SILICON DEEP-DIVE:
UPDATE AND OVERVIEW

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ARGONNE NATIONAL LABORATORY
JUNE 1-4, 2020
US DOE VEHICLE TECHNOLOGIES OFFICE
2020 ANNUAL MERIT REVIEW

Project ID BAT388

OVERVIEW

Timeline

- Start October 1, 2017
- End: September 30, 2020
- Percent Complete: 89%

Barriers

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

Budget

- Funding for FY20: $3000K
- Presentations

  BAT388, BAT439, BAT440

Partners

- Argonne National Laboratory
- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Pacific Northwest National Laboratory
- *Academic Partners*: UMass-Boston, Western Michigan University, University of Illinois-Chicago, University of Tennessee, University of California

RELEVANCE

We seek to create a long cycle and calendar life silicon based anode for lithium ion batteries through an understanding of cell design, electrode design and formation, failure analysis, and silicon surface stability.

The **Silicon Deep Dive Next Generation Anode Program** addresses the cost and performance issues preventing the inclusion of silicon into a commercial lithium-ion cell

- Elemental silicon can theoretically store > 3500 mAh/g
- BatPaC modeling indicates a silicon-based electrochemical cell coupled with a high-capacity cathode presents a pathway to less than \$125/kWh$_{use}$
- Silicon-based electrodes require different components than graphitic carbon anodes due to differences in surface chemistry, SEI stability, conductivity, and volume expansion.
- Stabilizing the surface of silicon is a pathway towards limiting detrimental side reactions with electrolyte on cycling.

MILESTONES AND ACTIVITIES

FY19Q3	Demonstrate the utility and limitations of anode pre-lithiation in a full cell configuration; extend cycle life of silicon-based baseline electrode by at least 10%. (***Completed 06/19***)
FY19Q4	Construct and evaluate cells based on optimizing lithium inventory, binder, electrolyte formulation, and testing protocol to achieve a 300 Wh/kg cell design based on BatPaC modeling. (***Completed 11/19***)
FY20Q1	Evaluate two new binder - slurry – silicon laminate combinations that lead to improved stability and a 15% improvement in performance compared to baseline for a high silicon-loading (>60%) electrode (***Completed 12/19***)
FY20Q2	Assess and evaluate multiple surface driven coatings that utilize a multivalent surface substitution. Develop an understanding of the formation mechanism on the cycling stability of the underlying silicon electrode; propose a mechanism of formation. (***Completed 2/20***)
FY20Q3	Assess the stability of electrode level silicon baseline materials on cycling and determine the range of species that solubilize and leach into the electrolyte. (***on-going***)
FY20Q4	Combine the advancements made over various aspects of the silicon electrode by the Silicon Deep Dive team evaluate them at the full system level and optimize a best full cell with a commercial cathode that using BatPaC can be determined to deliver > 350 Wh/kg for 120 cycles; Evaluate the energy fade on standing for 2 mos and demonstrate an improvement over baseline of 20%. (***on-going***)
FY20Q4	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 SEISta*). (***on-going***)

APPROACH & ORGANIZATION

A Coordinated Five National Laboratory Research Program

The program is designed to address issues associated with the commercialization of a LIB silicon anode. This effort uses a series of multi-lab research joint efforts to reach our goals.

Silicon and Cell Design

BAT388 Jack Vaughey (ANL)

Silicon Surface Functionalization, Binders, & New Electrolytes

BAT440 Zhengcheng (John) Zhang (ANL)

Slurries, Laminate Structure, Electrode Design

BAT439 Beth Armstrong (ORNL)

SEI Formation on Silicon and its Stability

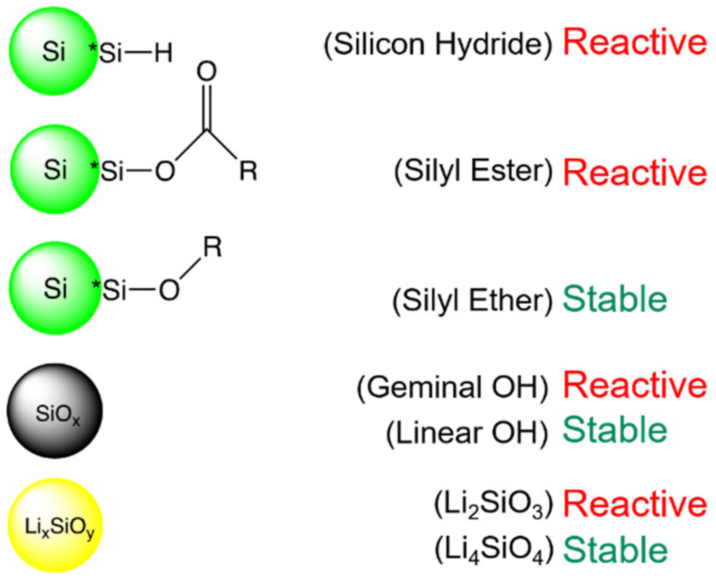
BAT388 Jack Vaughey (ANL)

SILICON AND CELL DESIGN

Silicon Sources: Organic Coatings

Batch to batch variability has been an issue for many silicon R&D efforts as the surface of silicon is active towards water, air, and organics. We have been evaluating silicon scale-up production methods for possible use in the DeepDive program.

- HEBM of commercial silicon boules leads to the formation of active surfaces during the processing. If done in the presence of various organics - these materials act to sacrificially passivate the surface leading to a stabilized & functionalized Si surface



