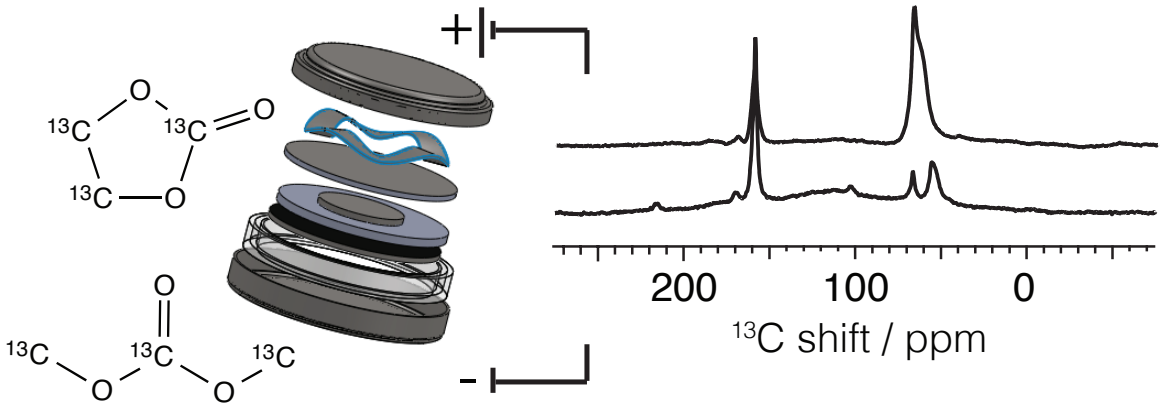
NMR and Pulse Field Gradient Studies of SEI and Electrode Structure

P.I. Name: Clare P. Grey

University of Cambridge

4/10/2015



Project ID
ES055

Overview

Timeline

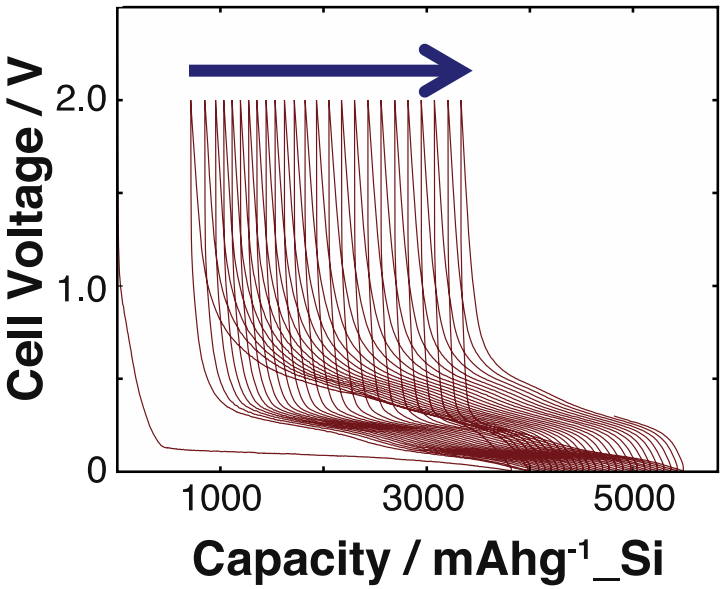
- Project start date: 1/1/13
- Project end date: 12/31/16
- Percent complete: 60%

Barriers

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

Budget

- Total project funding: $1.1M
- Funding received in FY14: $272,197
- Funding for FY15: $277,954



Partners

- Brett Lucht (Rhode Island)
- Jordi Cabana (UIC)
- Kristin Persson (LBNL)
- Guoying Chen (LBNL)
- Stan Whittingham (Binghamton)
- Ram Seshadri (UCSB)
- Anton Van der Ven (UCSB)
- Stephan Hoffman (U. Cam)
- Andrew Morris (U. Cam)
- Nigel Brandon (Imperial)
- Paul Shearing (UCL)
- Peter Bruce (Oxford)
- Elizabeth McCord, Bill Holstein (DuPont)

Relevance:

Overall objectives:

•Design a stable SEI

•Reduce overpotential (e.g., interfacial resistance, “structural hysteresis”)

•Optimise performance of high capacity anodes and cathodes

Specific Objectives - 2014/15

•Complete structural/mechanistic studies of Si (performance – very high energy density)

•Identify major solid electrolyte interphase (SEI) components on SI, and their spatial proximity, Li^+ transport through SEI, and how these changes with cycling (capacity fade)

•Contrast with graphite (capacity fade)

•Investigate local structural changes of high voltage/high capacity electrodes (e.g., Li-S) and electrode reaction mechanisms (e.g., spinels) on cycling (performance/capacity fade)

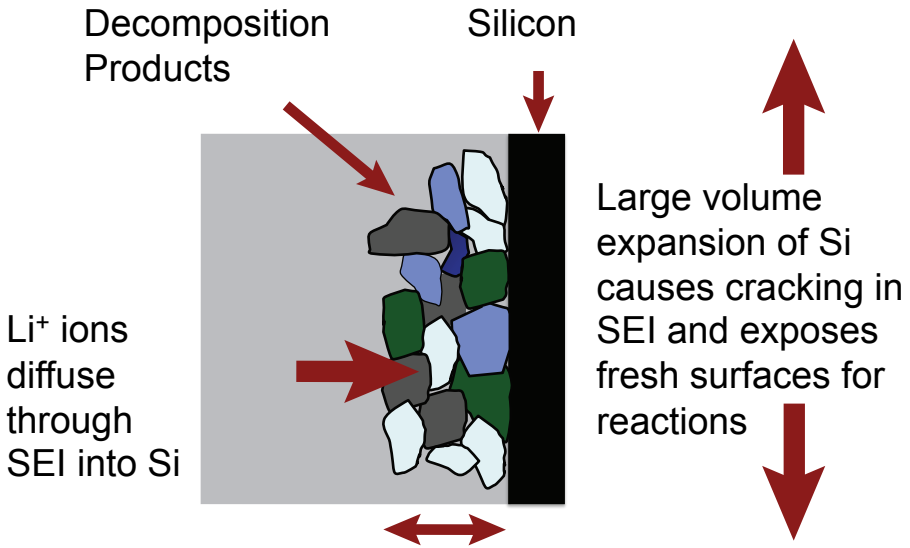
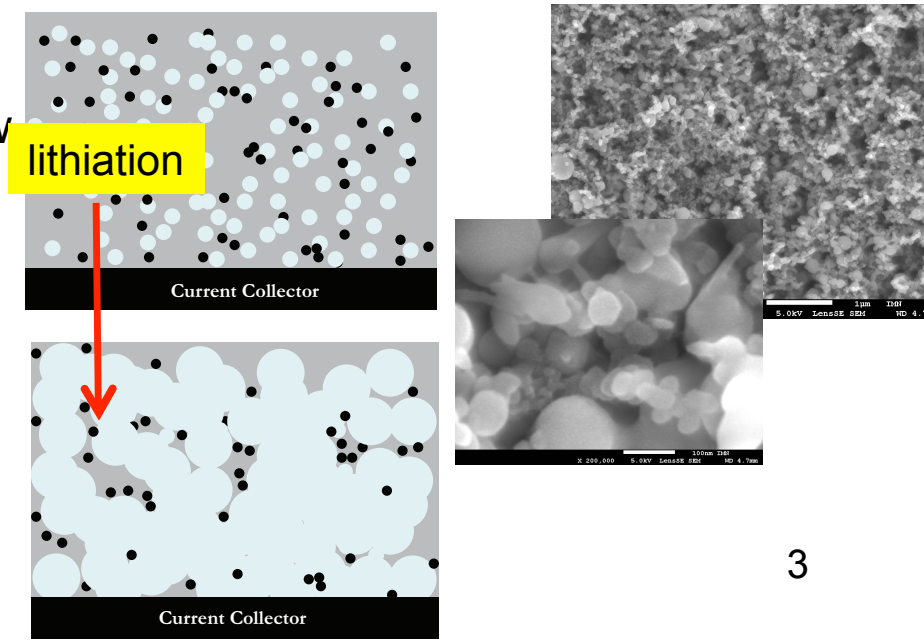


Figure based on E. Peled et al. *J. Electrochem. Soc.* 144, L208 (1997)



Milestones

FY 2014 Q1. Identify major components (LiF, phosphates, carbonates and organics) in Si SEI by NMR methods. (Dec-13). **Complete**

