First Principles Calculations and NMR Spectroscopy of Electrode Materials

Professor Clare Grey

University of Cambridge

6/17/2014

Project ID
es055

Overview

Timeline

- Project start date: 1/1/13
- Project end date: 12/31/16
- Percent complete: 33%

Barriers

- Life (capacity fade)
- Performance (high energy density)
- Rate

Budget

- Total project funding: $1.1M
- Funding received in FY13: $265,913
- Funding for FY14: $272,197

BATT collaborators

- Brett Lucht
- Jordi Cabana
- Kristin Persson
- Guoying Chen
- Stan Whittingham

Relevance: Objectives - 2013/14

•Identify major solid electrolyte interphase (SEI) components, and their spatial proximity, and how this changes with cycling (capacity fade)

•Complete structural/mechanistic studies of Si (performance)

•Investigate local structural changes of high voltage/high capacity electrodes on cycling (performance/capacity fade)

2015/16

•Contrast SEI formation on Si vs. graphite and high voltage cathodes (capacity fade)

•Correlate Li^+ diffusivity in particles and composite electrodes with *rate*

Approach/Strategy

- **Optimizing Si performance**
  - Structures formed on cycling
  - Reducing overpotential
  - Building a better SEI

  - Development of new platform for *in situ* studies.
  - Li and NMR studies of structure
  - NMR and electrochemical studies of Si coatings/surface treatments

- **SEI studies**
  - NMR studies of local structure as a function of cycling

  - ^{13}C NMR studies of ^{13}C enriched electrolytes to study SEI organic components; ^{19}F and ^{31}P studies of inorganics

- **Improving rate performance (electrode tortuosity studies)**

  - Develop pulse field gradient (PFG) approach to study electrode tortuosity ($LiCoO_2$ current model compound)

- **High voltage spinels**

  - Development of in situ methods to study phase transformations
  - In-situ and ex-situ NMR studies of Li^+ transport and structural changes

Approach/Strategy (cont.)

Milestones

- Identify major components (LiF, phosphates, carbonates and organics) in Si SEI by NMR methods. (Dec-13). **Complete**
- Correlate presence of SEI components with cycle number and depth of discharge of Si. Complete preliminary TOF-SIMS measurements to establish viability of approach. (Mar-14) **Ongoing. Difficulties encountered with sample reproducibility and Si cracking (TOF-SIMS)**
- Identify SEI components in the presence of FEC and VC in Si and determine how they differ from those present in the absence of additives. (Jun-14) **Ongoing**
- Go/No-Go: Stop Li+ PFG diffusivity measurements of electrodes. Criteria: If experiments do not yield correlation with electrochemical performance. (Sep-14) **PFG studies initiated of $LiCoO_2$.**

Technical Accomplishments and Progress

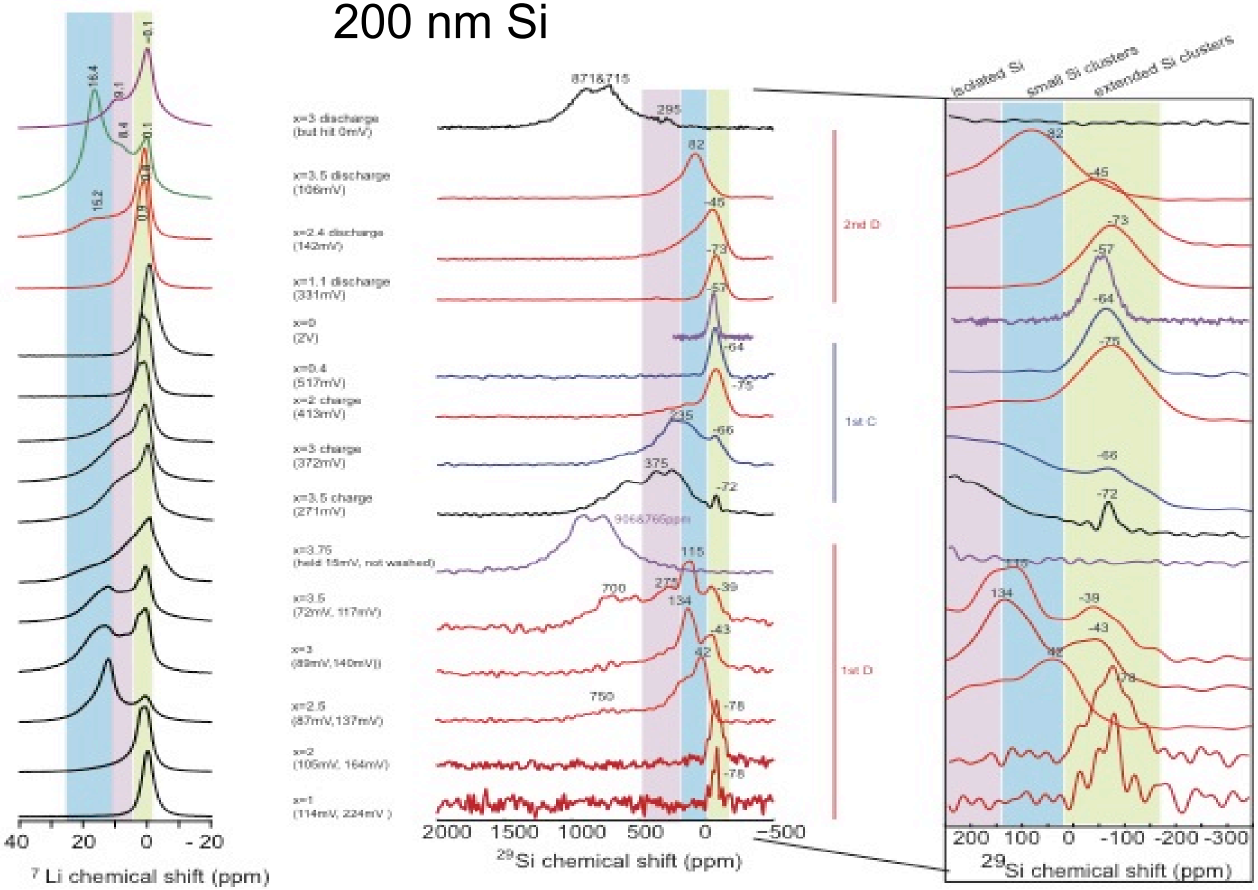
Optimizing Si performance: I

- Used ^{29}Si NMR and Li NMR to study Si cluster formation and bond breakage as function of state of charge
  - Showed that mechanisms for lithiation are different in smaller Si particles

^{7}Li NMR **^{29}Si NMR**

200 nm Si

15 nm

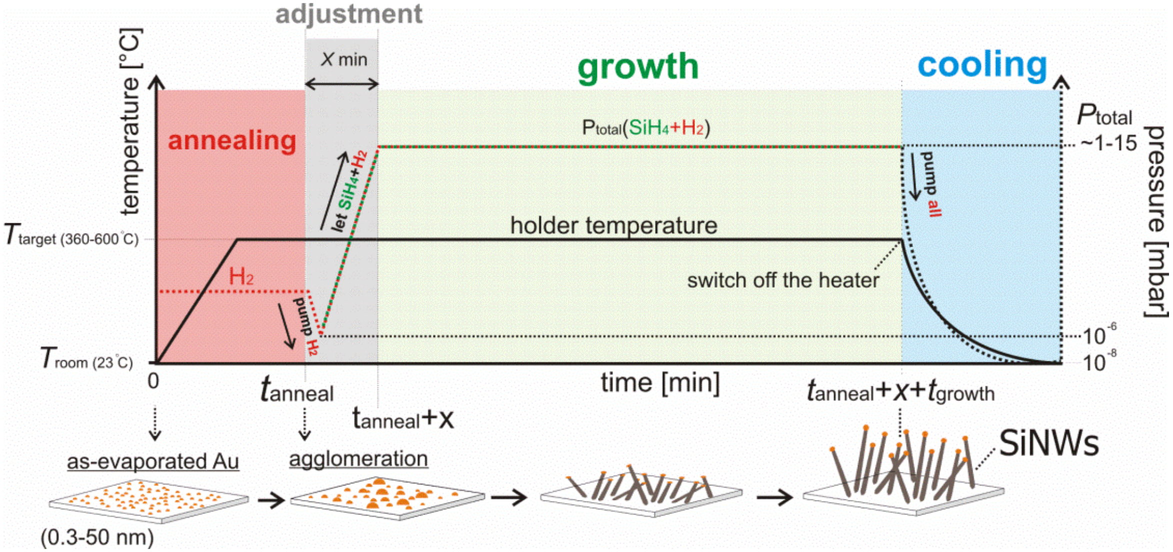


Salager et al. in prep.

- Investigated (Li) defects in Si by DFT-based computations

A.J. Morris et al., *Phys Rev B* (2012)

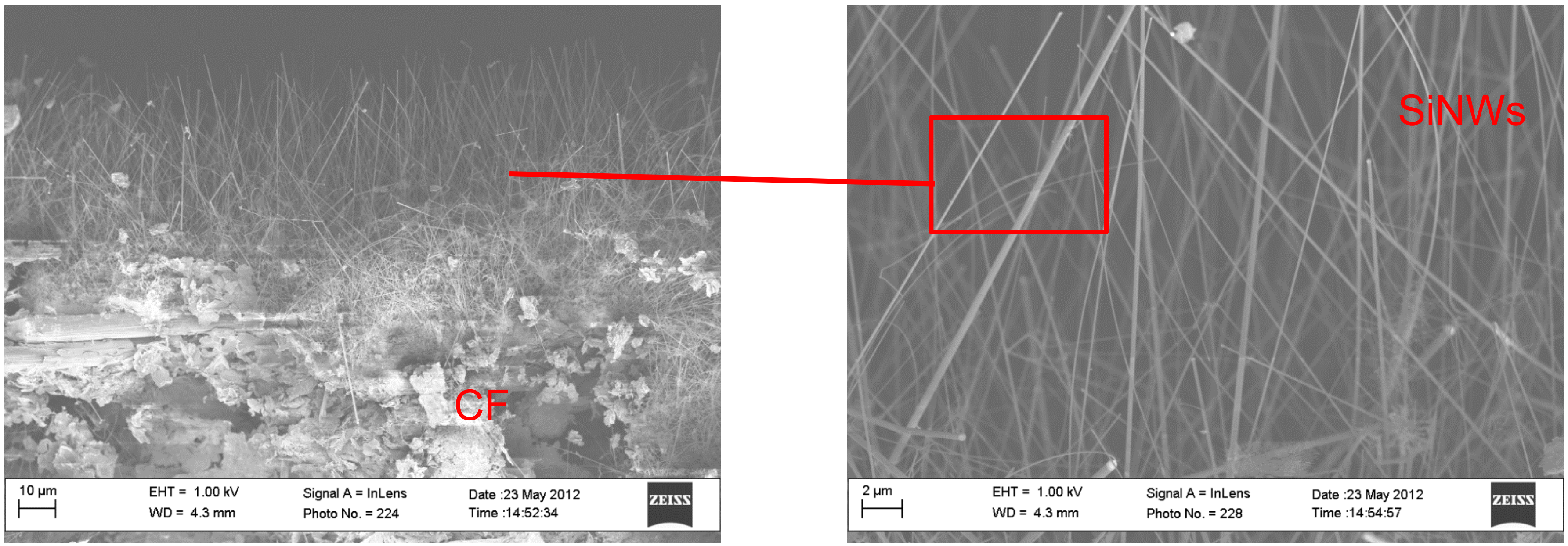
Optimizing Si performance II: Studying nanoparticles by in-situ NMR



