U.S. DEPARTMENT OF ENERGY'S (DOE) VEHICLE TECHNOLOGIES OFFICE (VTO) 2020 ANNUAL MERIT REVIEW (AMR)

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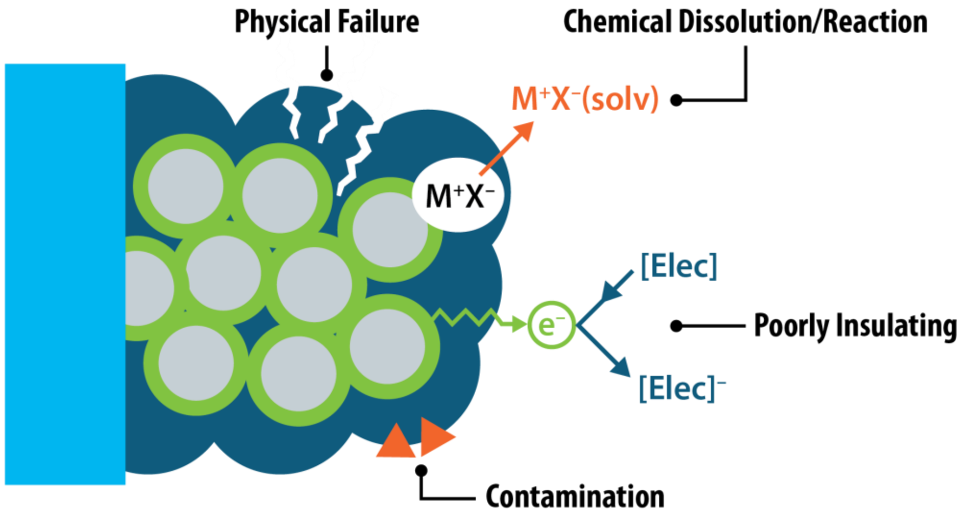
THE SILICON CONSORTIUM PROJECT: ELECTROCHEMISTRY OF SILICON ELECTRODES



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Poster ID: bat497
Presentation Date: 06/25/2021
Presentation Location: virtual

OVERVIEW

Timeline

- October 1st 2020 - September 30st 2025.
- Percent complete: 10%

Budget

- Funding for FY20: $7500K

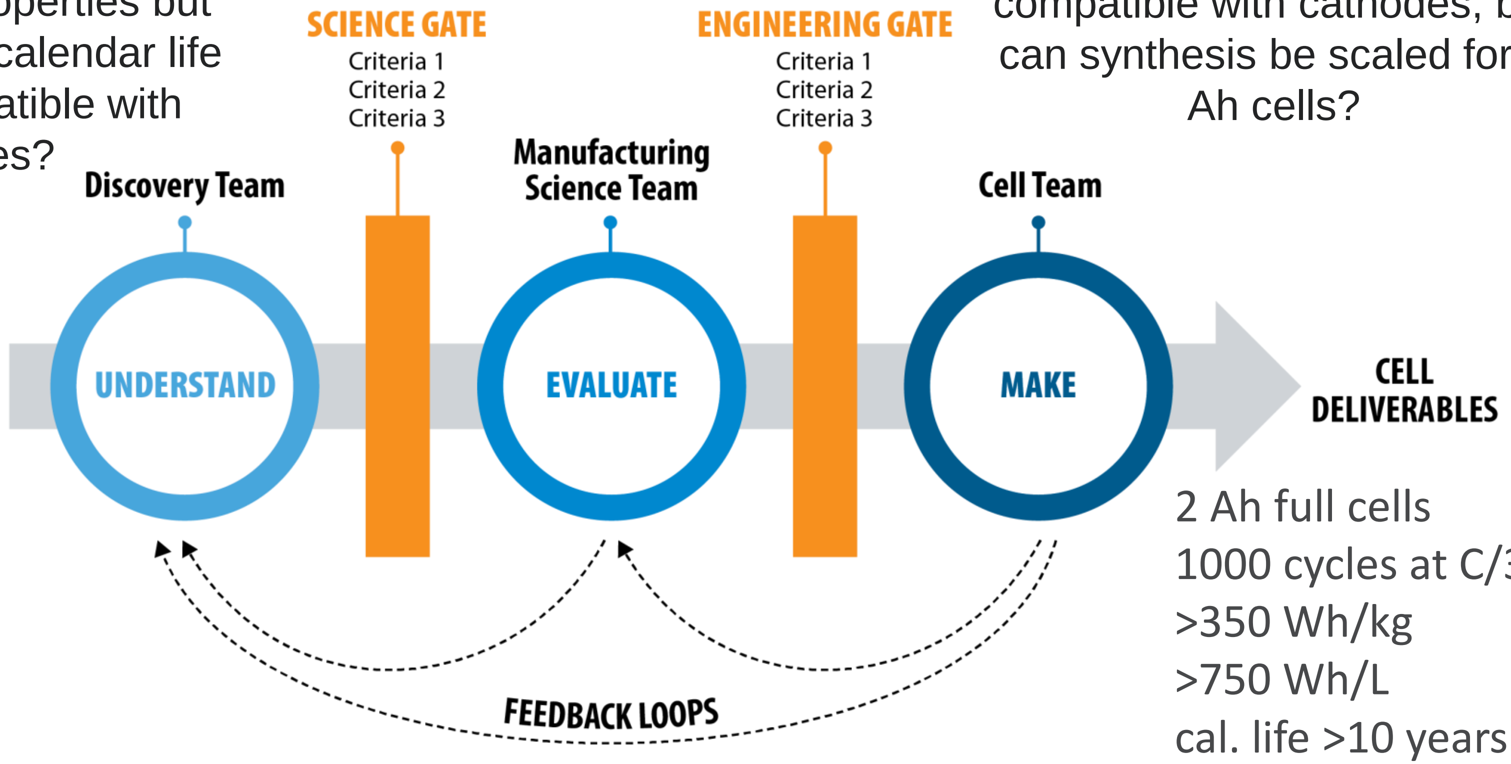
Electrochemistry Stability Thrust Focus

Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals. Specifically targeting the development of calendar life in silicon anode.
  - Cost, Performance and Safety

Example gate criteria:
Additive enables better SEI Li ion transport properties but does it improve calendar life and is it compatible with cathodes?

Example gate criteria:
Additive enables favorable SEI electrochemical stability, improves calendar life, is compatible with cathodes, but can synthesis be scaled for 2 Ah cells?



