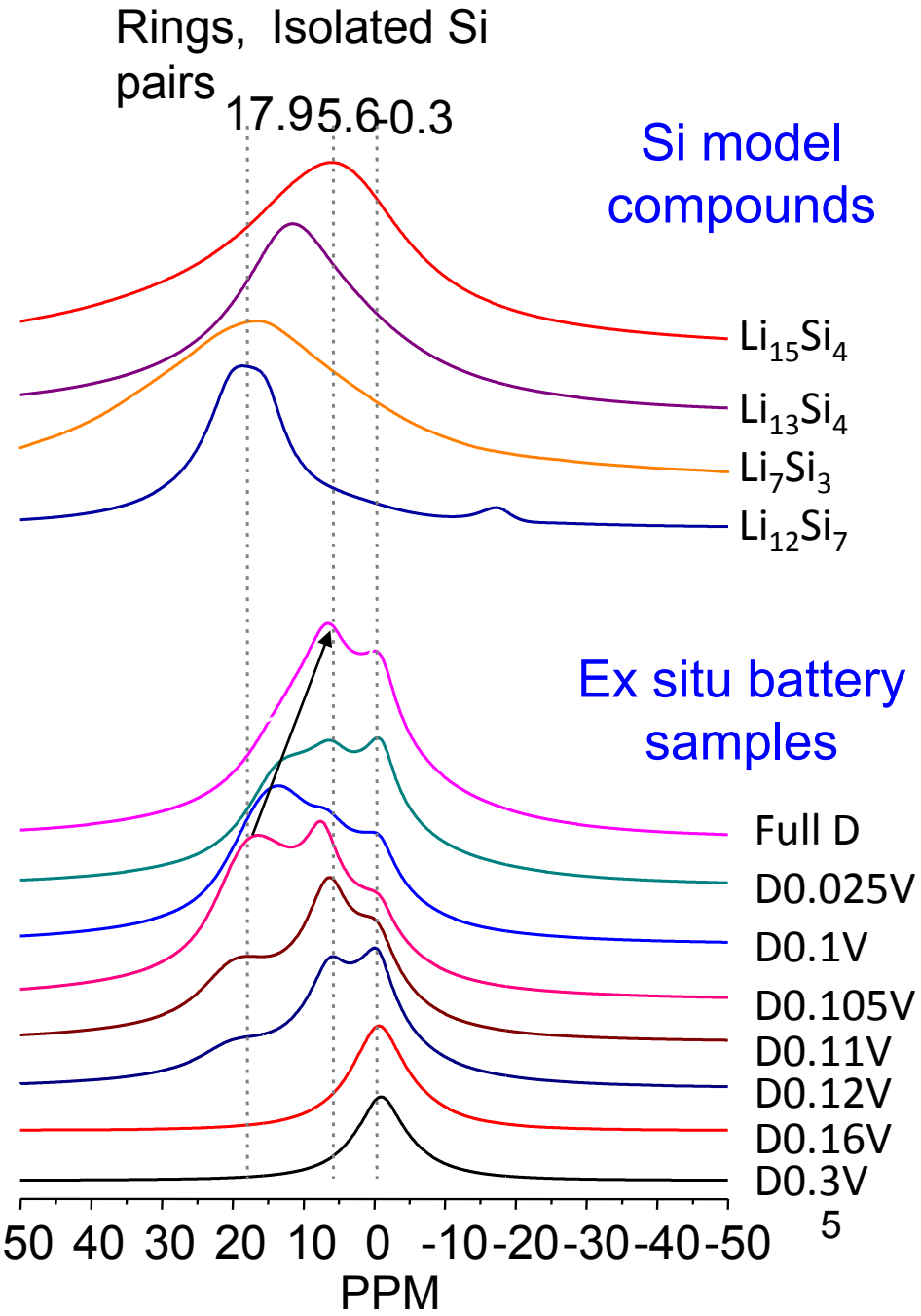
Anodes: 4. Silicon

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

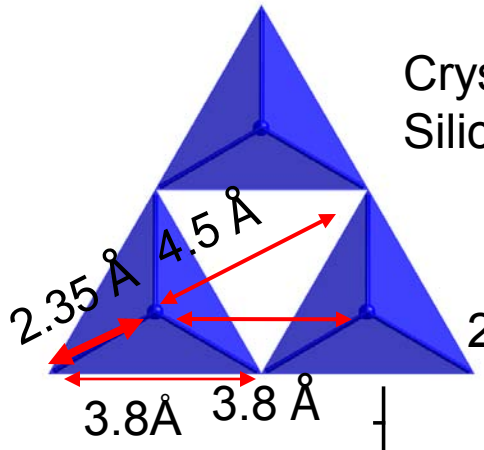
Barriers: Large hysteresis; poor rate performance; reactivity of Si with electrolyte

Status March 2009: Used *in-* and *ex-situ* Li NMR to identify structural changes in 1st discharge; identified self-discharge mechanism at low voltages; initiated PDF studies of 1st discharge.

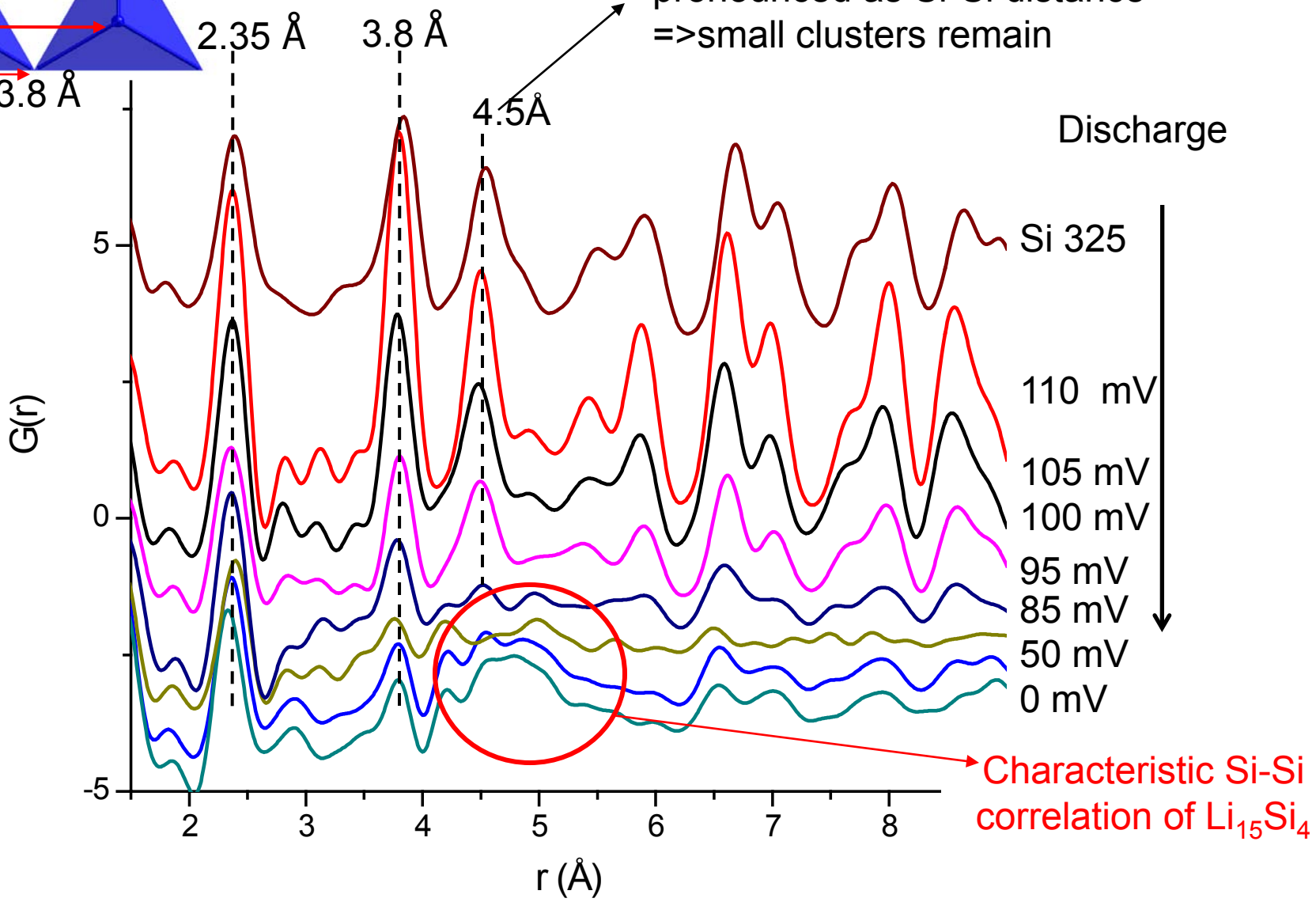
- Lithiation proceeds to form isolated Si and clusters
- Clusters broken up to form isolated Si anions (embedded in Li+)
- Formation of crystalline phase at full discharge