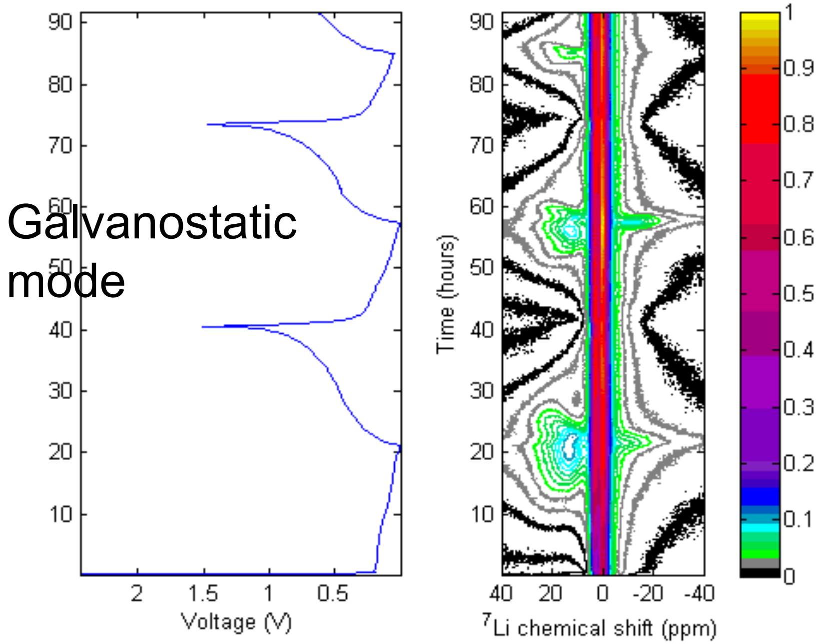
Inspired by:
C. K. Chan. … R. A. Huggins, Y. Cui, *Nature Nanotechnology*, 3, 31 (2008)

K. Ogata
C. Kerr
S. Hoffman

CF+50nm-Au+SiNWs   Cross sectional SEM images



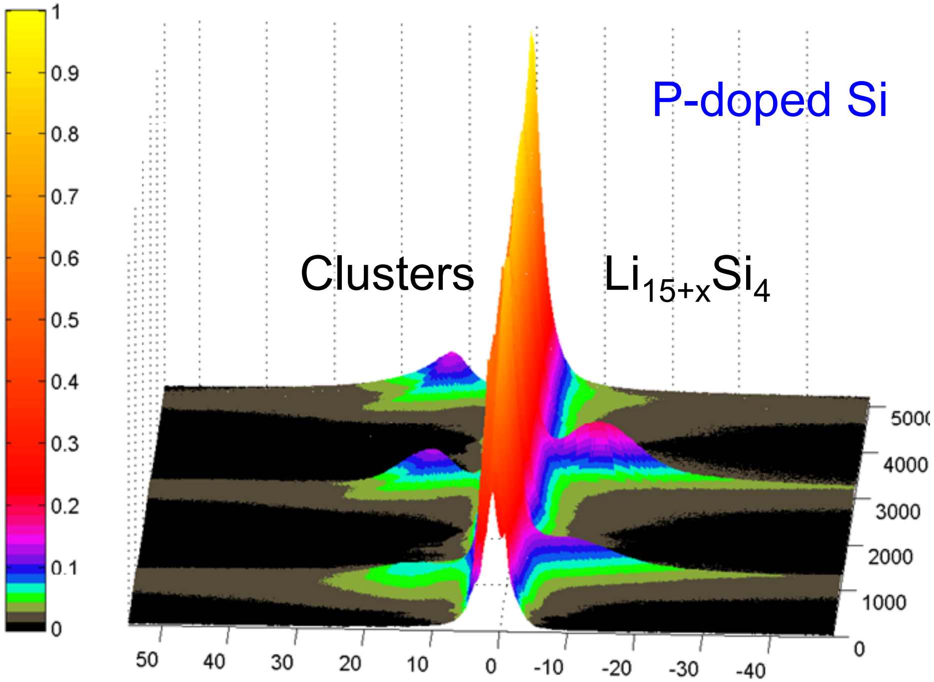
In-situ NMR of Si Nanowires:

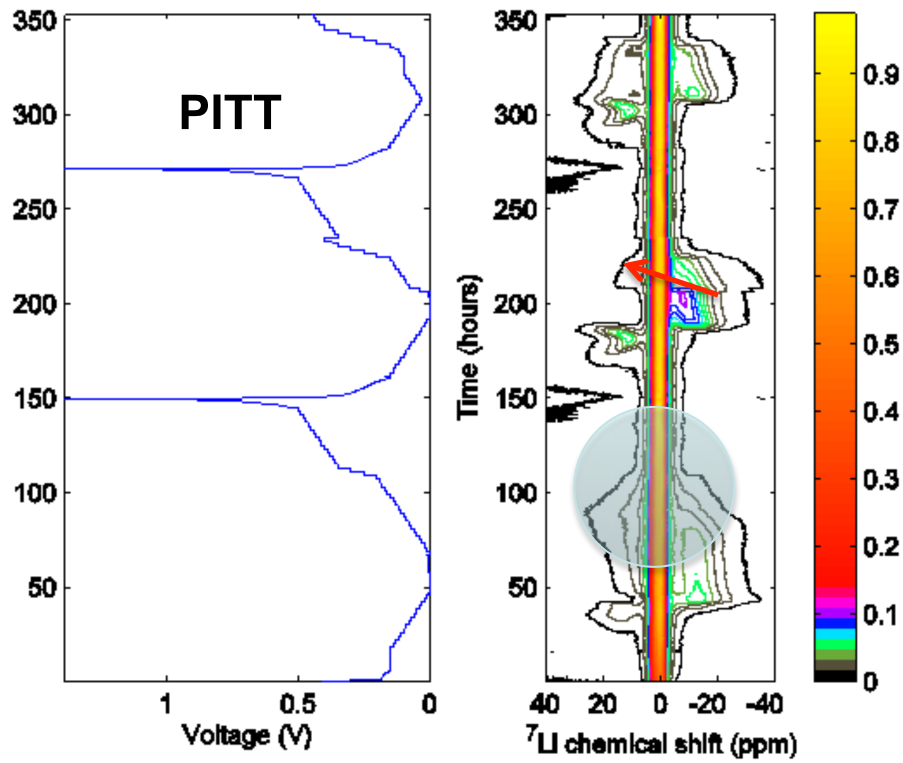


Ideal Model Systems for Studying Mechanisms – allow GITT and PITT experiments to be followed *in situ*

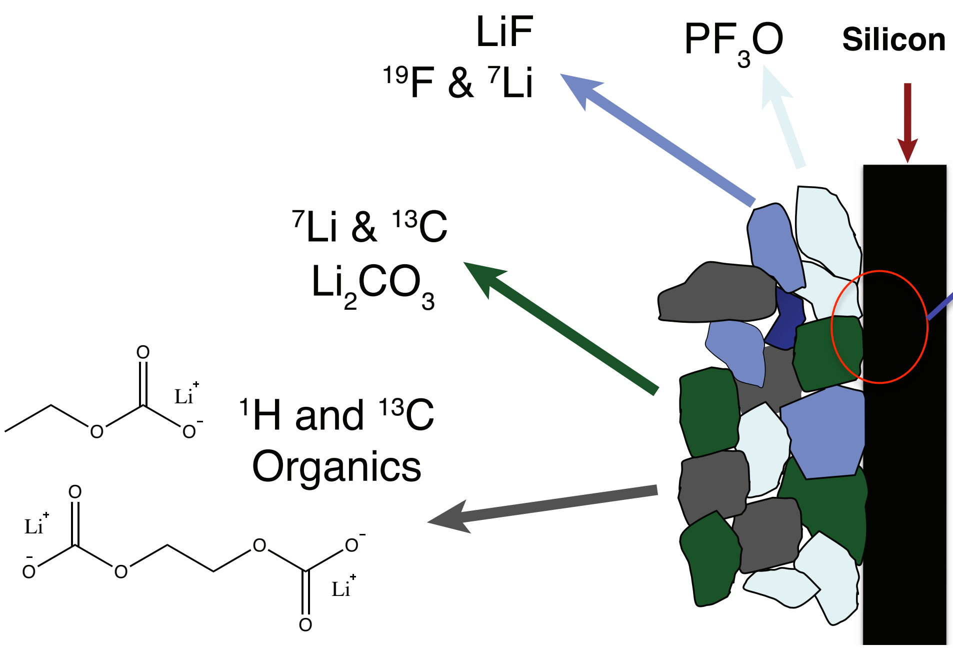
Ogata et al., *Nat. Commun*. (2014)

Detect Si=Si defects in $Li_{15}Si_4$
=> Set overpotential voltage on charge



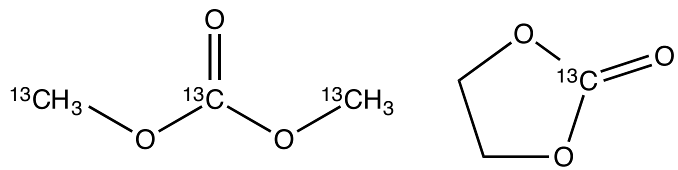


SEI Studies: Si

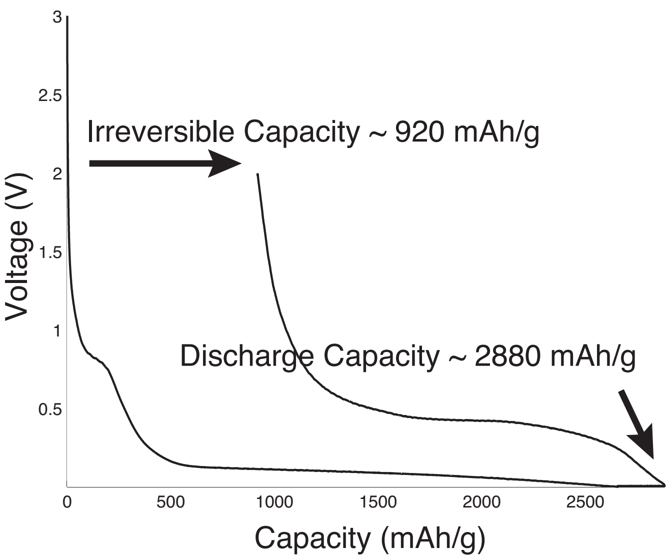


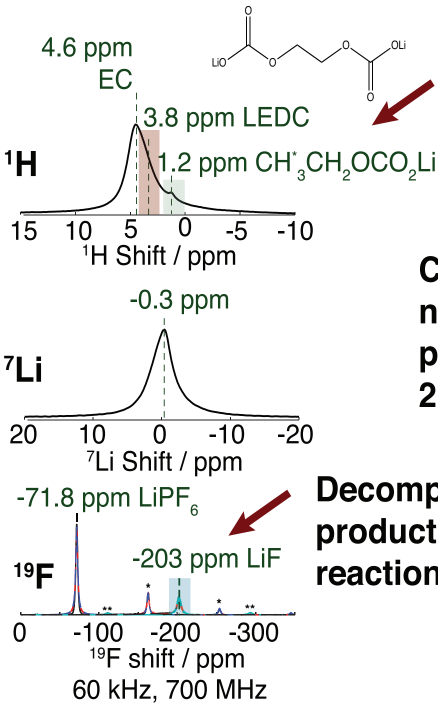
Structure of the interface?

- SEI as a function of voltage?
- SEI as a function of cycle number?



