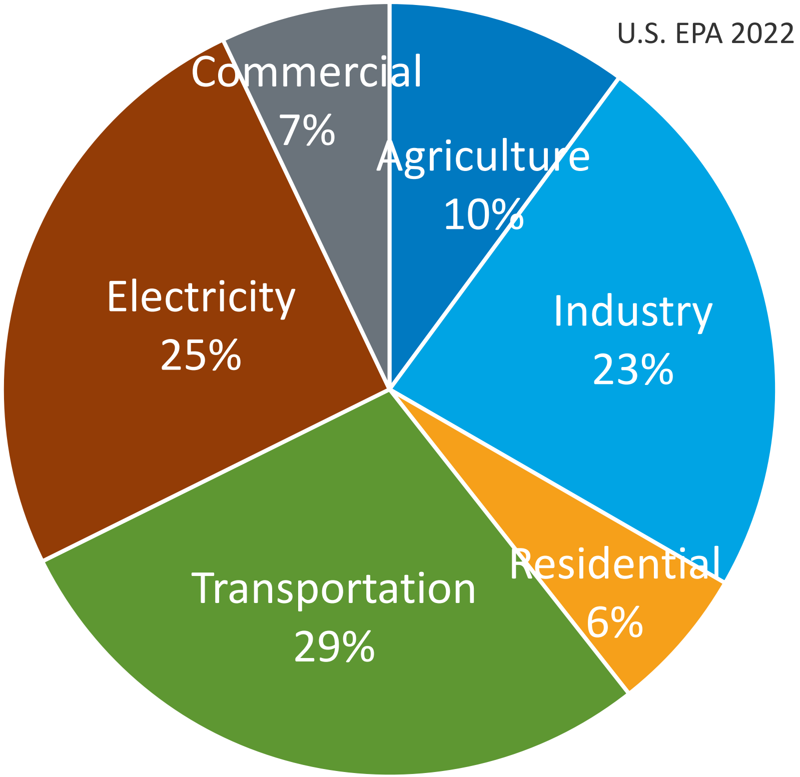
Using the Principals of Electrochemistry to Understand and Overcome the Complicated Degradation Mechanisms of Silicon Anodes in Lithium-Ion Batteries.

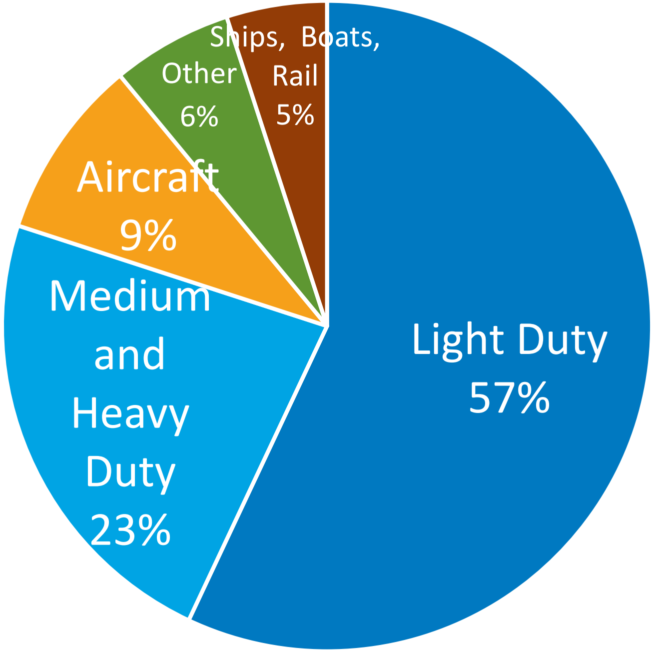
Mike Carroll
6/4/2024
2024 GRC Inorganic Chemistry

