NMR and Pulse Field Gradient Studies of SEI and Electrode Structure

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4/07/2016

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Overview

Timeline

- Project start date: 1/1/13
- Project end date: 12/31/16
- Percent complete: 80%

Budget

- Total project funding: $1.1M
- Funding received in FY14: $277,954
- Funding for FY15: $283,936

Barriers

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

Partners

- Brett Lucht (Rhode Island)
- Alexej Jerschow (NYU)
- Ram Seshadri (UCSB)
- Anton Van der Ven (UCSB)
- Stephan Hoffman (U. Cam)
- Andrew Morris (U. Cam)
- Dominic Wright (U. Cam)
- Erika Eiser (U. Cam)
- Cate Ducati (U. Cam)
- Paul Shearing (UCL)
- Peter Bruce (Oxford)
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 – March 2015-16
• 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)
• Extend to CEI
• Use recently developed in situ NMR/MRI metrologies to investigate Li (and Na dendrite formation), and the role that additives and different electrolytes play in controlling Li(Na) morphology.
• Develop new coatings for Si to reduce SEI formation
• Use NMR methodologies to study beyond Li cathodes (Na, Li-air)
Milestones

2014
Q2. Identify differences in Si SEI after one and multiple cycles. (3/31/15); paper submitted and under review
Q3. Identify major organic components on the SEIs formed on high surface area carbons by NMR. (6/30/15) Complete
Q4. Complete initial carbon-SEI interfacial studies (9/30/15) Complete
Go/No-Go: Determine whether NMR has the sensitivity to probe organics on the cathode side in paramagnetic systems (9/30/15) Stopped project temporarily

2015
Q1 Identify the major carbon-containing break down products that form on graphene platelets. Ongoing. Decision made to complete Si studies (Q3 milestone) first since student is graduating
Q2 Establish the difference between extrinsic and P-doped silicon nanowires Ongoing
Q3 Complete SEI study of silicon nanoparticles by NMR spectroscopy. Complete
Develop NMR methodology to examine cathode SEI Ongoing
Q4 Produce first optimized coating for Si electrode. 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

- 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)
  - Develop new coating strategies and chemistries (D. Wright, E. Eiser)

- MRI studies to correlate electrolyte concentration gradients with dendrite formation
Technical Accomplishments and Progress

1. Silicon SEI

First Studies Used Binder Free System – to remove $^{13}$C background and produce more SEI

Voltage Dependent Composition of the SEI:

Use DFT Methods to Provide Estimates for $^{13}$C/$^1$H/$^7$Li NMR Shifts of Predicted Products and Functional Groups:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Atom</th>
<th>ChemNMR</th>
<th>DFT</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEDC</td>
<td>C1</td>
<td>161</td>
<td>171.0</td>
<td>(solvent: AC-$d_6$/D$_2$O$^7$) 157/161.2</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>65.5</td>
<td>64.5</td>
<td>62.9/62.5</td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td>24.8</td>
<td>25.4</td>
<td>3.53/3.51</td>
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<tr>
<td></td>
<td>H2</td>
<td>4.42</td>
<td>4.1</td>
<td>3.65</td>
</tr>
<tr>
<td></td>
<td>H3</td>
<td>1.61</td>
<td>1.7</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>Li</td>
<td>-</td>
<td>1.0</td>
<td>na</td>
</tr>
<tr>
<td>LEC</td>
<td>C1</td>
<td>161</td>
<td>171.4</td>
<td>(solvent: D$_2$O$^8$) 163.7</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>63.5</td>
<td>62.8</td>
<td>60.1</td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td>13.8</td>
<td>11.9</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>4.21</td>
<td>4.1</td>
<td>3.65</td>
</tr>
<tr>
<td></td>
<td>H3</td>
<td>1.27</td>
<td>1.5</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>Li</td>
<td>-</td>
<td>1.0</td>
<td>na</td>
</tr>
<tr>
<td>LMC</td>
<td>C1</td>
<td>161</td>
<td>171.9</td>
<td>(solvent: AC-$d_6$/DMSO$^9$/D$_2$O$^8$) 160.97/157.02/163</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>54.1</td>
<td>51.5</td>
<td>62.40/51.51/54.6</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>3.68</td>
<td>3.8</td>
<td>3.56/3.27/3.35</td>
</tr>
<tr>
<td></td>
<td>Li</td>
<td>-</td>
<td>0.9</td>
<td>na</td>
</tr>
<tr>
<td>PEO</td>
<td>C2</td>
<td>61.3</td>
<td>62.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td>70.3</td>
<td>70.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H1</td>
<td>5.4</td>
<td>0.1</td>
<td></td>
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<tr>
<td></td>
<td>H2</td>
<td>3.7</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H3</td>
<td>3.54</td>
<td>3.7</td>
<td></td>
</tr>
</tbody>
</table>