Q2. 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) **Complete**

Q3. 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) **. Studies on reduced VC and FEC model compounds complete.**

Q4. Establish proximity between different Si SEI components by NMR. **Complete**

Go/No-Go: Stop Li+ PFG diffusivity measurements of electrodes. Criteria: If experiments do not yield correlation with electrochemical performance. (Sep-14)**.**

FY 2015 Q1. Complete initial Si SEI work and submit for publication. **Paper in prep.** Complete 4V spinel work (*in situ* NMR) and submit for publication (12/31/14) **Complete; paper in prep.**

Q2. Identify differences in Si SEI after one and multiple cycles. (3/31/15) **^{1}H NMR complete**

Q3. Identify major organic components on the SEIs formed on high surface area carbons by NMR. (6/30/15) **On track**

Q4. Complete initial carbon-SEI interfacial studies (9/30/15) **On track**

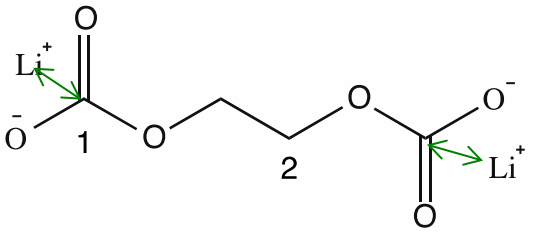
Go/No-Go: Determine whether NMR has the sensitivity to probe organics on the cathode side in paramagnetic systems (9/30/15) **On track**

Approach/Strategy

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

- **SEI studies**
  - NMR studies of local structure as a function of cycling
  - 2 dimensional and double-resonance NMR studies to establish proximity between species

e.g., ^{7}Li -> ^{13}C CP to detect C nearby Li



LEDC

- **Improving rate performance (electrode tortuosity studies)**
- **High voltage/capacity cathodes**

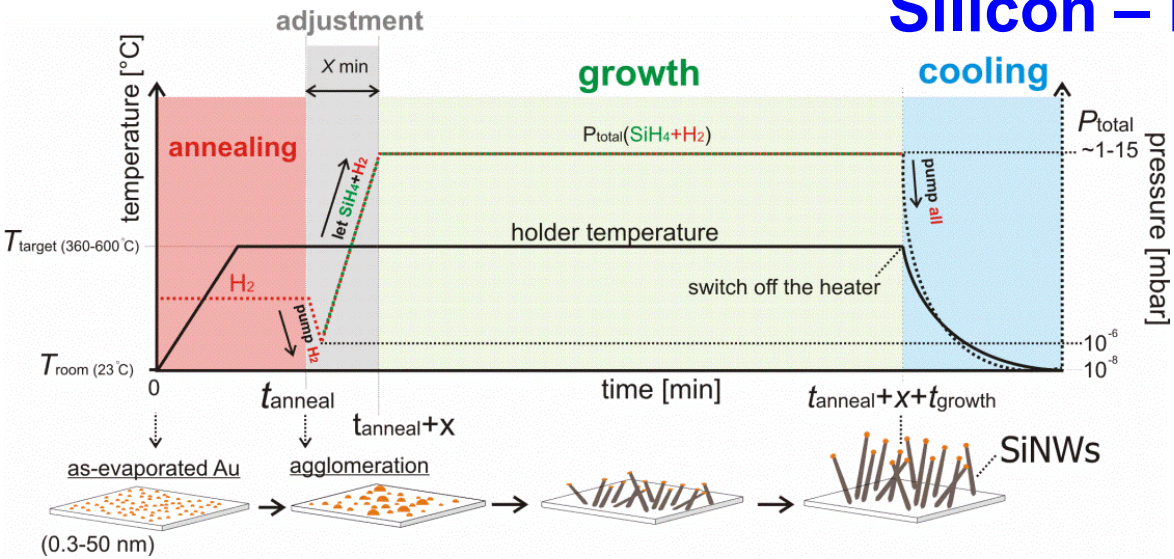
- Development of new platform for *in situ* studies.
- ^{6,7}Li NMR studies of structure
- NMR and electrochemical studies of Si coatings/surface treatments

- ^{13}C NMR studies of ^{13}C-enriched electrolytes to study SEI organic components; ^{7}Li, ^{19}F and ^{31}P studies of inorganics
- ^{13}C NMR studies of reduced VC and FEC additives with naphthalene (B. Lucht)
- Explore the use of DNP for signal enhancement (*new)*

- Develop pulse field gradient (PFG) approach to study electrode tortuosity (carbon model compound)
- Development of in situ methods to study phase transformations and Li dynamics
- In-situ and ex-situ NMR studies of Li^{+} transport and structural changes

Technical Accomplishments and Progress

Silicon – reaction mechanisms



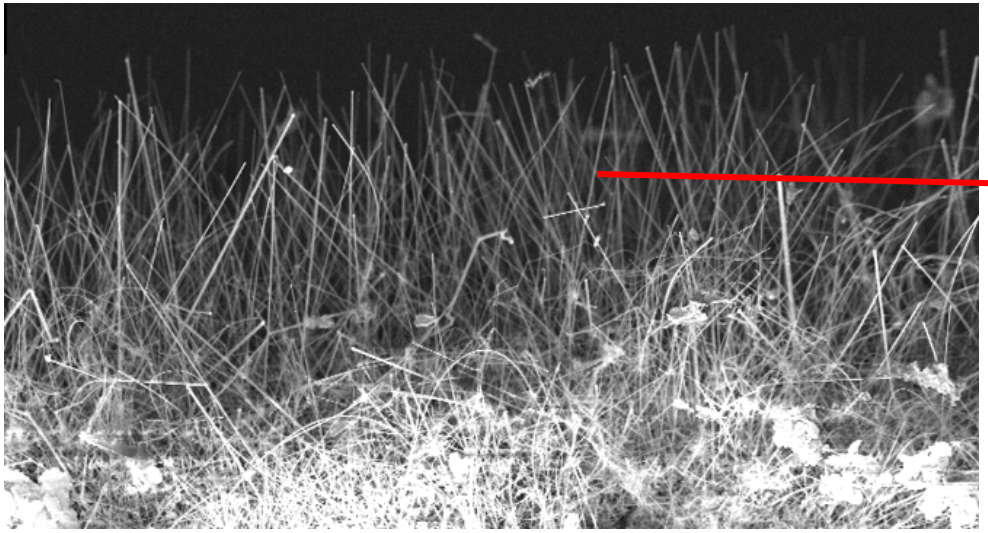
"Platform" for NMR studies

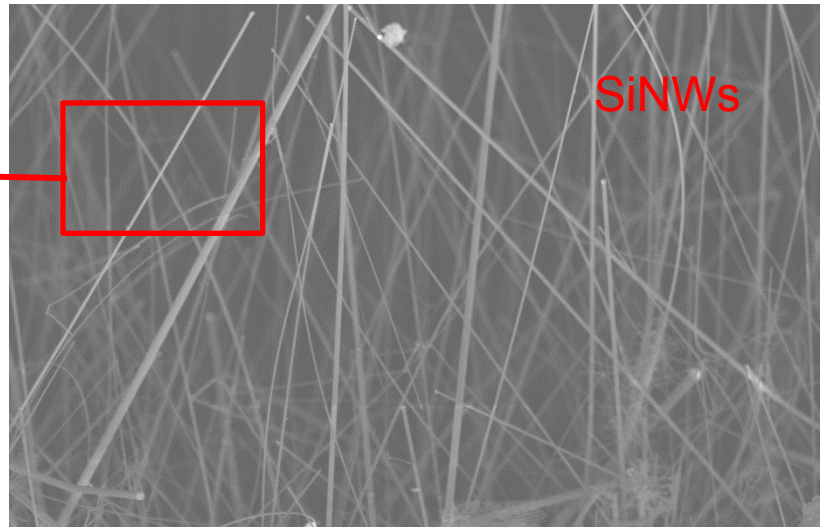
Inspired by:
C. K. Chan. … R. A. Huggins, Y. Cui, *Nature Nanotech.* 3, 31 (2008)