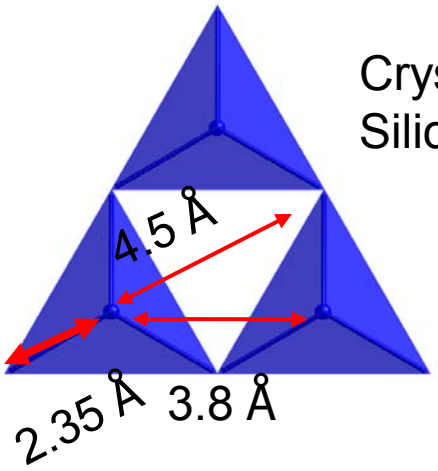


PDF analysis



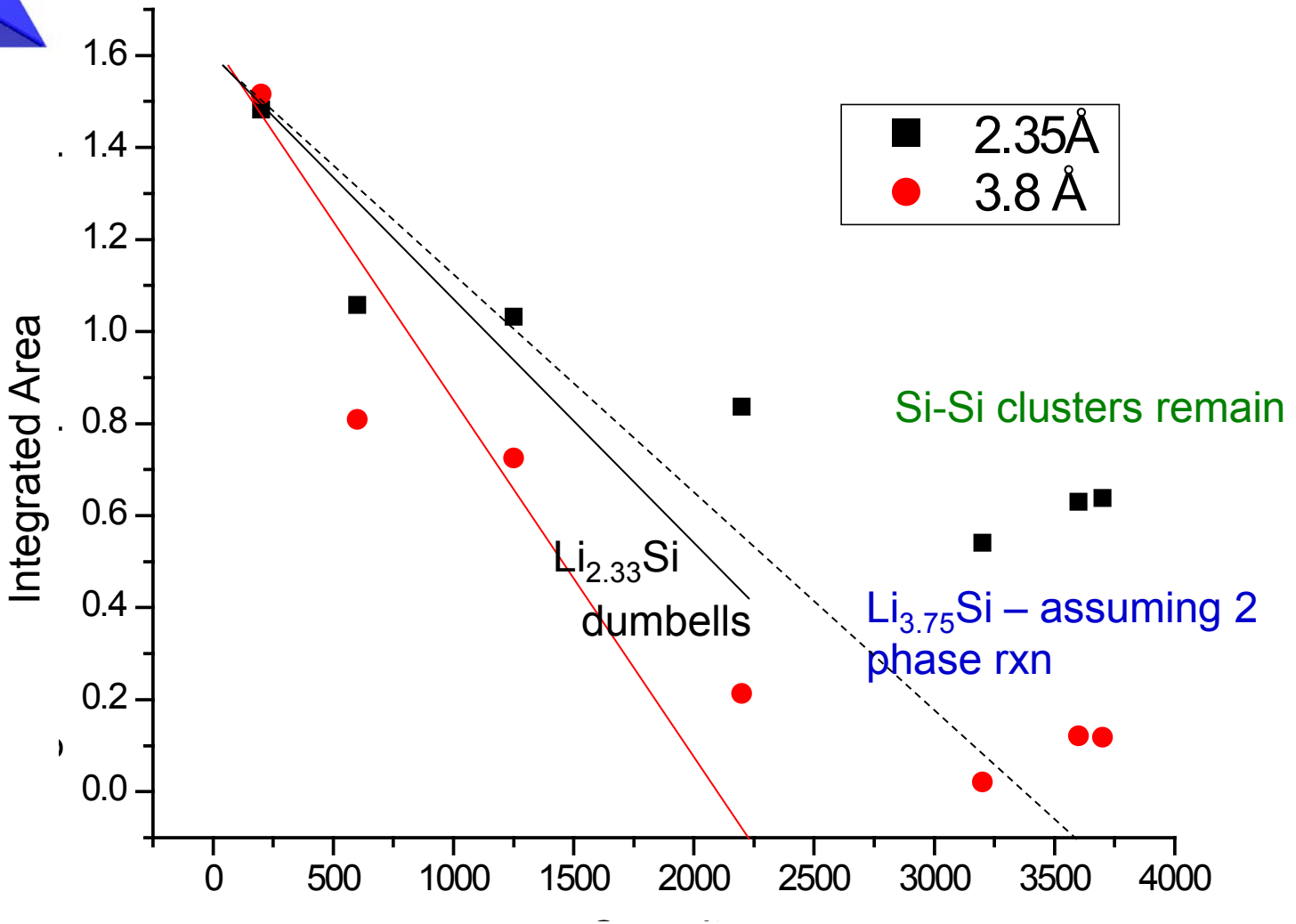
Intensity loss of Si-Si contacts more pronounced as Si-Si distance =>small clusters remain