2 Ah full cells
1000 cycles at C/3
>350 Wh/kg
>750 Wh/L
cal. life >10 years

THRUST TASKS

Timeline

- October 1st 2020 - September 30st 2025.
- Percent complete: 10%

Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals. Specifically targeting the development of calendar life in silicon anode.
  - Cost, Performance and Safety

Budget

- Funding for FY20: $7500K

Tasks

- Advanced Characterization of the Si/SEI/Electrolyte Interface Function
- **Electrochemical Stability of the SEI**
- Mechanical Characterization of the SEI
- Next-Generation Materials discovery and development
- The Science of Manufacturing
- Cell manufacturing

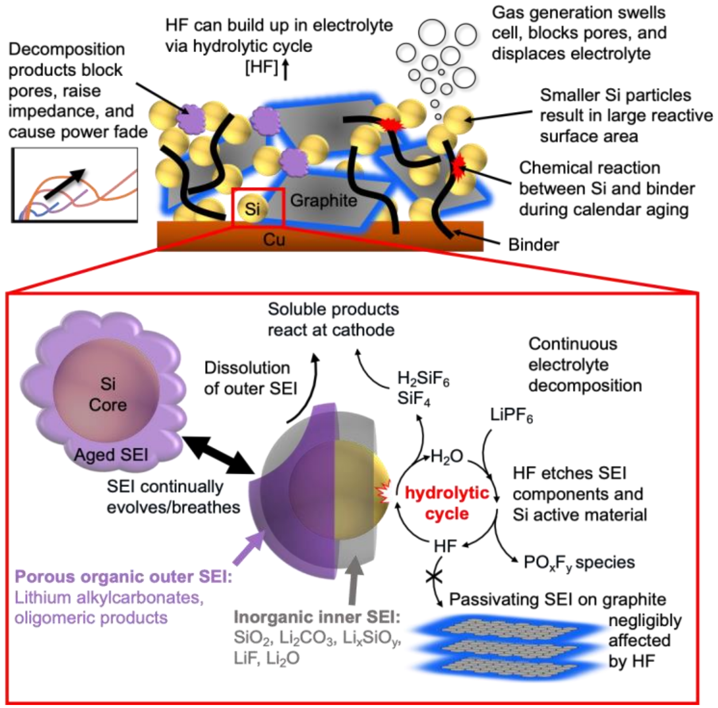
SEI = solid electrolyte interphase

MILESTONES

- Establish a Pre-lithiation protocol that can be utilized by all partners Q1 (complete)
- Go/no-go on HF etching of Silicon Oxide-silicon as viable route to silicon Q2 (complete)
- Go/No go on the Moire interferometry at as a method of probing the calendar life of the silicon SEI? Q3 (complete)
- Produce 20 grams of next generation silicon's with at least two different coatings, at least one of which exhibits enhanced calendar life over the baseline commercial silicon (NREL-centric) Q4
- **Advanced version of the calendar life protocols that quantifies calendar life in silicon-based anodes within 20% of the "real" calendar life predictions of calendar life. Q4**
- Synthesis and testing of 5 different metallic glasses with theoretical capacities > 1000 mAh/g Q4
- **Identify active cell components and cell designs to achieve stable calendar life electrode performance with a cell build demonstrating 300 cycles with <20% capacity fade. Q4**

ELECTROCHEMISTRY STABILITY THRUST OBJECTIVES

Thrust objective is to understand the electrochemical behavior of the Si SEI and collect electrochemical data to support calendar life estimates, protocols and provide parameter inputs for an electrochemical physics model of the SEI



Schematic of composite electrode processes that affect calendar life

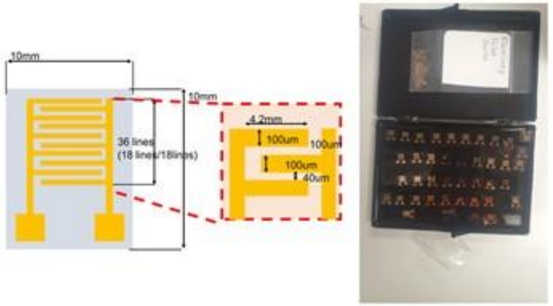
- **Objective 1**
  - Determine electrochemical protocols to project Si calendar life
  - Model the Si calendar life
- **Objective 2**
  - Use electrochemical detection of soluble components
- **Objective 3**
  - Measure Li ionic conductivity parameters
- **Objective 4**
  - Test Si SEI stability by (1) CV, (2) DPV, methods, and (3) temperatures and (4) voltages of V_{hold}
- **Objective 5**
  - Determine Si SEI porosity & integrity, and its electronic conductivity
- **Objective 6**
  - Develop an electrochemical transport model for Si calendar life

- Li_xSi chemical reactivity can affect electrochemical viability and robustness of the SEI
- Calendar life is likely impacted by electrode kinetics issues and current leakage (self-discharge)

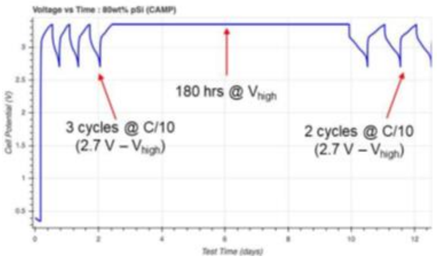
ELECTROCHEMISTRY STABILITY THRUST APPROACHES

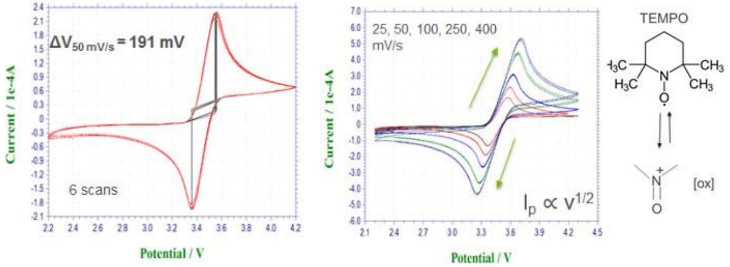
Thrust approach is to measure, quantitate and predict the (1) electrode kinetics of Si SEI formation, and (2) collect electrochemical data to support calendar life estimates, protocols and provide parameter inputs for an electrochemical physics model of the SEI

- **Approach 1**
  - Measure leakage current at 0.1 V vs. metallic Li equivalent; < 1.826*10^{-5} Amps/Ah Li-consumption for best Si calendar life
- **Approach 2**
  - Use IDE electrode arrays to determine kinetic parameters of Si electrode and measure soluble species
- **Approach 3**
  - Measure GITT properties of down-selected Si electrode materials -> Li ionic conductivity parameters
- **Approach 4**
  - Develop new electrochemical protocols & methods for testing Si SEI stability
- **Approach 5**
  - Redox probes and other methods to provide insight into intrinsic properties of Si SEI, such as porosity, and amorphicity, & its integrity and electronic conductivity



- measure i_{lim}
- SEI stability
- Provide transport numbers
- Li_xSi reactivity
  - side products





SI CALENDAR LIFE: TESTING PROTOCOLS

Cell building methods, and materials specified; capacity and lithium inventory maximized