K. Ogata
C. Kerr
S. Hoffman

CF+50nm-Au+SiNWs

Cross sectional SEM images



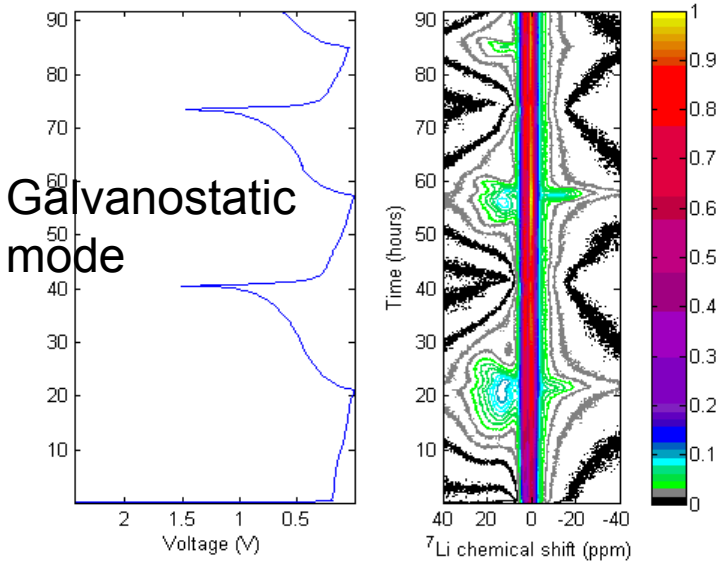


In-situ NMR of Si Nanowires:

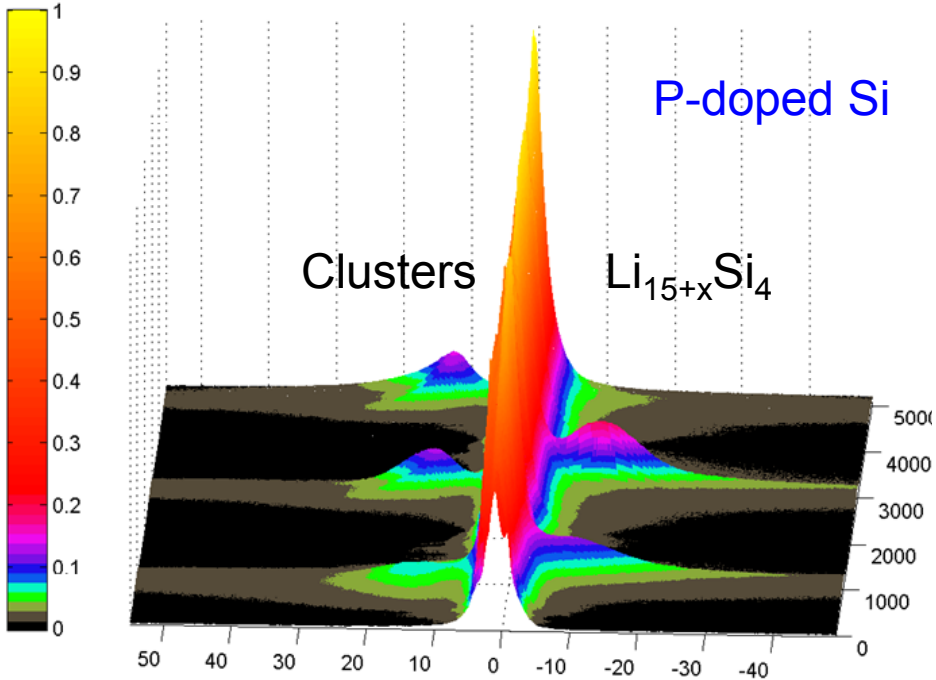
Ideal model systems for studying mechanisms – allow GITT and PITT experiments to be followed *in situ*

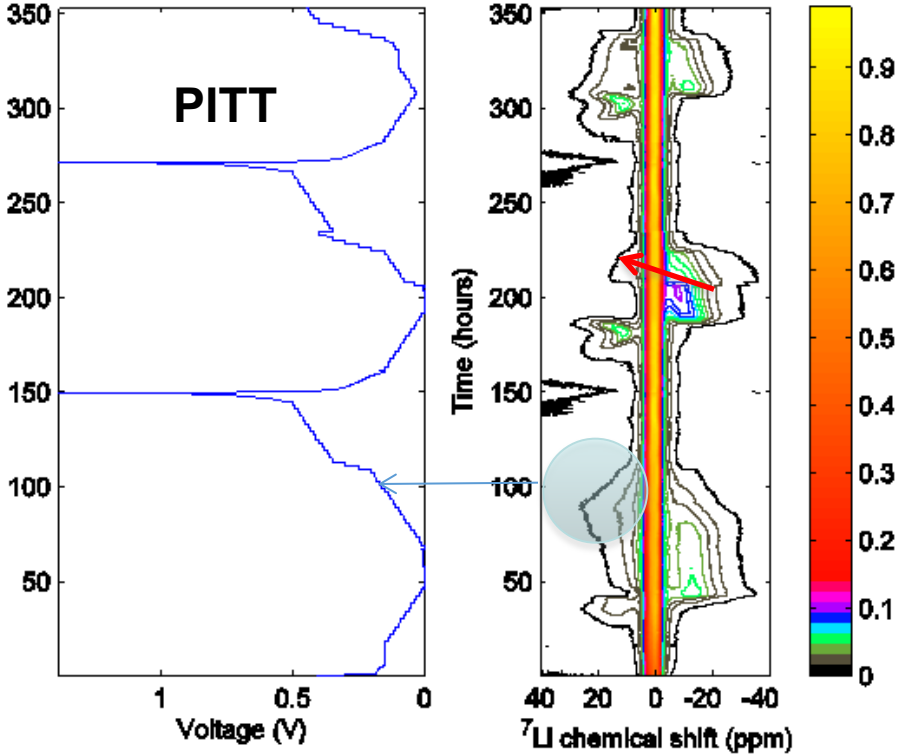
Ogata *et al.*, *Nat. Commun.* (2014)

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



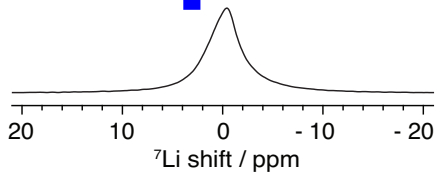
- Investigated effect of P-doping on reaction mechanisms



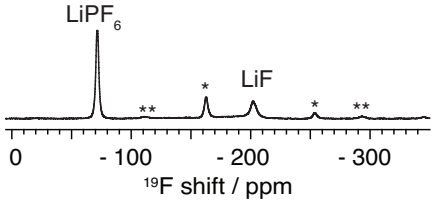


Composition of the SEI on Silicon

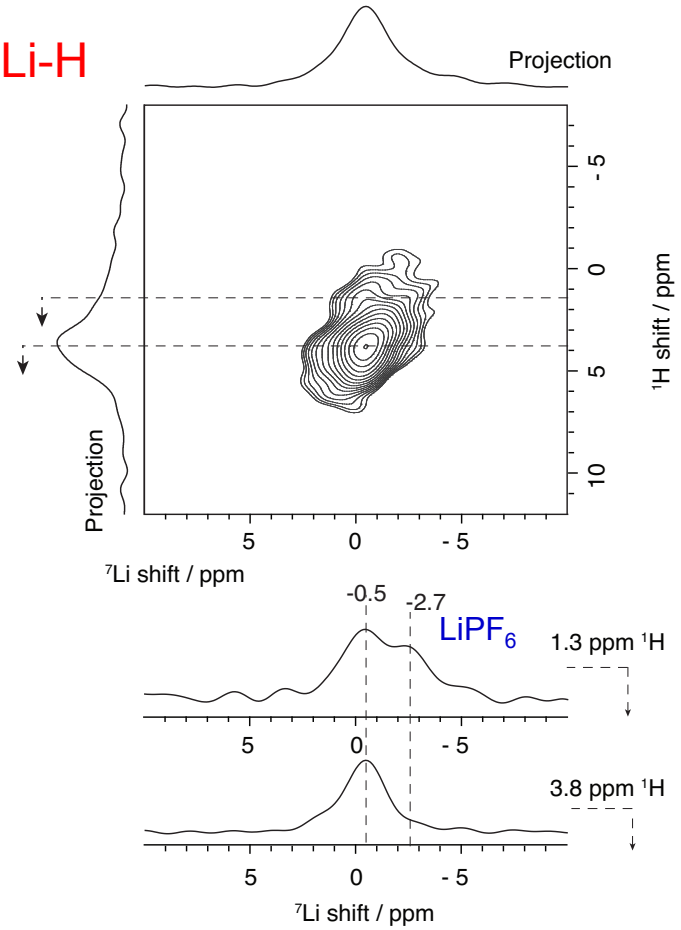
Li



F



Li-H



"Simple" 1-D and 2-D nmr studies to track SEI composition with voltage and cycle no.