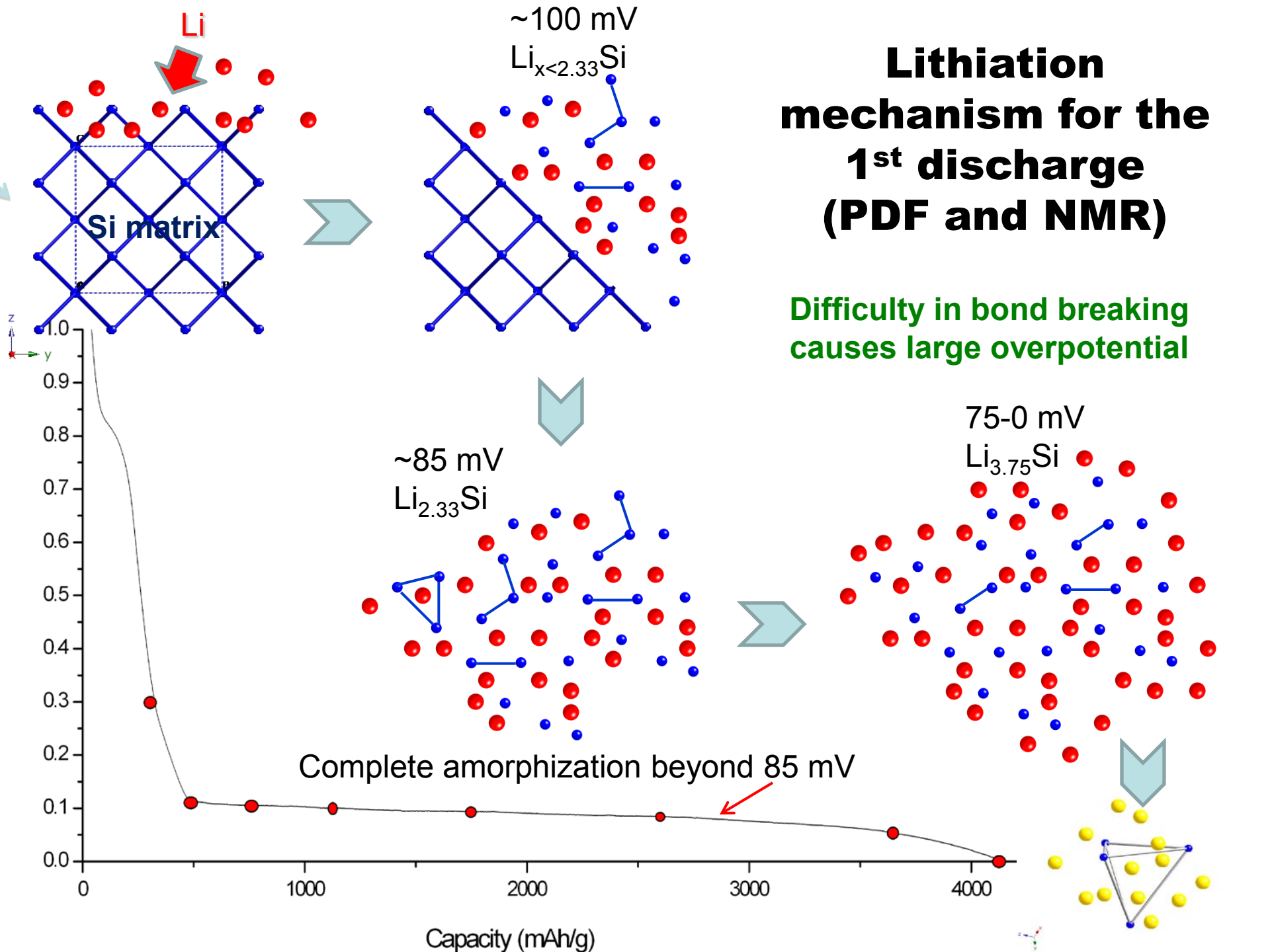




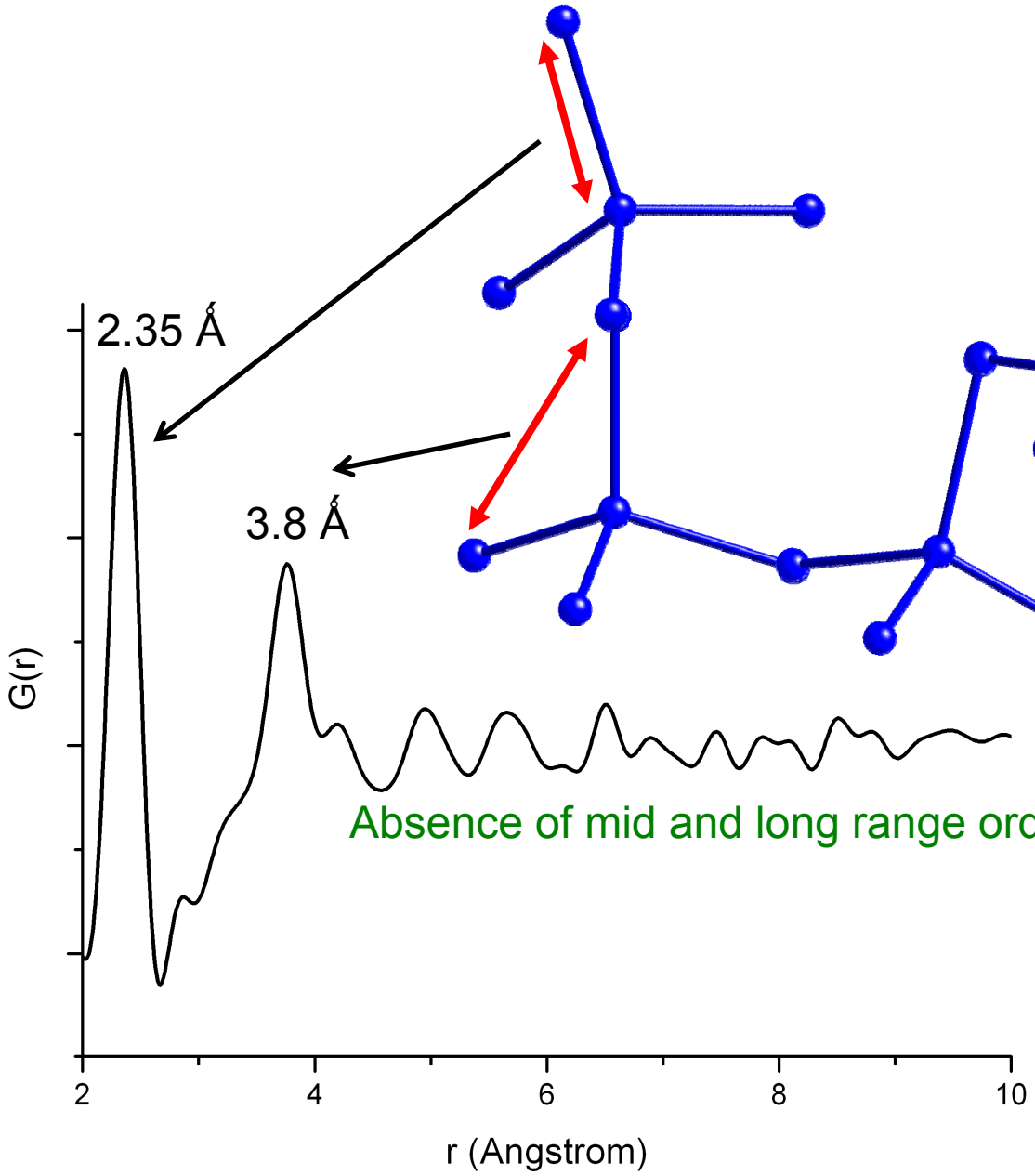
Crystalline Silicon

PDF data is consistent with breakage of Si bonds to form isolated Si and clusters



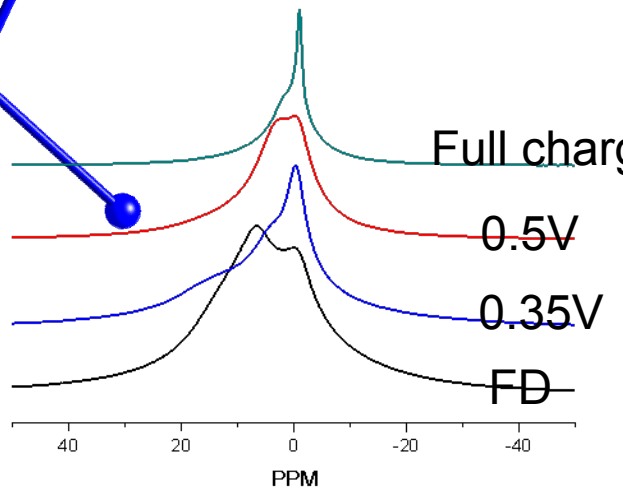

Li
Si matrix
~100 mV
$Li_{x<2.33}Si$
~85 mV
$Li_{2.33}Si$
75-0 mV
$Li_{3.75}Si$
Lithiation mechanism for the 1st discharge (PDF and NMR)
Difficulty in bond breaking causes large overpotential
Complete amorphization beyond 85 mV
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
1000
2000
3000
4000
Capacity (mAh/g)