(Silicon Hydride) Reactive

(Silyl Ester) Reactive

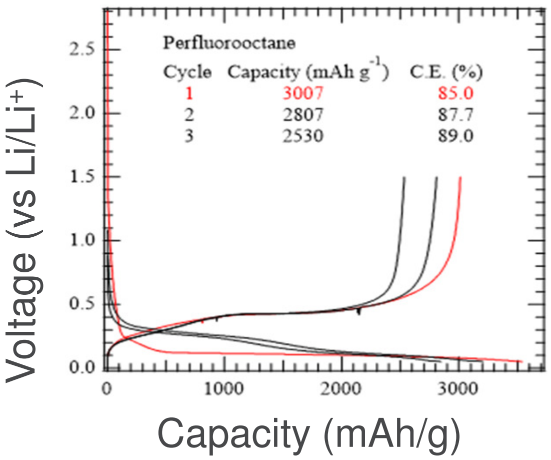
(Silyl Ether) Stable

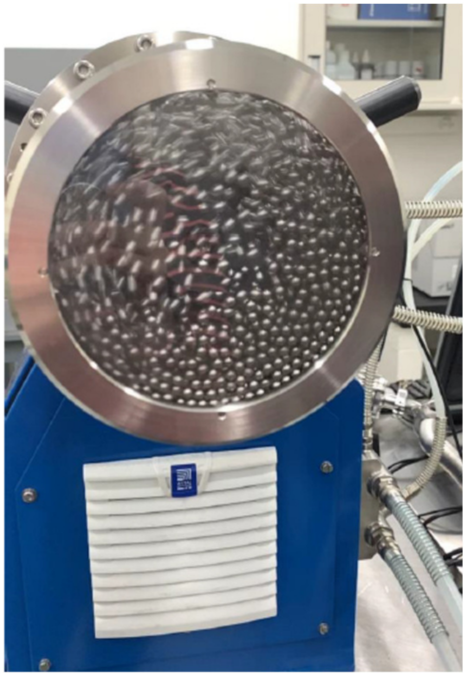
(Geminal OH) Reactive

(Linear OH) Stable

(Li_2SiO_3) Reactive

(Li_4SiO_4) Stable



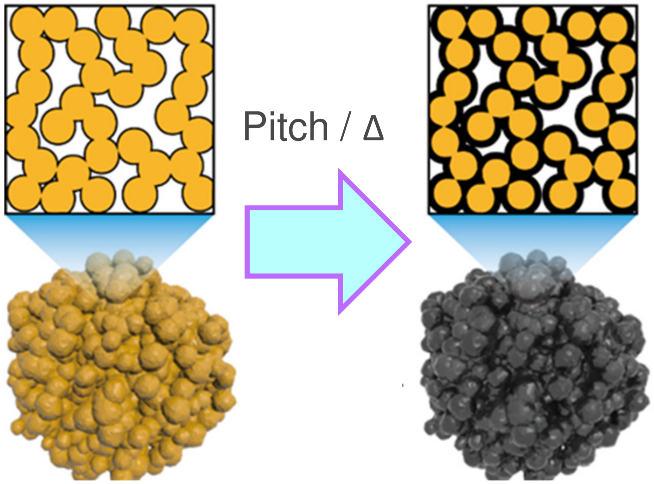


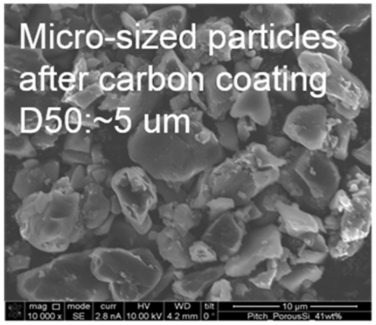
SILICON AND CELL DESIGN

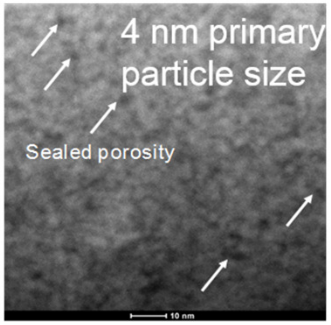
Silicon Sources : Conformal Carbon Coatings

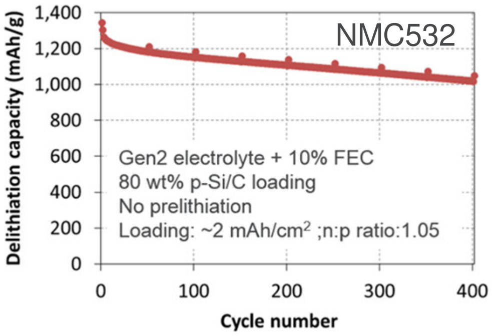
A controlled silicon microstructure is an approach to limit side reactions and reactivity by controlling the silicon-electrolyte interface. We have developed a method to make a carbon coated porous silicon powder starting from a commercial SiO sample

Process: After annealing at 900 ^{0}C; sample was acid etched to dissolve SiO_2 followed by pitch infusion and heating to drive decomposition to carbon. Product is about 50% Silicon.







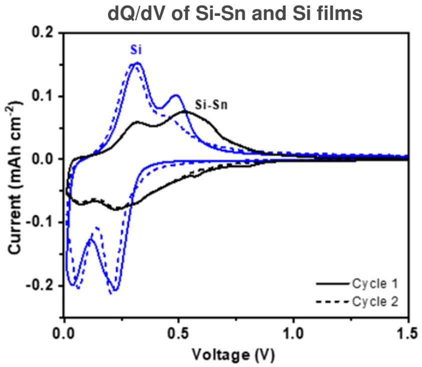


Evaluation at these SOCs has demonstrated the stability and performance of the porous framework

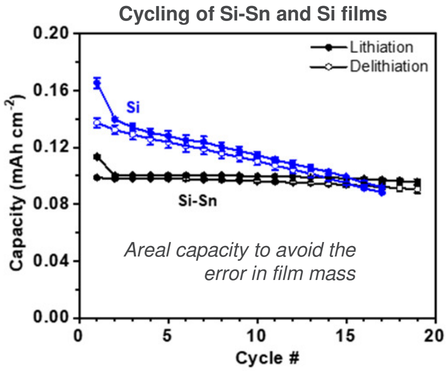
SILICON AND CELL DESIGN

Silicon Sources : Silicon – Tin Composites

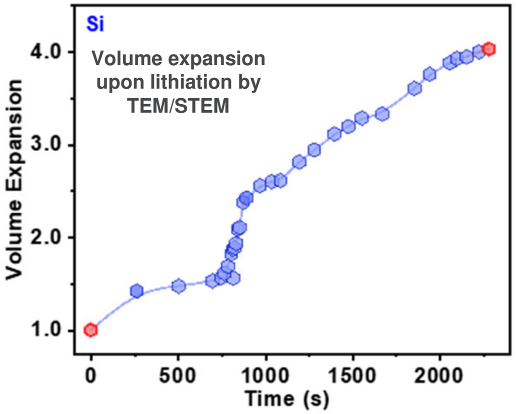
The activity of silicon can be maintained and extended by embedding it in a tin matrix. The Li_xSn ion conducting matrix helps separate and buffer the nanoscale silicon during cycling- extending cycle life.

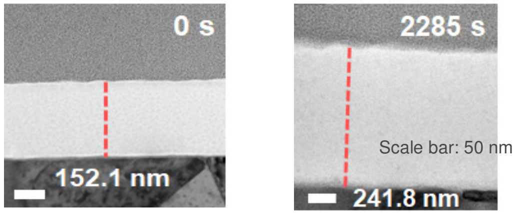


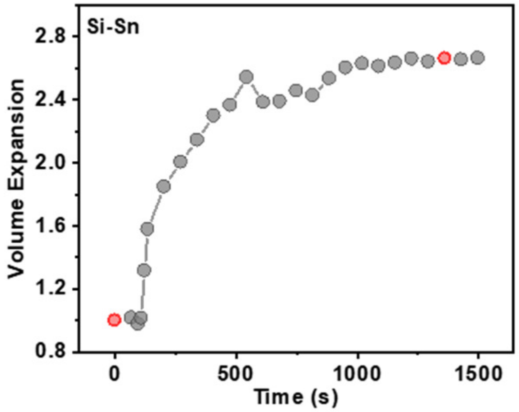
Li_xSn occurs at higher V than Li_xSi

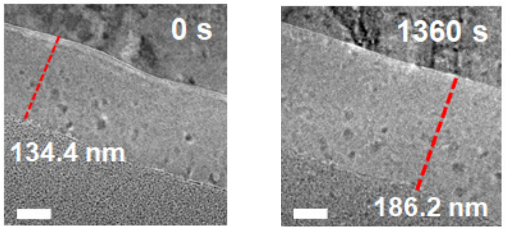


Si-Sn exhibits better cycling stability than a Si film (both ~160 nm)