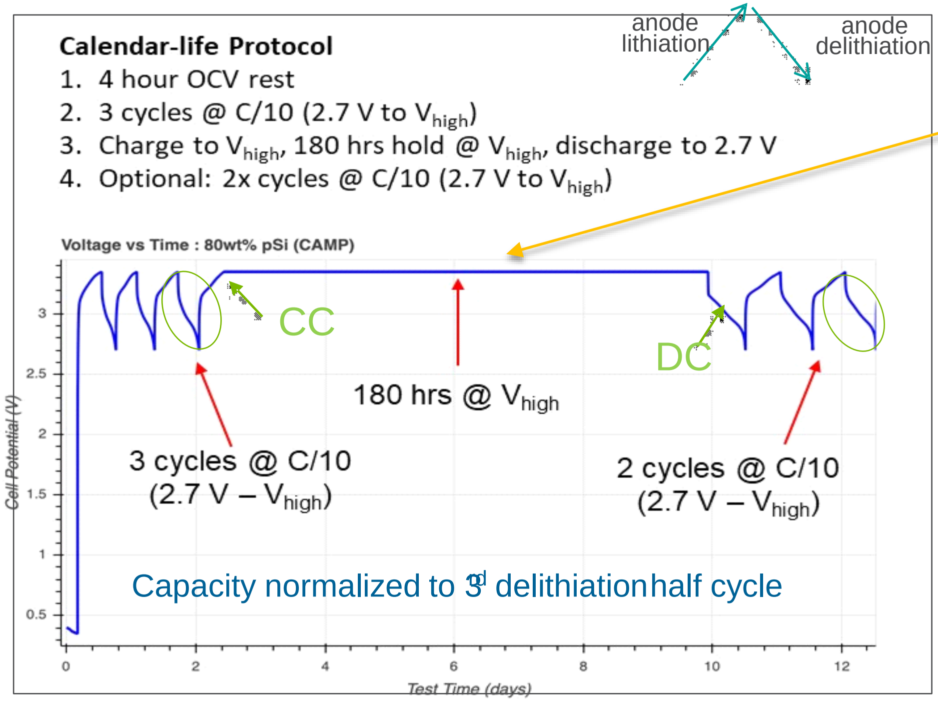
Si(C)/LFP full cell

Formation cycles

Charge to 3.35 V and hold 180 h

Discharge to 2.7 V (measure delithiation anode capacity)

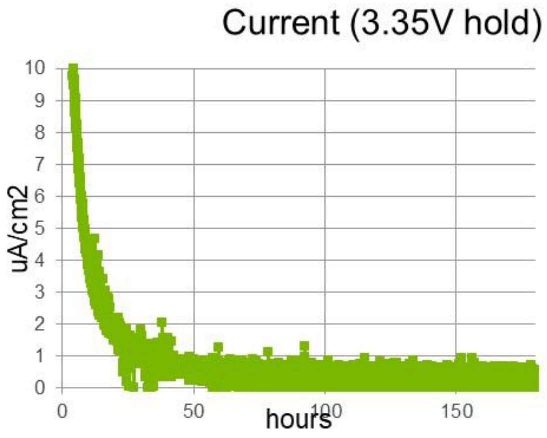
Conduct analysis (mean terminal current) by normalizing for capacity as A/Ah



METHOD:

- Large capacity from V_{hold} + 4th CC charge
- Capacity normalized to 3rd delithiation half cycle before hold
- Capacity normalized to 6th delithiation half cycle after hold

- Can calculate a Q_{rev} and Q_{irrev} and plot versus no. of days of V_{hold}



SI-CONTAINING SYSTEMS: CELL CALENDAR LIFE

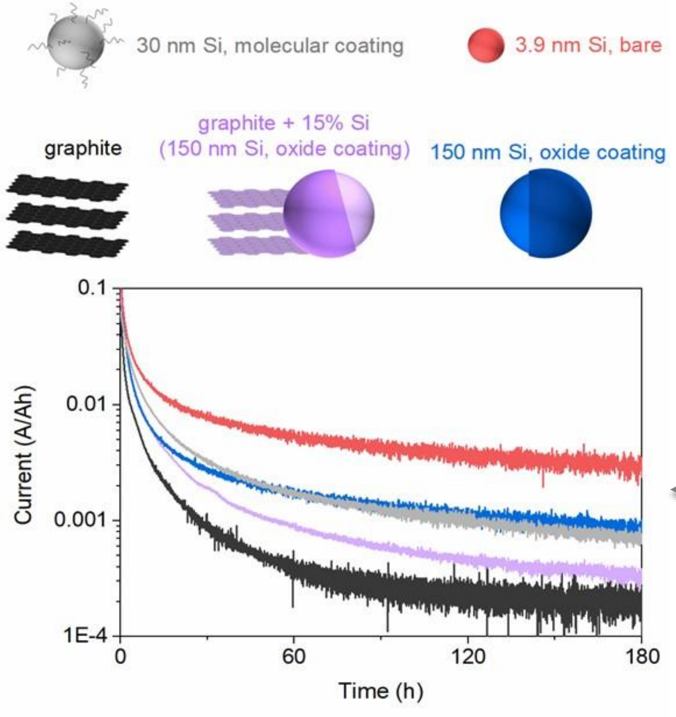
Different Si materials show different mean terminal currents: graphite system lowest, naturally

Cell Design

Table 1: Requirements of test and counter electrodes

Electrodes	Chemistry	Capacity	Diameter
Test Anode:	Si material	<1.3 mAh/cm^2	15 mm diameter (14 mm vs. Li)
Preferable cathode:	Lithium iron phosphate (LFP)	>2.5 mAh/cm^2	14 mm diameter
Acceptable counter electrode:	Lithium metal	>2.5 mAh/cm^2	15 mm diameter

Examples:



Example reporting:

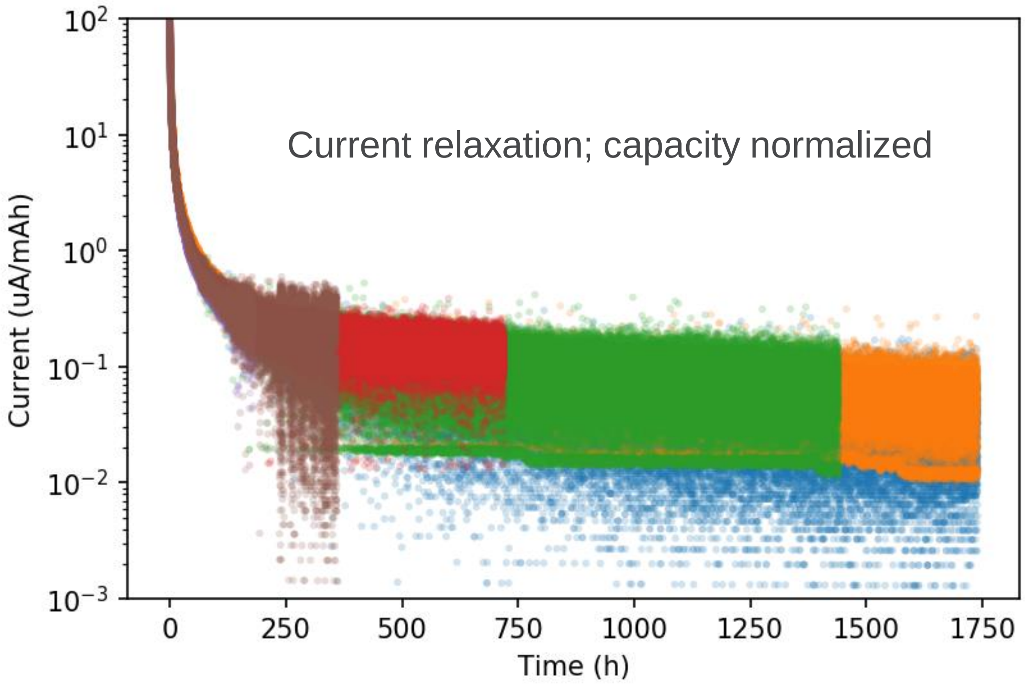
Graphite baseline electrode
1.17 mAh/cm^2
91.83 wt% Superior Graphite SLC1520P
2 wt% Timcal C45 carbon
6 wt% Kureha 9300 PVDF Binder
0.17 wt% Oxalic Acid
Electrolyte: 1.2 M $LiPF_6$ in ethylene-carbonate:ethyl-methyl-carbonate 3:7 + 10 wt% FEC
Mean terminal current = 0.23 mA/Ah

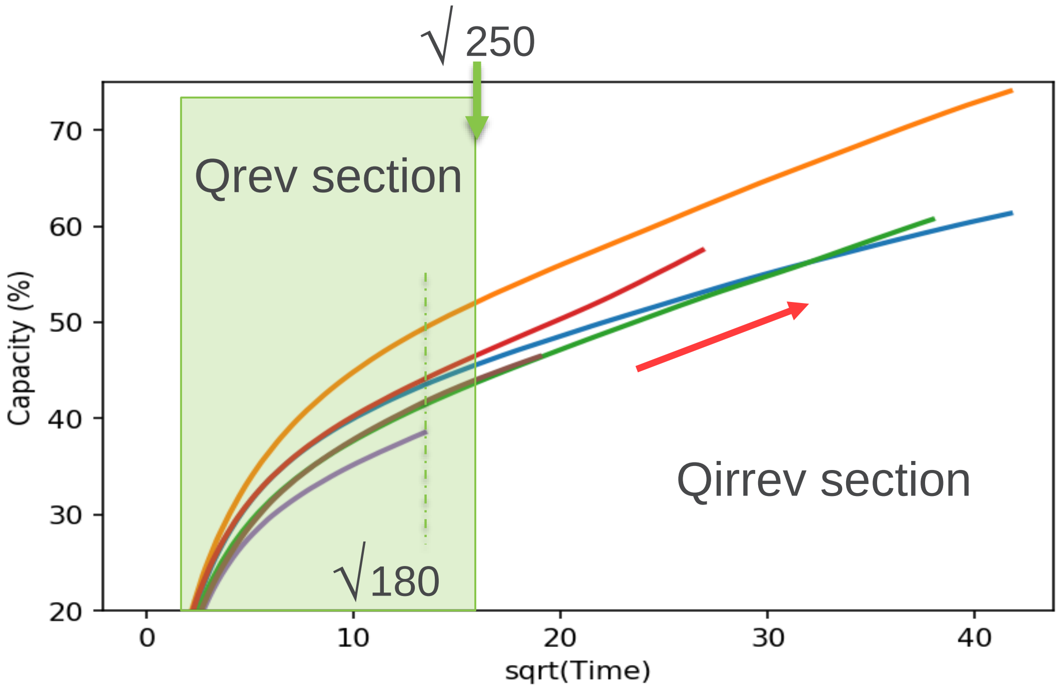
Nano Silicon
0.3 mAh/cm^2
20 wt% 3.9 nm diameter Si nanoparticles
65 wt% Timcal C65 carbon
15 wt% PAA Binder
Electrolyte: 1.2 M $LiPF_6$ in ethylene-carbonate:ethyl-methyl-carbonate 3:7 + 10 wt% FEC
Mean terminal current = 2.62 mA/Ah

Mean terminal
Currents -> lead to qualitative assessment of Si SEI reactivity

LONG TERM HOLD – VALIDATION TO A TIME DEPENDENCE FUNCTION

15% Si-Gr (A019), LFP, GenF



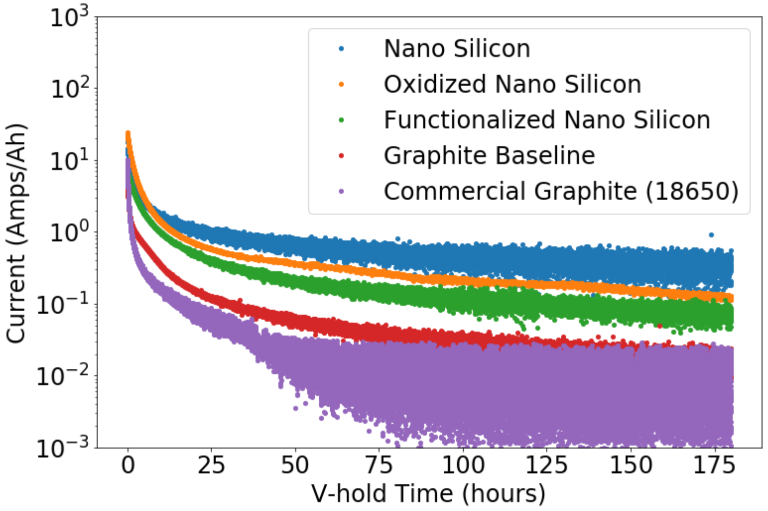


$$Q_{hold}(t) = Q_{irrev}(t) + Q_{rev}(t)$$

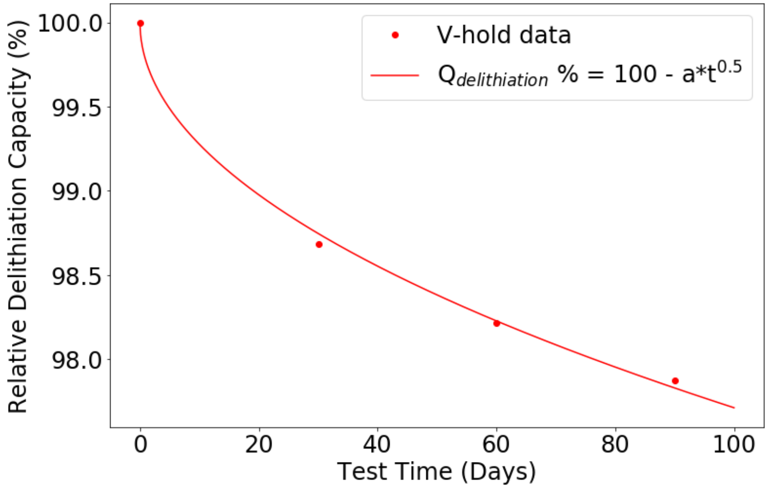
- Qrev very slow for Si (slow equilibration)

