SILICON ELECTROLYTE INTERFACE STABILIZATION (SEISTA): ELECTROCHEMICAL METHODS

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OVERVIEW

Timeline
• October 1st 2016 – September 30th 2019.
• Percent complete: 80%

Budget
• Funding for FY 20: $3800

Barriers
• Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals
  • Cost, Performance and Safety

Partners
• Six Laboratory Team lead by NREL:
  • Sandia National Laboratory
  • Argonne National Laboratory
  • Oak Ridge National Laboratory
  • Lawrence Berkeley National Laboratory
  • Pacific Northwest National Laboratory
• UC Berkeley, Colorado University Boulder, Colorado School of Mines, University of Rhode Island
RELEVANCE: OBJECTIVES

Si anodes exhibit ca. 3x higher volumetric energy density than graphite anodes

1. Si anodes have three major challenges to commercialization
   - Rapid capacity fade
   - Poor shelf life
   - Electrode formulation/manufacturability/stability

2. SEI formation in Si is much more complex than in graphite, and seems to be dependent on initial state and history
   - Inherently non-passivating in organic carbonate electrolytes
   - Large volume expansion on alloying
   - Extensive gas formation

Improve calendar life and understand initial stages of SEI formation by understanding intrinsic chemical reactivity of Si electrodes
**Approach**

**Critical Questions:**
- What are the unique basic properties of the Li_x Si/electrolyte interface?
- What is the mechanism of the SEI formation?
- How fast does the silicon SEI grow?
- Does it stop growing?
- Role of soluble components?
- What is the composition, structure and function of the surface film?
- How to stabilize SEI on silicon?

**Team work:**
- Close coordination with the Deep Dive Program
- Fundamental understanding is critical
- Multiple approaches on the same problem
- Well defined samples
- Standardized experimental protocols
- Reproducibility across the team (multiple labs)
- Rapid communication
  - All information is stored on BOX
  - Weekly team meetings (video)
  - Quarterly face to face
  - Multiple side phone meetings
  - Site visits by researchers to other labs
MILESTONES IN FY20

1. Have demonstrated ability to make model electrodes of Mg-Si zintl compounds and compared SEI chemistry to silicon using XPS, STEM-EDS and FTIR/Raman. **Q1 Complete**
2. Have established experiments and protocols for understanding the factors that affect safety in silicon anodes, with a specific focus on highly exothermic reactions that occur at silicon electrodes. **Q1 Complete**
3. Have determined the affect that CO2 has on the stability of SEI formation on model electrodes, but examining the changes in the nature of the SEI (XPS, and FTIR/Raman and quantitate electrochemical measurement) as a function of CO2 concentration. **Q2 Complete**
4. Have determined zintl phase formation mechanism and its effect on SEI with model systems including Si NPs, Si wafer, a-Si thin film using XPS, AFM/SSRM, STEM-EDS and FTIR/Raman. **Q2 Complete**
5. **Go/NoGo** on production of tin-silicon alloys to be determined by the ability of the alloys to be prepared in 1g quantities and a demonstration that the alloys exhibit greater cyclic life than the pure metals alone. **Q2 Complete**
6. Have determined the chemistry and interfacial properties (e.g. nature of the chemical bonding at the surface of Si and the organic material) of LiPAA/Si interfaces as a function of charge (OCV, 0.8V, 0.4V, 0.15V, 0.05V) and drying temperature (100, 125, 150, 175, 200°C). **Q3**
7. Have determined how binder changes the stress/strain on silicon electrodes as a function of state of charge by varying Si NP size and surface functionally utilizing both 2 or three dimensional model systems. **Q3**
8. Have implemented protocols that enable comparisons of safety responses in silicon anodes as a metric for improving safety in silicon cells. **Q3**
9. Have published a document that will enable other research and development groups to analyze stability of the SEI on a silicon-based anode, thus enabling developers or researchers to continually improve silicon cell stability (joint milestone with the Silicon Deep Dive). **Q4**
10. Have understood how the nature and amount of formed/soluble SEI species varies with electrolyte, binder, and Si anode (with surface functionalization) using GC-MS, (in-situ) FTIR/Raman and XPS. **Q4**
Overarching Mission: Develop a stable SEI layer for Silicon Anodes to enable the use of intermetallic anodes for lithium ion batteries. This is not a new challenge but we believe that the difficulties working with silicon have precluded a “quick fix” to long term stability of silicon electrodes.