Amorphous Si formed on charge

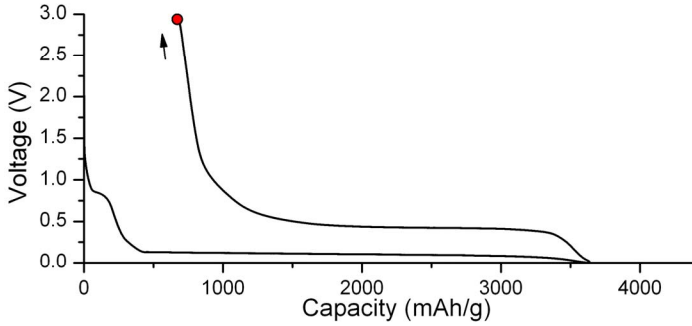


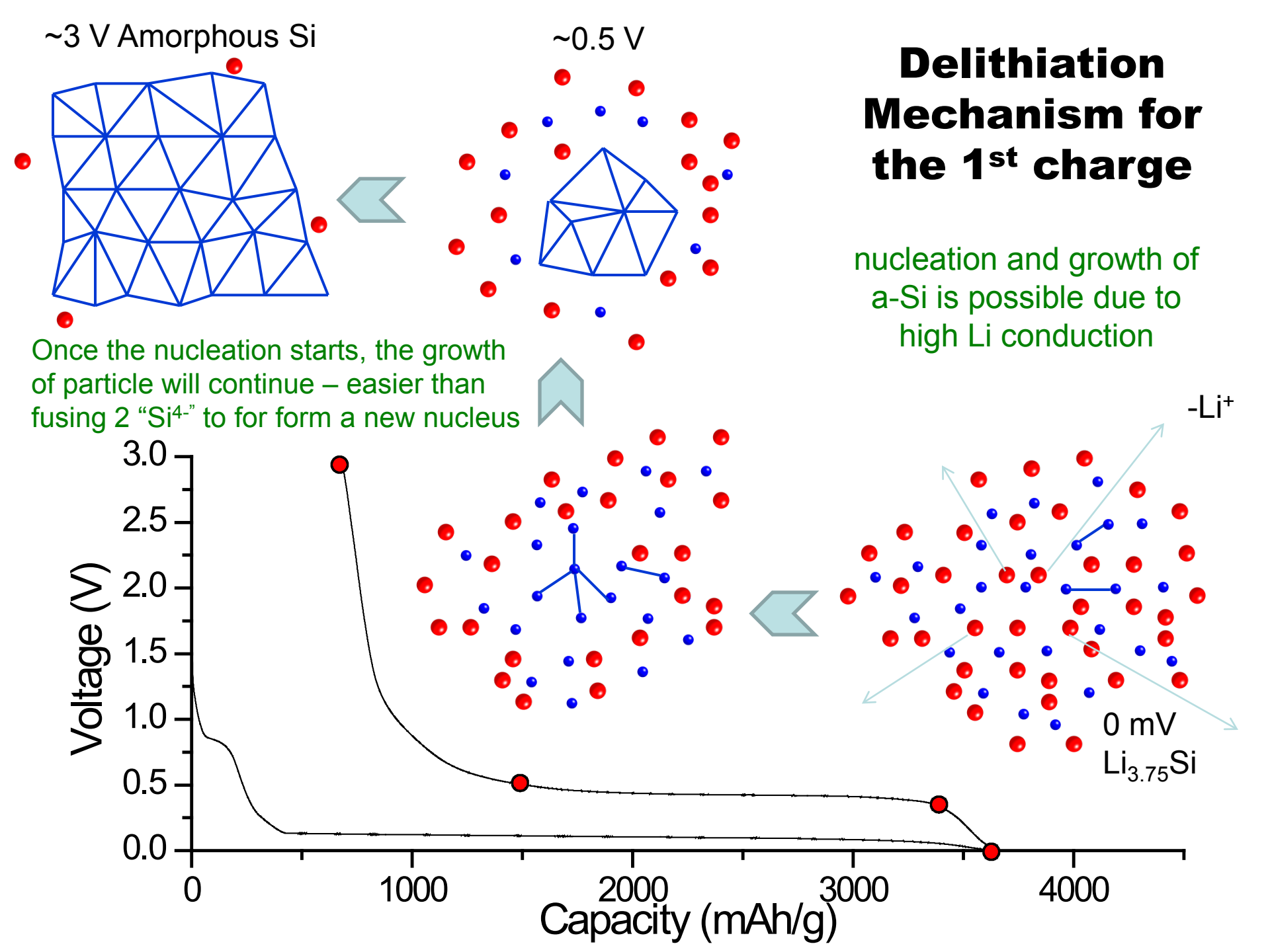
Absence of mid and long range order

Li NMR
•No significant cluster formation

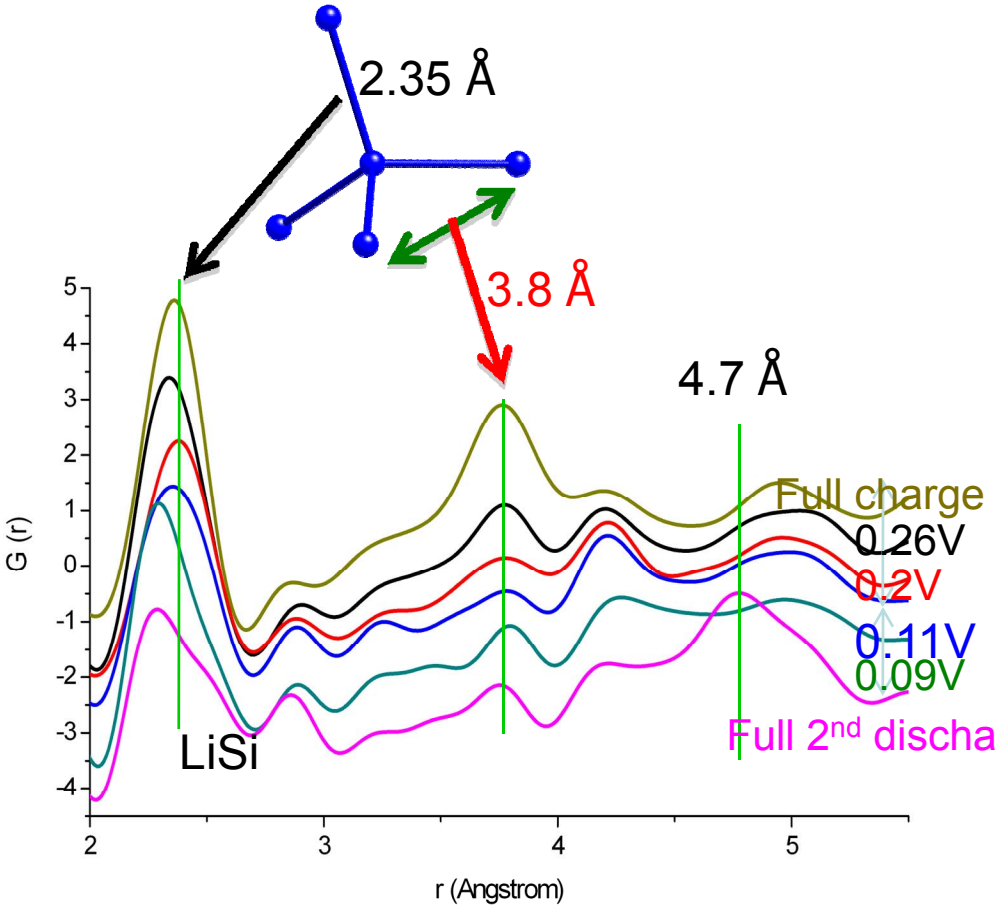


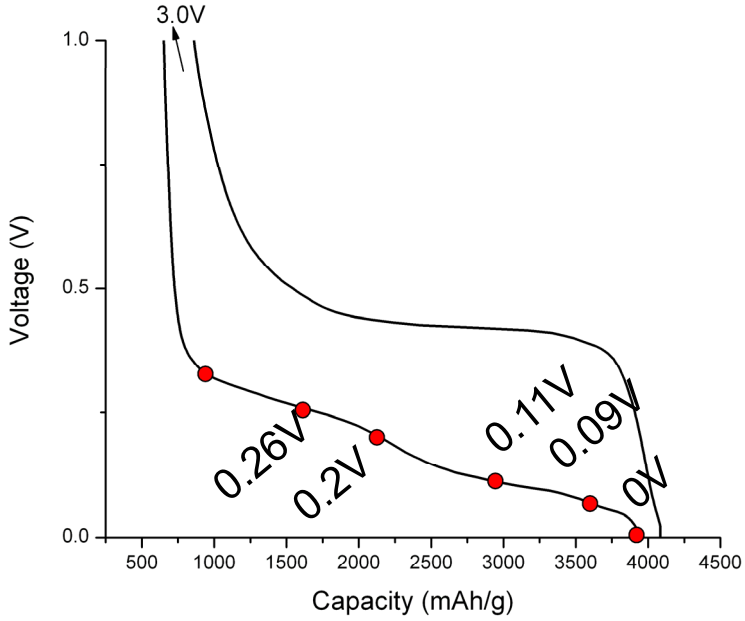
FD then Full Charge

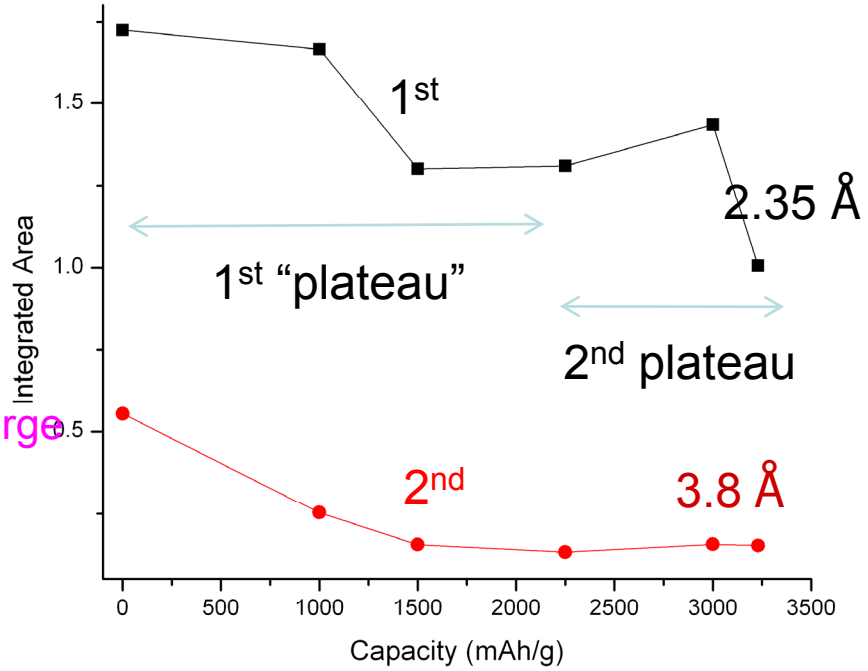



~3 V Amorphous Si
~0.5 V
Delithiation Mechanism for the 1st charge
nucleation and growth of a-Si is possible due to high Li conduction
Once the nucleation starts, the growth of particle will continue – easier than fusing 2 "Si4-" to for form a new nucleus
-Li+
0 mV
Li3.75Si
Voltage (V)
Capacity (mAh/g)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1000
2000
3000
4000