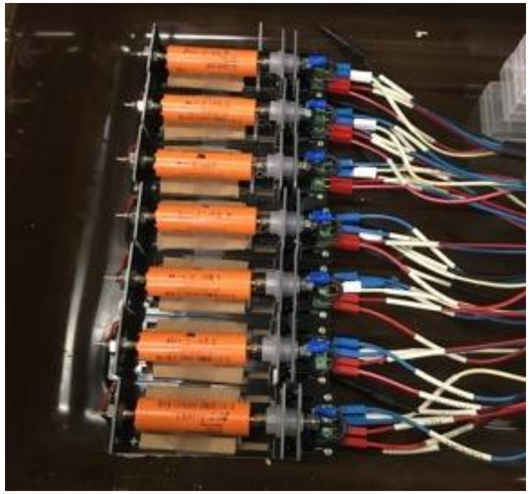
- Qirrev is reasonable accordance with $t^{0.5}$ dependence
- Must fit first 180 h
- Scatter in data – coin cell is an issue -> moving to pouch cells for V_{hold} measurements

ACCELERATED CALENDAR LIFETIME PROTOCOL



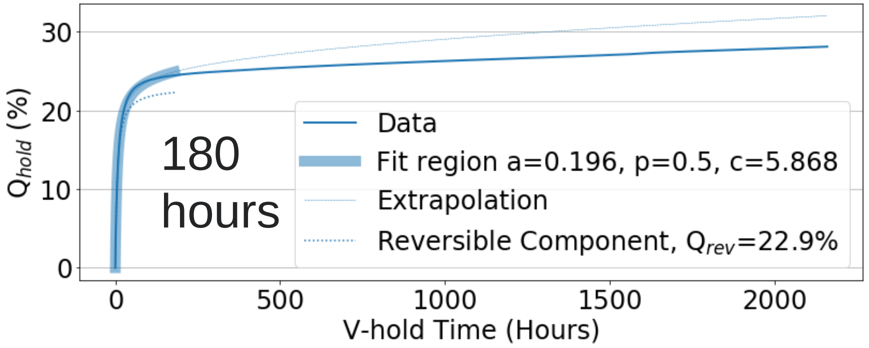
Voltage hold currents as a qualitative assessment of calendar aging rates

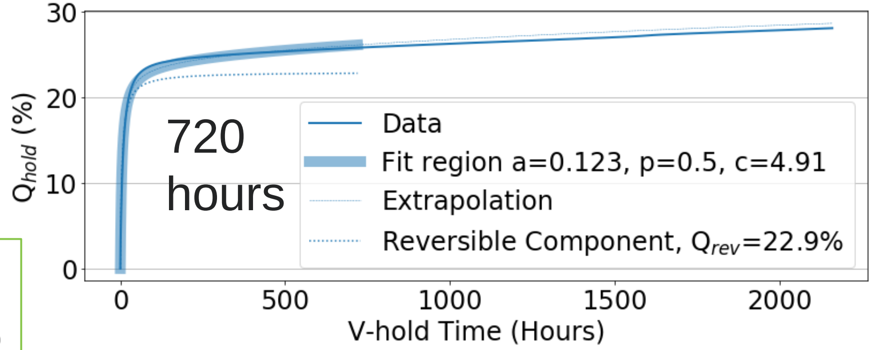




Voltage holds of commercial cells allow us to develop functional forms for quantitative calendar lifetime modeling

Long voltage holds allows us to determine the minimum experiment length to accurately predict future calendar aging behavior





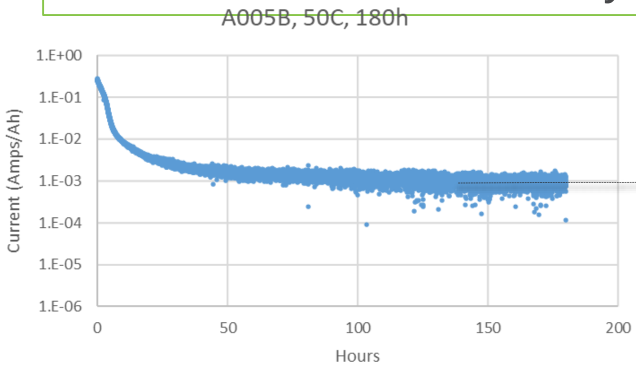
$$Q_{hold}(t) = at^{p} + \frac{Q_{rev}(c + t_{final})t}{t_{final}(c + t)}$$

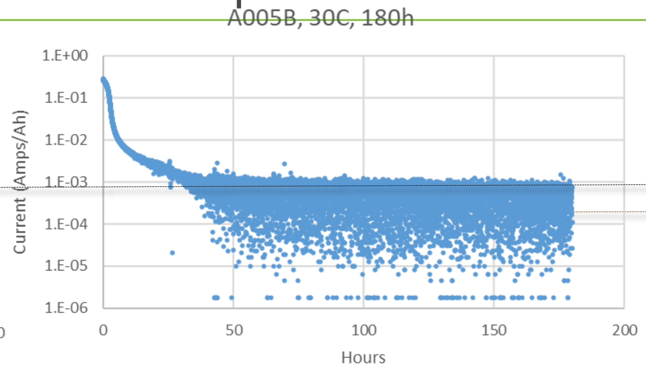
CALENDAR LIFETIME PROTOCOL – VARIABLE TEMPERATURES AND VOLTAGES

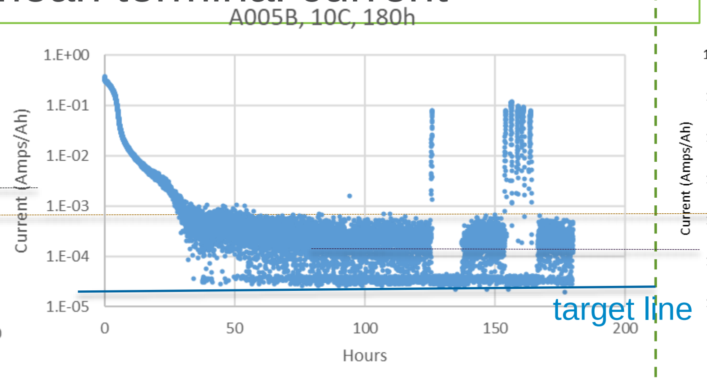
Cell: **Graphite vs LFP** (A005B vs LN3237-59-7), 10wt% FEC/Gen2
Protocol: C/10x3 then hold at 3.335 or 3.35 V for 180 h
Conclusion: 3.335V-hold would not push into 3rd plateau of graphite at all temperatures (3.35V would)