$^1$H NMR: New species at 1.3 ppm (saturated CH groups) emerges at lower voltages
Composition of the SEI on Silicon after 1 cycle

- Detailed $^{13}$C measurements of selectively labeled molecules yield composition of organics
  - High concentration of EC trapped in SEI
- Li-$\rightarrow$ C CP detects lithiated carbonates (ROCO$_2^-$), Li$_2$CO$_3$, formates (H- and RCO$_2$Li)
- A number of ether carbons from EC/DMC decomposition products are detected beneath the EC resonances

$^{13}$C-enriched EC

DMC

\[
\begin{align*}
&\text{ethers} \\
&\text{(a) } ^{13}\text{C}_3 \text{ EC Sample} \\
&\text{(b) } ^{13}\text{C}_1 \text{ EC Sample} \\
&\text{(c) } ^{13}\text{C}_3 \text{ DMC Sample}
\end{align*}
\]
Quantification of the signals/species

<table>
<thead>
<tr>
<th>Proposed Decomposition Products</th>
<th>Total $^{13}$C Signal (%)</th>
<th>Molecular Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) $^{13}$C$_3$ EC Sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEO $-O$CH$_2$CH$_2$O$-$</td>
<td>51</td>
<td>25</td>
</tr>
<tr>
<td>LEDC ($CH_2OC_2Li$)$_2$</td>
<td>28</td>
<td>7</td>
</tr>
<tr>
<td>LEC $CH_3CH_2OCO_2Li$</td>
<td>18</td>
<td>6</td>
</tr>
<tr>
<td>and LBDC ($CH_2CHOCO_2Li$)$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RCO$_2$Li</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(b) $^{13}$C$_3$ DMC Sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LMC $CH_3OCO_2Li$</td>
<td>58</td>
<td>29</td>
</tr>
<tr>
<td>Non-labelled EC and products</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>RCO$_2$Li</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>
Proposed Decomposition Mechanisms of EC & DMC

PEO

\[
\begin{align*}
2 \text{O} & \xrightarrow{\text{n e}^-} \left(1 \text{O} \right)_n + n \text{CO}_2 \\
2 \text{O} & \xrightarrow{\text{e}^- + \text{Li}^+} \text{O}^{\text{Li}^+} \xrightarrow{\text{and/or}} \text{Li}^{+} + \text{CH}_2=\text{CH}_2 \\
2 \text{O} & \xrightarrow{2 \text{e}^- + 2 \text{Li}^+} \text{Li}_2\text{CO}_3 + \text{CH}_2=\text{CH}_2 \\
2 \text{O} & \xrightarrow{\text{e}^- + \text{Li}^+} \left(1 \text{O} \right)^{\text{Li}^+} + \text{CH}_3.
\end{align*}
\]

Our results showed experimental evidence of decomposition products, consistent with theoretically predicted reduction mechanisms.

LEDC is widely believed to be an important EC decomposition product. We also observe evidence for LBDC and LEC (\text{CH}_2\text{R}/\text{CH}_3\text{R} \sim 30/25 \text{ ppm, C3}).

Note that:
- some \text{CH}_2(/\text{CH}_3)\text{CH}_2-\text{O} comes from DMC reactions not described above
- $^1\text{H}$ NMR suggest that these species are formed during the low V plateau

PEO species dominate EC decomposition products.

Chem Mater 2016
“Extended” cycling with CMC

Steady growth in SEI
No distinct difference seen by NMR

No $\text{SiO}_y\text{F}_x$

Minor organics on 1st cycle
Significant LiF on 1st cycle
Identification of longer chain organics

2D correlations between bonded carbon atoms
(CMC, 15 cycle sample)

Double-Quantum $^{13}$C shift / ppm

1D $^1$H-$^{13}$C CP

Ether and saturated carbons

Correlations with like (ether) carbons

PEO Oligomers

LEDLC
## Identification of longer chain organics

Assignments for the $^{13}$C spectra of the 15 cycle sample

<table>
<thead>
<tr>
<th>Resonance</th>
<th>$^{13}$C Shift/ppm</th>
<th>Fragment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A:</td>
<td>179</td>
<td>$RCO_2Li$, HCO$_2$Li/CH$_3$CH$_2$CO$_2$Li Li$_2$CO$_3$</td>
</tr>
<tr>
<td>B:</td>
<td>170</td>
<td>ROCO$_2$Li, residual EC/DMC C=O</td>
</tr>
<tr>
<td>C:</td>
<td>160</td>
<td>ROCO$_2$Li, residual EC CH$_2$, PEO –OCH$_2$CH$_2$O– CH$_3$OLi</td>
</tr>
<tr>
<td>D:</td>
<td>67</td>
<td>residual DMC CH$_3$</td>
</tr>
<tr>
<td>E:</td>
<td>53</td>
<td>RCH$_2$R'</td>
</tr>
<tr>
<td>F$_x$:</td>
<td>30</td>
<td>CH$_3$CH$_2$R</td>
</tr>
<tr>
<td>F$_y$:</td>
<td>23</td>
<td>CH$_3$R</td>
</tr>
<tr>
<td>F$_z$:</td>
<td>14</td>
<td>CH$_3$R</td>
</tr>
<tr>
<td>G$_x$:</td>
<td>30</td>
<td>RCH$_2$R'</td>
</tr>
<tr>
<td>G$_y$:</td>
<td>23</td>
<td>CH$_3$CH$_2$R</td>
</tr>
<tr>
<td>G$_z$:</td>
<td>14</td>
<td>CH$_3$R</td>
</tr>
</tbody>
</table>