Decarbonization

US GHG emissions by sector

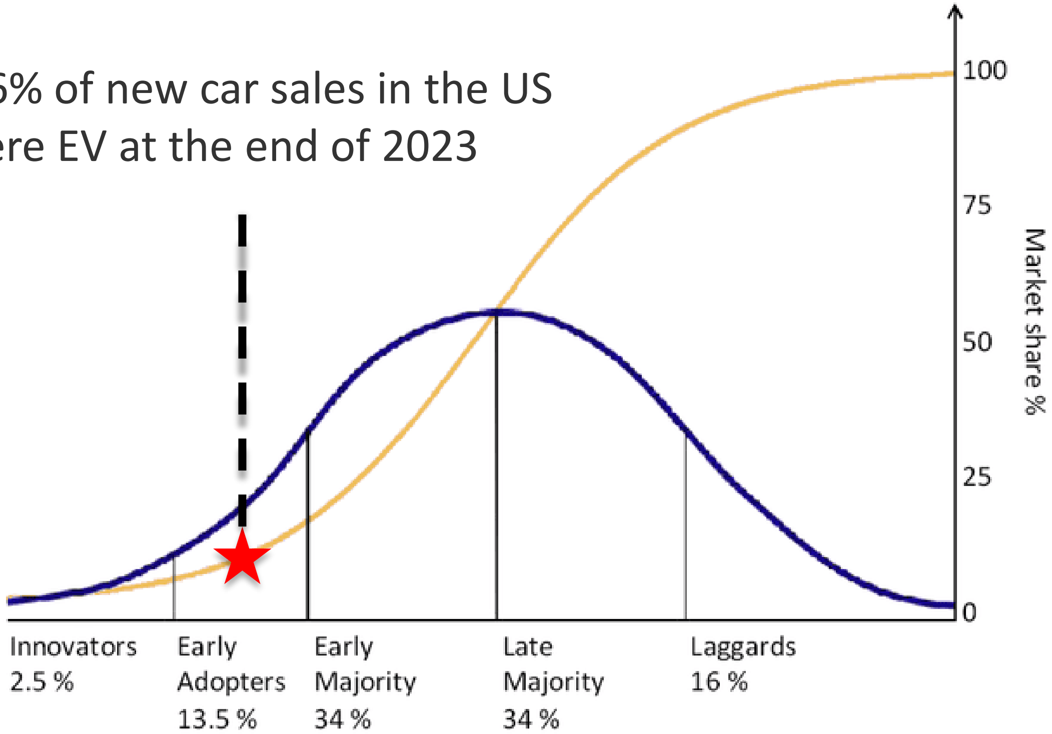


US transportation emissions



EV Adoption

7.6% of new car sales in the US were EV at the end of 2023

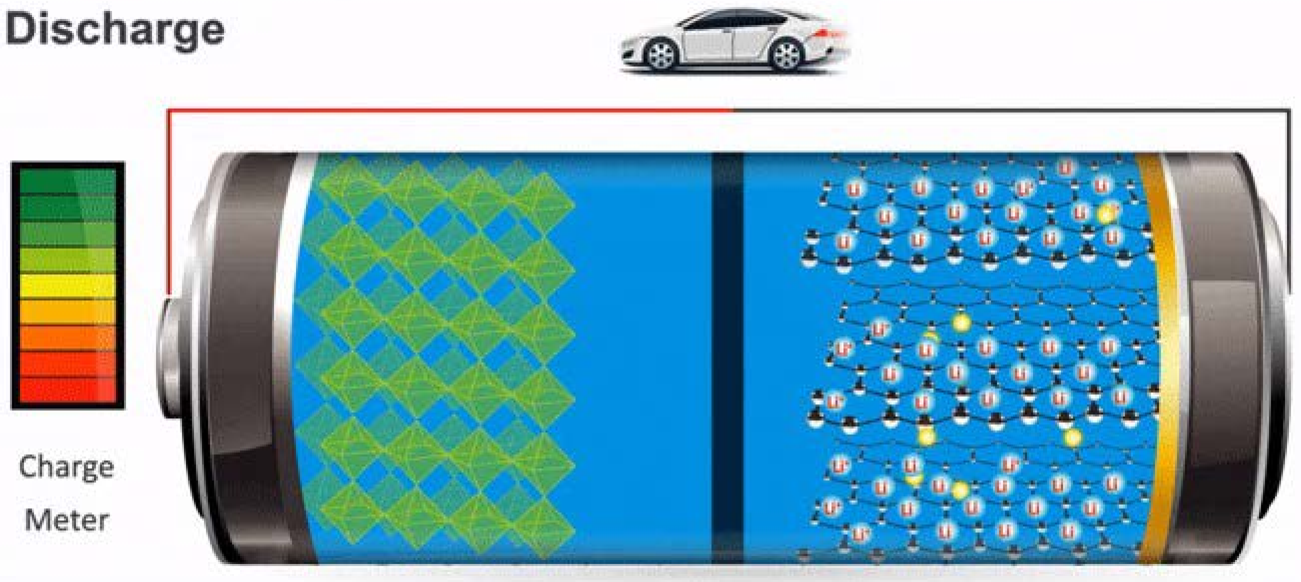


Major headwinds for EVs:

(1) Range anxiety
(2) Too expensive
(3) Developing charging infrastructure

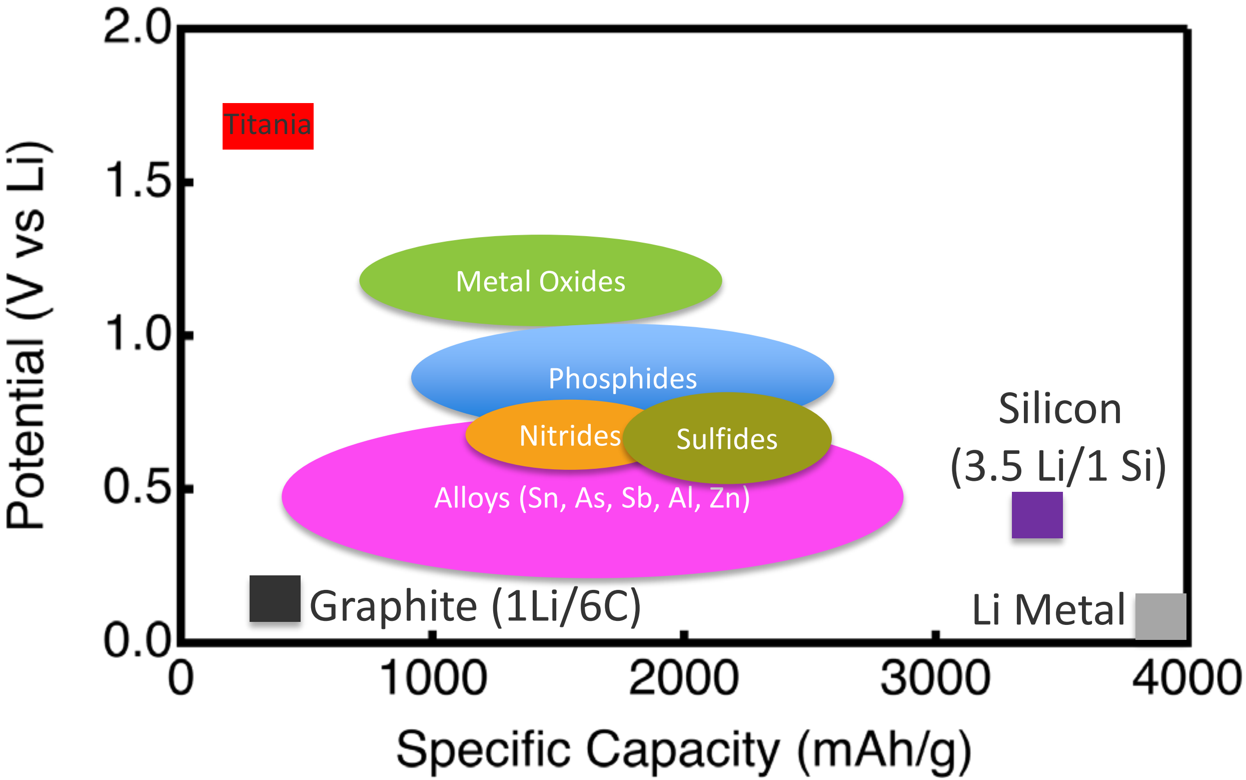
Battery technology is the bottleneck

How Lithium-ion Batteries Work

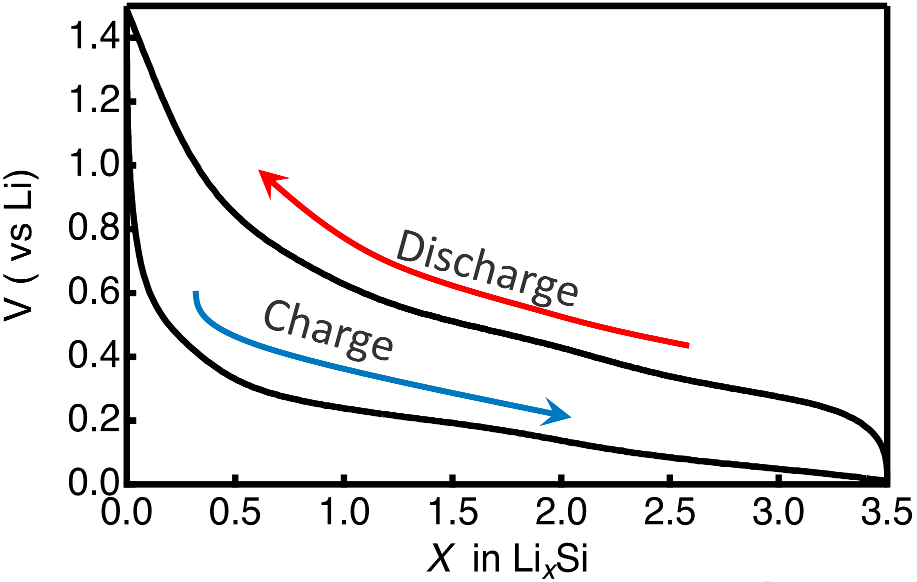


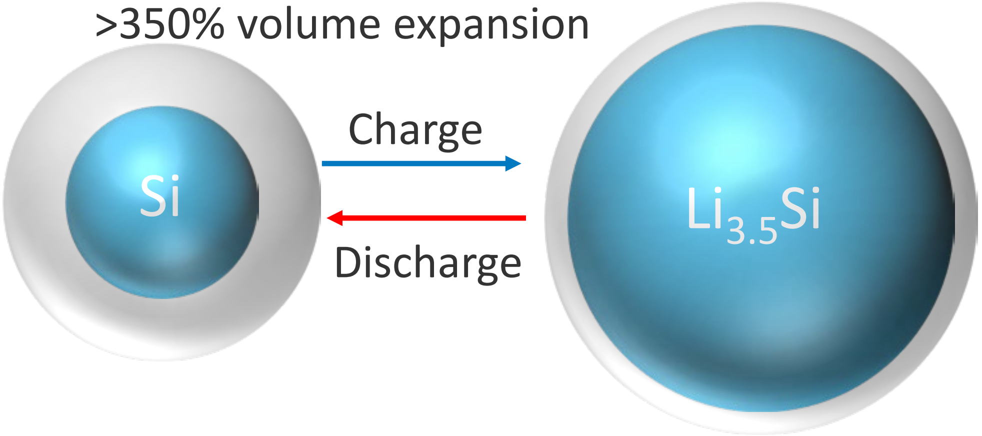
U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

Anode Active Materials

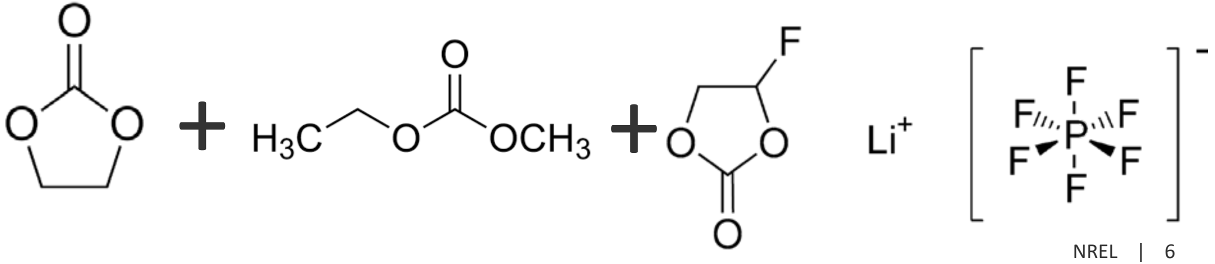


Cycling Silicon Under Battery Operation

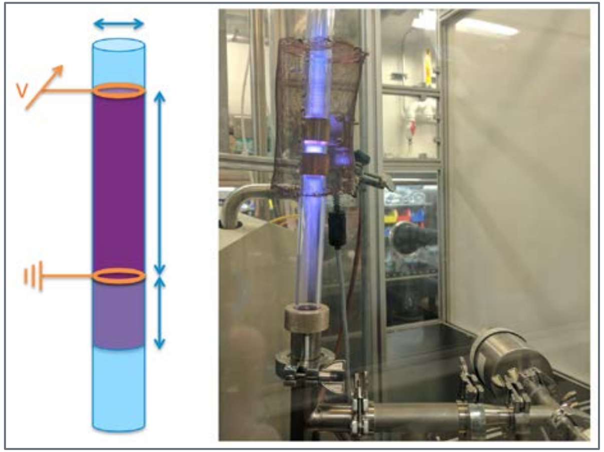




Solid Electrolyte Interphase



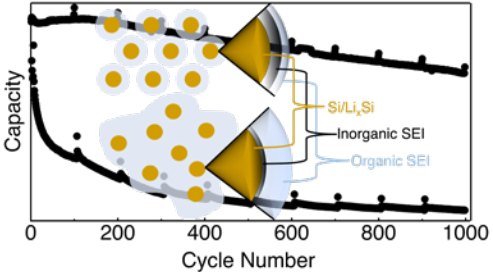
Plasma Enhanced Chemical Vapor Deposition Si NPs



-PECVD synthesis enables precise control over silicon size, surface chemistry, and composition

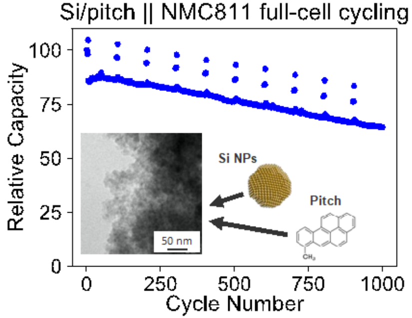
-Surfaces are terminated with SiH_x functional groups

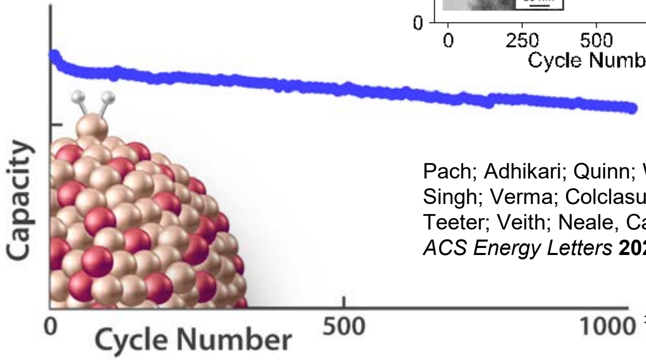
-Radical chemistry to functionalize the silicon surface



Schulze; Urias; Dutta; Huey; Coyle; Teeter; Doeren; Tremolet de Villers; Han; Neale; Carroll: *J. Mater. Chem. A.* **2023.**