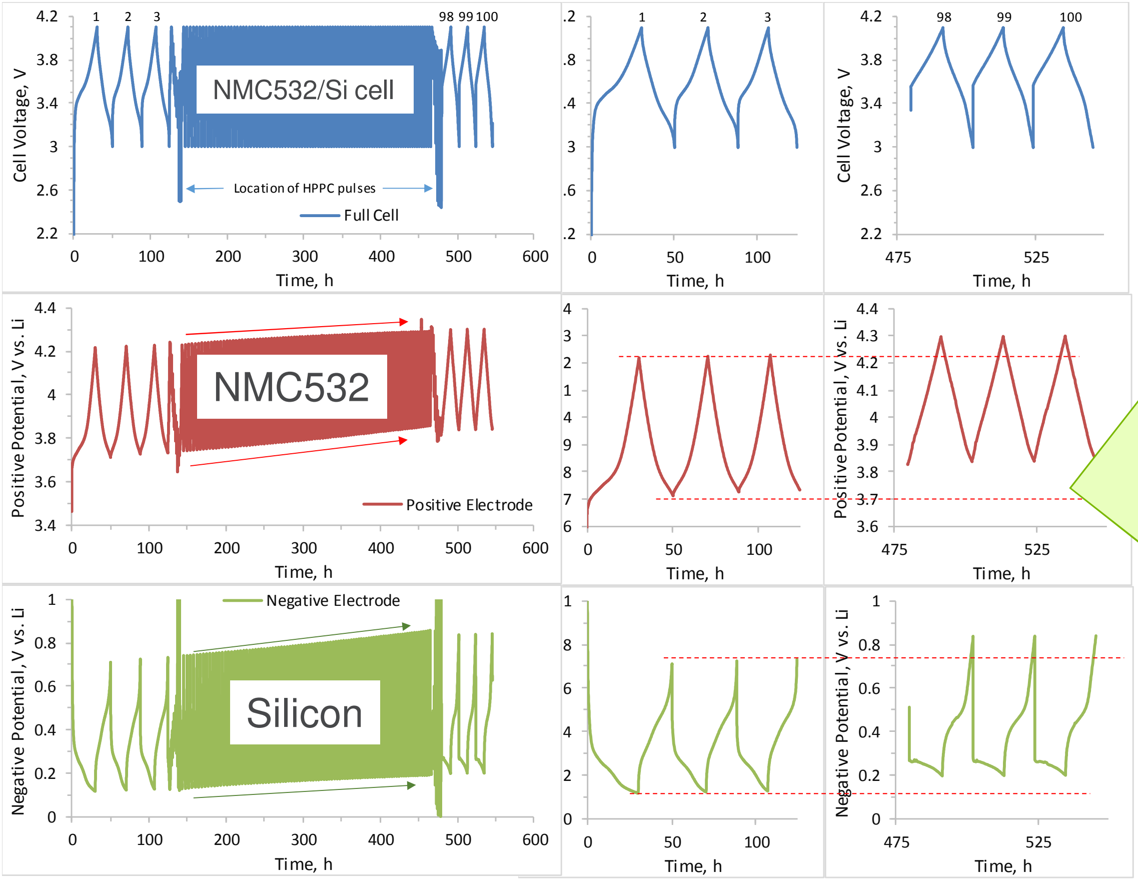








SILICON: CELL DESIGN

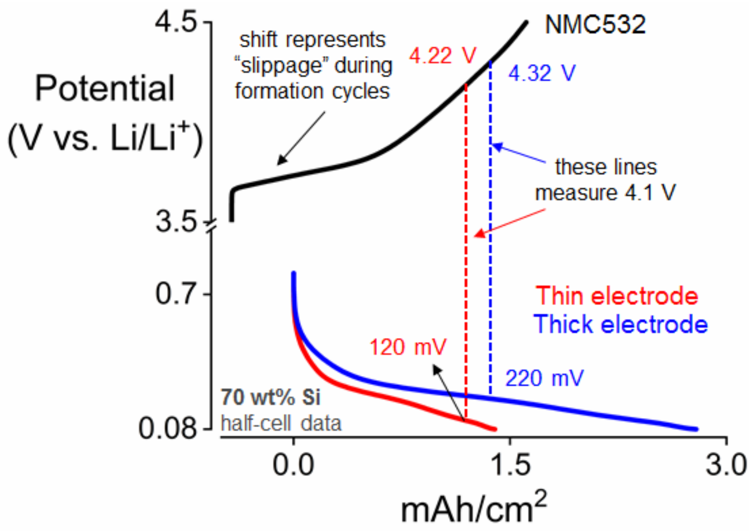


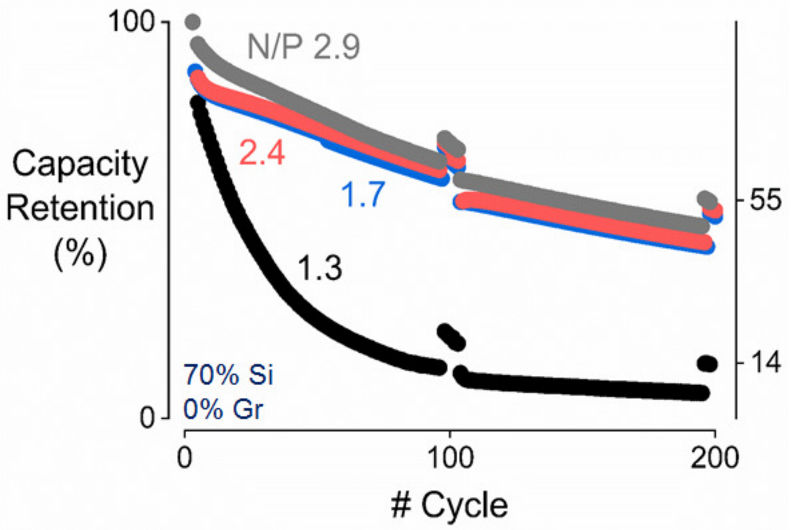
- **The positive and negative electrode potentials increase during the cycle-life aging**.
  - The positive potential increase could accelerate electrolyte oxidation.
  - Less Si is cycled as the negative cycling window changes; this would decrease the electrode volume expansion and reduce the rate of capacity fade as the aging progresses.
- An increase in voltage hysteresis is seen for both electrodes. The change is more significant for the Si electrode,
- The initial impedance of the Si electrode is more than twice that of a typical graphite electrode.
  - The increase in cell impedance is seen for both electrodes and is greater for the Si electrode
  - it is increasingly difficult to lithiate the cathode and delithiate the Si as the cycle-life aging progresses.

SILICON: FULL CELL DESIGN – N/P RATIO

Limiting Si utilization can have significant impact on electrode expansion and cell longevity

Cell Design





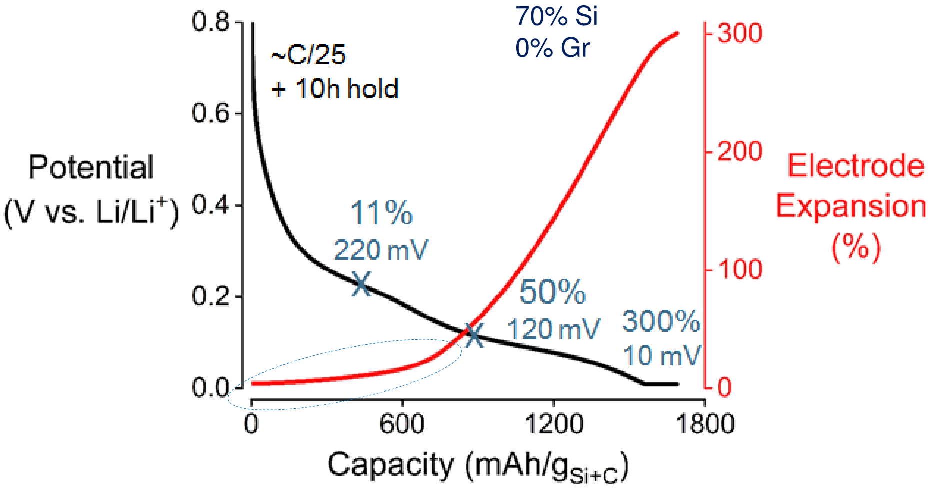
For the same cathode, doubling the anode capacity (N/P increased by a factor of 2), increases anode potential by ~100 mV (from 0.12 V to 0.22 V). This potential increase lowers Si utilization in the electrode.

Increasing N/P from 1.3 to 1.7 has a significant effect on capacity retention. Further increases (from 1.7 to 2.9) do not make a major difference.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

SILICON: FULL CELL DESIGN - ELECTRODE EXPANSION

Limiting Si utilization can have significant impact on electrode expansion and cell longevity



Si utilization can have a huge effect on electrode expansion. Limiting electrode expansion to lower values (dashed oval) can improve capacity retention. For N/P ratios of 1.3 and 1.7, estimated electrode expansions (at the beginning of cycling) are 225% and 92% respectively, which may explain observed differences in capacity retention.