We require a foundational understanding of the formation and evolution of the SEI on silicon

Understand first, fix later!
INTRODUCTION

Intrinsic non-passivating behavior of Si anodes in organic carbonate electrolytes

• SEI layer (electro)chemical instability leads to high “leakage” or “corrosion” current
• Surface composition of Li$_x$Si electrode is constantly changing during cycling
• Si particle decrepitation and fresh surface exposure during cycling

Three strategies to stabilize Si/electrolyte interface

Electrolyte Modification

Effect of CO$_2$ on SEI behavior
Saturate electrolyte with CO$_2$ (one of electrolyte reduction products) to alter formation of the SEI of the SEI and gain control over the SEI composition, structure and passivating behavior

Interface Modification

Si-Mg Zintl phase *in situ* formation
Modify *in situ* the surface of Si anode by electrochemical formation of Si-Mg Zintl phase to promote formation of stable SEI

Advanced Materials Development

Si-based Amorphous Alloys
Synthesize a new class of Si-based amorphous electrode active materials with greatly improved interfacial and mechanical properties
• Corrosion current measured for model Si thin-film electrodes corresponds exactly to the parasitic current from Si anode in full Li-ion cells under steady-state conditions
• Si interfacial instability is primarily responsible for the observed lithium inventory shift and capacity fade in Li-ion cells
Dynamic growth and dissolution of the SEI layer on silicon during lithiation/de-lithiation, respectively

- SEI layer “breathing effect” is directly related to formation of LiEDC and P-F and P-O-F containing compounds at low potentials and their disappearance upon de-lithiation
- SEI layer gets enriched with inorganic compounds, mainly LiF, during cycling

Overall composition and morphology of the film and its interactions with the Li$_x$Si electrode and electrolyte, appears to be strongly dependent on the electrolyte potential
**ROLE OF SiO$_2$ ON PASSIVATING BEHAVIOR OF SI IN Li-ION CELLS**

- SiO$_2$ is omnipresent on Si surface
- Effect of SiO$_2$ on interfacial properties of silicon varies with the film thickness, phase composition and morphology, which depend on film growth methods e.g., native, thermal, sputtered, etc.
- SiO$_2$ exhibits some activity toward Li$^+$ i.e., a fraction of the film may undergo physical and chemical changes during charge/discharge processes

*SiO$_2$ film alone does not appear to help promote growth of a stable SEI layer on Si electrodes*
THREE STRATEGIES TO STABILIZE SI/ELECTROLYTE INTERFACE

**Electrolyte Modification**

(i) \( \text{(CH}_2\text{O)}_2\text{CO}(\text{EC}) \xrightarrow{2e^-} (\text{CH}_3\text{OCO}_2\text{Li})_2 + \text{CH}_2 = \text{CH}_2 \)

(ii) \( \text{(CH}_2\text{O)}_2\text{CO}(\text{EC}) \xrightarrow{2e^-} \text{LiOCO}_2\text{CH}_3\text{H}_2\text{OCO}_2\text{Li} \)

(iii) \( \text{(CH}_2\text{O)}_2\text{CO} + 2e^- + 2\text{Li}^+ \rightarrow \text{Li}_4\text{C}_2\text{O}_4 + \text{CH}_2 = \text{CH}_2 \)

(iv) \( \text{Li}_2\text{O} + \text{EC} \rightarrow \text{LiOCH}_2\text{CH}_2\text{OCO}_2\text{Li} \)

(v) \( \text{CH}_3\text{OCO}_2\text{CH}_2\text{DMC} + e^- + \text{Li}^+ \rightarrow \text{CH}_3\text{OCO}_2\text{Li} + \text{CH}_3\text{O} \)

(vi) \( \text{CH}_3\text{OCO}_2\text{CH}_2\text{DMC} + e^- + \text{Li}^+ \rightarrow \text{CH}_3\text{OLi} + \text{CH}_3\text{OCO} \)

(vii) \( 2\text{ROCO}_2\text{Li} + \text{H}_2\text{O} \rightarrow \text{Li}_2\text{CO}_3 + 2\text{ROH} + \text{CO}_2 \)

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**Effect of CO\(_2\) on SEI behavior**

Saturate electrolyte with CO\(_2\) (one of electrolyte reduction products) to alter formation of the SEI of the SEI and gain control over the SEI composition, structure and passivating behavior

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**Interface Modification**

Si-Mg Zintl phase *in situ* formation

Modify *in situ* the surface of Si anode by electrochemical formation of Si-Mg Zintl phase to promote formation of stable SEI

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**Advanced Materials Development**

Si-based Amorphous Alloys

Synthesize a new class of Si-based amorphous electrode active materials with greatly improved interfacial and mechanical properties