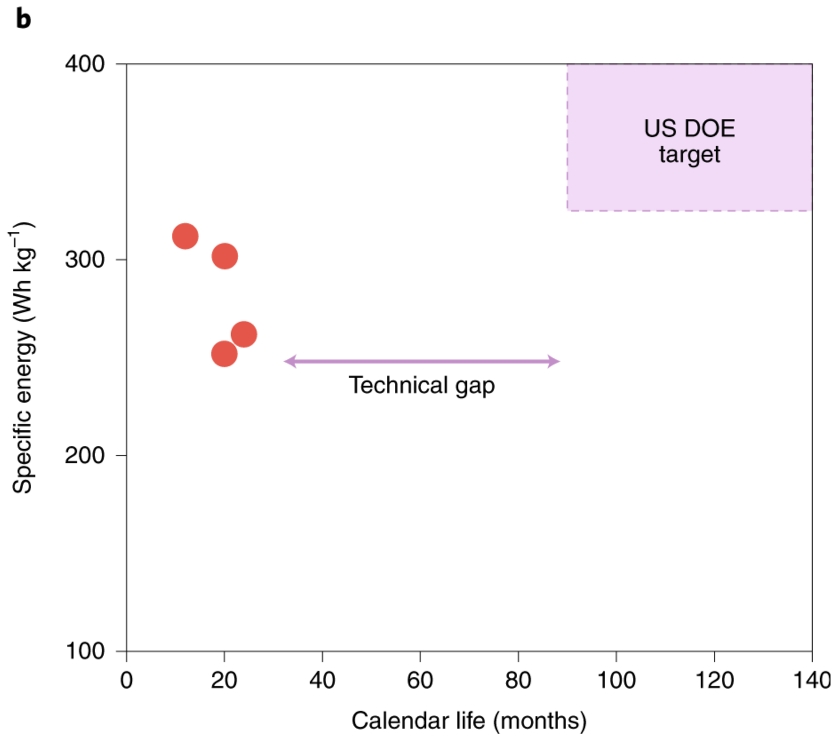
Schulze.; Fink; Palmer; Carroll; Dutta; Zwiefel; Engtrakul; Han; Neale, Tremolet de Villers: *Batteries and Supercaps,* **2023.**

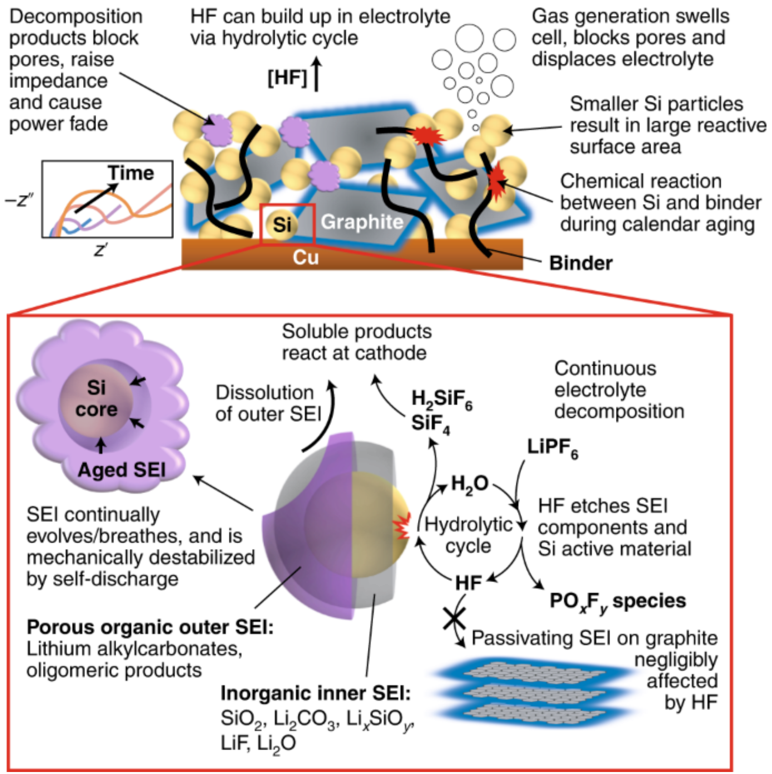




Pach; Adhikari; Quinn; Wang; Singh; Verma; Colclasure; Kim; Teeter; Veith; Neale, Carroll: *ACS Energy Letters* **2024**

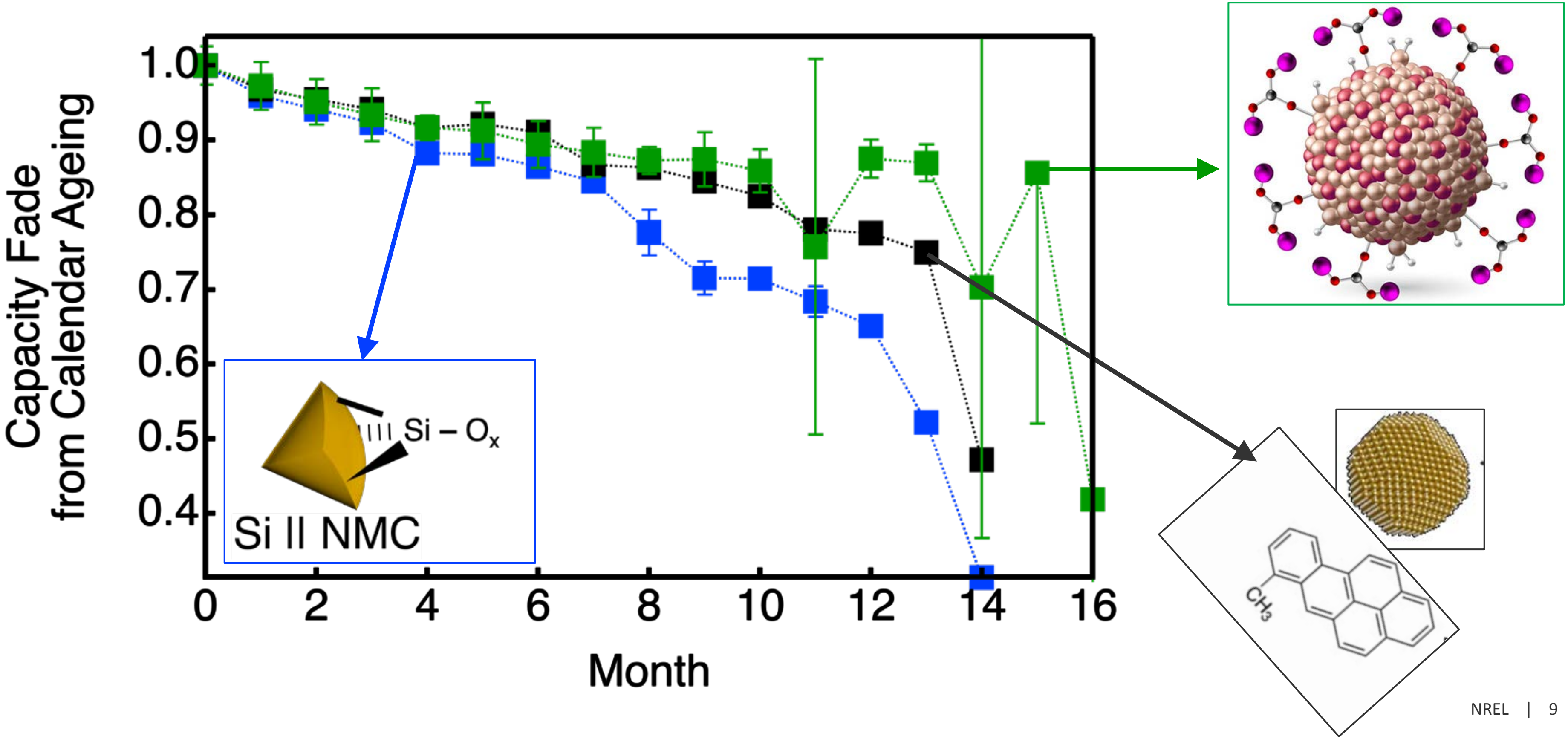
Calendar Life in Silicon Containing Anodes