For high capacity silicon electrodes, capacity retention is related to

(1) the thickness of the electrode and cell balancing as gradual lithium loss can drive up the silicon's potential as well as the cathodes,

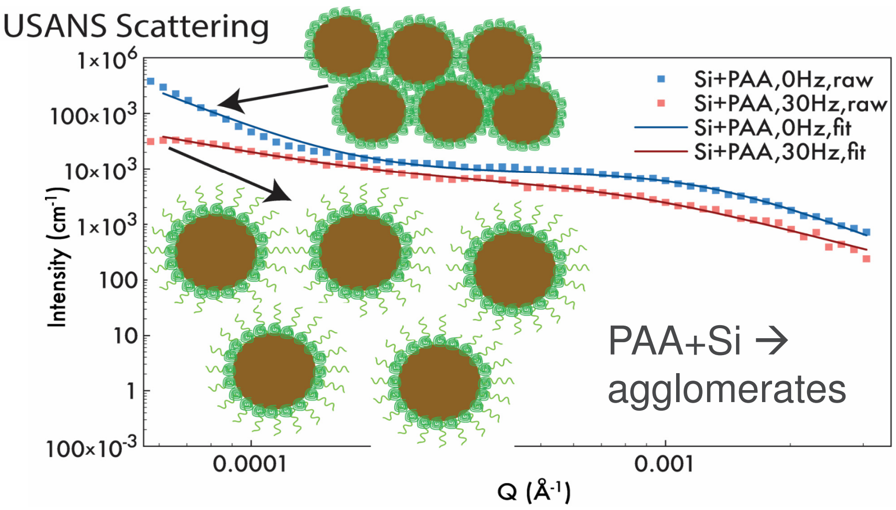
(2) As volume expansion is related to SOC for silicon, it also drives cell stability and performance

ELECTRODE STUDIES

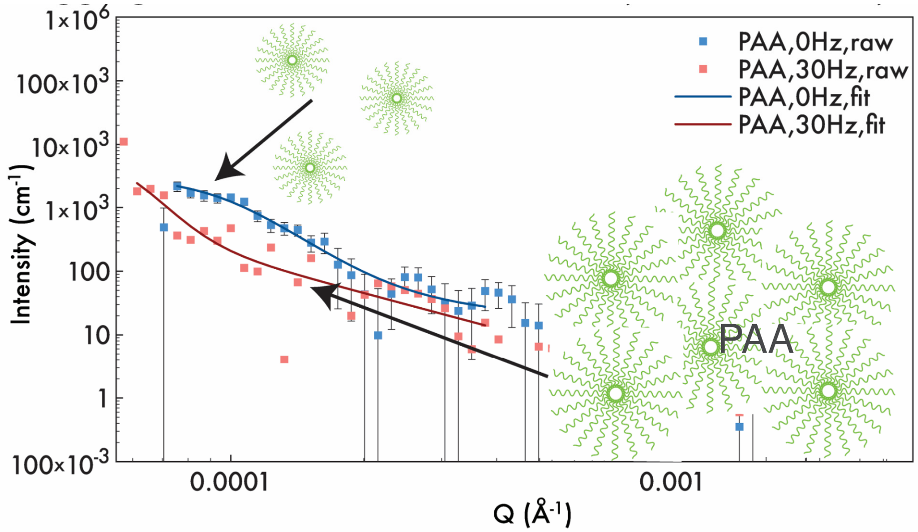
From silicon to electrode studies. Understanding how the surface of silicon interacts with the binder at various pHs, how drying changes distribution? How do the conductive additive and binder interact?

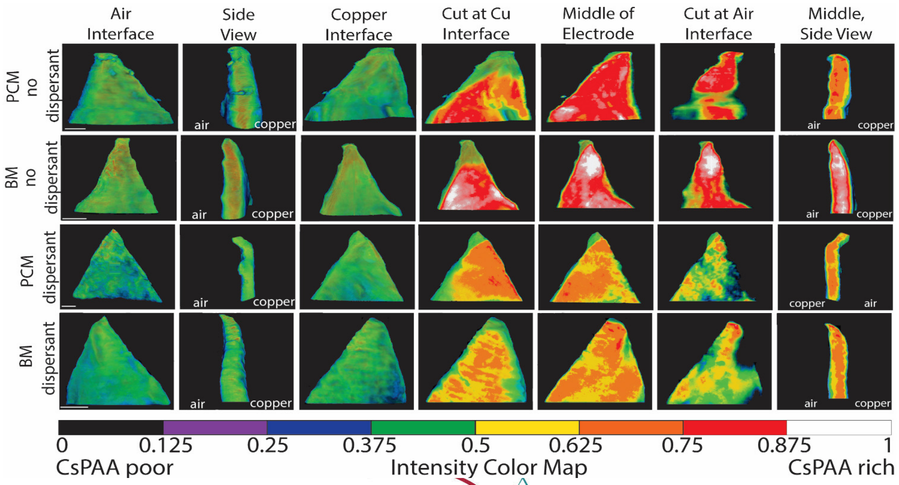
Slurries, Laminate Structure, Electrode Design

BAT439 Beth Armstrong (ORNL)

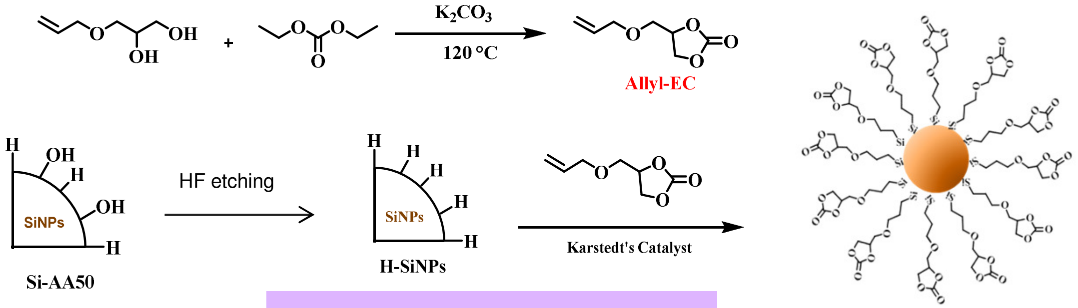


PAA+Si → agglomerates

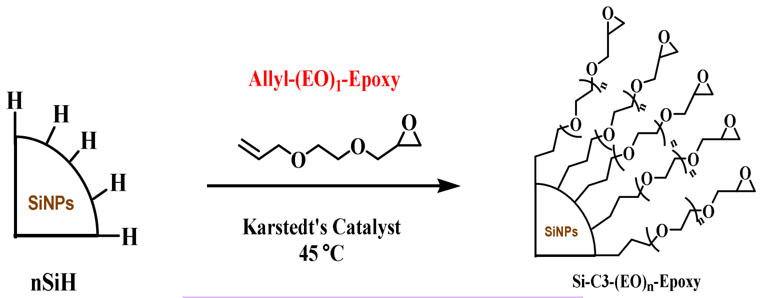




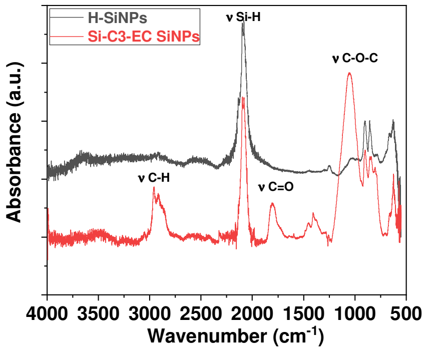
SURFACES AND BINDERS



SEI Functionality

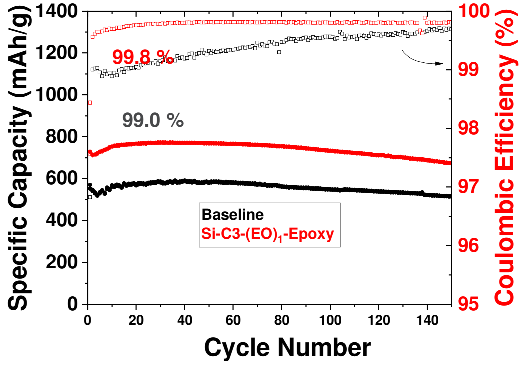


Binder Functionality



Silicon Surface Functionalization, Binders, & New Electrolytes

BAT440 Zhengcheng (John) Zhang (ANL)



- Si nanocrystal structure was well maintained after functionalization.
- HRTEM, FT-IR, XPS and TGA analysis confirmed the attachment of the organic carbonate monolayer on the surface of SiNPs.