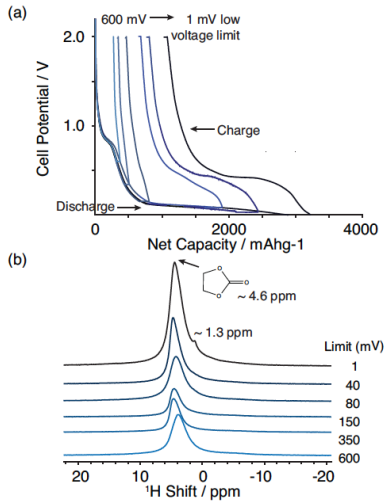
To wash or not to wash… washing removes residual $LiPF_6$ and EC, but need to be very careful to ensure no traces of water introduced during washing (results random LiF concentrations). Longer washing will remove large fragments of SEI

Initial experiments on non-washed samples

EC seen in ^{1}H NMR spectra but absent in Li-H correlation NMR experiments

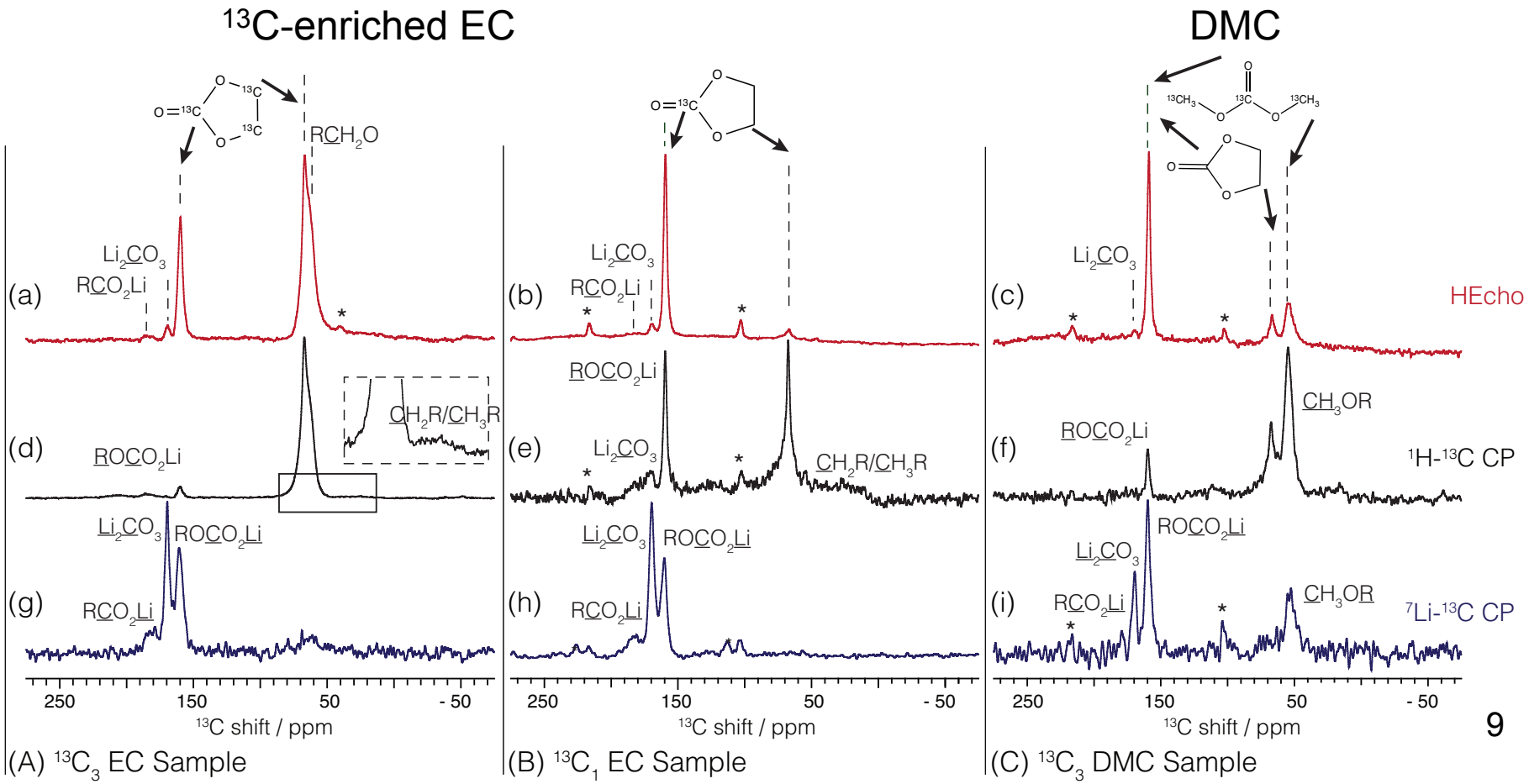
3.8 ppm ^{1}H signal assigned to RCH_2O-

Need ^{13}C NMR to provide more detailed assignments

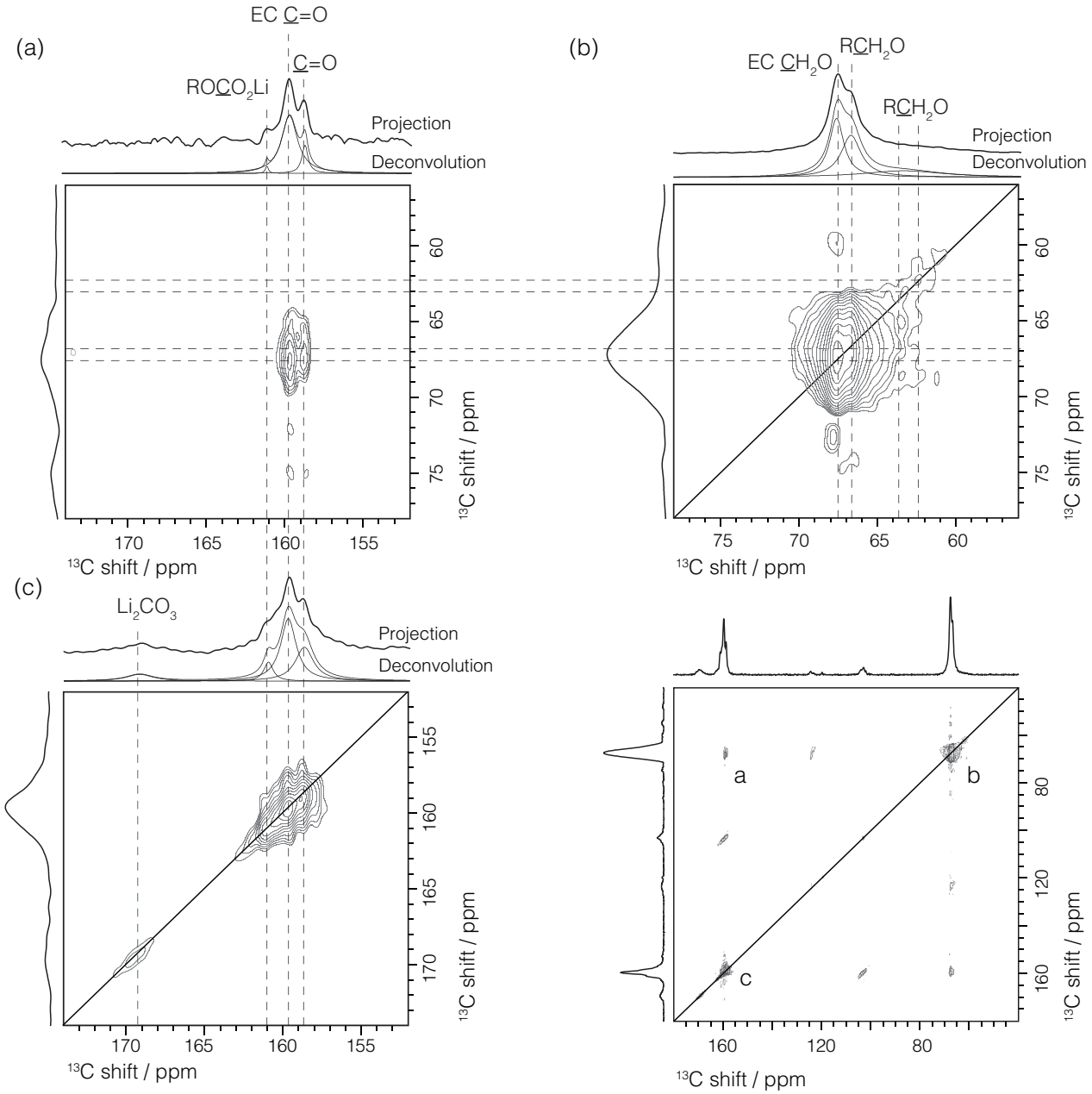


Composition of the SEI on Silicon

- Detailed ^{13}C measurements yield composition of organics in SEI
- High concentration of EC trapped in SEI
- Li-C CP detects lithiated carbonates, Li_2CO_3, formates
- A number of ether carbons from EC/DMC decomposition products are detected beneath the EC resonances