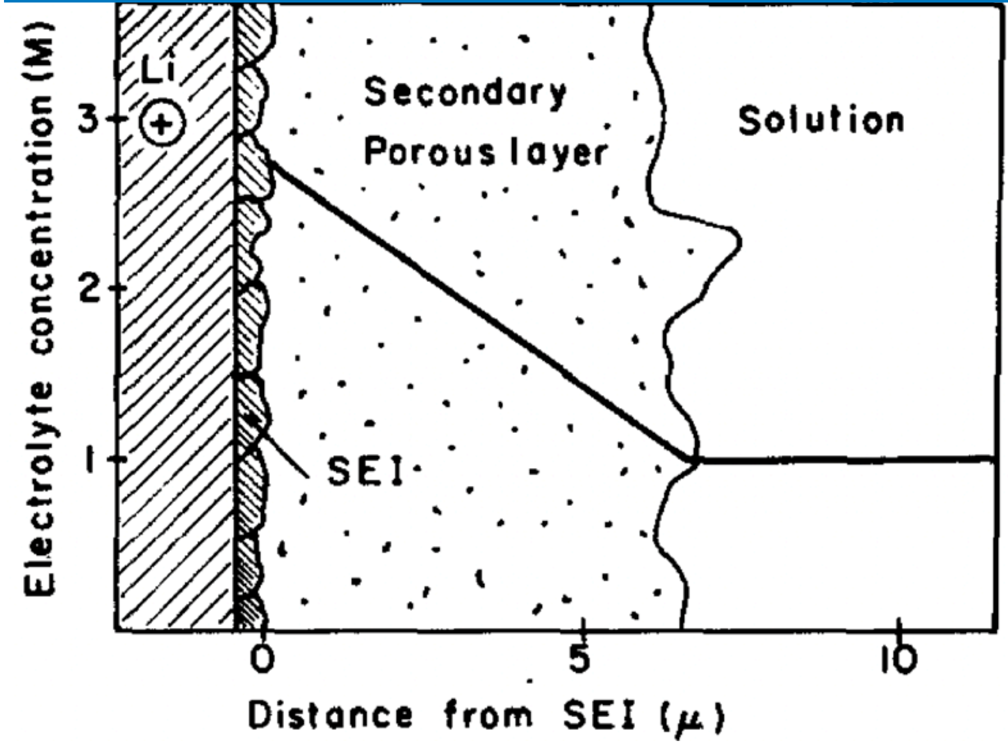


McBrayer; Rodrigues; Schulz; Abraha; Apblett; Bloom; Carroll; Colclasure; Fang; Harrison; Liu; Minteer; Neale; Veith; Johnson; Vaughey; Burrell; Cunningham: *Nature Energy* **2021**

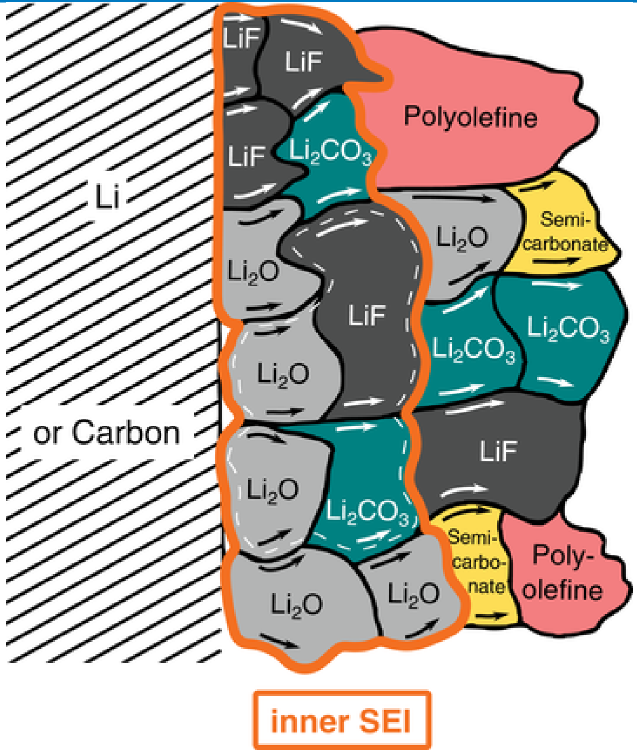
Calendar Life Issues in Silicon Containing Anodes