**Pristine**

**30 cycles**

**60 cycles**
Cycling with CMC

Li⁺ ion diffusion in the increasingly dense electrode structure: expansion on lithiation reduces transport through top of electrode.

Capacity loss and evolving kinetics: high voltage process lost due to increased tortuosity through electrode.

- Cycle 2-30: Uniform lithiation
- Cycles 30-60: Surface particle lithiation

- a-Si 2 V
- a-LiₓSi 250 mV
- a-Liₓ₋ₓ⁺Si 100 mV
Correlating Dendrite Formation with Concentration Gradients: MRI Studies

High current (0.76 mA cm\(^{-2}\))

(a) Pristine  
(b) \(t = 10.5\) hours  
(c) \(t = 18.6\) hours  
(d) \(t = 32.7\) hours

Low current (0.16 mA cm\(^{-2}\))

(a) Pristine  
(b) \(t = 23.1\) hours  
(c) \(t = 52.8\) hours  
(d) \(t = 73.1\) hours

With A. Jerschow, NYU

Correlating Dendrite Formation with Concentration Gradients: MRI Studies

Sands time, $\tau_s$

Time the anion concentration at the anode drops to zero (@ high current densities)
Electroneutrality breaks down and dendrites grow from anode

$$\tau_s = \pi D \left( \frac{C_0 e}{2Jt_a} \right)^2$$

$C_0$ = initial electrolyte concentration
$t_a$ = transport no. of anion
$J$ = Current density
$D$ = ambipolar diffusion time


NMR Sands Time?

Two mechanisms for microstructure growth clearly seen

- High currents – Sands time mechanism holds
- Low currents – Transition to dendritic structure still occurs- local Li depletion @ SEI/Li interface?

Role of additives and electrolyte?

D. Aurbach et al. SSI (2012)
Li air chemistries in the presence of H$_2$O and LiI additives cycle via the formation of LiOH – not Li$_2$O$_2$. 

A: XRD

B: ssNMR

C: Images of pristine, discharged, and charged samples.
The reviewer’s comments were generally extremely positive, Reviewer 3 noting that “Clare Grey’s nuclear magnetic resonance (NMR) work and method development seemed truly groundbreaking” and Reviewer 2 saying that “those developing new methods seem to be rushed to apply them to lots of materials right away, presumably to show relevance and highlight the importance of the work. The reviewer fears the project teams are rushing into the application field too quickly, before the teams have really done a thorough job of validating the method. The reviewer was happy to see that Clare Grey’s group took a time-out to look at their methods in such detail.”

In response to Qu 1, reviewer 2 stated “The only aspect the reviewer would question is the breadth of studies conducted under this effort, which the reviewer noted is attacking a lot of very difficult problems.”

In response to this we stress that the major focus of this project is and continues to be the SEI. However, we continue push the use of our in-situ metrology to examine different, relevant battery chemistry, to expand the applicability of the method, to learn increasingly new and varied information from a wider class of battery systems and materials.

Reviewer 3 stated “Li-ion conductivity in SEI should be investigated using NMR, and noted that no study on electrode tortuosity was reported.” We agree, and these studies are in progress. To this end we have performed FIB SEM studies of electrode morphology, and PFG/MRI/tomography experiments are in progress. The conductivity studies (by NMR) are more challenging and we will seek to develop approaches to this within the coming year (i.e., before the termination of the current funding cycle).

Reviewer 1 “described the future planned work as very ambitious”, while Reviewer stated that “The Si SEI work is excellent and highly relevant, .. referring to earlier comments on whether the Si SEI is truly passivating. Another valuable focus, in this reviewer’s opinion, would be trying to understand the effect of additives, such as FEC, on the SEI makeup. The reviewer was unsure about the purpose of the Na dendrite study, because Na offers no obvious benefit for transportation applications, in the reviewer’s view.”