Composition of the SEI on Silicon



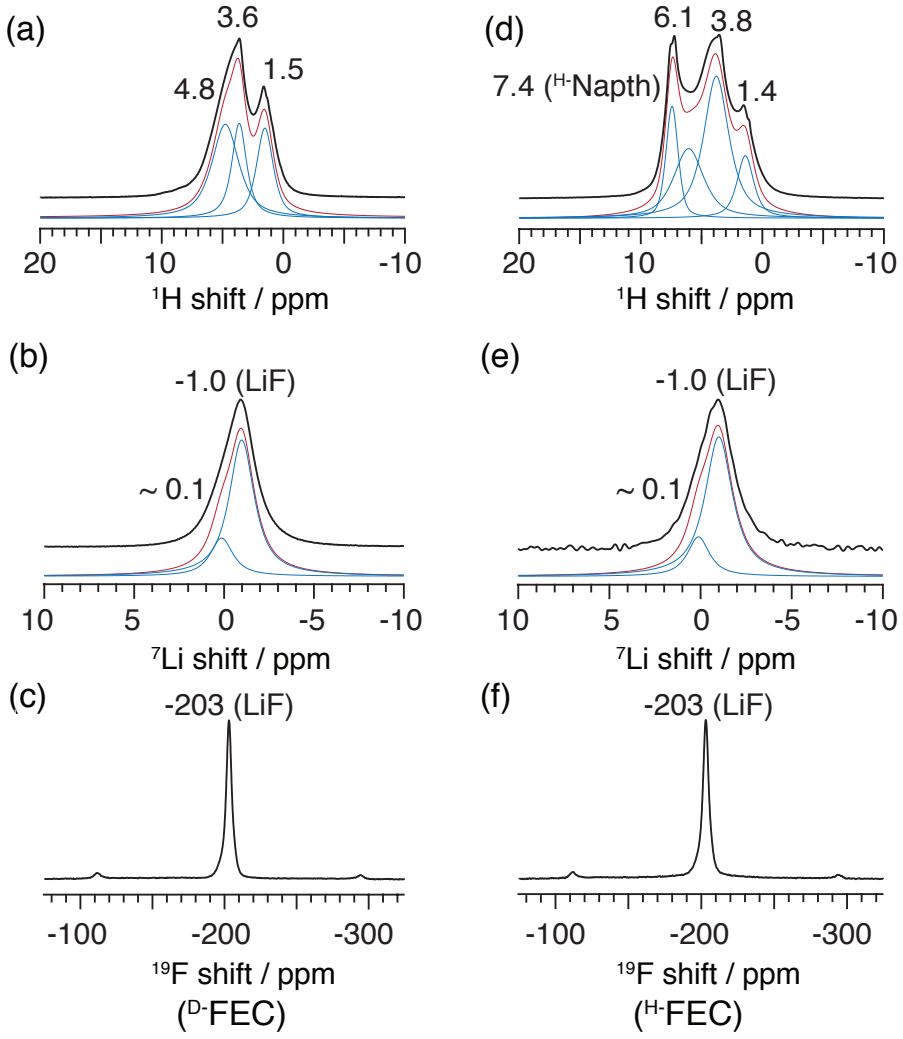
Assignments confirmed by DFT shift calculations and 2D/double resonance experiments

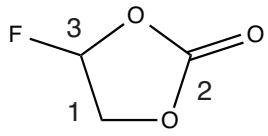
e.g., ^{13}C-^{13}C Correlation experiments on enriched EC/Si sample

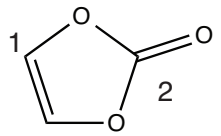
Manuscript in prep.

Role of Additives in SEI?

1st strategy (in collaboration with B. Lucht) – examine bulk samples of reduced FEC and VC to obtain "fingerprints" for potential SEI components





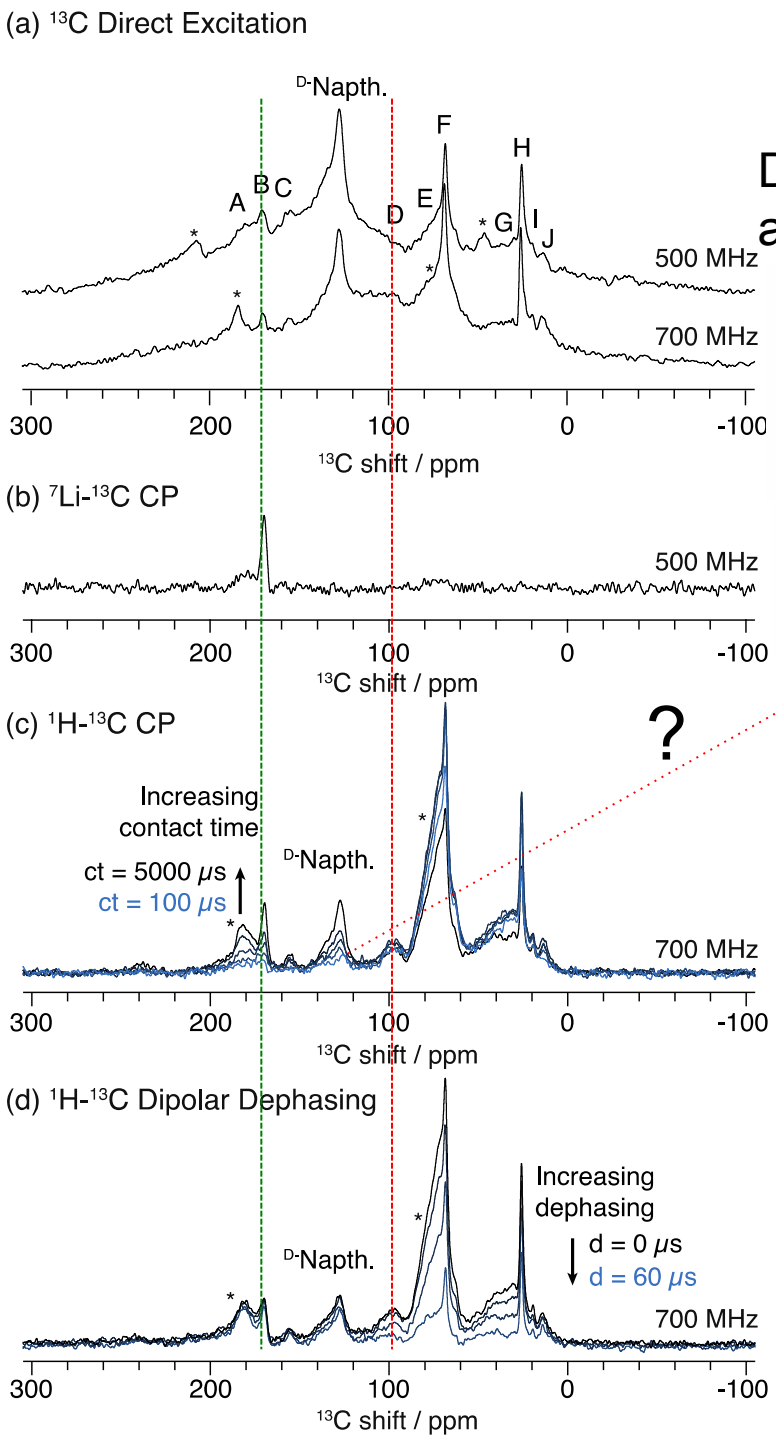


- Reducing agent (naphthalene) incorporated into solid composite of reduced FEC/VC (proved this by studying composites with deuterated naphthalene).
- F in reduced FEC only present as LiF – i.e., quantitative reduction
- ¹H NMR provides useful fingerprints e.g., formate seen for VC but not FEC

- Similar NMR acquired for VC

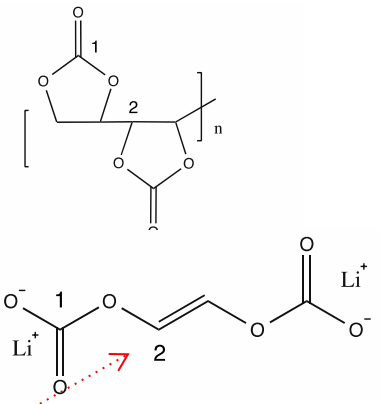
Manuscript in prep.