The SEI Model

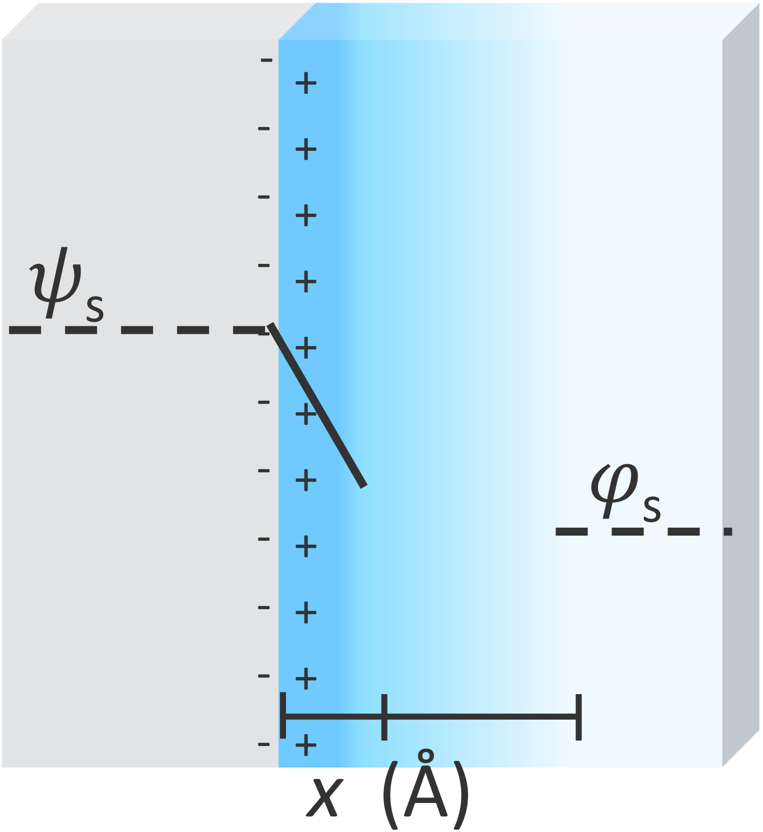


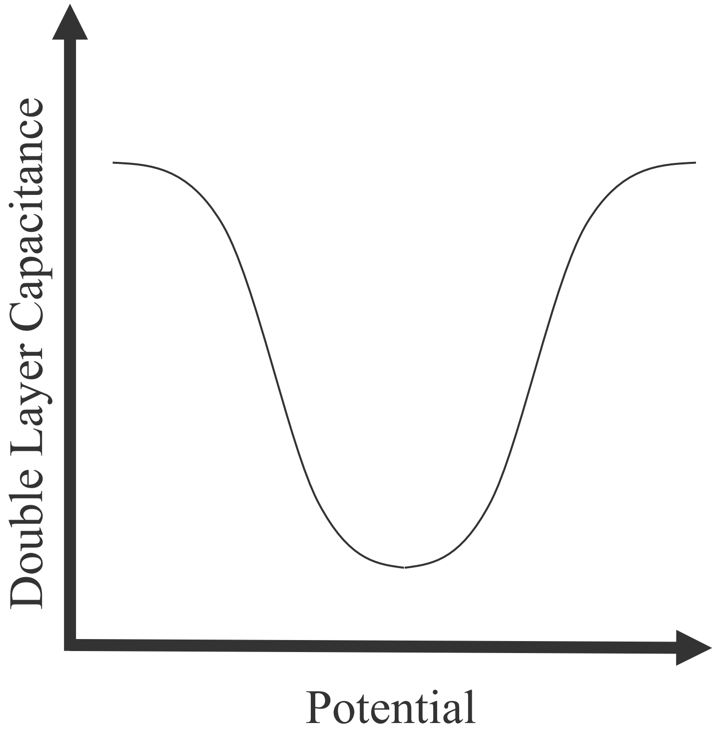
Emanuel Peled, *JPS* **1982**



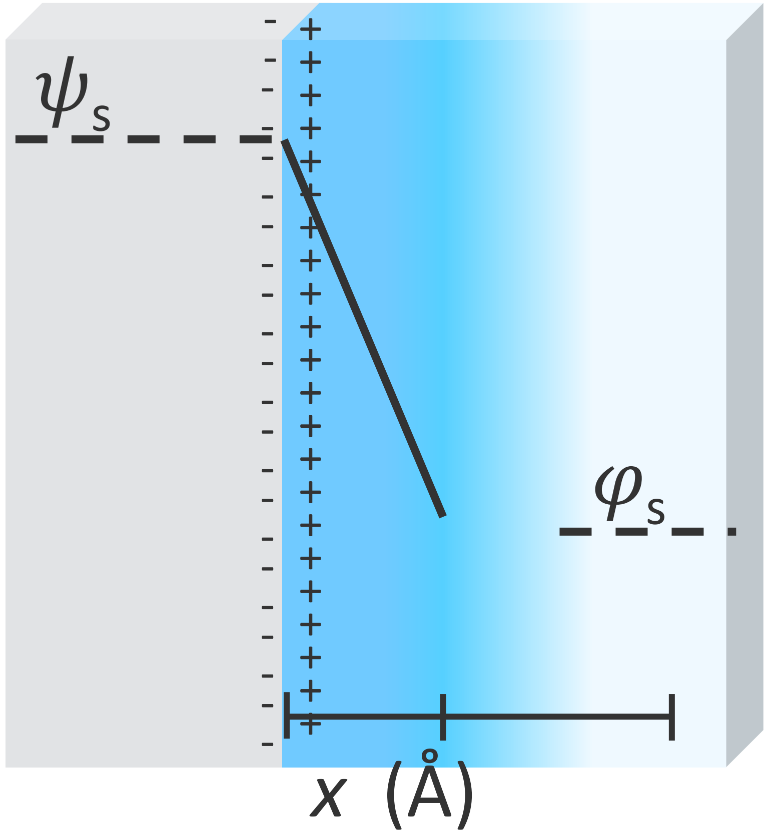
Krauss, et al., *Adv. Mater. Int.* **2022**