2 Processes are clearly seen on the 2nd discharge







Lithiation Mechanism for the 2nd discharge

~3 V Amorphous Si

250 mV plateau

Amorphous, more open structure allows Li conduction into the particle

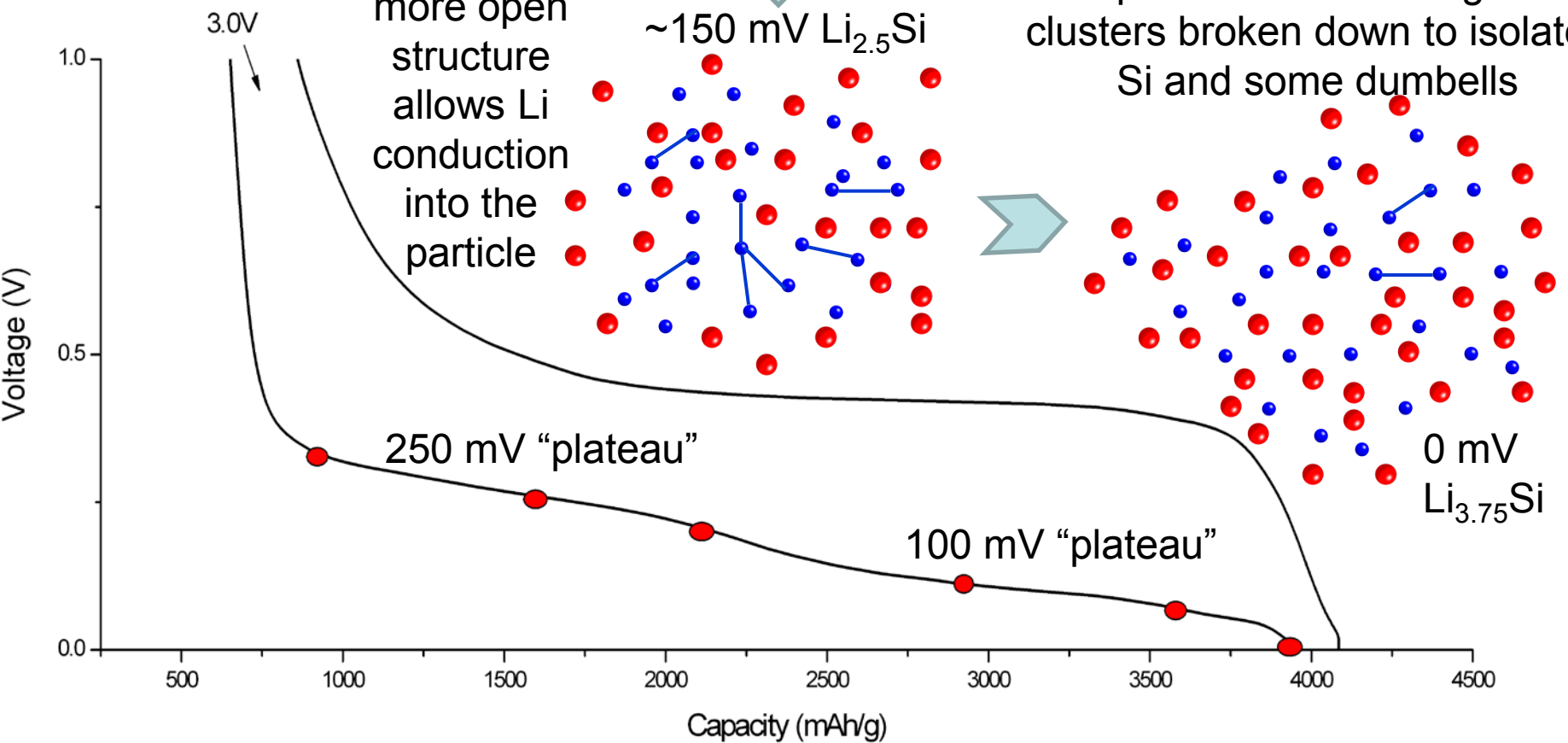
~150 mV $Li_{2.5}Si$

0 mV $Li_{3.75}Si$

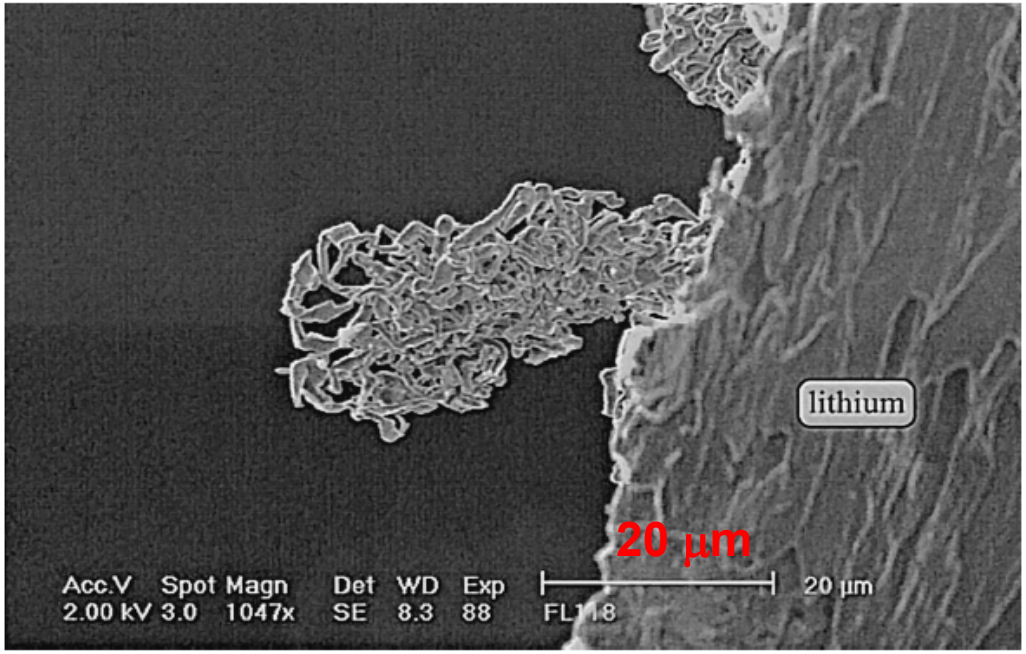
Two processes

1st process - Breaking down of a Si tetrahedra into smaller fragments

2nd process – remaining Si-Si clusters broken down to isolated Si and some dumbells



5. *In Situ* NMR: Detection of Li Dendrites and Mossy Li



SEM after one charge at 2.2 mA/cm^2

F. Orsini, J. M. Tarascon, P. Notten, et al.

J. Power Sources, 76, (1998)

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)