System: C + Si, 1 : 1

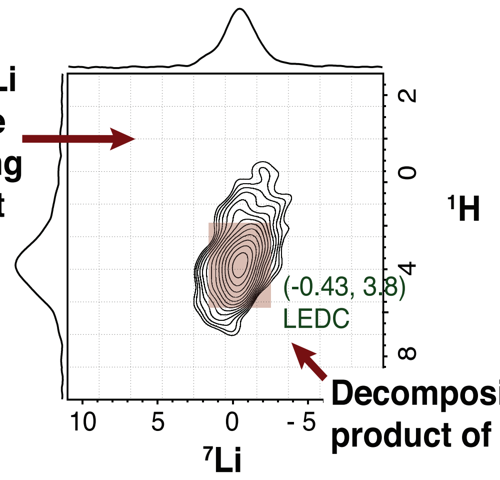




Decomposition products of EC

Decomposition product a result of reactions with H_2O

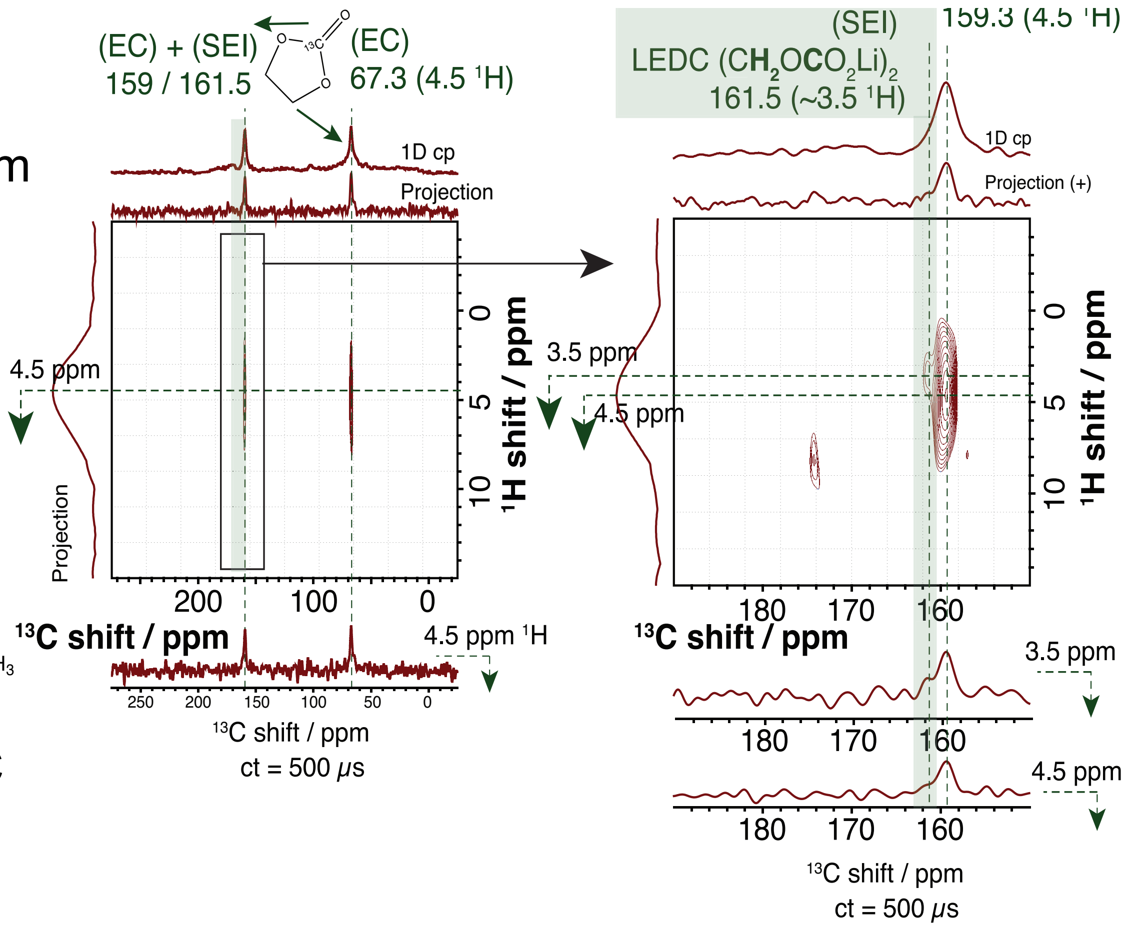
Correlate ^{1}H-^{7}Li nuclei in close proximity using 2D experiment

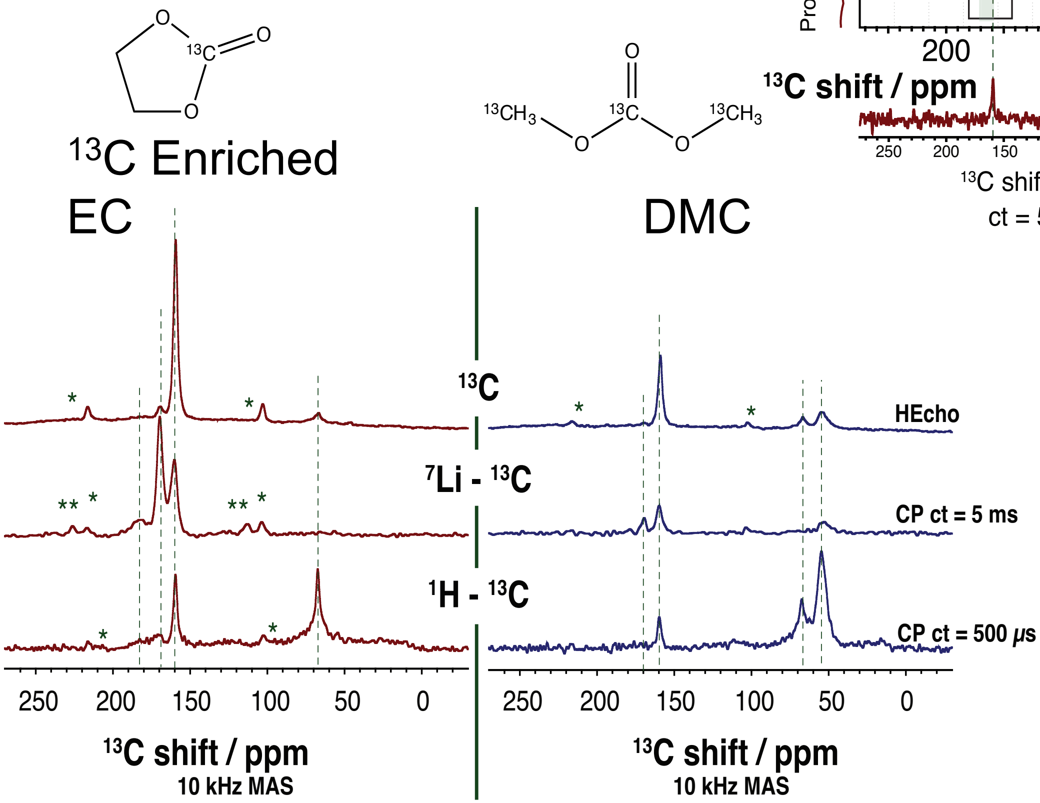


Decomposition product of EC

^{13}C Solid State NMR – SEI Composition

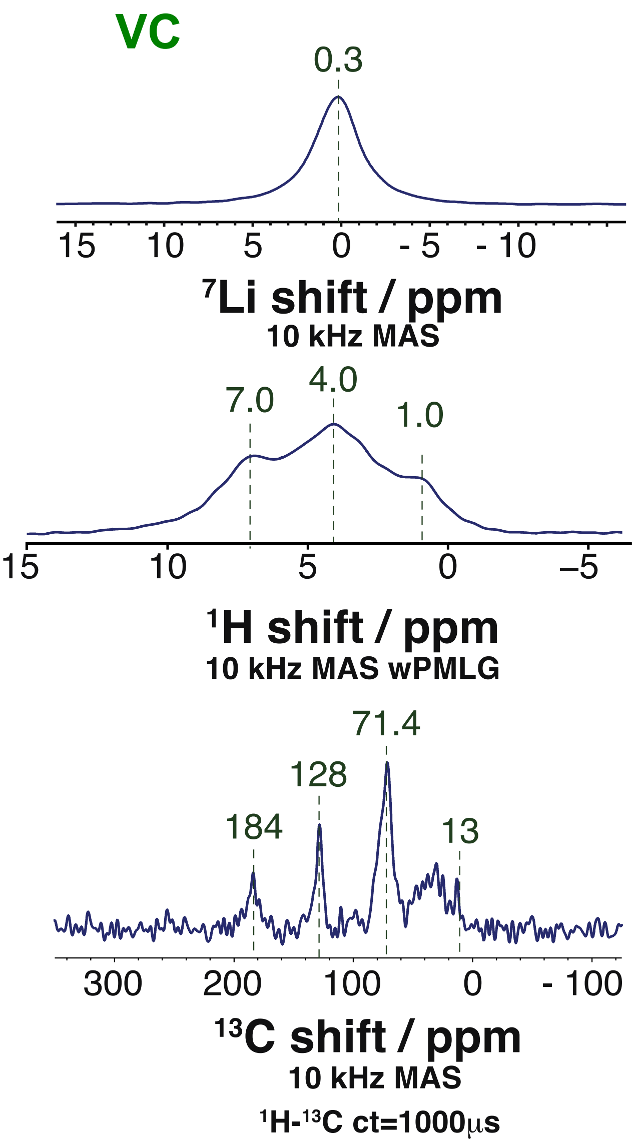
EC: 2D experiments confirm assignments of LEDC (similar experiments performed for DMC)

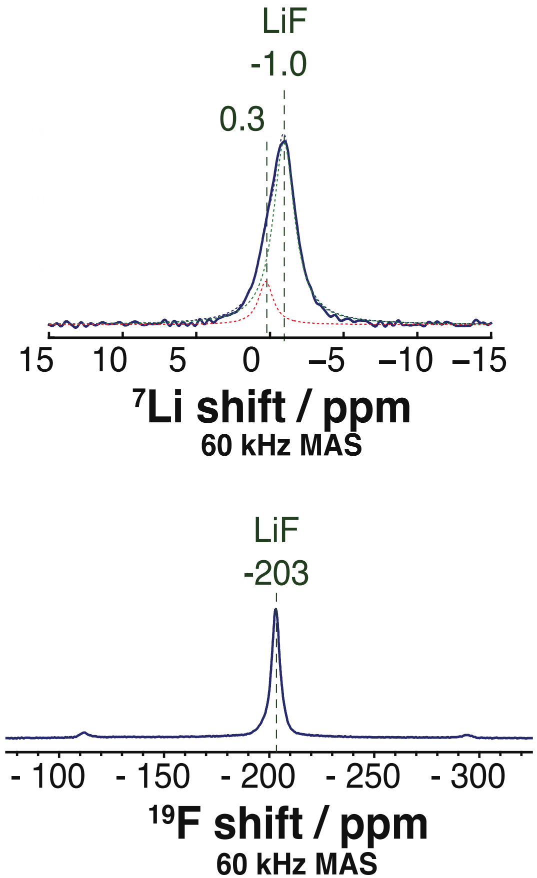


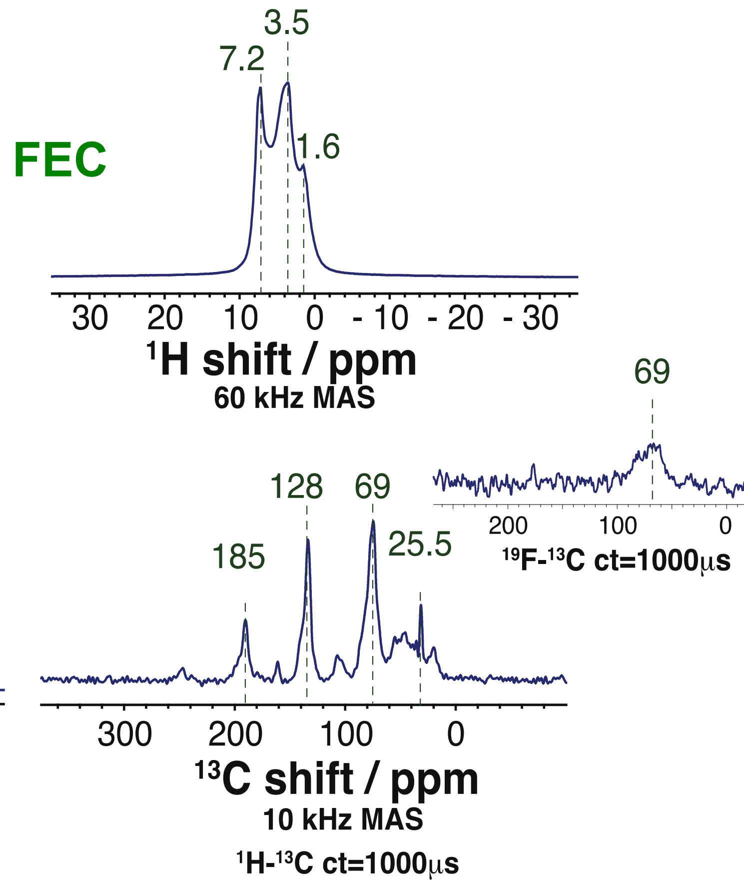


Use correlation NMR experiments (cross-polarization (CP)) to establish spatial proximity between atoms

Collaboration with B. Lucht: Structures of reduced VC and FEC





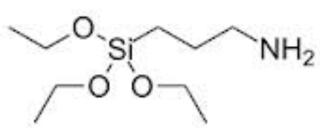


185 = RCO_2
128 = C=C
69 – 71 = OCH_2

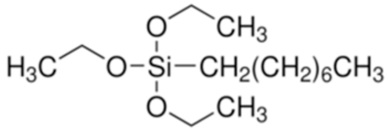
Very similar polymers ..