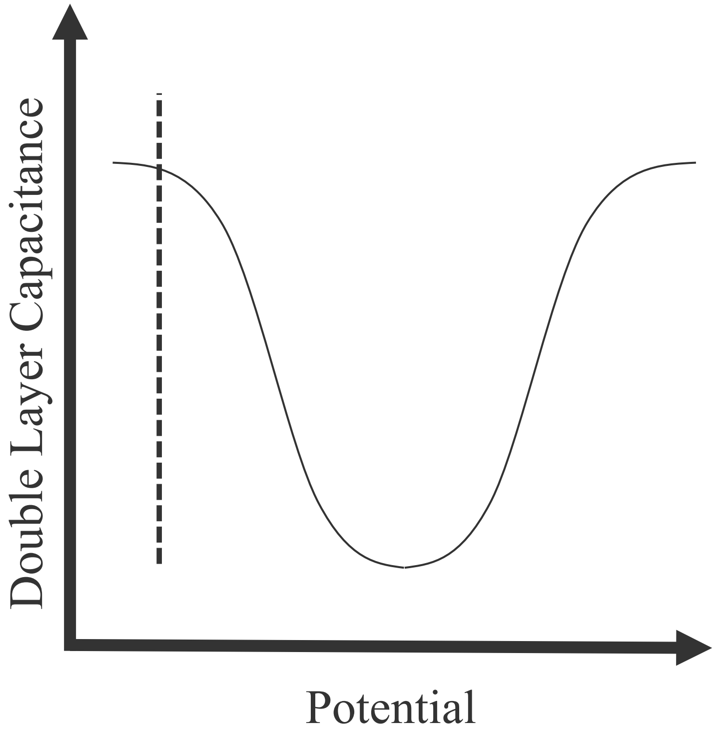
The Classical Model



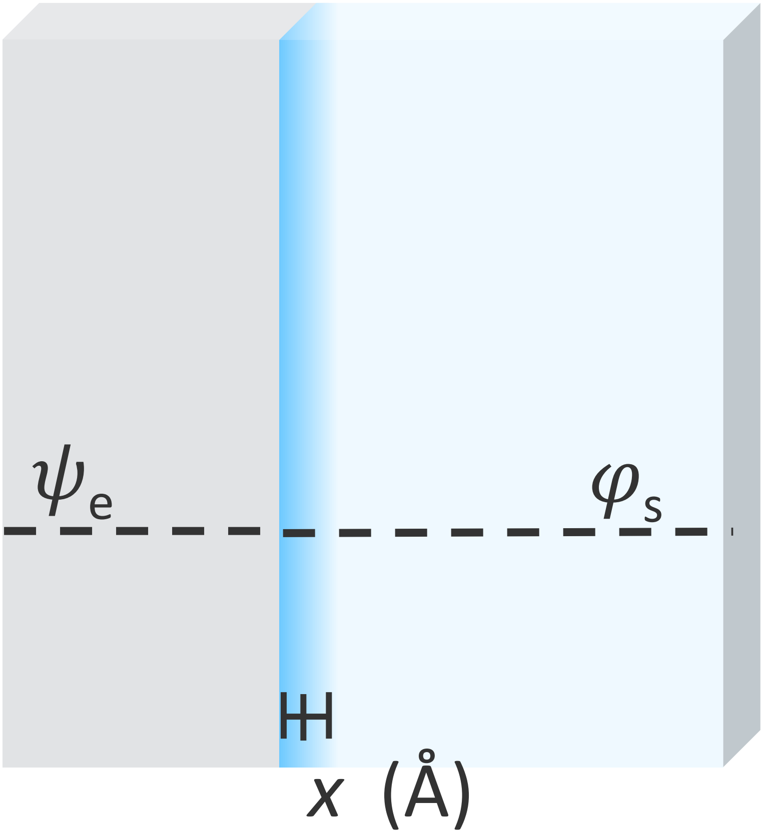


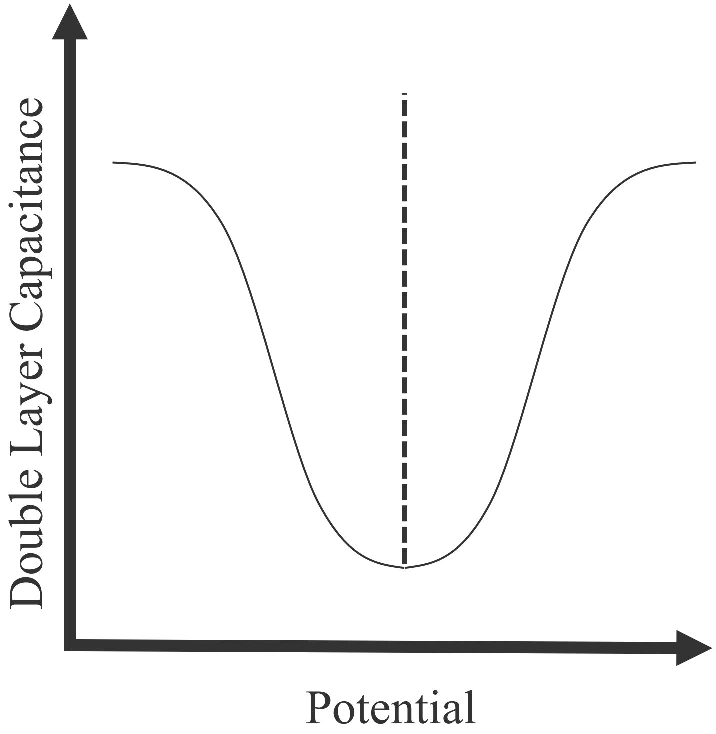
The Classical Model



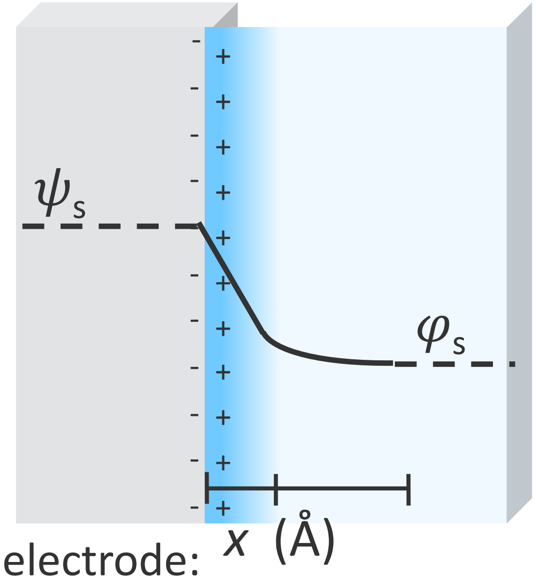


The Classical Model

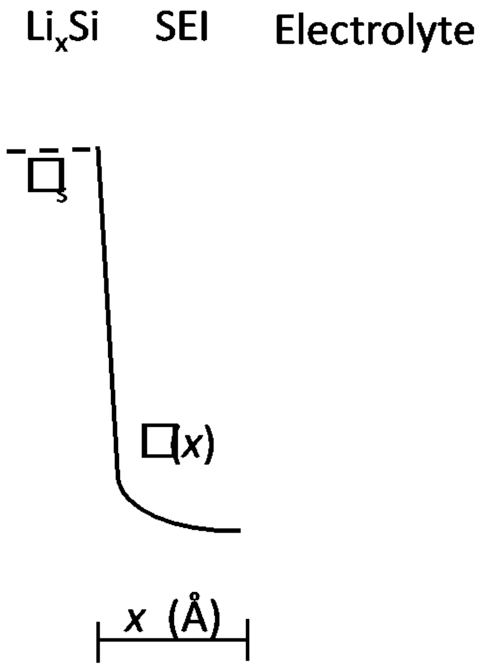




(Re-)Connecting Li_xSi to Model Interfaces

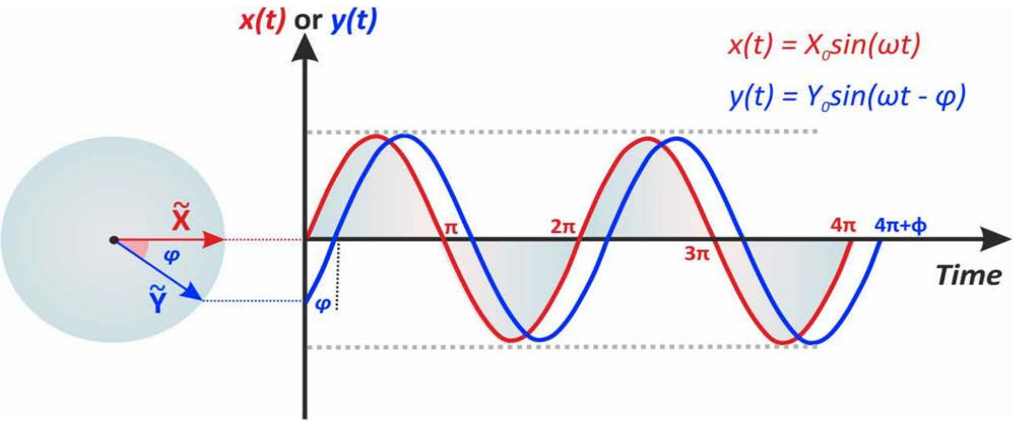


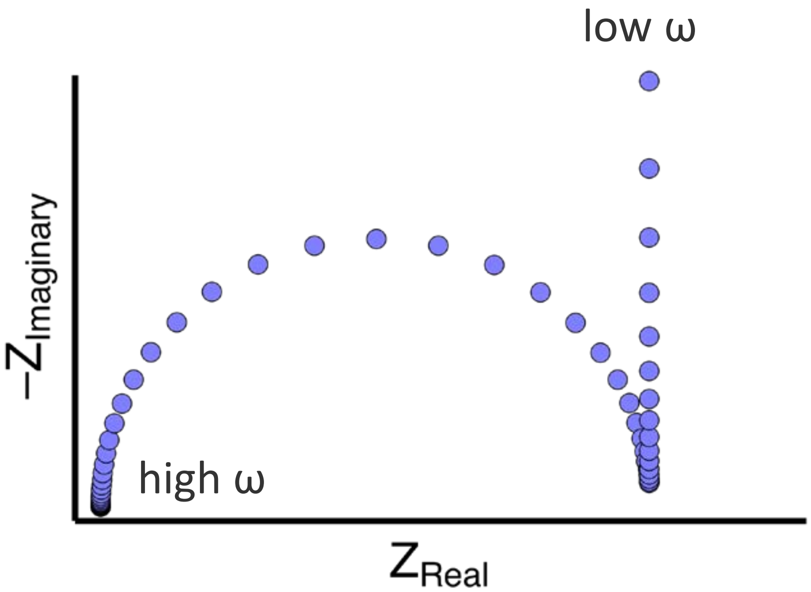
Ideal electrode:
(1) Static and well-defined electrode interface
(2) No hysteresis between cycling