The FEC/VC work is on going the challenge for NMR being the difficulty in enriching these materials in $^{13}$C. We have worked with Prof. B Lucht to prepare and characterize bulk reduced FEC and EC and a paper describing this work is about to be submitted. We are developing approaches to examine FEC/VC systems and we hope to report on this later on in the year.

With respect to the Na work, we stress that this was part of the in situ metrology development and the study led to insight into the nucleation and growth of dendrites that has value for the LIB chemistry as well.
Collaboration and Coordination with Other Institutions

- Brett Lucht* (Rhode Island) – SEI and additives; provided reduced FEC/VC samples (BMR)
- Elizabeth McCord, Bill Holstein (DuPont) – input on SEI and electrolytes
- Jordi Cabana* (UIC); Stan Whittingham* (Binghamton), Shirley Meng*, Peter Bruce - Na cathodes (samples, magnetism)
- Stephan Hoffman, Cate Ducati, Andrew Morris (U. Cam) – Synthesis of Si nanowires, TEM, theory (Si)
- Dominic Wright, E. Eiser (U. Cam), new electrode coatings
- 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). – comprehensive study takes time!
- Cannot simply obtain \(^{13}\)C enriched FEC/VC – need to rely on \(^{1}\)H and \(^{19}\)F studies.
- 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, limited resolution of MRI experiments means thick samples need to be prepared. Continue on graphites and Si. Explore very low field measurements. Have now built 18 relevant e-chem cells
Proposed Future Work

- Complete graphite/graphene SEI study
- Continue Si-coating studies; investigate SEI in presence of coatings
- Continue tortuosity PFG and MRI experiments with focus on graphite and Si electrodes.
- Investigate effect of additives and different electrolytes on Li dendrite growth
- Complete (Ni,Mn)O Na-layered materials study
- Investigate catalytic OER reactions in the Li-air system
Silicon SEI:
• Selective labeling and a series of 1 and 2D NMR experiments have been used to identify a series of products in the SEI.
• Correlations identify species in close proximity (e.g., Li---X and C – C connectivity).
• PEO-type oligomers are in high abundance – some are removed on washing indicating that they are in the fragile/organic more porous part of the SEI
• LiF, Li$_2$CO$_3$, RCO$_2$Li are seen in addition to the semicarbonates LMC, LEDC, LBDC and LEC
• SEI growth is voltage dependent – and a new local environment (with saturated groups as expected in LBDC and LEC) is observed @ very low voltages
• Some evidence that some saturated CH$_3$ groups are formed from DMC in addition to EC.
• Same species seen with CMC binder – but organic SEI formation much slower – LiF formed on 1$^{st}$ cycle; very little growth thereafter

Li Dendrites:
• Two mechanisms for microstructure growth clearly seen
• High currents – Sands time mechanism holds – dendrites grow when electrolyte depletion near current collector observed
• Low currents – Clear transition from mossy Li to dendritic growth is still observed. Thick SEI causes electrolyte depletion near Li metal?

Li Air:
• LiOH formed in the presence of LiI additives, the protons coming from added H$_2$O and not the electrolyte (DME).
• Reversible chemistry seen over multiple cycles indicating that LiOH can be removed
Technical Back-Up Slides
Investigation of the organics in the SEI: structural information

$^{13}C_3$ DMC Sample

$^{13}C$ shift / ppm

Rinsing electrode samples to remove excess electrolyte is a commonly used technique for ex-situ SEI studies.

Our preliminary rinsing studies suggested PEO-type organics are removed by rinsing. These fragile organics are likely on the outermost layer of the SEI.
Use 2D experiments to help assignments:
E.g., $^{13}$C-$^1$H Correlation NMR Experiments with enriched DMC

E.g., 1H-13C Correlation NMR Experiments with enriched DMC

(DMC) CH$_3$O + SEI
54.5

(DMC) CH$_3$OCO$_2$Li
53.3 (3.3 $^1$H)

(DEI) CH$_3$O
67.3 (5.5 $^1$H)

(EC) CH$_2$O
67.3 (5.5 $^1$H)

(DMC) CH$_3$O
55.7 (3.7 $^1$H)

(SeI) CH$_3$OCO$_2$Li
53.3 (3.3 $^1$H)

At least one DMC product
CH$_3$-O-CO$_2$-

Distinct from EC products
\textbf{\textsuperscript{13}C-\textsuperscript{13}C Correlations: EC products}

Correlate ether and carbonate regions to separate components.

- \textsuperscript{13}CH\textsubscript{2}OCO\textsubscript{2}-

At least 2 components.

Correlate ether and carbonate regions to separate components.

\textbf{Carbonates}

\textbf{Ethers}
$^{13}$C-^1$H$ Correlation NMR Experiments – EC Products

Formates and CH$_x$CH$_2$-O seen

CH$_x$ seems to come from both EC and DMC

Formates and CH$_x$CH$_2$-O seen

CH$_x$ seems to come from both EC and DMC