Now we can compare spectra with those obtained when using VC and FEC as additives

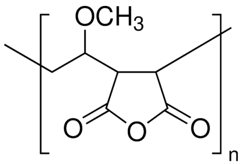
Reducing SEI Formation: Si surface coatings improve capacity retention



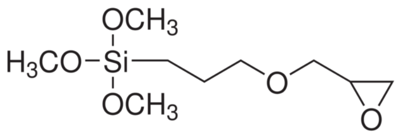
APTMS



TEOOS

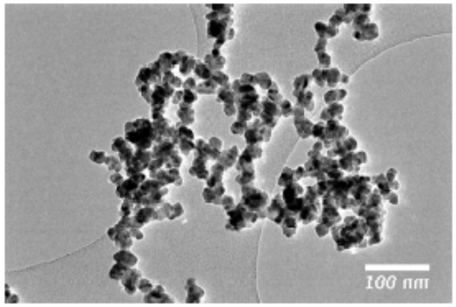


PMVEMA

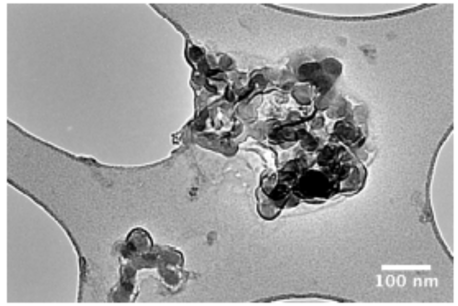


(3-Glycidyloxypropyl)trimethoxysilane

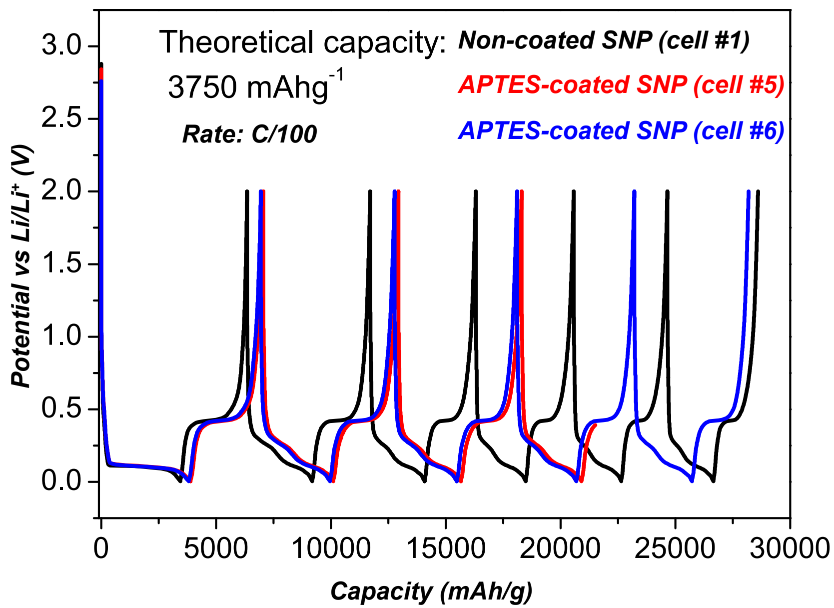
$Si(OCH_2CH_3)_2CH_2CH_2CN$

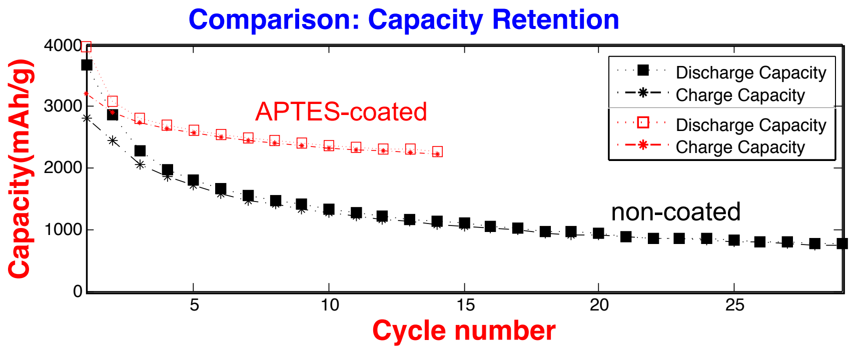


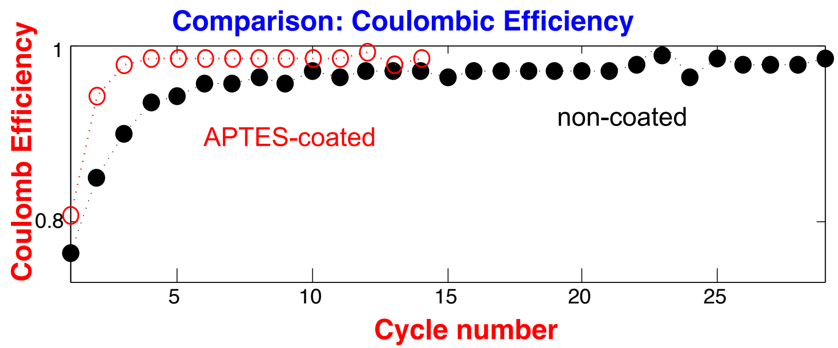
Si without coating



Si-TEOOS



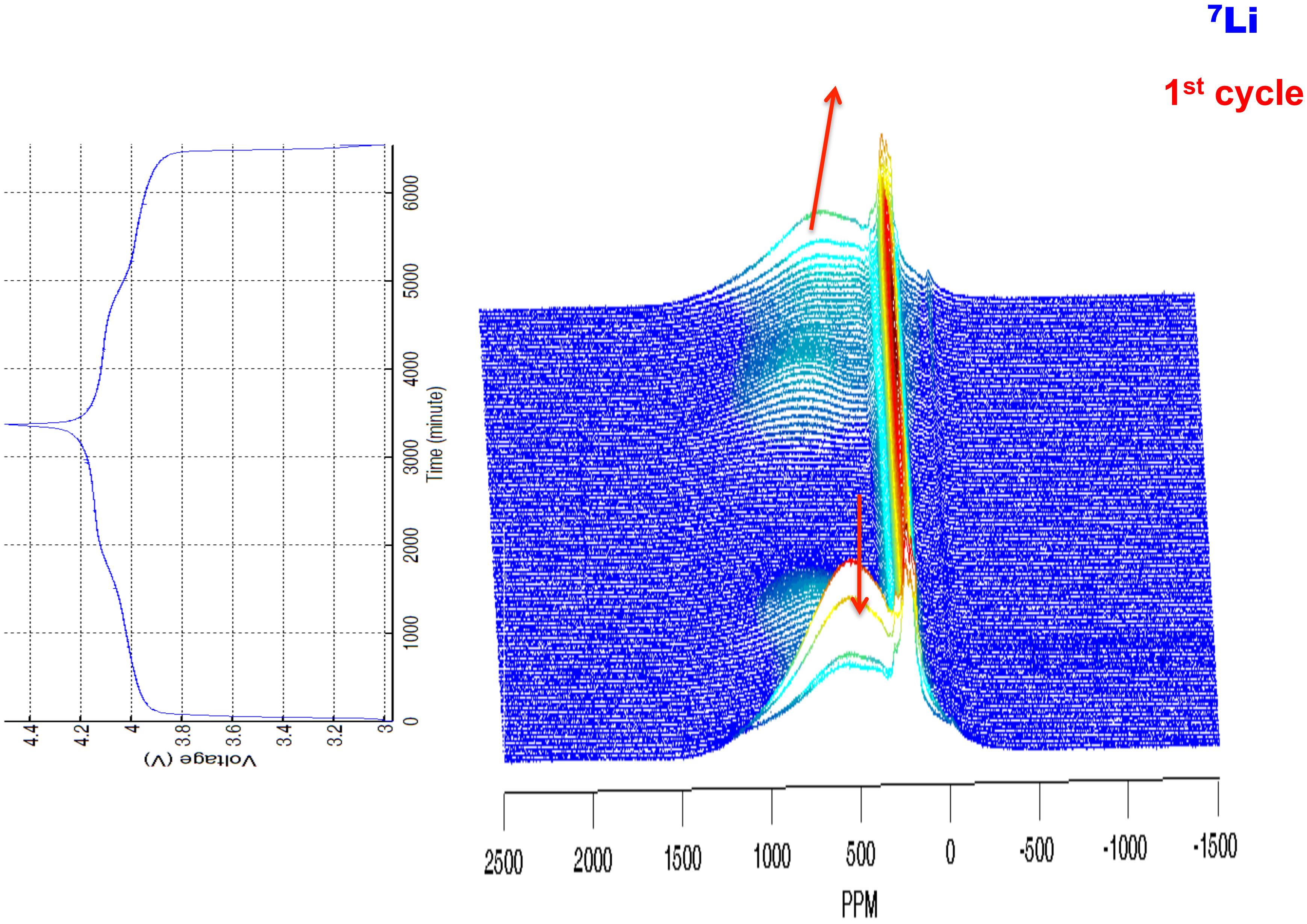




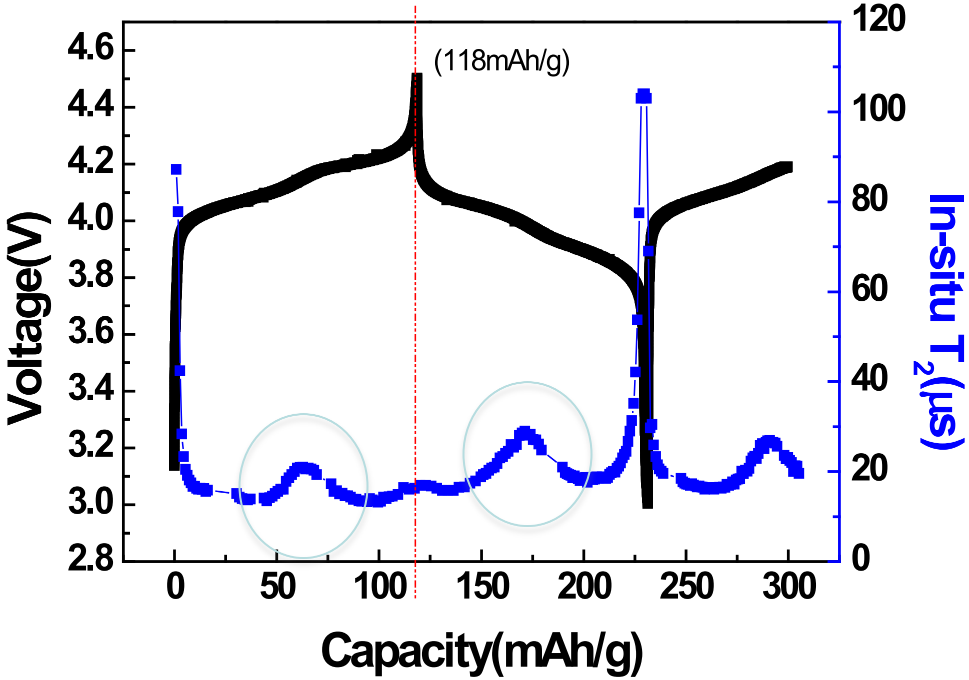
NMR studies in progress to study nature of grafting

- Echem performance improvement: APTMS> $Si(CH_2)_2CN$>TEOOS> PMVEMA> >$Si(CH_2)_7CH_3$ > non-coated

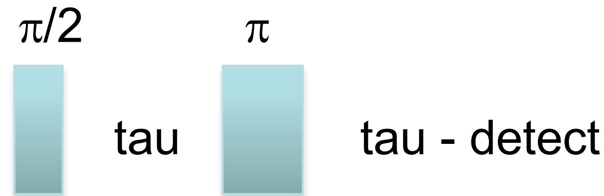
Development of In situ NMR method for Paramagnetic Cathode Materials: $Li_{1.08}Mn_{1.92}O_4$ Electrode Orientation = 54.7 Degrees