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SILICON SEI STABILITY

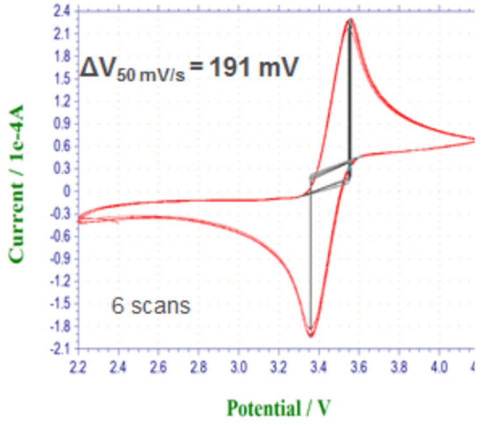
SEI Conductivity and Solubility: New Approaches and Methodologies

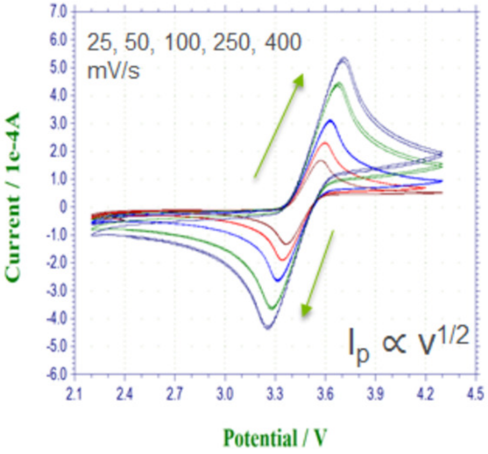
Rotating Ring Disk Electrode (RRDE) studies detect by-products from electrochemical reactions and can determine the location of the electron transfer during (de)lithiation: whether it's exterior to the SEI, within the SEI, or at the interface of SEI/Si or SEI/SiO_2/Si

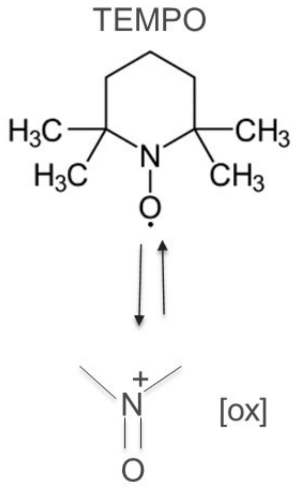
Si disk
Pt ring

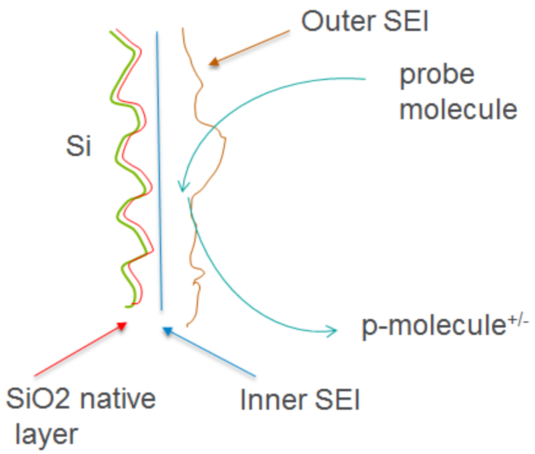
What is the (1) chemical, (2) electrochemical*, and (3) morphological behavior of Si electrode material SEI under operando conditions

Goal: Establish probe molecule electrochemistry (TEMPO) at **Si n-type electrode disk** to interrogate Si SEI







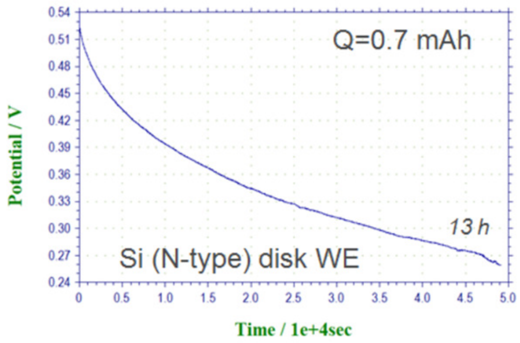


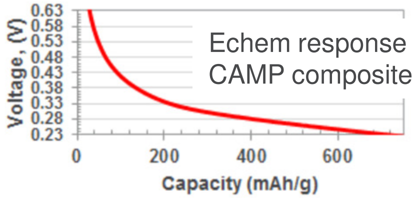
- TEMPO: good stability (> 2 weeks) and reversibility at Si electrode in Gen2

Grow Si SEI -> Run CV (TEMPO) -> oxidize Si SEI -> Run CV (TEMPO)

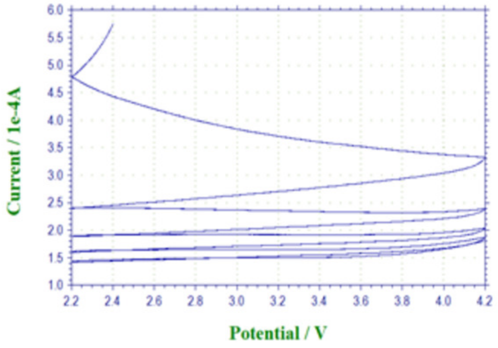
SILICON SEI STABILITY

SEI Conductivity and Solubility: New Approaches and Methodologies





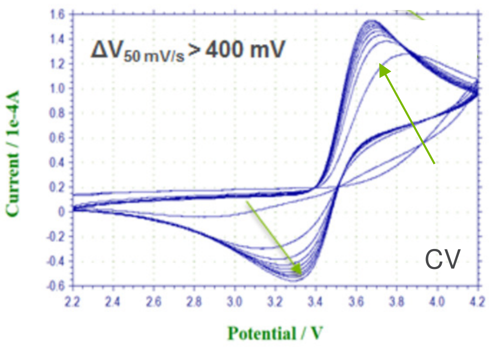
Echem response similar to ANL CAMP composite Si electrode



High resistance and blockage

CV

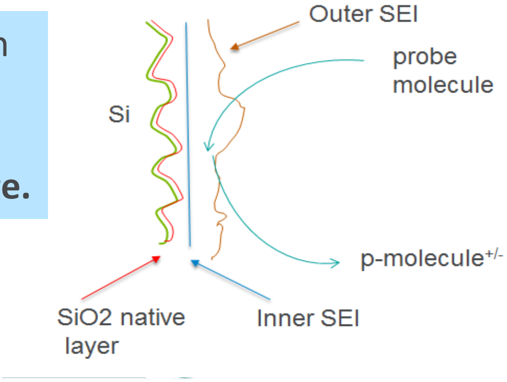
Disk charged back to 0.6 V



Si n-type electrode disk discharged in Gen2

TEMPO molecule electro-activity returns upon Si SEI oxidation with signal growth indicating slow partitioning through SEI

Cyclic voltammetry with redox probe molecule indicates that at low voltage the SEI depth and electrical resistivity exceeds the ability of TEMPO to partition through the film and reduce or even reduce at the exterior of the SEI; on charge the SEI thins and the electrochemical reactivity of TEMPO returns. **Parts of the SEI may be dissolving on charge.**