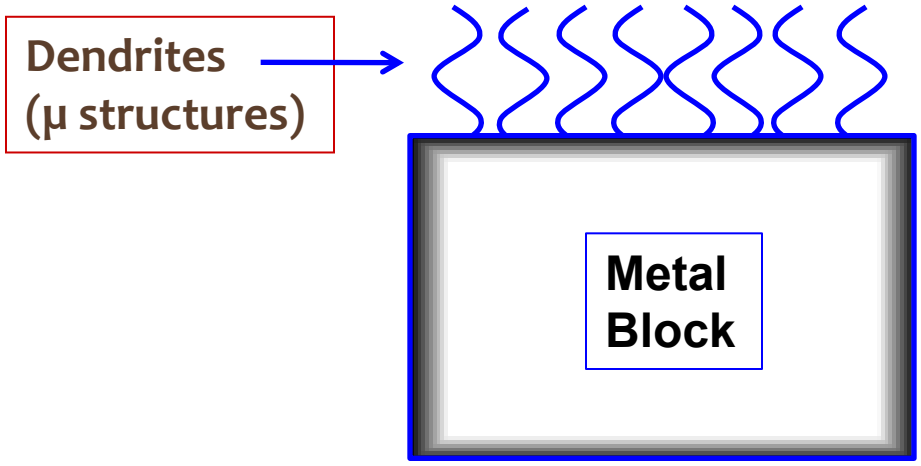
Barriers:

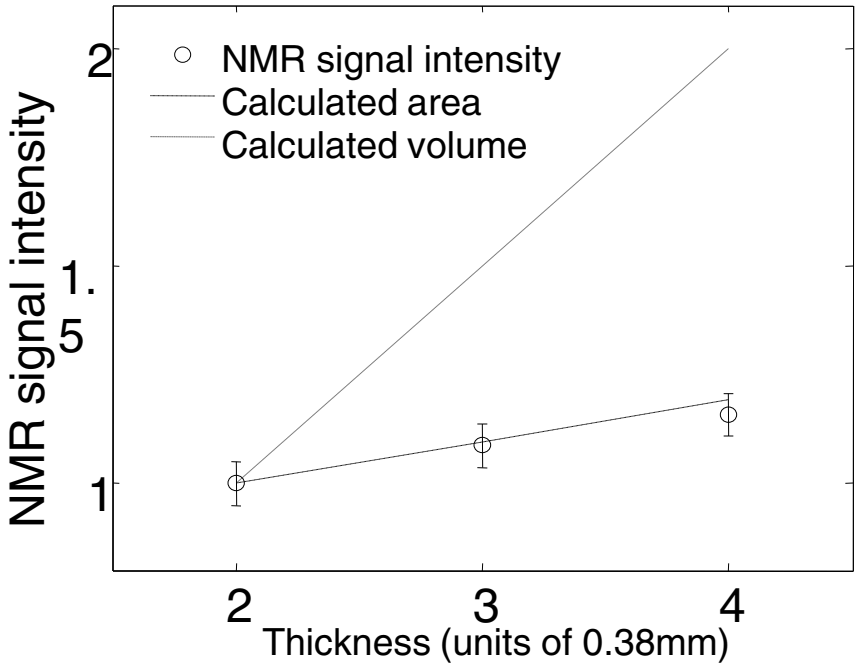
- No simple, non-destructive method for monitoring and *quantifying* dendrite formation in Li cells and for readily determining the conditions under which these dendrites form

Status March 2009: Project commenced in FY2010

In Situ NMR: R.f. fields can penetrate through an entire dendrite, but not through the Li anode

•NMR of Li block correlates with surface area

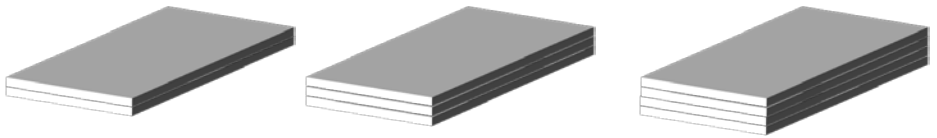




Skin depth:

$$d = \frac{1}{\sqrt{\pi \mu_o}} \sqrt{\frac{\rho}{\mu_r f}}$$

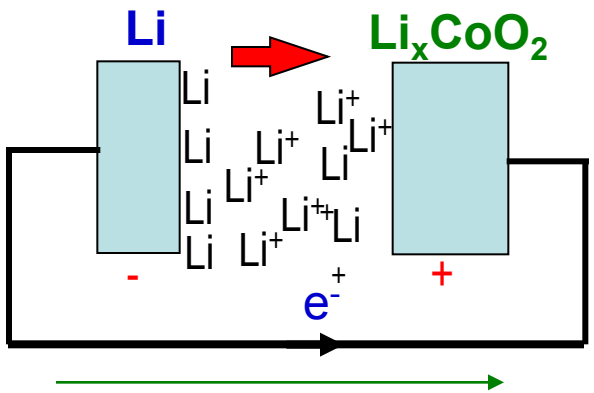
d : skin depth
μ_o : permeability of vacuum
μ_r : relative permeability of Lithium
ρ : resistivity of Lithium
f : carrier frequency



***Skin depth, d* = 15 μm for *f* = 77 MHz (Low field NMR)**

•NMR experiments can be used to monitor dendrite formation

$LiCoO_2$: Intensity Changes consistent with mossy Li formation



(d) I_{expt} = NMR signal intensity

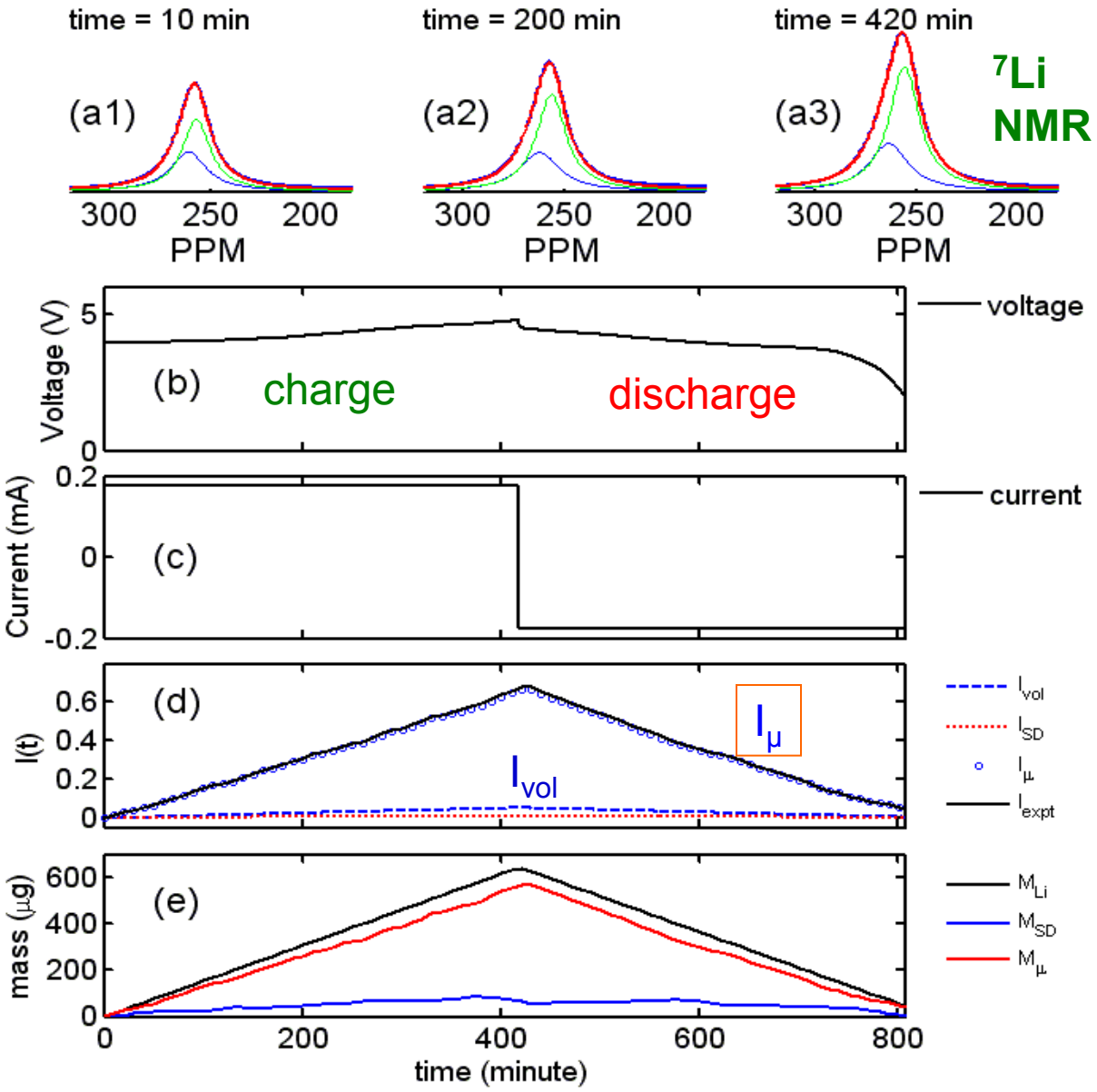
I_{vol} = intensity change calculated by assuming that Li signal depends on volume (mass) of Li ☒