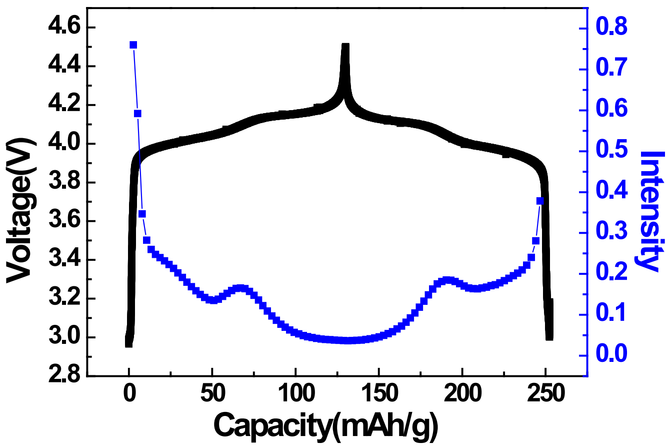


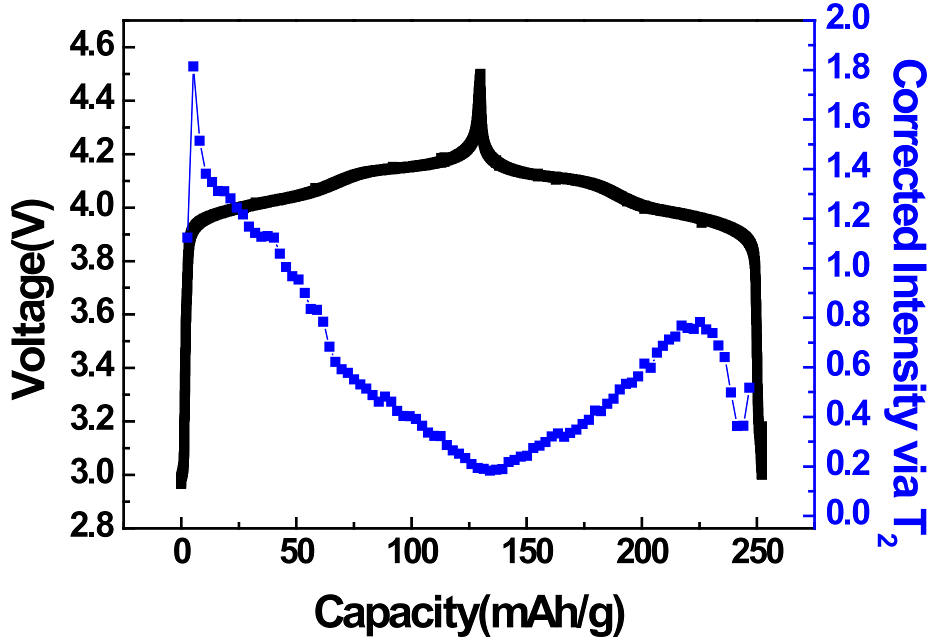
Relaxation (T_2) effects – and thus spectral intensity - are strongly affected by Li motion



Spin-spin relaxation (T_2) measurements:



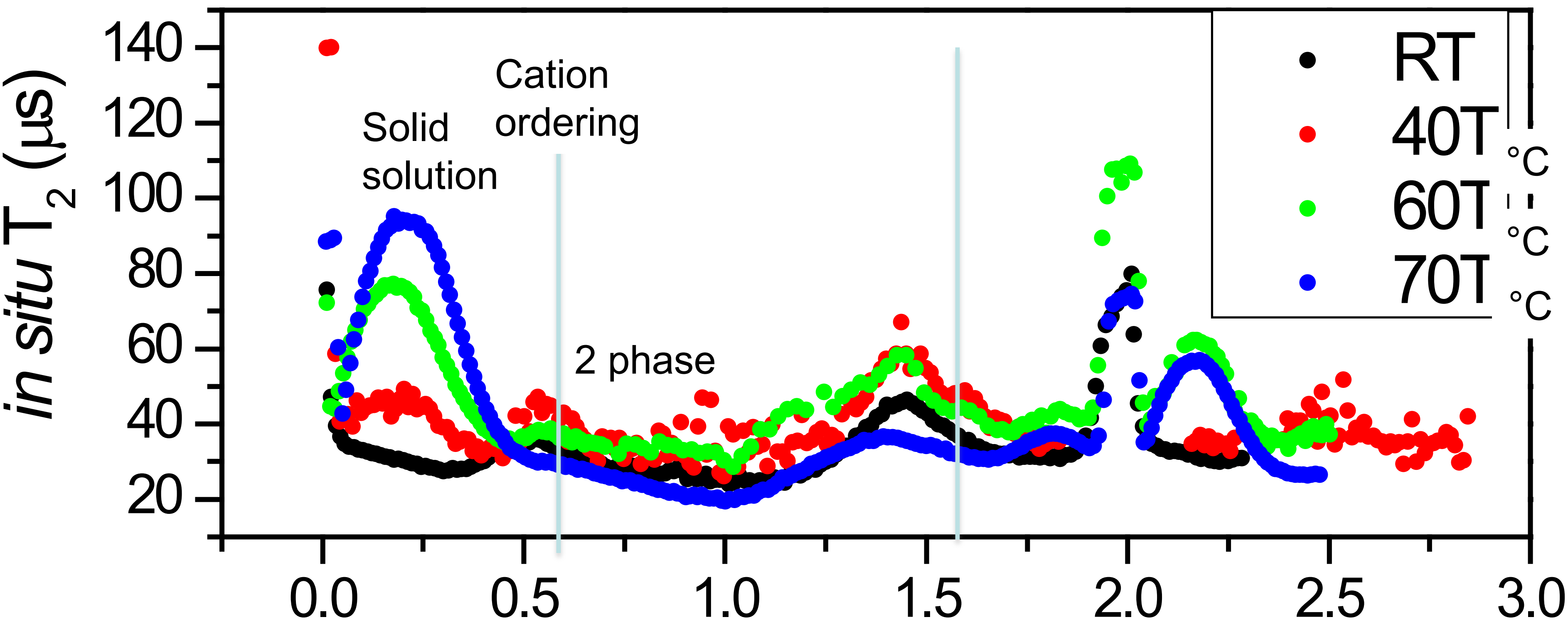




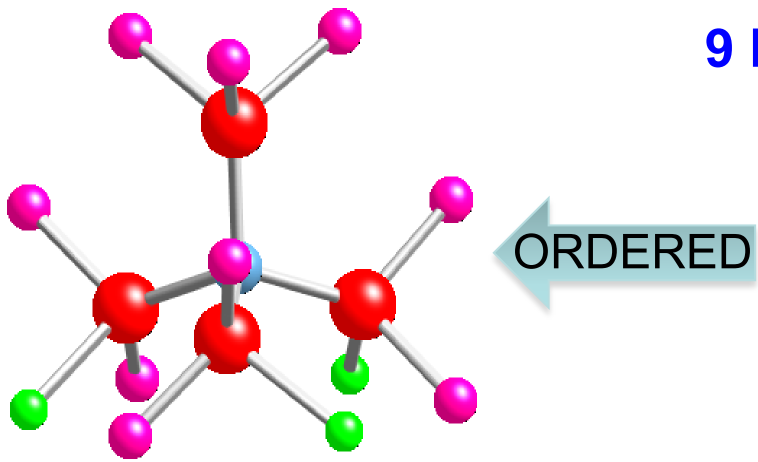
Use In-situ T_2 Measurements to Study Li Dynamics as a Function of Temperature

- Rapid Li^+ and electronic motion in partially charged samples
- Clear evidence for solid solution from 1 Li to 0.5 Li
- Ordering tendency @ 0.5 Li -

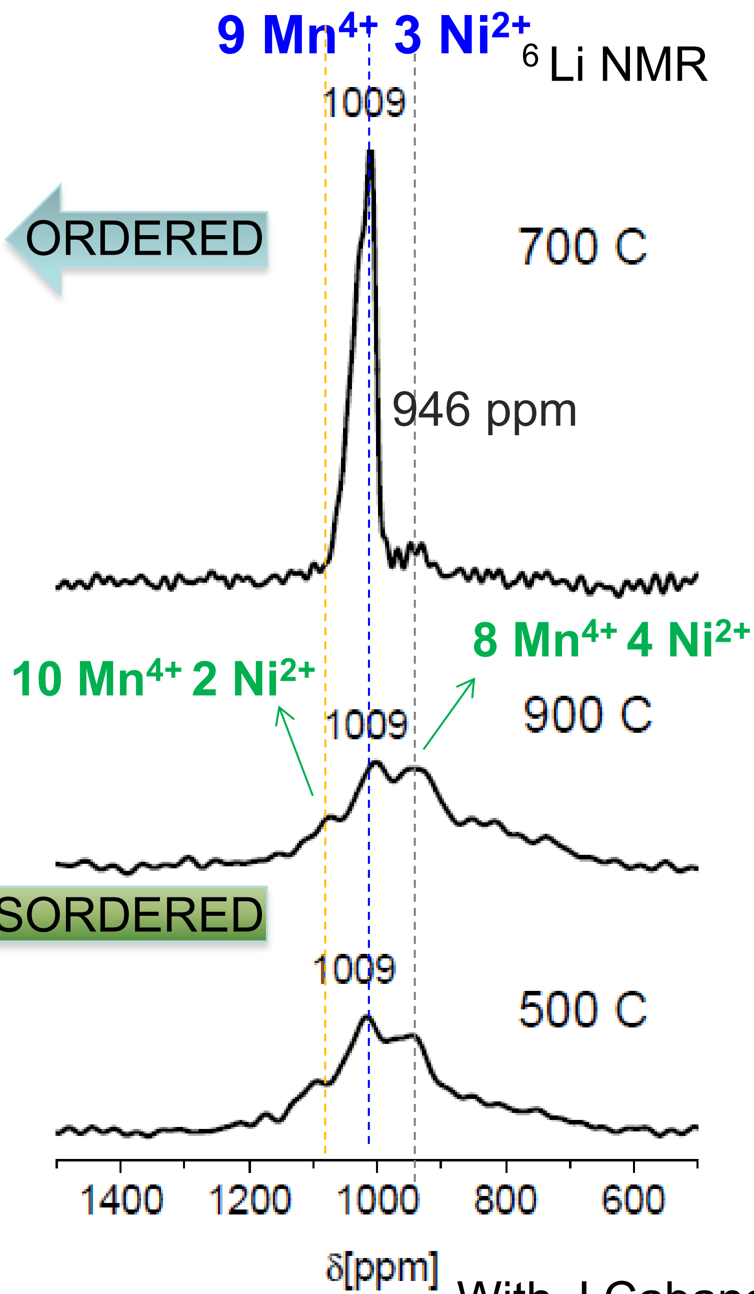
- Method can be used to study dynamics during (de)lithiation

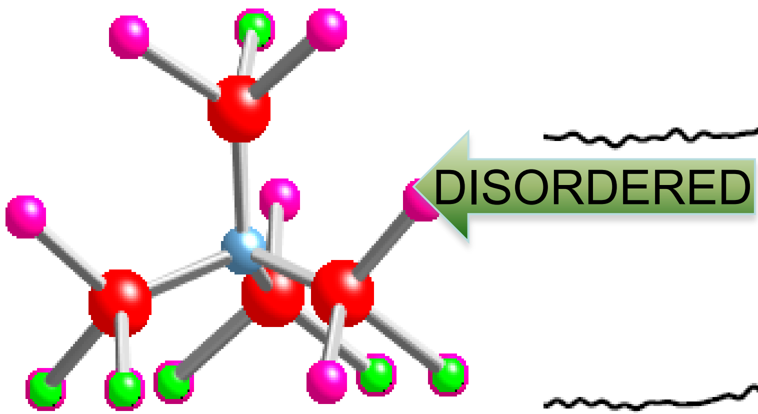


High Voltage Spinels ($Li(Ni_{0.5}Mn_{1.5}O_4)$) - Ordering affects the electrochemistry @ the 4.8 V process