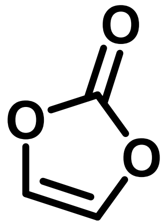


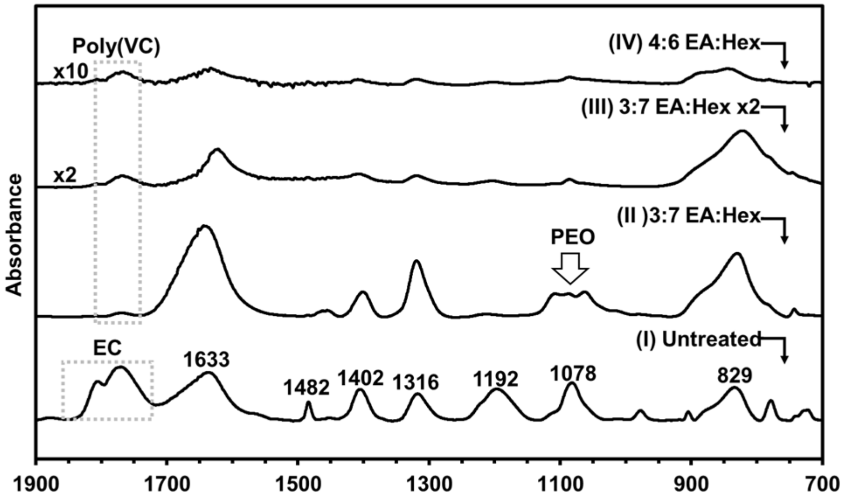
SILICON SEI STABILITY

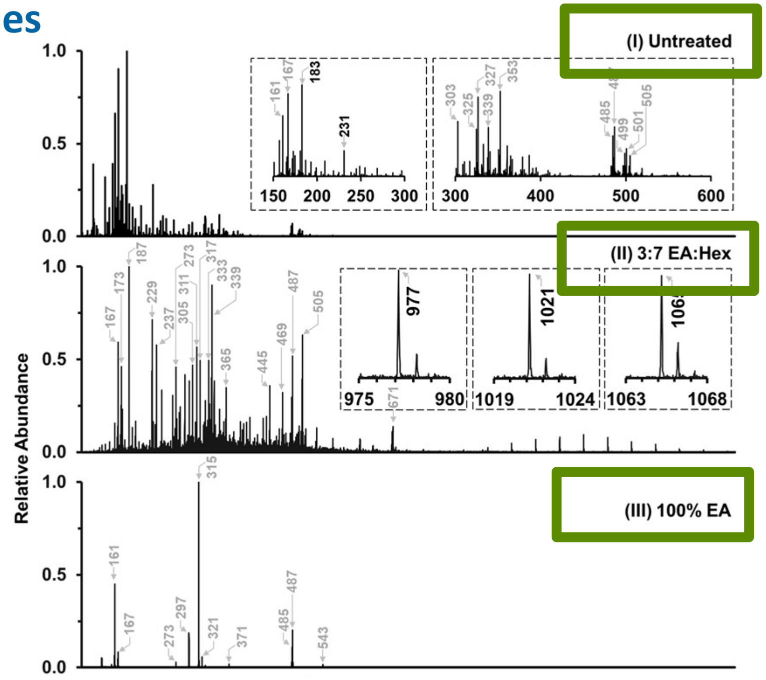
SEI Conductivity and Solubility : New Approaches and Methodologies

A gradient polar solvent wash approach to dissolve the initially insoluble SEI components as a function of polarity has been developed. The materials are separated and identified using FTIR and MALDI-MS.

INITIAL MODEL: the common cell additive Vinylene Carbonate (VC) in 1.2M $LiPF_6$ EC/EMC







Polar solvents (ethyl acetate) tend to dissolve out organic salts and more polar species while nonpolar solvents (hexane) dissolve the neutral and non-polar species. Separation can be achieved with a solvent gradient

SILICON SEI STABILITY

SEI Conductivity and Solubility: Role of FEC vs Temperature

Initial capacity

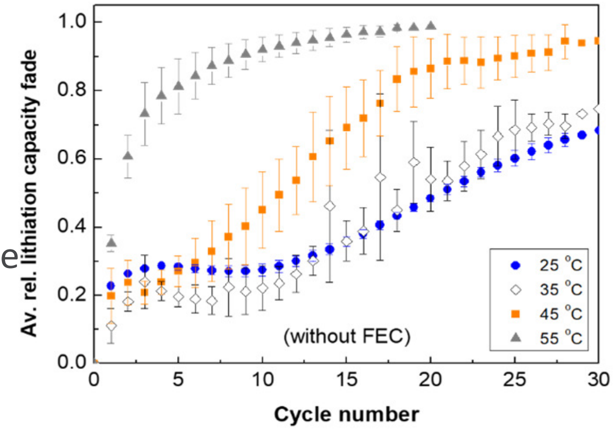
- **Without FEC** : Sensitive to temperature. Initial capacity increases as temperature increases
- **With FEC** : Insensitive to temperature. Larger initial capacity than the cell without FEC, regardless of temperature
- FEC has a critical role to improve the reaction kinetics (SEI Film resistance)

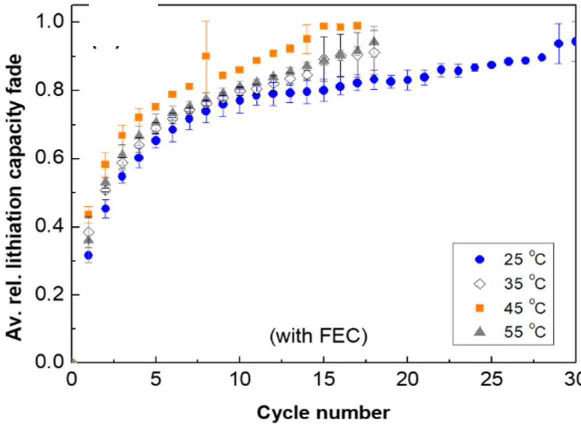
Average, initial capacity, mAg (g-Si)$^{-1}$	Without FEC	With FEC
25ºC	1306.2	2328.6
35ºC	1030.8	2519.7
45ºC	1531.2	2493.0
55ºC	2630.1	2447.3

Average relative capacity loss vs. cycle

Without FEC

- Sensitive to temperature
- Data fit needs a combination of two different model depending on temperature





With FEC

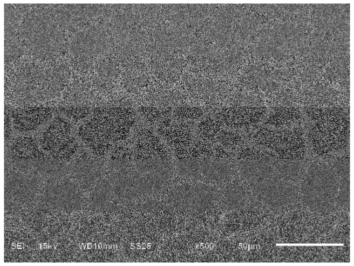
- Insensitive to temperature
- Change in capacity loss mechanism by FEC addition into the electrolyte: Can model with a Natural logarithm of cycle
- At high lithiation yields higher degradation of material, and shortening of cycle life

SILICON SEI STABILITY

SEI Conductivity and Solubility: Role of FEC vs Temperature

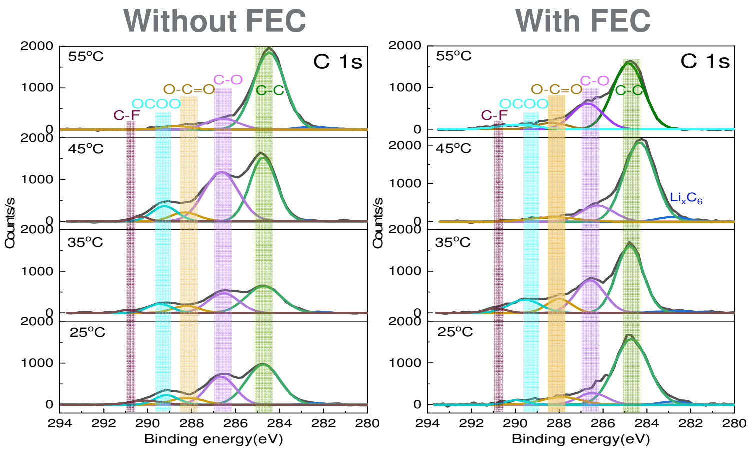
XPS analysis on SEI formation

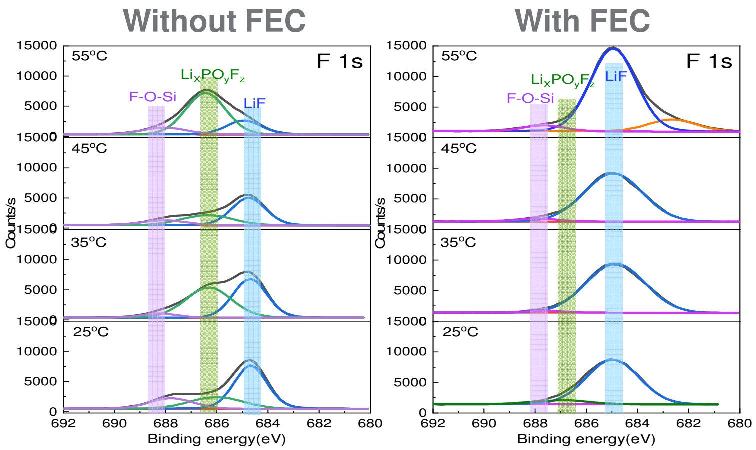
- Different chemical species of SEI by FEC addition
- Less organic species in Si-rich with FEC cell : Suppression of EC/EMC decomposition by FEC addition (C-O, C=O)
- Strong LiF peak in Si-rich cell with FEC
- Relatively less temperature-sensitivity of SEI chemistry in the Si-rich cell with FEC
- SEI with FEC : Stable and better withstand the changes with temperature



SEM

- The growth of the SEI causing a loss of electrical contact between individual silicon particles
- Crack/fracture in Si-rich anode cell with FEC after 5cycles at 25^{o}C