I_{SD} = intensity calculated assuming a skin depth (SD) issue and that all the Li is deposited as a smooth film ☒

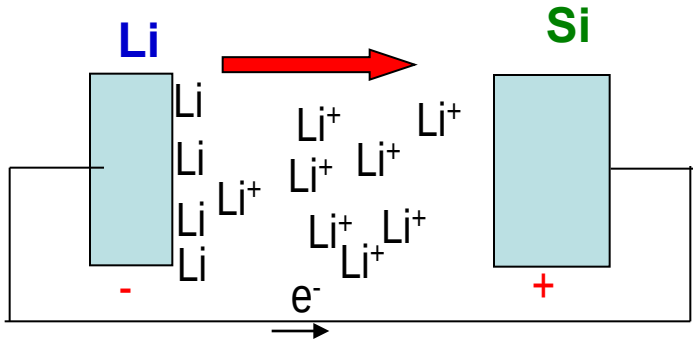
I_{μ} = Intensity calculated assuming SD issue, and deposition as micron sized Li ☑

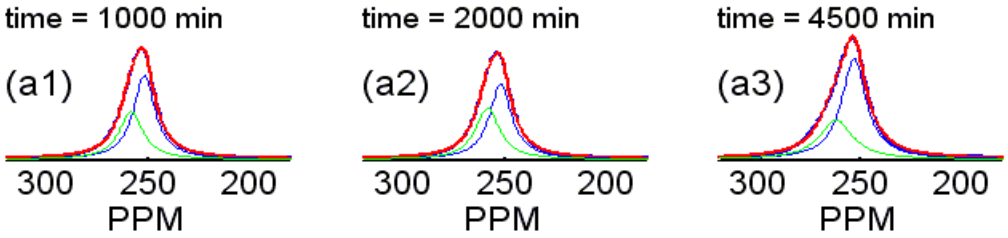
(e) Total mass of Li deposited M_{li} (from e-chem), and the Mass of dendritic/mossy Li M_{μ} and smooth deposit, M_{SD}, from NMR.

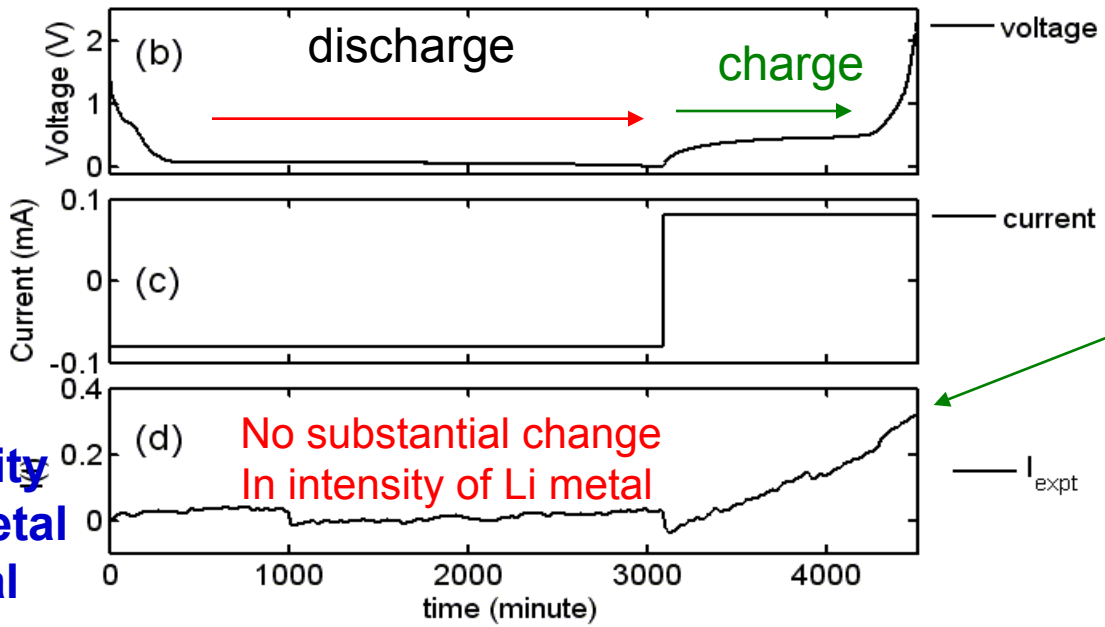
Mossy Li participates in the electrochemistry – in the 1st cycle



Very different Li intensities seen in Li – Si cells







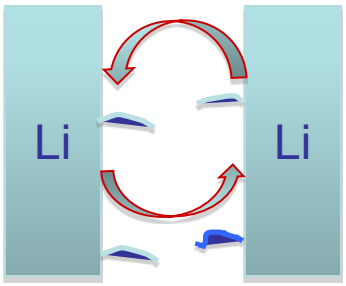
Intensity of Li Metal signal

Intensity growth indicates that mossy Li is formed

Subsequent decrease (not shown) indicates that it participates in the next discharge

Symmetric Cells

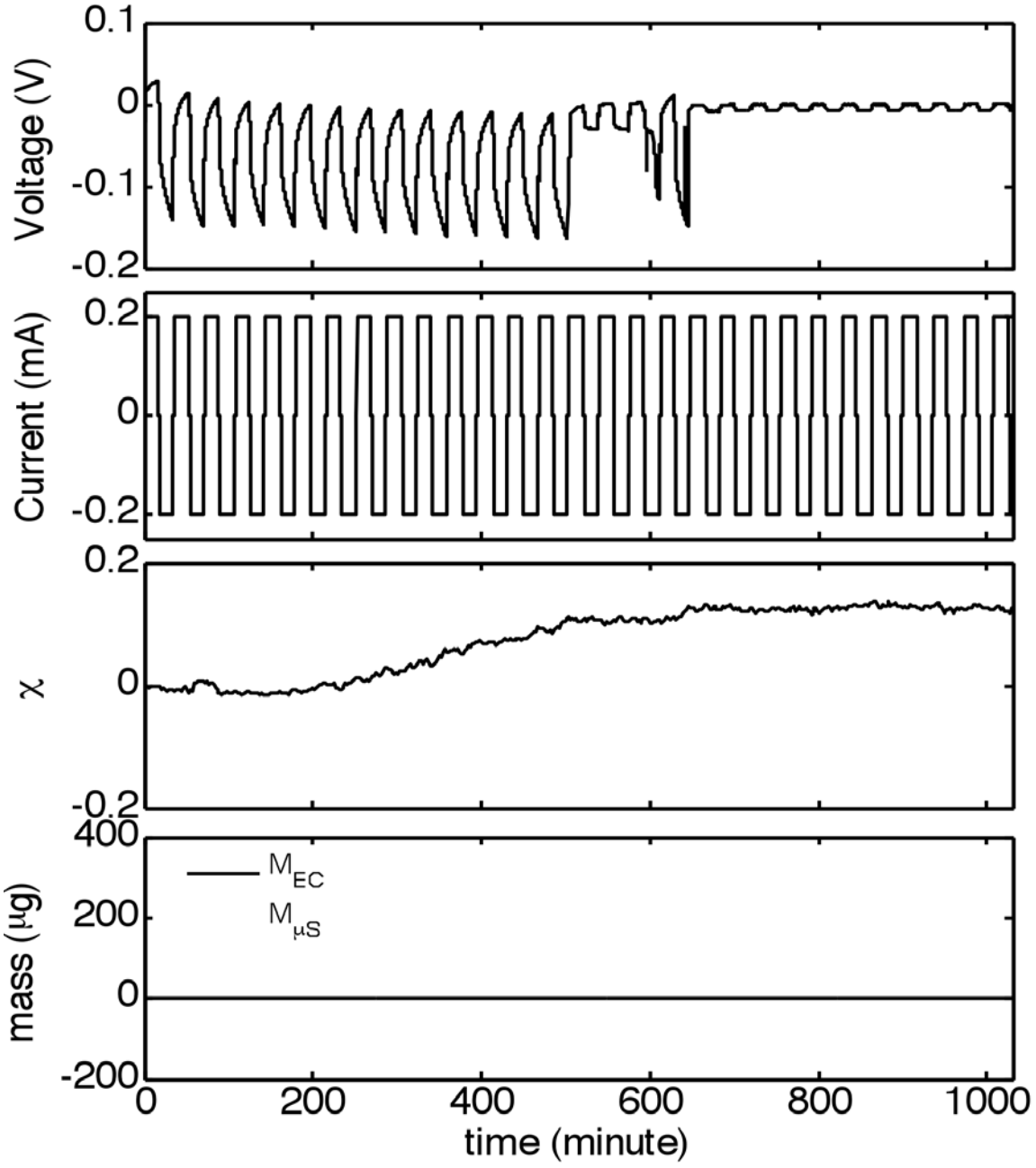
•Convert Li signal intensity into %age of dendritic/mossy Li