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Baris et al., *ACS Appl. Mater. Interfaces* 2019, 11, 29780

EFFECT OF CO$_2$ ON INTERFACIAL PROPERTIES OF SI ANODE

Ex situ XPS of Si/SEI

- Presence of CO$_2$ in Gen2 electrolyte substantially changes SEI composition on Si:
  - Promotes LiF and suppresses Li$_2$CO$_3$ formation
  - Promotes formation of aldehyde/ketone-like organic species and PEO oligomers

Ex situ ToF-MS of SEI on Si
EFFECT OF CO$_2$ ON INTERFACIAL PROPERTIES OF SI ANODE

- SEI film formed in the presence of CO$_2$ tends to be thinner and less electronically resistive
- CO$_2$-saturated Gen2 electrolyte does not improve Si cycling performance
THREE STRATEGIES TO STABILIZE SI/ELECTROLYTE INTERFACE

**Electrolyte Modification**

- (i) (CH₃O)₂CO (EC) + 2e⁻ → (CH₃OCO)Li₂ + CH₄↑
- (ii) (CH₃O)₂CO (EC) + 2e⁻ → LiOCO₂CH₂OCO₂Li
- (iii) (CH₃O)₂CO (EC) + 2e⁻ + 2Li⁺ → Li₂CO₃ + CH₂=CH₂↑
- (iv) Li₂O + EC → LiOCH₂CH₂OCO₂Li
- (v) CH₃OCO₂CH₂(DMC) + e⁻ + Li⁺ → CH₃OCO₂Li₂ + CH₂
- (vi) CH₃OCO₂CH₂(DMC) + e⁻ + Li⁺ → CH₂O Li₂ + CH₂OCO
- (vii) 2ROCO₂Li + H₂O → Li₂CO₃ + 2ROH + CO₂

**Interface Modification**

- Discharged in Li-only traditional electrolyte
- Highly reactive Li-Si binaries
- Relatively stable Li-Mg-Si ternaries
- Twice more capacity retention after 270 cycles

**Advanced Materials Development**

- Si-Mg Zintl phase in situ formation
  - Modify in situ the surface of Si anode by electrochemical formation of Si-Mg Zintl phase to promote formation of stable SEI

**Si-based Amorphous Alloys**

- Synthesize a new class of Si-based amorphous electrode active materials with greatly improved interfacial and mechanical properties
MECHANISM OF ZINTL PHASE FORMATION ON SI ANODE

Mg(TFSI)$_2$ electrolyte additive alters composition of the Si/electrolyte interface

Lithiation: 3 working hypotheses
1. Exchange:
   $3.75\text{Li} + \text{Si} \rightarrow \text{Li}_{3.75}\text{Si}$
   $\text{Li}_{3.75}\text{Si} + 0.1\text{Mg}^{2+} \rightarrow \text{Li}_{3.55}\text{Mg}_{0.1}\text{Si} + 0.2\text{Li}^+$

2. Co-alloying
   $\text{Li}_{3.5}\text{Si} + \text{Mg}^{2+} \rightarrow \text{Li}_{3.5}\text{Mg}_{0.1}\text{Si}$

3. Co-insertion followed by equilibration:
   $\text{Li}_{3.75}\text{Si} + \text{Mg}^{2+} \rightarrow \text{Li}_{3.75}\text{Mg}_{0.1}\text{Si}$
   $\text{Li}_{3.75}\text{Mg}_{0.1}\text{Si} \rightarrow \text{Li}_{3.5}\text{Mg}_{0.1}\text{Si} + 0.2\text{Li}^+$

Delithiation:
$\text{Li}_{3.75-2x}\text{Mg}_x\text{Si} \rightarrow \text{Mg}_x\text{Si} + (3.75-2x)\text{Li}$

NMR indicates no removal of Mg when delithiation is carried out in GENFM, consistent with Mg strong coordination to Si
**EFFECT OF ZINLT ON SI ANODE INTERFACIAL BEHAVIOR**

- Improved in Si electrode capacity retention in GenFM electrolyte
- \( \text{Li}_x\text{Mg}_y\text{Si} \) phase formation on the electrode/electrolyte interface
- Lower parasitic current at 10 mV, indicating better passivating properties of the SEI on Si in presence of Mg(TFSI)$_2$

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Baris et al. ACS Appl. Mater. Interfaces 2019, 11, 29780
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(ii) \((\text{CH}_3\text{O})_2\text{CO} (\text{EC}) \xrightarrow{2\text{Li}^+} \text{Li}_2\text{O} \cdot \text{CH}_3\text{O} \cdot \text{CO}_2\text{Li}) + \text{Li}^+ = \text{Li}_2\text{O} \cdot \text{CH}_3\text{O} \cdot \text{CO}_2\text{Li} + \text{Li}^+ \)

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**Si-Mg Zintl phase in situ formation**

Modify in situ the surface of Si anode by electrochemical formation of Si-Mg Zintl phase to promote formation of stable SEI.