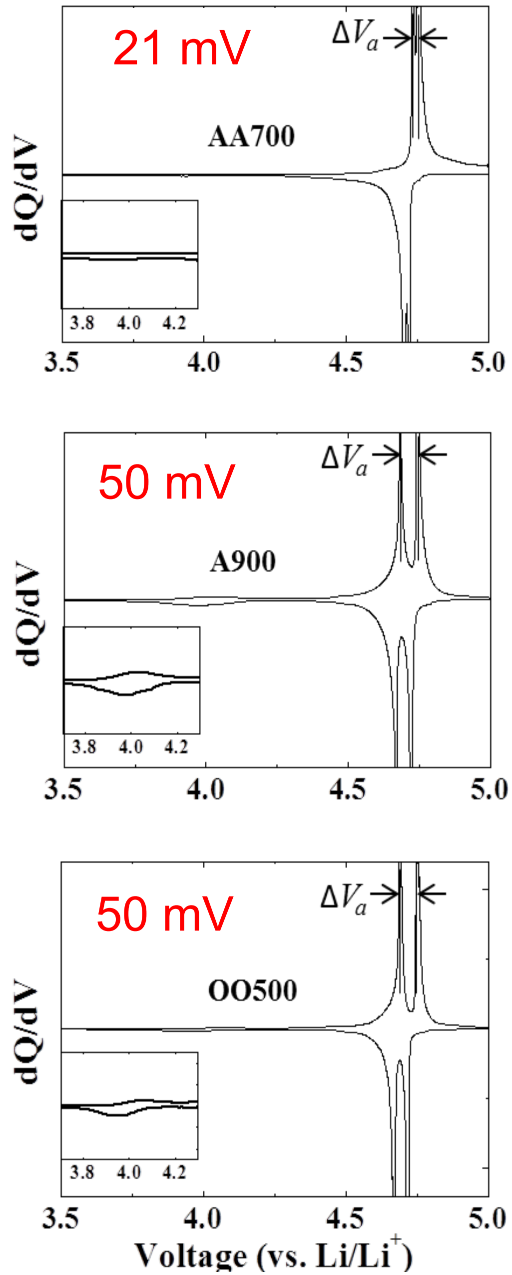


$P4_332$: Ni^{2+} and Mn^{4+} ordering





Fd-3m: Ni^{2+} and Mn^{4+} randomly distributed

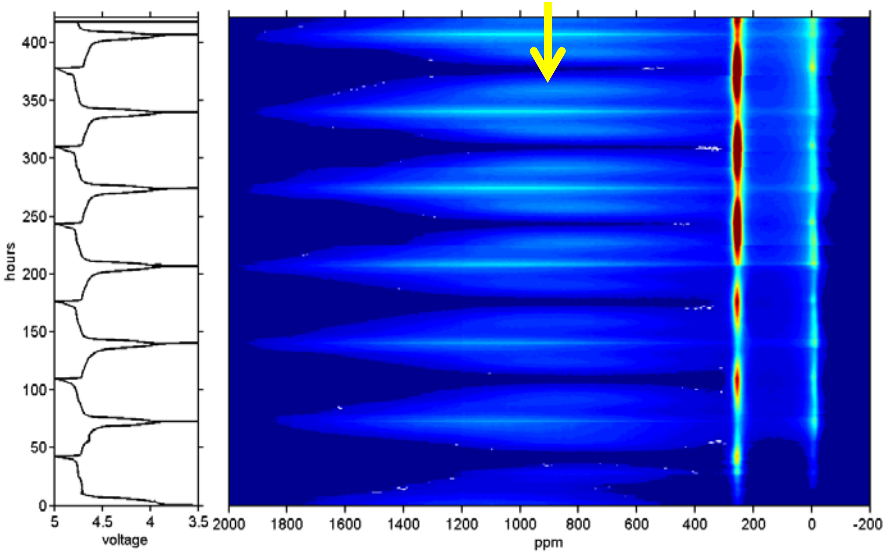


With J Cabana (LBNL/UIC) C Kim (LBNL)

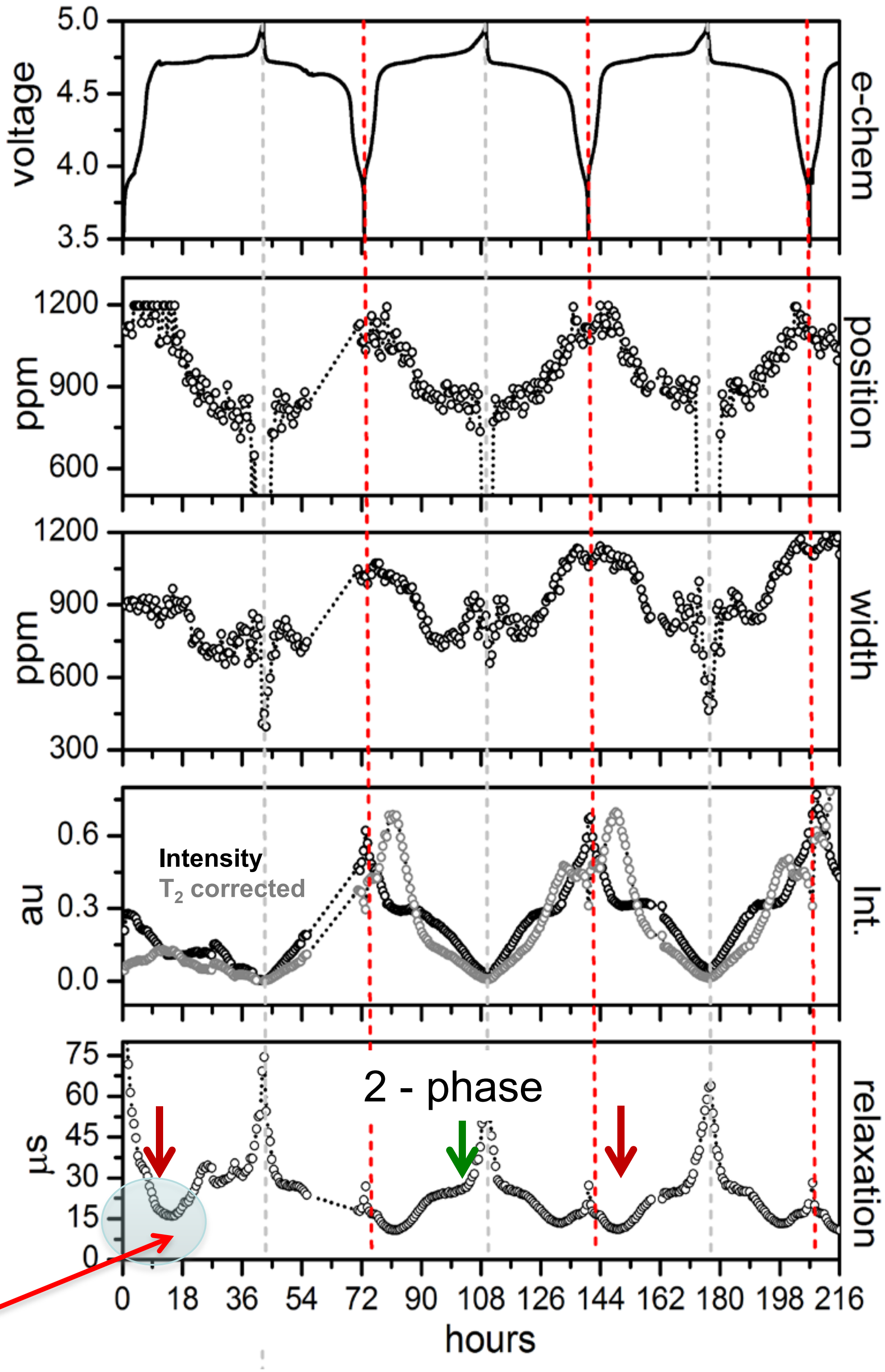
In-situ ^{7}Li NMR – Mechanisms of (de)lithiation

Disordered 900 C spinel

Cation ordering @ x = 0.5



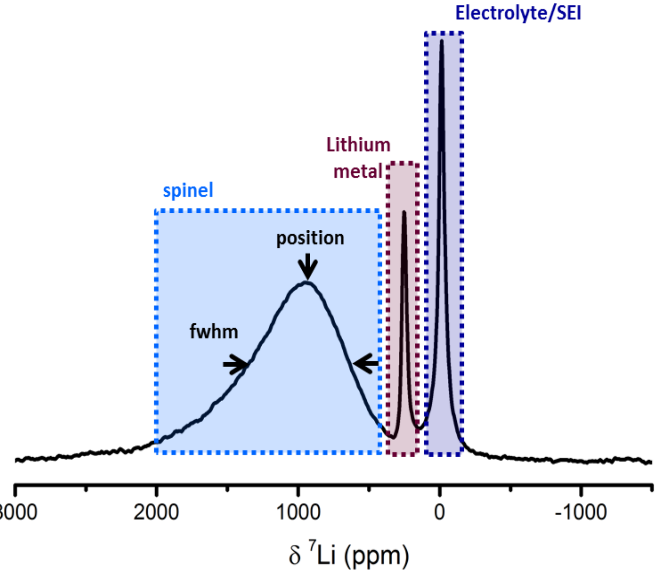
Intensity vs. cycling



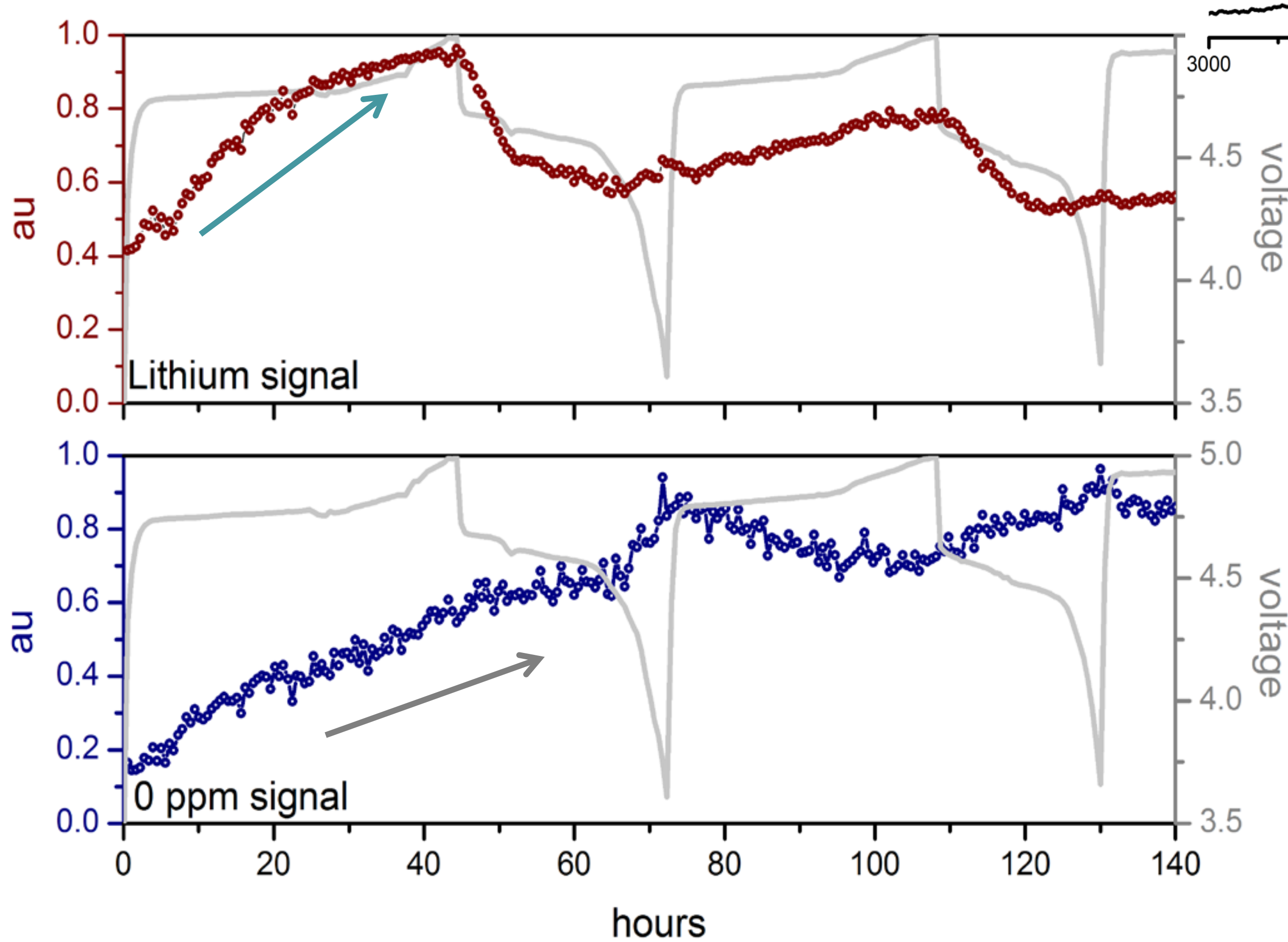
"T_2" Relaxation studies show solid solution followed by 2 phase

Increased Li mobility
Solid solution

In-situ ^{7}Li NMR – Lithium & electrolyte region: Follow Li dendrite formation and electrolyte decomposition *in situ*



Ordered



Dendrite formation

Electrolyte decomposition

Summary

- **Silicon – structural work essentially complete.**
- Used ^{29}Si NMR to study cluster formation on lithiation
- Developed in-situ NMR method for studying nanowires
- Identified source over large "overpotential" on charging fully lithiated $Li_{15}Si_4$ phase
- **Si SEI – NMR methodology has been developed.**
- Clear NMR signatures of many SEI components identified
- **Si Coatings – Grafting of small molecules helps improve capacity retention.**
- **Tortuosity – PFG method demonstrated**
- **High Voltage spinels – Demonstrated novel NMR methodology to study paramagnetic materials**
- Approach can be used to study Li ion dynamics, cation ordering, solid solution vs. 2-phase behaviour
- Used to study nature of electrode reactions for the high voltage spinel $Li(Ni_{0.5}Mn_{1.5})O_4$, electrolyte decomposition and Li dendrite formation
- Ex-situ NMR highly sensitive to cation (Ni/Mn) order

Future Work

•Silicon structure

Future work will focus on (i) Reverse Monte Carlo simulations of amorphous phases (with pair distribution function analysis) to quantify Si amorphous structures and (ii) the effect of P doping on rate, overpotential (energy efficiency) and lithiation mechanisms.