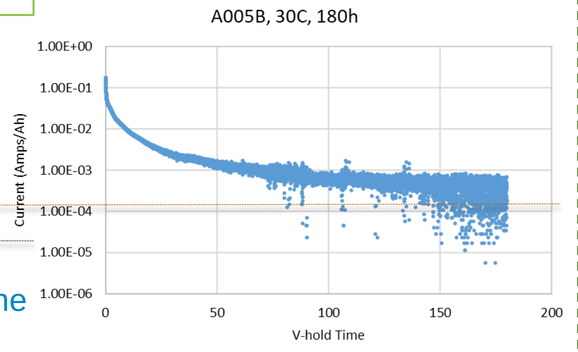
@3.335 V Voltage-Hold is more reliable measurement for predicting life stability of anode SEI. Better stability at low temperatures – lower mean terminal current

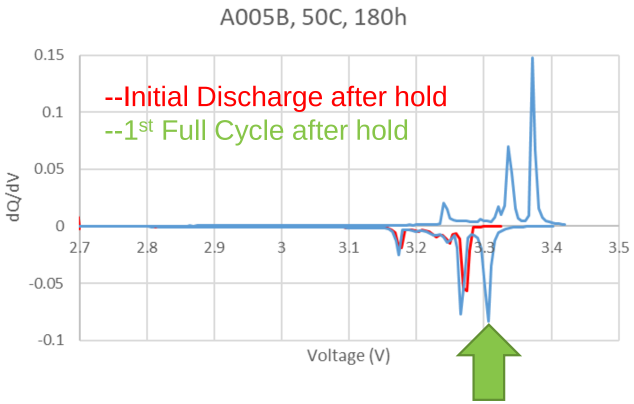
@3.35 V Voltage-Hold

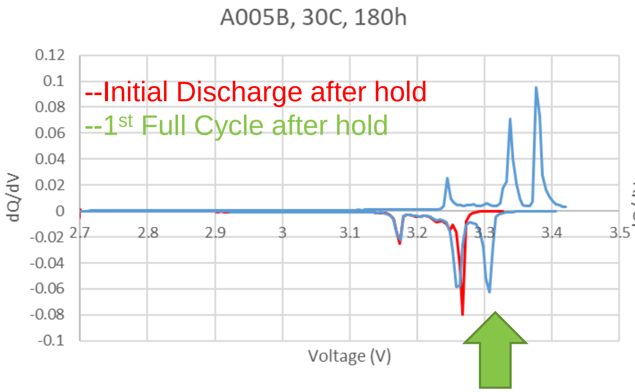


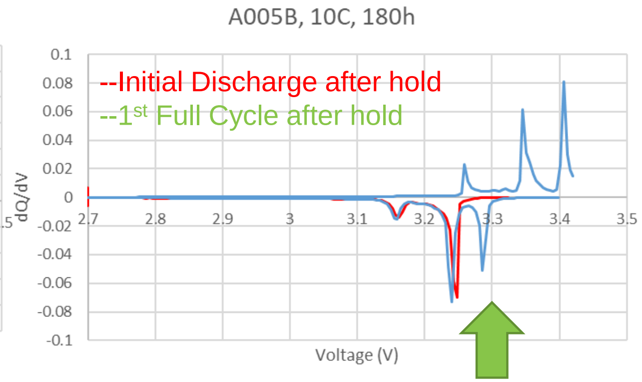




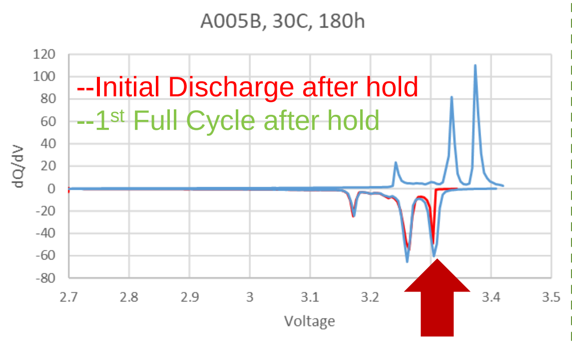








3rd Plateau not seen for initial discharge

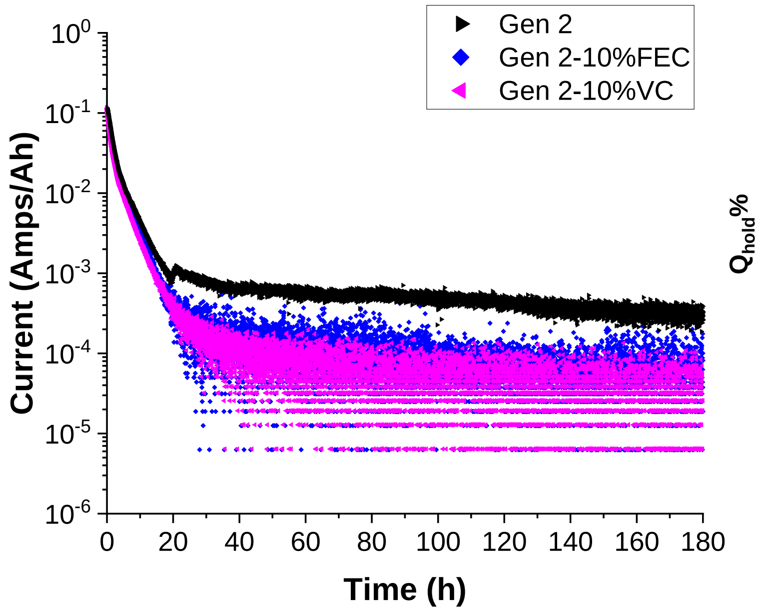


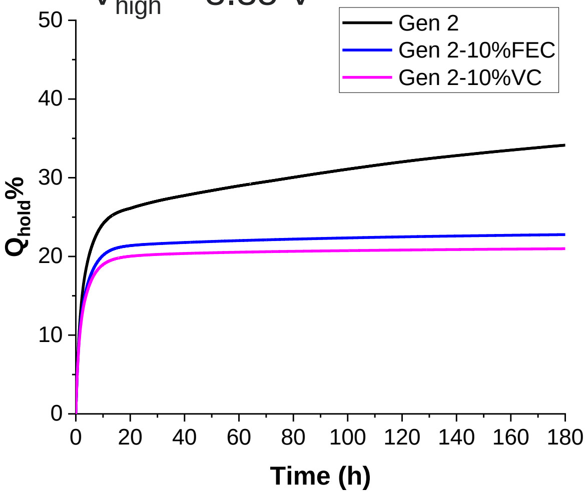
3rd Plateau seen for initial discharge

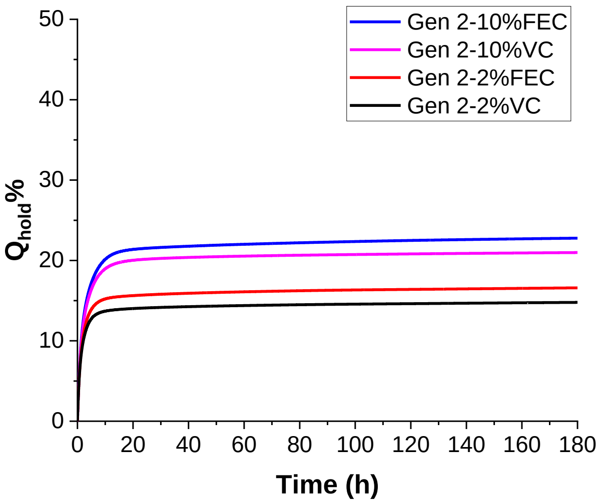
IDENTIFICATION OF ROLES OF ADDITIVES TOWARDS IMPROVED CALENDAR LIFE

Standard calendar-life protocol using Si anode and LFP cathode

V_{high} = 3.35 V







Electrolyte	Mean Terminal Current (Amps/Ah)	Q_{hold} (%)	CE (%)
Gen 2	2.97E-4	34.1	83.7
Gen 2-10%FEC	4.77E-5	22.8	90.3
Gen 2-10%VC	2.40E-5	20.9	89.8

The lower mean terminal current and accumulated capacity during holding (Q_{hold}) indicates VC may work better than FEC is Si SEI stabilizer.

Since Si lithiation may occur during the holding, the CE values (delithiation/lithiation + holding) is a another good indicator for comparing calendar life, and both FEC and VC outperform Gen 2.