Additives in SEI?



?

D is not seen in EC/DMC studies on Si. Possible assignment:



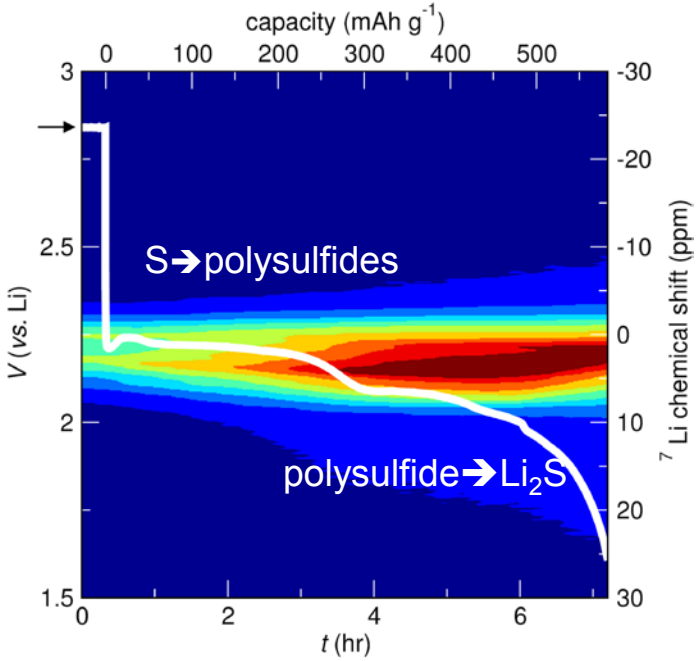
Ouatani, El, L.; Dedryvere, R.; Siret, C.; Biensan, P.; Reynaud, S.; Iratçabal, P.; Gonbeau, D. *J. Electrochem. Soc.* **2014**, *156*, A103.

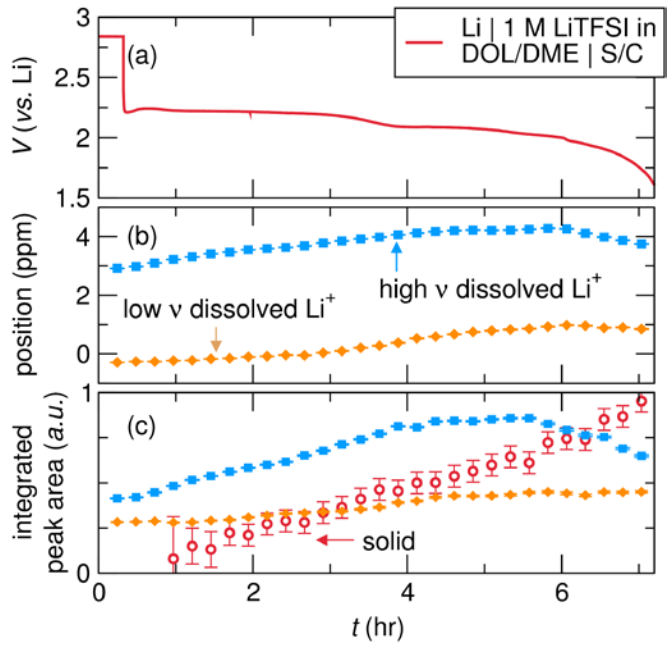
- v. little if any LVD $(=CH\text{-}OCO_2Li)_2$

Label in Spectra*	Chemical Shift / ppm	Proposed Assignment
A	181.7	HCOOLi
B	170.0	$R\bar{O}CO_2Li$ and Li_2CO_3
C	155.4	$-O\bar{C}O_2$ ("Polymer Radical")
D	99.7	-OCHCHO- ("Polymer Radical")
E	73.3	$\bar{C}H_2$-O
F	68.3	Residual THF
G	35.4	C-CH_2-C
H	25.4	Residual THF
I	19.4	$R\bar{C}H_3$
J	12.8	$R\bar{C}H_3$
D-Napth	134.5	Naphthalene
D-Napth	127.5	Naphthalene

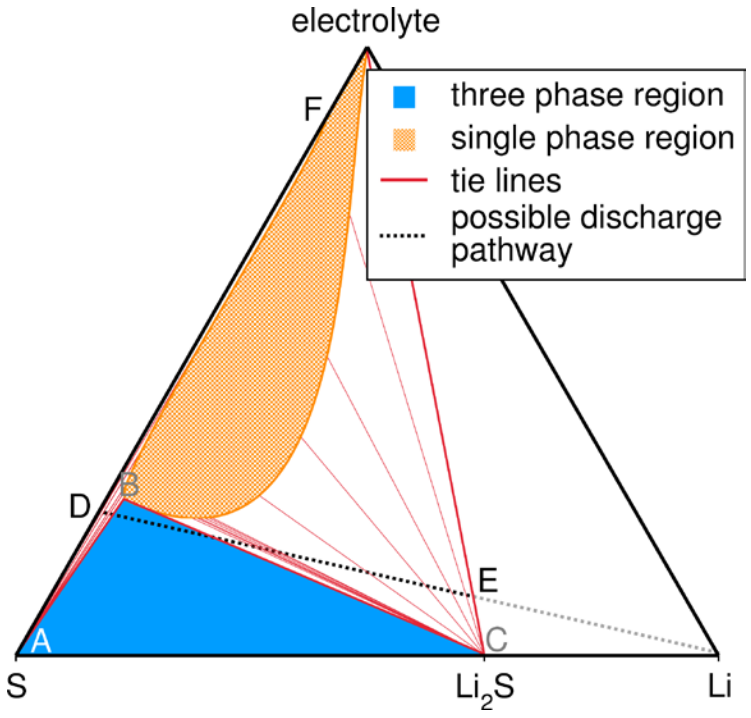
- Similar NMR acquired for FEC

Mechanisms of high capacity cathodes: Li-S





- In situ NMR used to separate solid and liquid components
- Li_2S observed even in 1st plateau
- Developed phase diagram for S, Li, electrolyte system
- Electrolyte concentration in cell will impact Li_2S – polysulfide equilibrium and reaction mechanism, and (some) inconsistencies between results in literature