•Si SEI

•Further 2D NMR experiments of fully enriched EC will be performed for more detailed structure solution of decomposition products (including reduced FEC/VC)

•Future work will focus on cycling studies, and structure f(voltage) and VC/FEC

•C-Si experiments will be initiated to investigate SEI/Si interface

•Si Coatings

•Detailed NMR studies will be performed to understand nature of grafting and how that changes with cycling. Use results/understanding to investigate different molecules

•Tortuosity

•PFG method will be applied to cycled/discharged samples to explore how SEI growth affects tortuosity (and rate)

•Investigation of Si/conducting polymer samples prepared by Gao Liu (LBNL) – particularly to investigate conductivity in pores and binder – are planned

•High Voltage spinels

•Separate equilibrium from non-equilibrium processes in NMR

•Initiate work on SEI of HV spinels. Combine with graphite carbon for full cell studies.

•Extend method to other high voltage systems.

Collaboration and Coordination with Other Institutions

- Dupont CR&D (E. McCord and W. Holstein)
  - Investigation of electrolyte stability and SEI formation
- Brett Lucht (Rhode Island)
  - Investigation of SEI
- Jordi Cabana (UI Chicago)
  - synthesis, XRD of high voltage spinels
- Stanley Whittingham (Binghamton)
  - magnetism of spinels
- Stephan Hoffman (Cambridge)
  - Si nanostructures
- Andrew Morris (Cambridge)
  - DFT structures of LixSi
- Guoying Chen (LBNL)
  - synthesis of high voltage spinesl

Responses to Previous Year Reviewers' Comments

- N/A – not reviewed last year

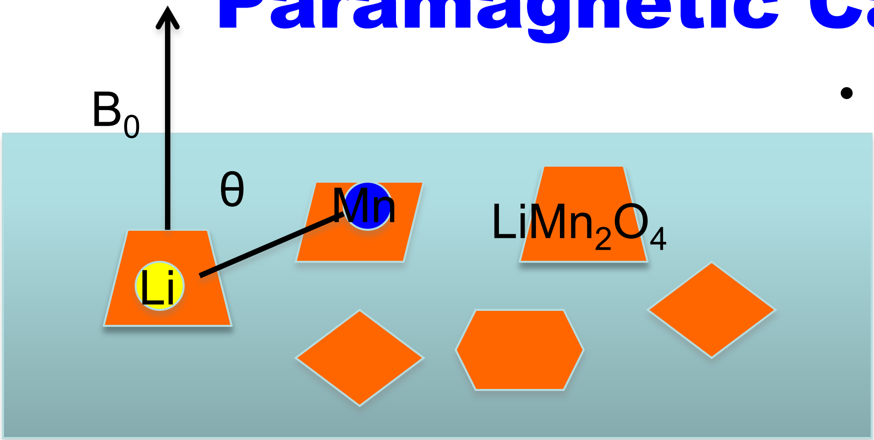
Technical Back-Up Slides

Publications and Presentations

- “Structure of aluminum fluoride coated $Li[Li_{1/9}Ni_{1/3}Mn_{5/9}]O_2$ cathodes for secondary lithium-ion batteries”, K.J. Rosina, M. Jiang, D. Zeng, E. Salager, A.S. Best, C.P. Grey, *J. Mat. Chem*., **22,** 20602-20610, (2012).
- “Scanning x-ray fluorescence imaging study of lithium insertion into copper based oxysulfides for Li-ion batteries”, R. Robert, D. Zeng, A. Lanzirotti, P. Adamson, S.J. Clarke, and C.P. Grey, *Chem. Mat*., **24**, 2684-2691, (2012).
- “Sidorenkite ($Na_3MnPO_4CO_3$): A new intercalation cathode material for Na-ion batteries”, H. Chen, Q. Hao, O. Zivkovic, G. Hautier, L.-S. Du, Y. T, Y.-Y. Hu, X. Ma, C.P. Grey, and G. Ceder, *Chem. Mat*., **25**, 2777-2786 (2013).
- “Study of the transition metal ordering in layered $Na_xNi_{x/2}Mn_{1-x/2}O_2$ ($2/3 \le x \le 1$) and consequences of Na/Li Exchange”, J. Cabana, N.A. Chernova, J. Xiao, M. Roppolo, K.A. Aldi, M. Stanley Whittingham, and C. P. Grey, *Inorg. Chem.,* **52**, 8540-8550 (2013).
- “Paramagnetic electrodes and bulk magnetic susceptibility effects in the *in situ* NMR studies of batteries: Application to $Li_{1.08}Mn_{1.92}O_4$ spinels”, L. Zhou, M. Leskes, A.J. Ilott, N.M. Trease, and C.P. Grey, *J. Mag. Res*., **234**, 44-57 (2013).
- “Lithiation of silicon via lithium Zintl-defect complexes from first principles”, A.J. Morris, R.J. Needs, E. Salager, C.P. Grey, C.J. Pickard, *Phys. Rev. B,* **87**, 174108-1 – 174108-4, (2013).
- “Revealing the kinetics of key Li_xSi phase transformations in nano-structured Si based Li-ion batteries via *in situ* NMR”, K. Ogata, E. Salager, C. J. Kerr, A. J. Morris, A. Fraser, C. Ducati, S. Hofmann, C. P. Grey, Nature Communications, 5:3217 | DOI: 10.1038/ncomms4217 (2014).

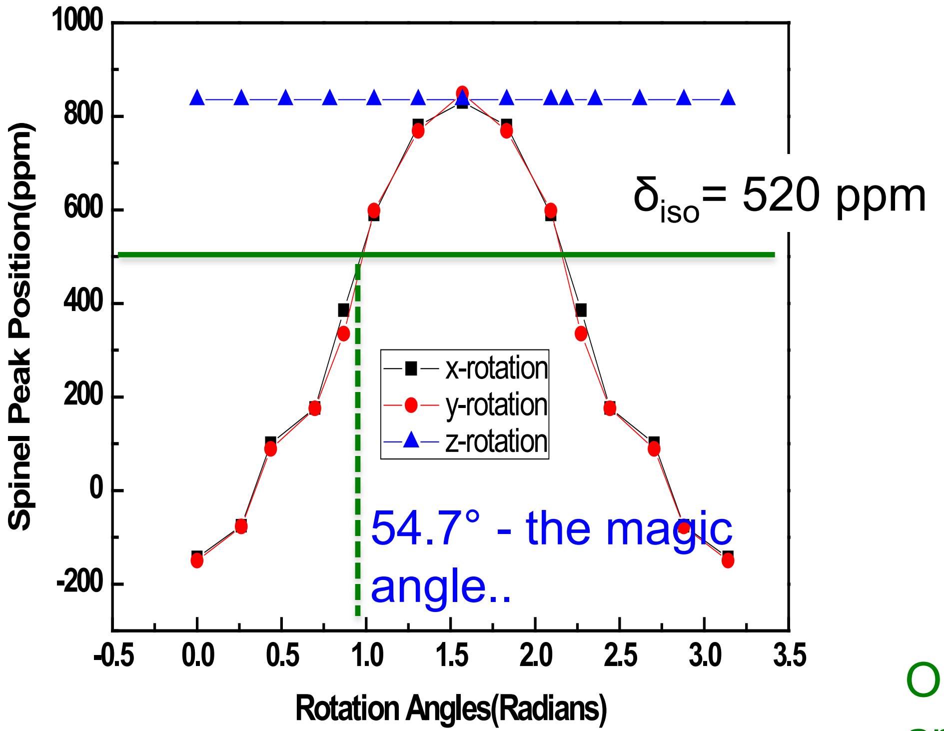
“Following Function in Real Time: New NMR and MRI Methods for Studying Structure and Dynamics in Batteries and Supercapacitors”
Talk (or related talk) given at the following meetings in 2013:
iNano Opening, Plenary Talk, Billund, January; Chemistry Department, ENS Lyon, January
RS, Theo Murphy International Scientific Meeting, 28 & 29 January; Chemistry Department, University of Wisconsin, February;
IBA2013, Research Award Address, Barcelona, March; ACS, New Orleans, March
54th ENC, Laukien Award Address, Asilomar, CA, April; ISMAR 2013, Rio de Janeiro, Brazil, May
University of Basel, Basel, May; SSI-19 Conference, Kyoto, June
RSC MC11, Warwick University, July; ICMRM, Cambridge, August
Electrochem2013, Southampton University, Southampton, September; RSC ISACS12, Cambridge, September
8th Alpine Meeting on Solid State NMR, Chamonix, September; LG Chemicals, Daejeon, Korea, October
Korea Basic Science Institute, Daegu, Korea, October; Department of Energy Science, Sungkyunkwan University, Korea, October
Samsung Advanced Institute of Technology (SAIT), Seoul, Korea, October
Institute of Energy & Climate Research, Forschungszentrum Juelich, Germany, November
MRS, December (2013).

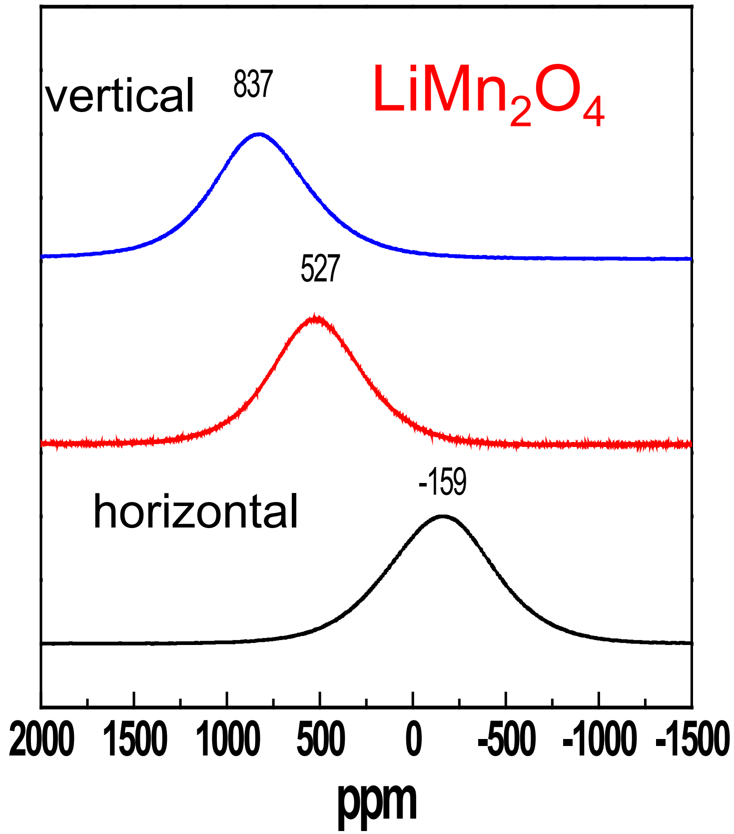
Challenges for In-situ NMR: Paramagnetic Cathode Materials



- Susceptibility effects and dipolar broadening are significant for paramagnetic samples