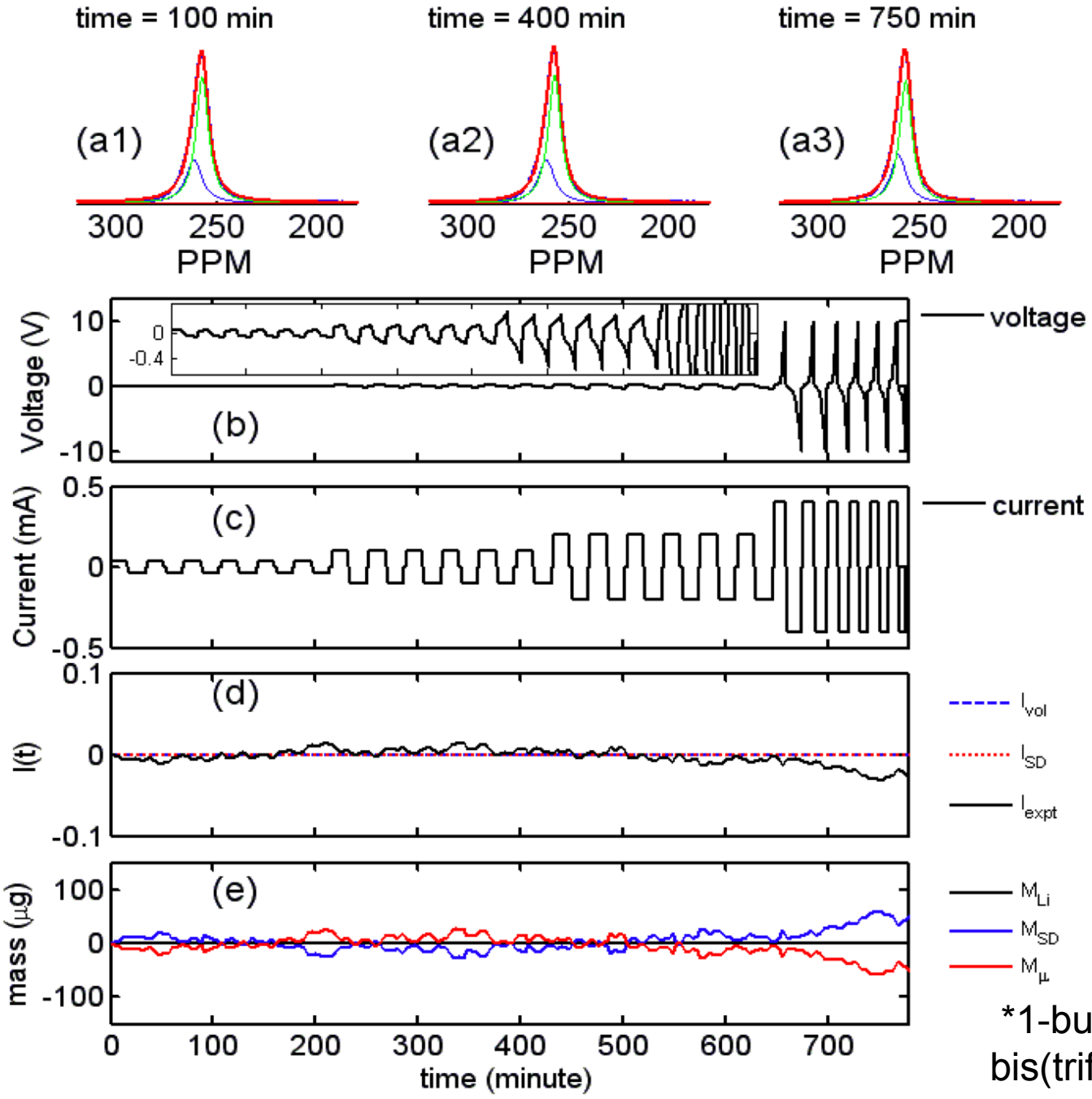
direct method to quantify Li microstructure formation

$C_2MIm\ BF_4^*$ + $LiBF_4$ + VC

(1-ethyl-3-methylimidazolium tetrafluoroborate)



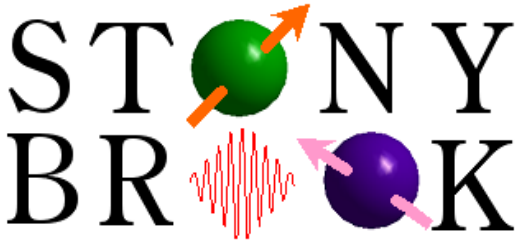
With A. Best, A. Hollenkamp CSIRO



C_4mpyr TFSI* + LiTFSI.

*1-butyl-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide

Acknowledgements



Baris Key
Rangeet Bhattacharyya
Hailong Chen
Ben Zhou
Nicole Trease
Derek S. Middlemiss
Dongli Zeng

Amiens
Mathieu Morcrette
Vincent Seznec
Jean-Marie Tarascon

CSIRO
Tony Hollenkamp,
Adam Best

LBNL
Jordi Cabana
Guoying Chen
Thomas J. Richardson

Collaboration and Coordination with Other Institutions

Gerbrand Ceder (MIT) – co PI

- Olivines; Layered oxides; Conversion reactions; Nanoparticles

BATT collaborators:

J. Cabana, T. Richardson, G Chen (LBNL)

- Olivines, characterization, conversion materials

M. M. Thackeray (Argonne)

- Characterization of composite spinel/layered materials

M. S. Whittingham (Binghamton)

- magnetism, doped phosphates

Other collaborators:

J. M. Tarascon, M. Morcrette (Amiens)

- Silicon, SEI formation, New materials

C. Masquelier (Amiens)

- Phosphates

A. Best, T. Hollenkamp (CSIRO)

- Ionic liquids, dendrite formation

Proposed Future Work

- Complete work on Si nanoparticles – identify how Li_xSi structures formed on cycling vary with size
- Explore correlations between structure and rate (in Si)
- Extend to other intermetallics
- Examine SEI formation on Si nanoparticles
- Explore in more depth correlations between rate, electrolytes and additives and Li dendrite formation
- Complete work on $LiCoO_2/LiMn_2O_4$ composites to explore effect of rate and high rate pulses on structural changes
- Continue to examine new materials

Summary Slide

New Diagnostics Methods

- In-situ NMR – a relatively straightforward, direct method for studying self-discharge processes and for capturing reactive species or microstructures that may be destroyed by pulling cell apart
  - Application to dendritic Li/Li microstructures
  - Investigate at different field strengths to obtain more detailed information about size distributions

Anodes

- A combination of ex and in-situ NMR and PDF methods was used to determine the structures present in the Li_xSi amorphous phase formed on Li insertion in silicon.
- 2 processes seen on 2nd discharge are assigned to breakage of Si-Si bonds in amorphous Si to form (i) isolated Si and Si clusters. (iii) breakage of the cluster bonds to form isolated Si^{4-}. Processes less well resolved in 1st discharge due to the severe kinetic challenges associated with breakage of large Si_x (crystalline) units.
- Charge occurs via the reaction of isolated Si^{4-} to form amorphous Si
- Different structures formed on charge and discharge explain hysteresis.

Cathodes

- Continue to use NMR methods to investigate structure-function relationships in a diverse range of materials within the BATT program.