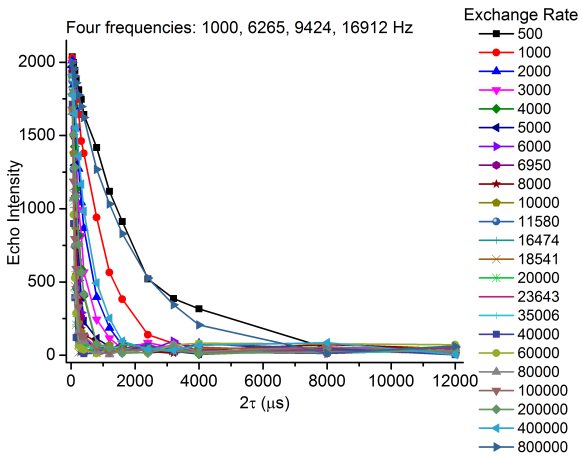


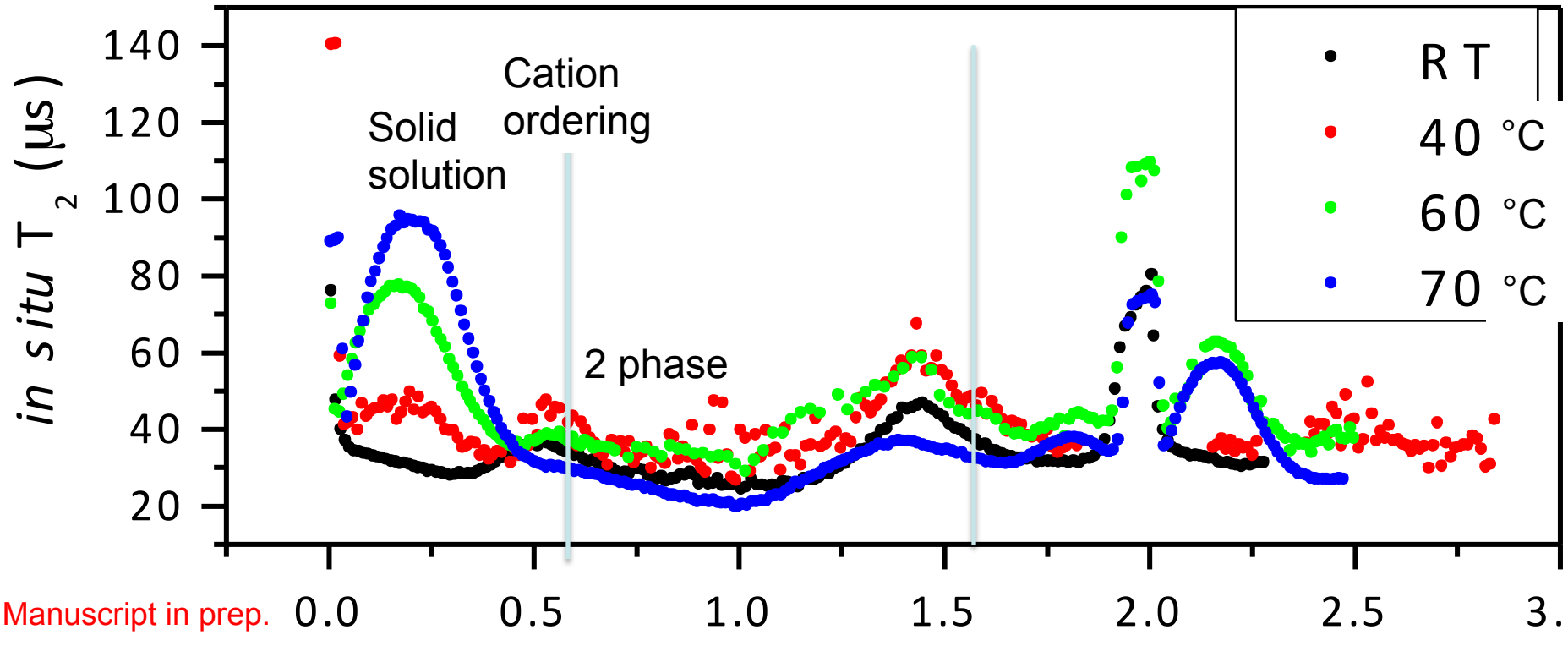
K. A. See et al. *J. Am. Chem. Soc.*, (2014)

In situ studies of spinels

- Development of a new NMR methodology to monitor Li dynamics on the fly.

- Spin-spin (T_2) lattice relaxation measures Li-Li dynamics
- Change in T_2 with Li concentration probes electrode transformation mechanism



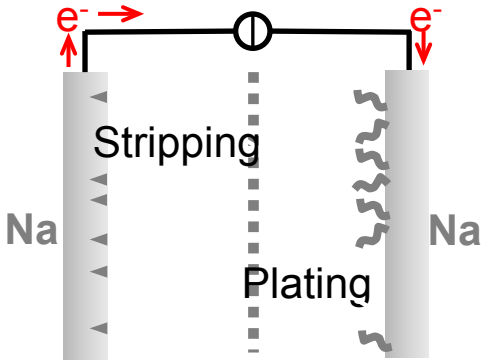


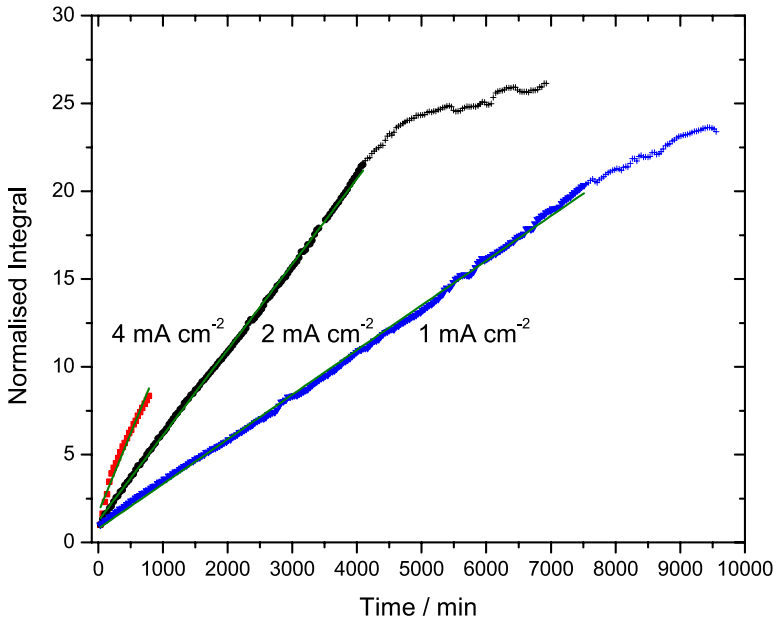
Manuscript in prep.

Na batteries

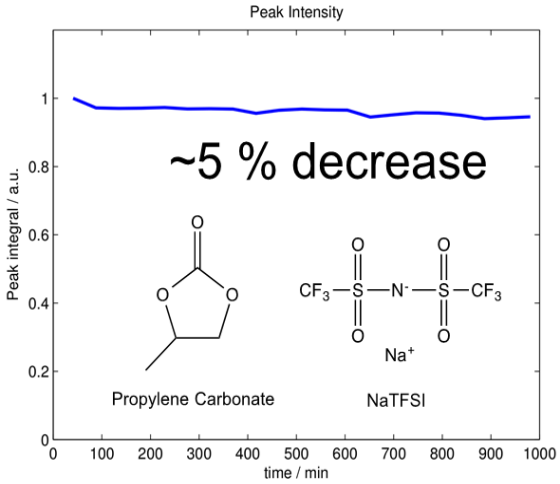
- Extended Li dendrite *in situ* NMR approach to Na batteries

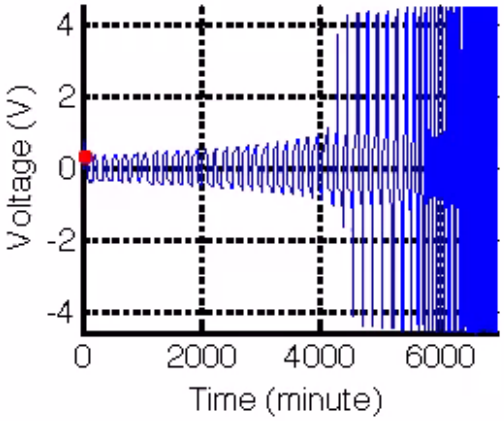
- Na dendrites formed even @ very low currents (problem much worse than for Li dendrites)
- Correlate dendrite formation with electrolyte decomposition
- Developed model to understand nucleation and growth





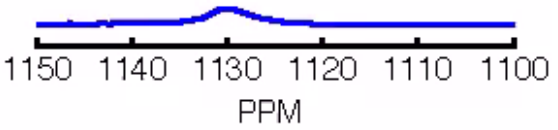
In situ quantification of Na^+ consumption from TFSI/PC





NMR studies of Na layered cathodes – use Na to examine cation ordering and dynamics

Manuscript in prep.



Responses to Previous Year Reviewers' Comments

- Reviewer 1 wondered whether we "could look at other state of the art materials other than the high voltage spinel that has been well studied in the literature by *in situ..* XRD."
- Work complete on HV spinel and is being written up for publication. Note NMR provides very different information concerning local structure and cation ordering – which is particularly relevant to the functioning of this system. (BATT work - "Composition-structure relationships in the Li-ion battery electrode material $LiNi_{0.5}Mn_{1.5}O_4$", J. Cabana, M. Casas-Cabanas, F.O. Omenya, N.A. Chernova, D. Zeng, M.S. Whittingham, C.P. Grey, *Chem. Mat.,* **24**, 2952-2964, (2012) – has been cited > 50 times). We stress – in situ NMR of paramagnetic materials is a novel diagnostic method & need to compare with complementary XRD studies. *In situ* work also focus on Li^+ dynamics not accessible by XRD. The high voltage spinel is also a good system for CEI studies. Note extension of *in situ* methods to Li-S, Na batteries (and Si) during FY 2014.