Lower the concentration from 10% to 2% (FEC or VC) affords lower mean terminal current and Q_{hold}, benefiting calendar life performance and implying a optimal concentration may be needed to achieve the balance between cycle life and calendar life.

Cell	Mean Terminal Current (Amps/Ah)	Q_{hold} (%)	CE (%)
Gen 2-10%FEC	4.77E-5	22.8	90.3
Gen 2-10%VC	2.40E-5	20.9	89.8
Gen 2-2%FEC	3.12E-5	16.6	90.3
Gen 2-2%VC	2.74E-5	14.8	91.9

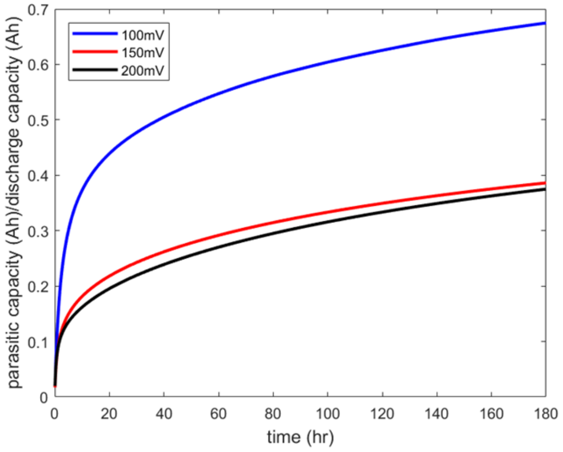
INTEGRATED MODELING OF SEI REACTIONS ON SILICON ANODE

Experimental voltage hold calendar life data shows high capacity at low voltage holds and detailed SEI modeling can help unravel this.

An atomistic-informed continuum-scale multiphase, multispecies mechano-electrochemistry model is developed

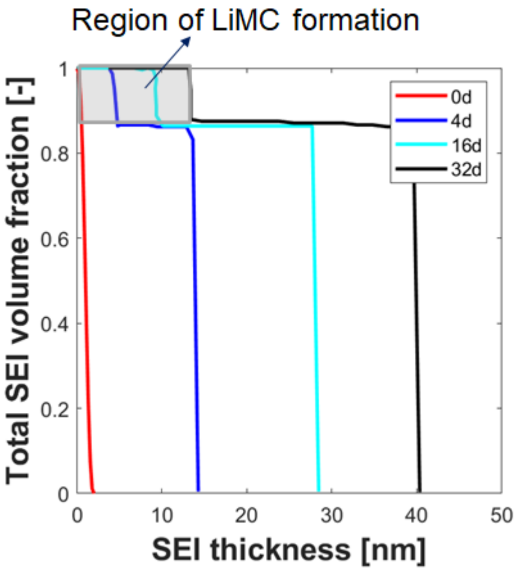
- Consider electrochemical and chemical reactions
- Resolve species transport to capture porous bi-layer SEI growth and compositional variations
- Resolve strong potential gradients in the solid SEI to determine solvent decomposition in the liquid electrolyte

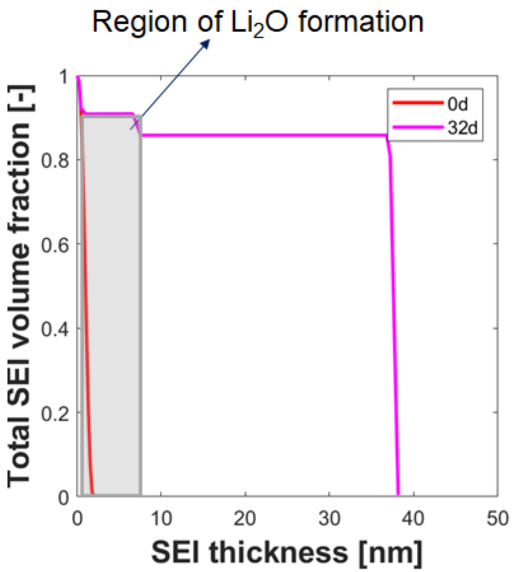
Co-solvent decomposition, and solid phase conversion reactions alongside primary solvent decomposition leads to the formation of bi-layer SEI with thickness evolution following square root of time dependence.