$Li_{1.1}Mn_{1.9}O_4$ electrode: rotation plot

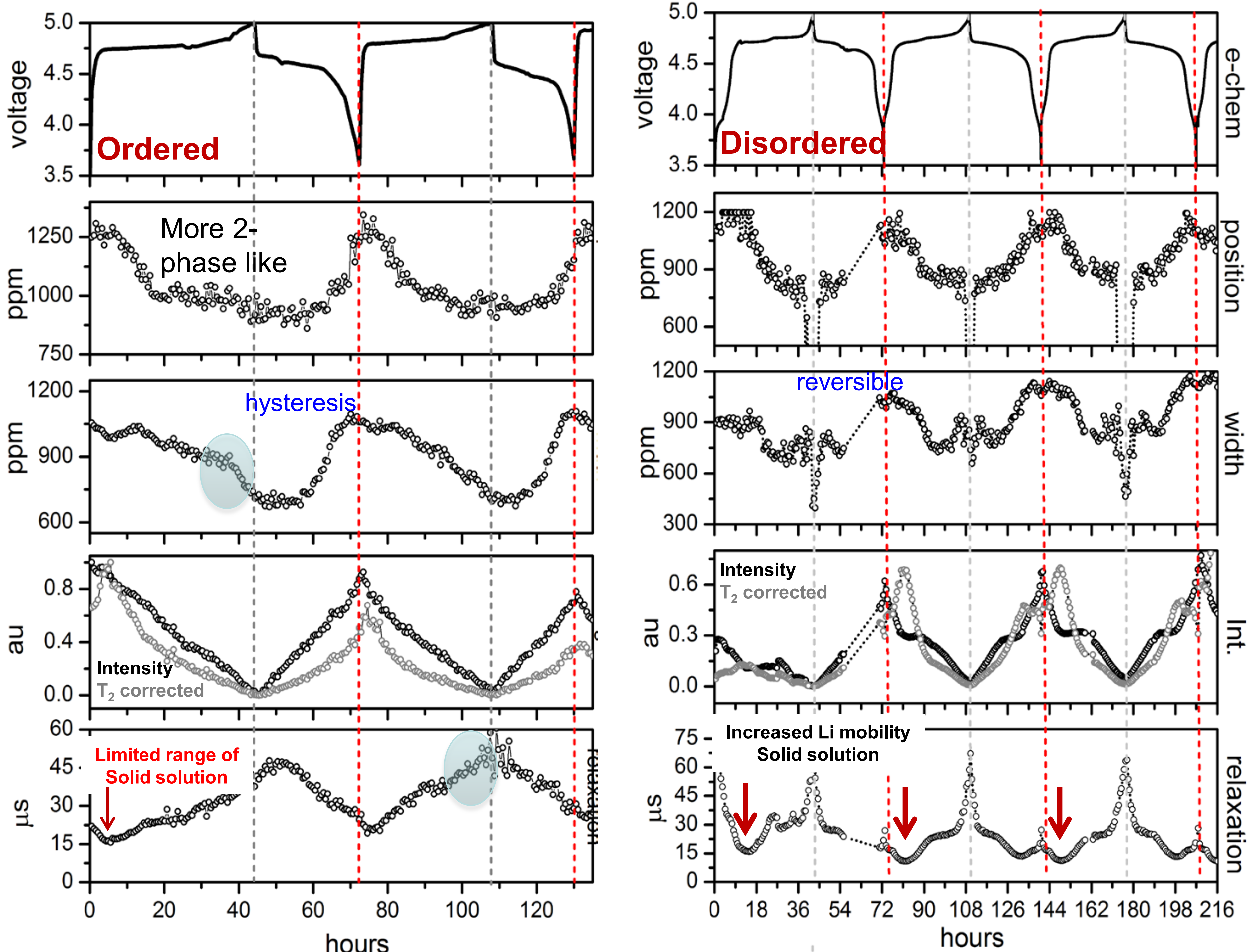




Orientation of battery film at the magic angle minimizes susceptibility effects

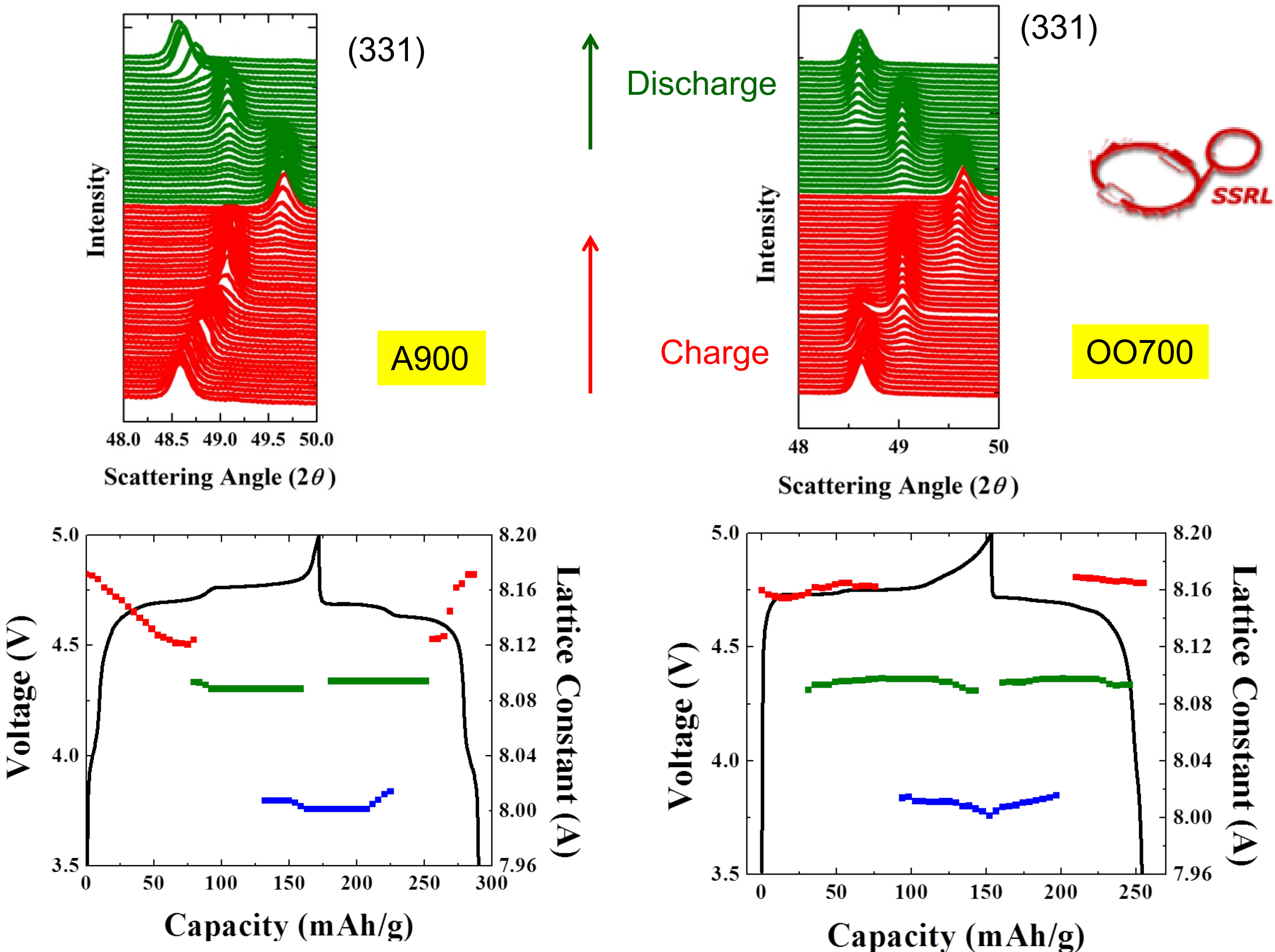
L. Zhou, et al. JMR 2013

In-situ ^7Li NMR – Ordered vs Disordered



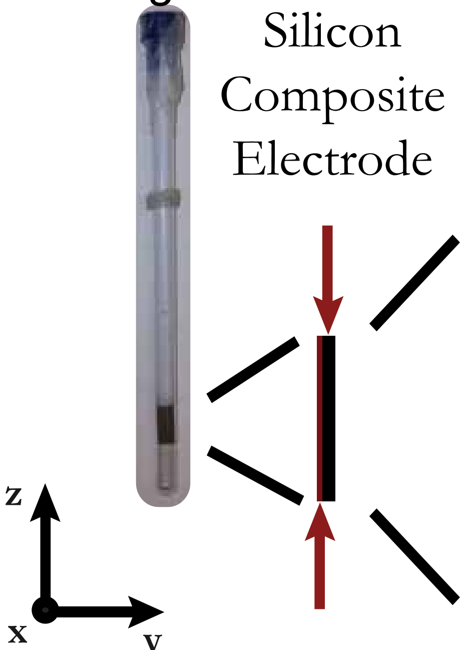
In-situ XRD: Ordered vs. Disordered

Chunjoong Kim, Jordi Cabana

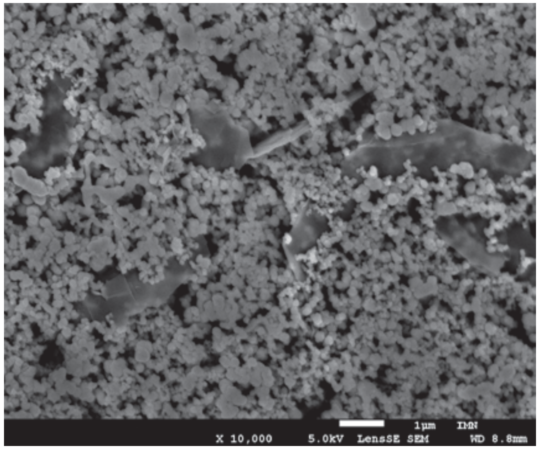


PFG NMR Experiments Si and $LiCoO_2$

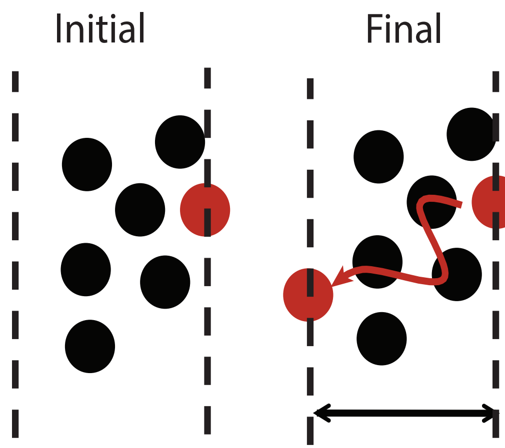
- Samples are saturated with electrolyte solvent (DMC) and diffusion is measured along the z-axis and length of sample



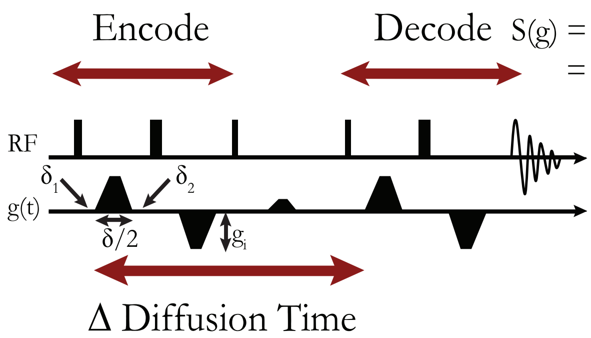
Surface of pristine electrode prior to saturation with DMC



Quantify tortuosity using $D_o = \tau D_{eff}$

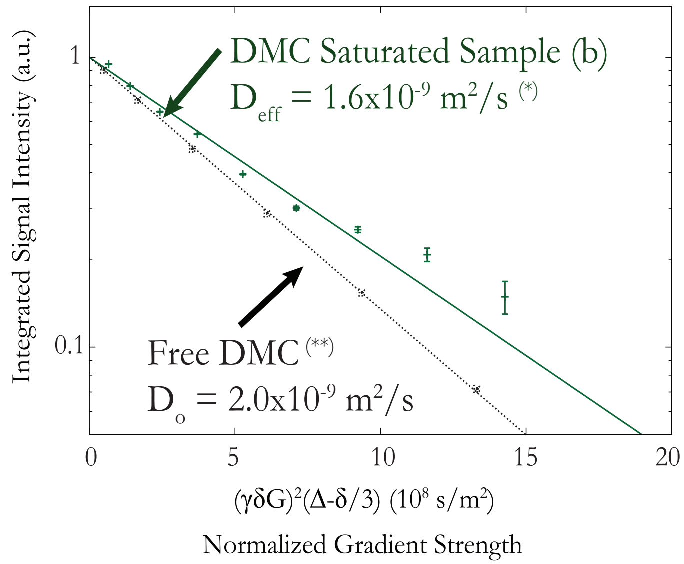


$$\langle (x'-x)^2 \rangle = 2Dt$$



$$S(g) = S(0)\exp[-D(\gamma\delta g_i)^2(\Delta-\delta/3)]$$
$$= S(0)\exp[-bD]$$

- Apparent tortuosity given by $\tau = D_o/D_{eff} = 1.3$ (room temperature)



- Unrestricted diffusion distance $(2D\Delta)^{1/2}$ >> average pore size in diffusion time $\Delta = 20$ ms