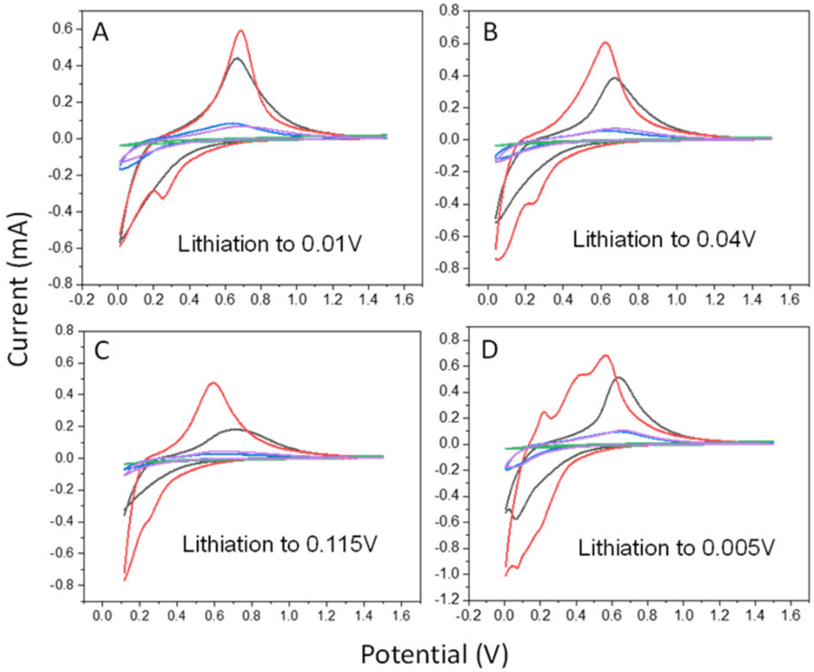




SILICON SEI STABILITY

SEI Conductivity and Solubility: Role of Mg(TFSI)$_2$

SEI formation and stability can also be tracked using Electrochemical Quartz Crystal Microbalance (EQCM) spectroscopy. We investigated the formation of the SEI, the role of Mg(TFSI)$_2$ additives, and SEI stability.



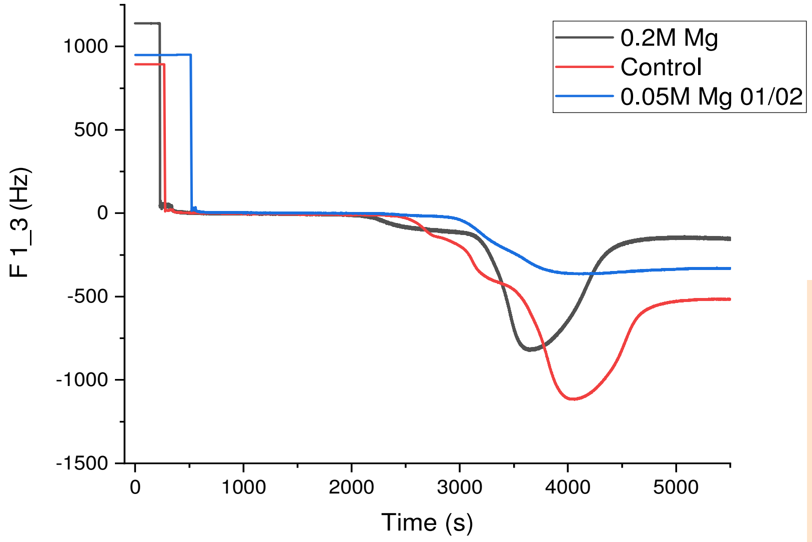
- 🟥 Control GEN2+10FEC
- 🟩 Control 0.2M Mg in EC:EMC 3:7, no lithium salt
- ⬛ 0.2M MgTFSI in GEN2+10FEC
- 🟦 0.5M MgTFSI in GEN2+10FEC
- 🟪 0.05M MgTFSI in GEN2+10FEC

- Without the lithium salt, just with Mg salt, there is no echem activity for Si anode. Only capacitive current is observed.
- For all the GEN2+10%FEC electrolytes with various Mg concentrations, complicated phase formation for Si is hindered.
- Electrochemical profile for lithiation and delithiation is not in linear relationship with Mg concentration

Current vs Potential at different intercalation voltage for various electrolytes

SILICON SEI STABILITY

SEI Conductivity and Solubility: Role of $Mg(TFSI)_2$

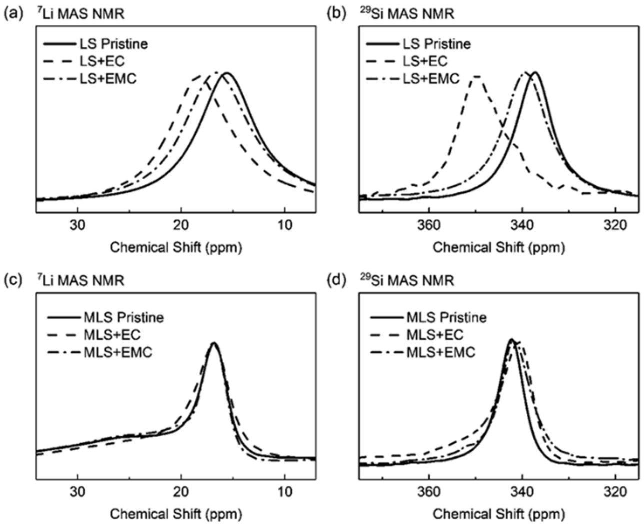


SEI formation for:

- 0.2M $Mg(TFSI)_2$ in GEN2+10FEC
- 0.05M $Mg(TFSI)_2$ in GEN2+10FEC
- Control GEN2+10FEC

- SEI formation is Mg concentration dependent
- Lowered Mg concentration results a thinner initial SEI layer formation
- Similar as 0.2 Mg salt, 0.05 M Mg is capable of reducing the initial SEI formation in the similar fashion as of 0.2 M Mg.

^7Li and ^{29}Si MAS NMR highlights that a surface magnesiated silicon electrode has far less reactivity towards the electrolyte than standard electrolyte at low voltage.



Mechanistically this data is supportive of a low voltage ion exchange reactions between $Li_{15}Si_4$ and soluble Mg^{+2} salts to form the stable Zintl coating.

RESPONSE TO REVIEWER COMMENTS (FY18)

- **Several reviewers commented on the advances individual components made versus baseline silicon cycling, including new electrolyte additives, silicon coatings, or LHCE electrolytes, however the presentation did not appear to discuss efforts to bring these individual advances together to assess them as a systems against baseline.**

  The program was designed to evaluate several electrode components, assess their properties and performance, and identify system level interactions that can limit cell performance. For instance baseline electrode development involved many variables including silicon morphology, processing conditions, passivation layer consistency, that was appropriate for the DeepDive effort in allowing us to have a representative electrode in full appreciation that it was not going to be as advanced as industrial efforts while allowing the program to make advances in various critical areas. As advances are noted in the program (or identified by the community) the baseline can be modified and assessments of how these changes affect the next level properties are identified. Examples include evolution of silicon baselines and role of particle size, electrolyte modifications to generate better surface protection, and screening various carbon conductive additives for their effect on electrode stability. At the end of FY18, our Q4 milestone brought together several advances to evaluate their symbiotic properties and help evaluate deficiencies in the materials program. For instance, higher cell stack pressure and Mg-based electrolyte additives, had a >10% improvement over baseline with extended cycling. BatPaC modeling of the data then identified electrode delamination as an area of needed effort that was extended into FY20 milestones.