$$2EC + 2\cdot(Li^+ + e^-) \rightarrow Li_2EDC + R$$

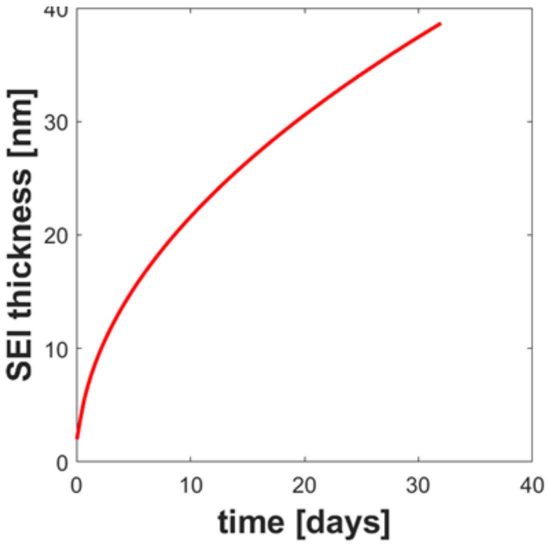
$$DMC + Li^+ + e^- \rightarrow LiMC + R$$





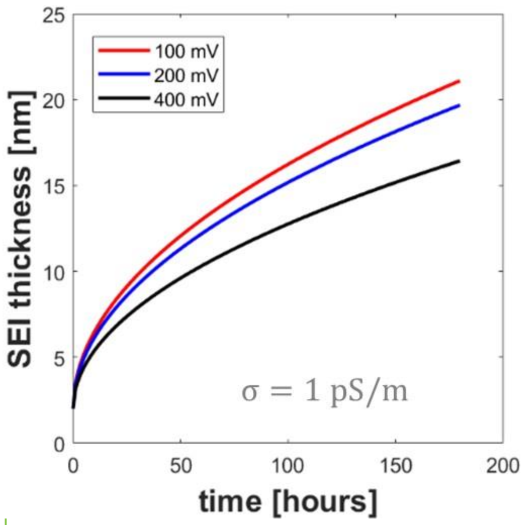
$$2EC + 2\cdot(Li^+ + e^-) \rightarrow Li_2EDC + R$$

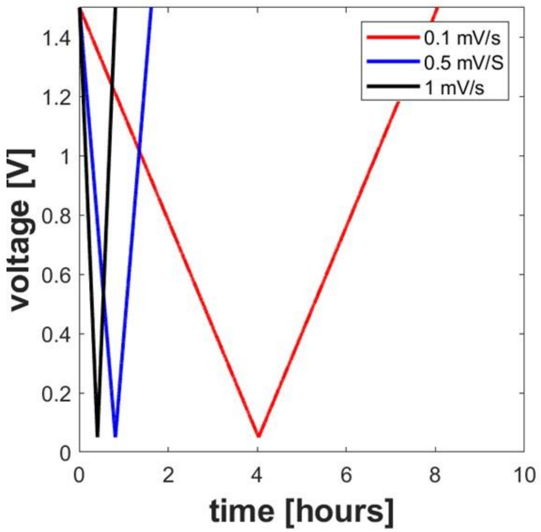
$$0.1Li_2EDC + Li^+ + e^- \rightarrow 0.6Li_2O + 0.4C$$

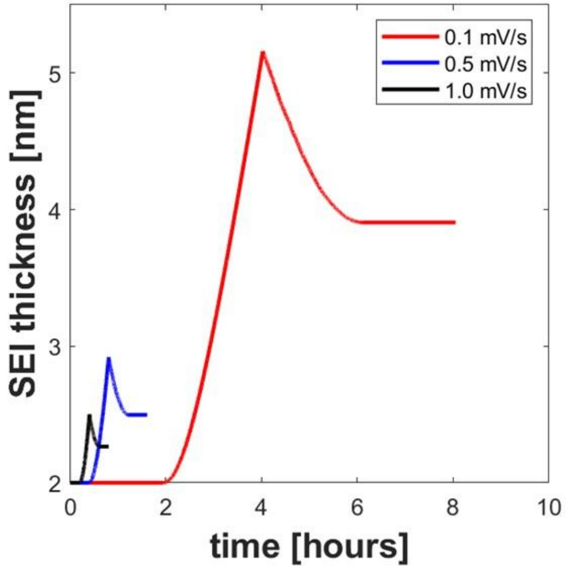


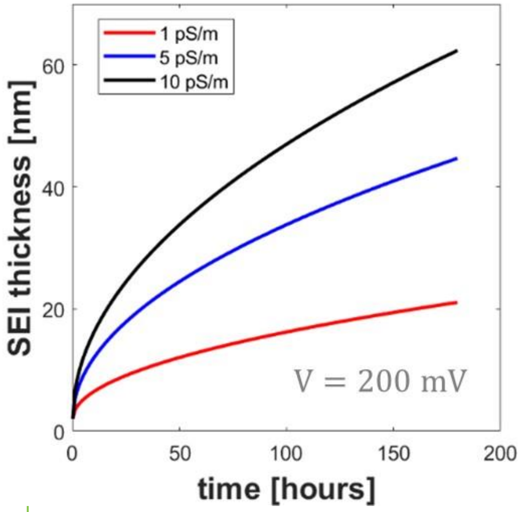
SEI ELECTRONIC CONDUCTIVITY AFFECTS CALENDAR LIFETIME

- Low voltage holds (high SOC of Si) result in thicker SEI formation due to the high driving force for Li_2EDC formation.
- Higher electronic conductivity of the SEI exacerbates the electronic current and drives faster SEI formation generating a thicker SEI.
- Voltage scan between 0.05 V and 1.5 V at different scan rates of 0.1, 0.5, and 1 mV/s are also performed.









- SEI thickness increases due to the reduction of electrolyte species to solid phase components.
- Allowing for reversible solid phase conversion reactions (Li_2EDC→Li_2CO_3 , Li_2EDC→Li_2CO_3 → Li_2O and vice versa) can explain observation of breathing seen in the SEI on silicon.

CONCLUSIONS AND NEXT STEPS

Conclusions:

- Si calendar life can be assessed via electrochemical methods utilizing V_{hold} for estimates of life
  - Mean terminal current is qualitative assessment of Si calendar life; higher current, lower Si calendar life
  - SEI electronic conductivity affects Si calendar life; more electronic current, then more SEI
- 30% of Si particle volume is SEI material based on synchrotron XRD results
- VC shows lower mean terminal current value than FEC; could have impact on Si calendar life
- 3-electrode current leakage study: LFP/Si cell shows better behavior than Si/LCO in mean terminal current level.

Next steps:

- Provide electrode parameters for electrochemical physics modeling
- Initiate semi-quantitative numerical modeling of Si calendar life projection from V_{hold}
- Complete IDE fabrication
- Conduct redox probe molecule assessment of SEI morphology
- Quantify mass fractions of crystalline SEI species for different stages during formation cycling.
- Work with the Mechanical team to measure how temperature affects the SEI species and compare results to calorimetry findings.
- Use more three-electrode cell designs to determine Si SEI electrochemical degradation vs. cathode behavior

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