- Reviewer 2 commented that "it was important to keep in contact with the research community to be sure to be working on the most important problems in batteries" and it "would be good to add collaborators in the tortuosity field"
- Note strong emphasis on SEI in FY2014 and extensive set of collaborators. (N.b., reviewer 1 commented "the PI is known to have an extensive collaboration network that involves the best battery materials scientists"). Collaborations with N. Brandon/P. Shearing on tortuosity to link NMR tortuosity with tomography measurements. Paper in prep.

- Reviewer 3 asked whether the PI had "any interest in ANL materials" and on "coatings"
- PI has published numerous DOE (BATT) supported papers on ANL and related materials. Has recently completed detailed study of "AlF_3" coatings (PhD Thesis, K. Rosina).

Collaboration and Coordination with Other Institutions

- Brett Lucht* (Rhode Island) – SEI and additives; provided reduced FEC/VC (BMR)
- Elizabeth McCord, Bill Holstein (DuPont) – input on SEI and electrolytes

- Jordi Cabana* (UIC); Guoying Chen* (LBNL); Stan Whittingham* (Binghamton). -Spinels (synthesis, magnetism)
- Kristin Persson* (LBNL) – Materials Project and spinels
- Jordi Cabana* (UIC); Stan Whittingham* (Binghamton), Shirley Meng*, Peter Bruce - Na cathodes (samples, magnetism)

- Ram Seshadri (UCSB), Anton Van der Ven (UCSB) - Li-S (materials, theory)
- Stephan Hoffman (U. Cam), Andrew Morris (U. Cam) – Synthesis of Si nanowires, theory (Si)
- Nigel Brandon (Imperial), Paul Shearing (UCL) – X-ray tomography

*BMR collaborators

Remaining Challenges and Barriers

- SEI studies are time consuming because the small sample sizes (poor S/N in NMR) and moisture/air sensitivity issues (cannot keep samples for long period of times). The experiments are strongly dependent on access to sufficient NMR time with particular hardware – comprehensive study takes time!

- Cannot simply obtain ^{13}C enriched FEC/VC – need to rely on ^{1}H studies. Exploring use of DNP (and synthesis approaches)

- Rinsing of SEI changes structure – careful studies of rinsed and non-rinsed samples performed as a function of drying time

- Sensitivity of NMR studies to study thin cathode SEI (CEI) - DFT studies to help assign spectra. Development of new NMR experiments for use at higher fields (increase sensitivity)

- Tortuosity measurements by magnetic resonance – difficult on highly paramagnetic/metallic samples. Continue experiments on $LiCoO_2$, graphites and Si. Explore very low field measurements. Just installed 300 MHz micro-imaging system (coils delivered in March 2015) which will speed up studies.

Proposed Future Work

- Complete Si SEI studies (focusing on affect of voltage, multiple cycles, (FY 2014) binder (CMC) and temperature (FY 2015))
- Compare with graphite SEI – explore higher surface area carbons to improve S/N and role of SEI on e.g., super P (FY14/15).
- Continue Si-coating studies (FY 2015)
- Complete Si-doping studies (FY 2014)

- Push NMR method development and application to study the CEI (FY2014/15)

- Continue tortuosity PFG experiments with focus on graphite electrodes. (FY14). Build cell for *in-situ* tortuosity studies (FY 15)

- Complete Na dendrite studies;
- Push the use of ^{23}Na NMR to study Na-(Ni,Mn)O layered materials. Complete $NaMnO_2$ study

Summary

- Detailed ^{13}C NMR study of the Si SEI has been performed to identify major organic components.
- Lithium ethylene dicarbonate observed along with PEO-type oligomers
- 1D and 2D measurements supported by careful DFT-based assignments of ^{13}C NMR shifts.
- Inorganics in SEI studied by heteronuclear NMR

- Major species in reduced VC and FEC have been identified by ^{13}C NMR

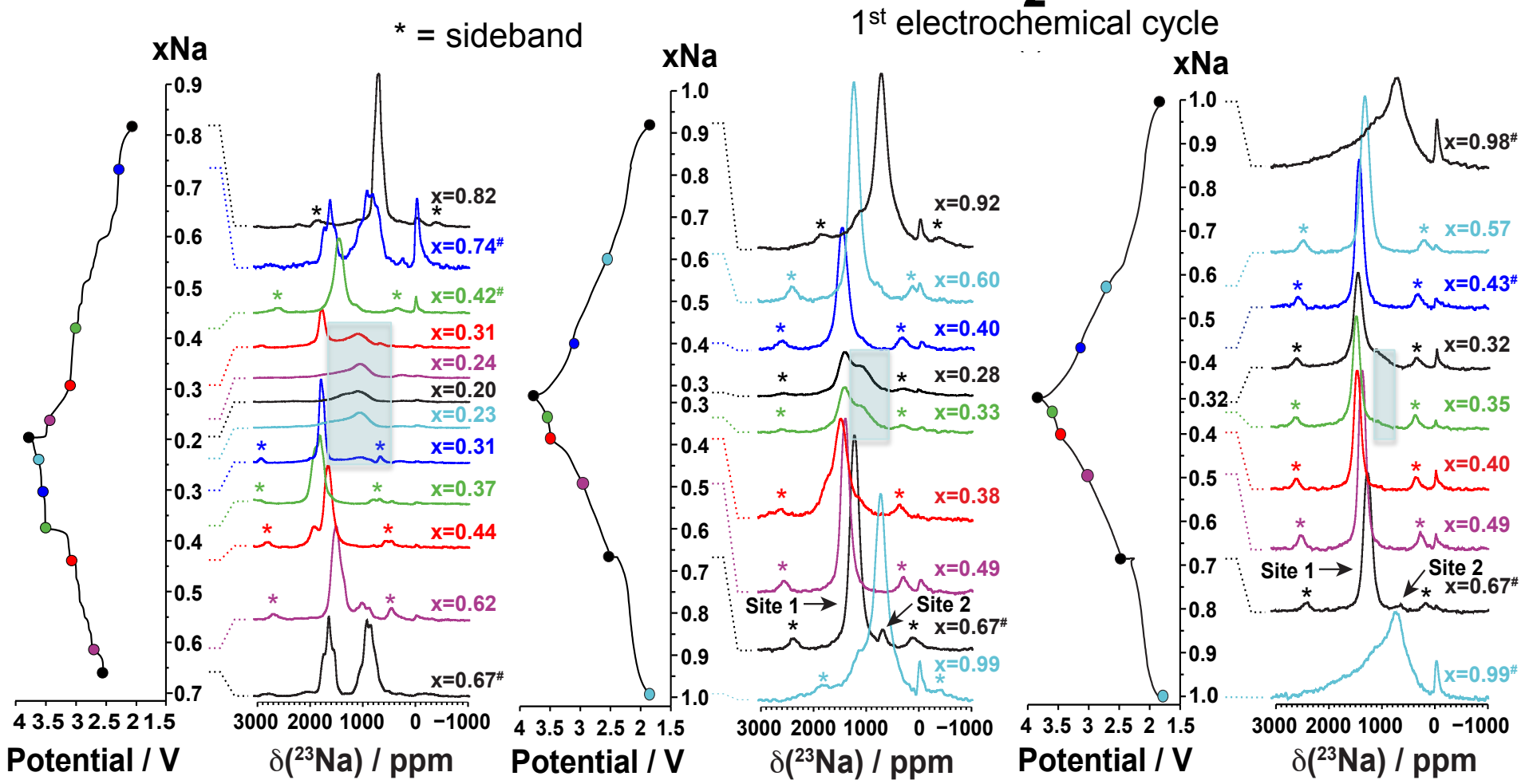
- In situ NMR methods have been extended to examine Li-S system and have helped develop a Li-S-electrolyte phase diagram.

- In situ NMR methods for paramagnetic materials can be used to study Li dynamics and electrode reaction methods

- Extended methodologies to study Na-dendrites and layered materials

Technical Back-Up Slides

Ex situ solid-state ^{23}Na MAS NMR at 200 MHz of Mg-substituted $NaMnO_2$



x = 0.0 **x = 0.05** **x = 0.1**

- More gradual structural changes + less extensive OP4 phase formation when Mg present.
- Na mobility increased noticeably!

With P Bruce (Oxford), T. Rojo (CIC)