**Interface Modification**

Discharged in Li-only traditional electrolyte

Highly reactive Li-Si binaries

Poor capacity after 270 cycles

Discharged in Li-Mg mixed-salt electrolyte

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Twice more capacity retention after 270 cycles

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**Advanced Materials Development**

**Si-based Amorphous Alloys**

Synthesize a new class of Si-based amorphous electrode active materials with greatly improved interfacial and mechanical properties.


Effect of CO₂ on SEI behavior

Saturate electrolyte with CO₂ (one of electrolyte reduction products) to alter formation of the SEI of the SEI and gain control over the SEI composition, structure and passivating behavior.
Splat quenching of a molten alloy droplet by splatting it with two cold metal surfaces at cooling rates of $10^5$-$10^6$ K/s produces amorphous alloys.

XRD, TEM and DSC results confirm successful fabrication of amorphous $\text{Al}_{64}\text{Si}_{25}\text{Mn}_{11}$ metallic glasses.

Lack of phase boundaries introduces new and unique materials properties.

<table>
<thead>
<tr>
<th>Known Binary System ($A_xB_y$ at.%)</th>
<th>$\text{Ti}<em>{0.84}\text{Si}</em>{0.16}$</th>
<th>$\text{Ni}<em>{0.75}\text{Si}</em>{0.25}$</th>
<th>$\text{Zr}<em>{0.8}\text{Si}</em>{0.2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>357 mAh/g</td>
<td>489 mAh/g</td>
<td>378 mAh/g</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ternary System ($A_xB_yC_z$ at.%)</th>
<th>$\text{Fe}_{1-x-y}\text{Si}_x\text{B}_y$ (x + y 25)</th>
<th>$\text{Ni}_{1-x-y}\text{Si}_x\text{B}_y$ (x + y 49)</th>
<th>$\text{Co}_{1-x-y}\text{Si}_x\text{B}_y$ (x + y 35)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>266 - 523 mAh/g</td>
<td>374 - 1152 mAh/g</td>
<td>300 - 730 mAh/g</td>
</tr>
</tbody>
</table>
Si-based amorphous alloys electrochemical behavior

Si-alloys retain volumetric energy density of Si and show much improved interfacial and mechanical stability

- SEI formation charge and current profile is comparable to copper
- Specific capacity ~900 mAh/g obtained for foil (2-4 μm) alloy sample. Higher values expected with properly engineered electrodes
SUMMARY

1. Inherent non-passivating behavior of Si in organic carbonate electrolytes confirmed and quantified
   • Corrosion/parasitic currents of 1 $\mu$A/cm$^2$ observed on model and composite Si electrodes
   • Gradual electrolyte consumption and lithium inventory shift in Si-based cells
   • SiO$_2$ film has to be carefully optimized to promote surface passivation

2. New routes to achieve interfacial stability of Si electrode explored and evaluated
   • SEI composition and structure can be altered by shifting reaction equilibria by soluble products of the electrolyte decomposition
   • ZINTL phase set s a new path for in situ modification of Si/electrode interface

3. Exploratory research of new Si-based high-energy electrode materials
   • A series of new Si-based binary and ternary amorphous alloys was synthesized and tested
   • Preliminary data show much improved interfacial behavior and mechanical properties
REMAINING CHALLENGES / FUTURE PLAN

Three Research Themes with Staggered Timelines

I. Use round robin electrodes for control and modification of physico-chemical properties
   • Characterize electrode surface reactivity, SEI layer composition and structure
   • Unveil hidden SEI layer components
   • Understand the mechanism of SEI layer operation and function

II. Correlate interfacial properties with electrochemical behavior
   • Formulate working hypothesis of the mass and charge transfer across the surface film
   • Develop methods to track Li\textsuperscript{+} in the film and electrode active material
   • Use and investigate chemical spillover effects from active and passive electrode components

III. Design rational Si electrode design principles to address performance challenges
   • Correlate modifications to specific challenges, e.g. surface reactivity to electrolyte, volume change, “cracking, etc.
   • Design and study model electrodes with tailored interfaces to control the kinetics i.e., rate and selectivity of interfacial processes.
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