- **A reviewer asked why does the 15% Si / 73% Gr cell degrades to gave the same performance as a 70% silicon cell after approximately 200 cycles with an NMC cathode?**

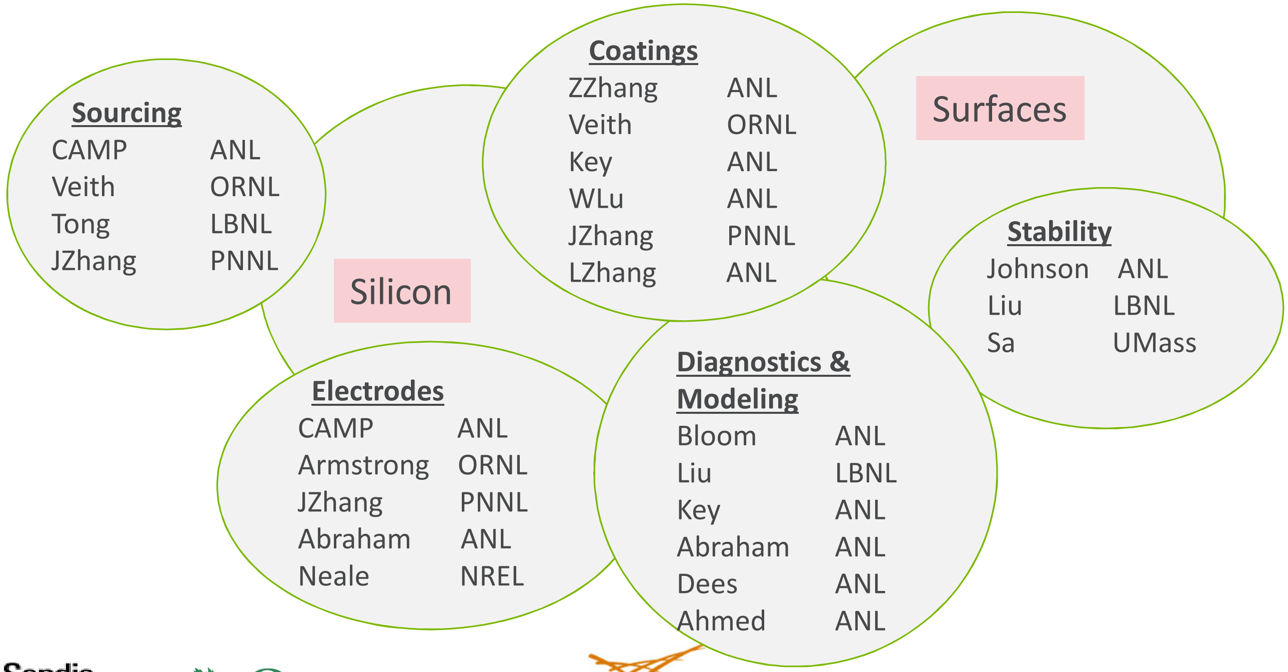
  The study was part of our full cell study and evaluating how the irreversible capacities associated with silicon gradually raise the operating voltage of the cathode by gradually shifting the operation plateaus to maintain the cell voltage. As the anode gradually loses lithium to side reactions, the cathode uses ‘deeper’ lithium to maintain voltage. This shift then gradually raises the anode voltage, and since the graphite insertion voltage is lower, the graphite slowly ceases participating in the cell reaction. Previously Johnson and Dose also showed that if against a lithium anode, the graphite capacity is maintained. The overlap of the capacities after 200 cycles is a consequence of the higher impedance of the higher content silicon cells evaluated. This is also being addressed as a CAMP milestone for FY20.

- **Several reviewers were concerned the program as described does not rule out components but continues in an exploratory manner**

  Initially, a baseline electrode system was organized by choosing the best available materials and components as determined by CAMP (ANL) evaluation studies. While evaluating other materials updating the baseline cell chemistry is evaluated on a regular basis. Earlier work identified a baseline silicon and we are on the third generation of silicon suppliers based on advances in morphology, processing, and coatings. We have moved from Gen2/FEC to Gen 2/FEC/additives for electrolytes while still evaluating the LHCE systems. Surface coatings have gone from simple silica natural passivation to functionalized organic layers, although due to scaling this has not yet displaced baseline Si from Paraclete. At the electrode level, in FY18 we went from silicon-graphite composites to high silicon after identifying several issues with surface binder chemistry that were detrimental to cycle life. As the effort advances, discoveries are made are evaluated and either added to the baseline or sent back for additional studies. Requirements for full cell evaluation with cell level goals have been added to the effort as Q4 end of year milestones.

COLLABORATION AND COORDINATION

The DeepDive effort is a multilab program designed to develop a better understanding of electrode structure and properties as they relate to cell performance. The effort is organized around various topics each with national lab participants, as well as select university collaborators. In addition to internal collaborations we are closely aligned, including joint milestones and projects, with the SEISTA silicon project, focused on early SEI formation and interfacial characterization.



Sourcing

CAMP	ANL
Veith	ORNL
Tong	LBNL
JZhang	PNNL

Silicon

Coatings

ZZhang	ANL
Veith	ORNL
Key	ANL
WLu	ANL
JZhang	PNNL
LZhang	ANL

Surfaces

Stability

Johnson	ANL
Liu	LBNL
Sa	UMass

Electrodes

CAMP	ANL
Armstrong	ORNL
JZhang	PNNL
Abraham	ANL
Neale	NREL

Diagnostics & Modeling

Bloom	ANL
Liu	LBNL
Key	ANL
Abraham	ANL
Dees	ANL
Ahmed	ANL

SEISTA Coordinated Collaborations include:

- Coatings,
- SEI Formation & Stability,
- Surface Characterization

REMAINING CHALLENGES AND BARRIERS

- The focus of the DeepDive effort has been on electrode level and cell level studies of silicon –based electrodes. We have efforts looking to understand the **surface/electrolyte reactivity** and their relationship to coulombic efficiency/cycle life, **SEI stability** in an electrochemical cell, **electrode formulations**, and other aspects of cell design and analysis
- We have highlighted the need for better slurry processing routes and identifying the role of additives and aging in slurry stability. We have multi-lab effort to identify and characterize these slurry issues and the variables that exist to influence them.
- Developing more in-depth cost Si-specific models in association with the BatPaC techno-economic modeling group to help guide long term research objectives that improve cycle life.
- SEI stability in systems that incorporate an alkaline metal salt (Zintl) additive shows significant improvement over baseline; on long term cycling it appears to diminish its effectiveness as the cation diffuses away from the surface. Methods to make the species less mobile would improve long term effectiveness.

FUTURE WORK

- Identify **soluble SEI spe**cies that are having a detrimental effect on cycle life. We've developed better analytical techniques to understand silicon SEI degradation and identify soluble species as a function of SOC. Synthesizing these materials and coordinating with the characterization teams identify their role in **the aging electrolyte**.

- Slurries constituents and the surface of silicon are important aspects of the final electrode product. For FY20/21 teams are coordinating the modification of the surface of the silicon particles to **create a more stable and functional connectivity** to enhance cycle life.

- As an oxophyllic element, the silicon surface evolves depending on its environment. This has a strong effect on reproducibility and evaluation. While we strive to use the same materials, we are working on **developing new scale up processes** for the baseline and functionalized silicon sample's used in the DeepDive effort.

SUMMARY

The EERE-VTO Deep Dive Silicon Project represents a cross-laboratory collaborative project that seeks to better understand the requirements to successfully develop a silicon-based electrode that meets DOE EERE VTO goals.

- Armstrong, Burdette-Trofimov, Zhang, Shi, and CAMP have identified several processing issues associated with silicon surface charge, functionality, surface reactivity, and passivation layer stability that are avenues for improvement in electrode quality and performance.

- Zhang, Key, and Tong have identified pathways to alter the way silicon interacts with the electrolyte by creating functionalized conformal coatings, inorganic surface Zintl gradients, or using novel methods to encase silicon in a lithium-ion conducting matrix. Improved performance has been noted and evaluated in conjunction with other team members. Preliminary calendar life studies have shown the parasitic side reactions at the heart of such tests are suppressed.

- Abraham, Fonseca Rodriguez, and Rodriguez Prado have identified a degradation mechanism based on the gradual loss of lithium that over-oxidizes the cathode. For silicon systems, the gradual shift also has a dramatic change in particle volume expansion as the lower voltage plateaus of silicon are not accessed, the volume expansion component of capacity fade is lowered.

CONTRIBUTORS AND ACKNOWLEDGMENT

Support for this work from Battery R&D, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – **Brian Cunningham, Steven Boyd, and David Howell**

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Research Facilities

- Post-Test Facility (PTF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- SLAC National Accelerator Laboratory
- Spallation Neutron Source (SNS-ORNL)
- Advanced Photon Source (APS-ANL)
- Battery Manufacturing Facility (BMF)
- Battery Abuse Testing Laboratory (BATLab)