→ No change to electrode surface
→ No change to electrolyte



Silicon electrode:
(1) Dynamic Si electrode interface with lithiation
(2) Poorly-defined interface (Li_xSi?, SEI?, $Li_xSi_yO_z$)
(3) Unstable (intrinsically reactive)
(4) Hysteresis between cycles
(5) Extremely heterogeneous

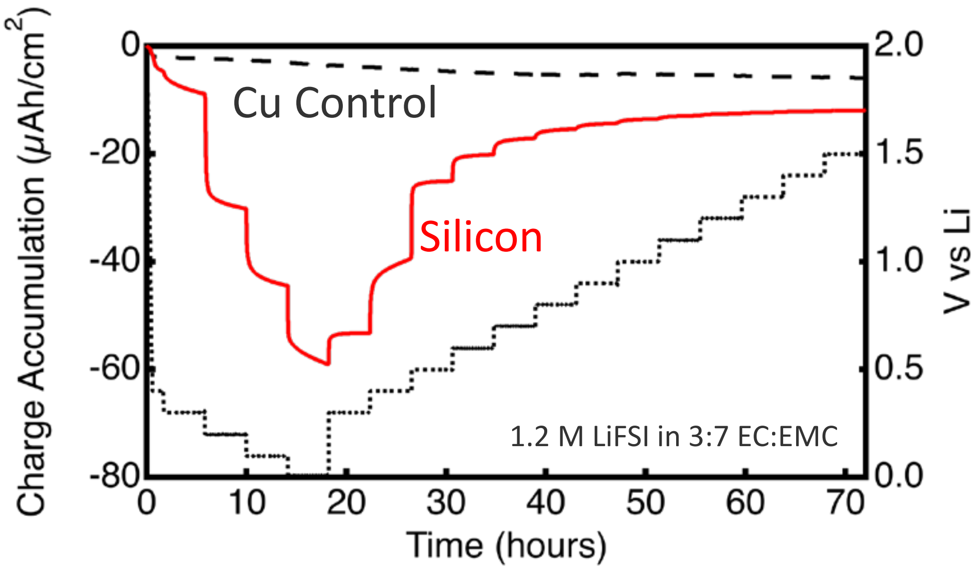
Electrochemical Impedance Spectroscopy

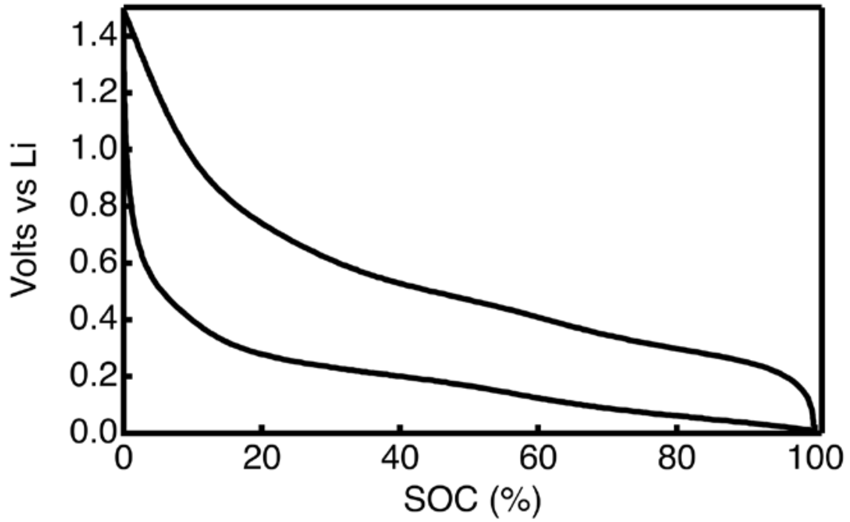




Lazanas, A. C.; Prodromidis, M. I: *ACS Measurement Science Au* **2023.**

SOC – Dependent EIS



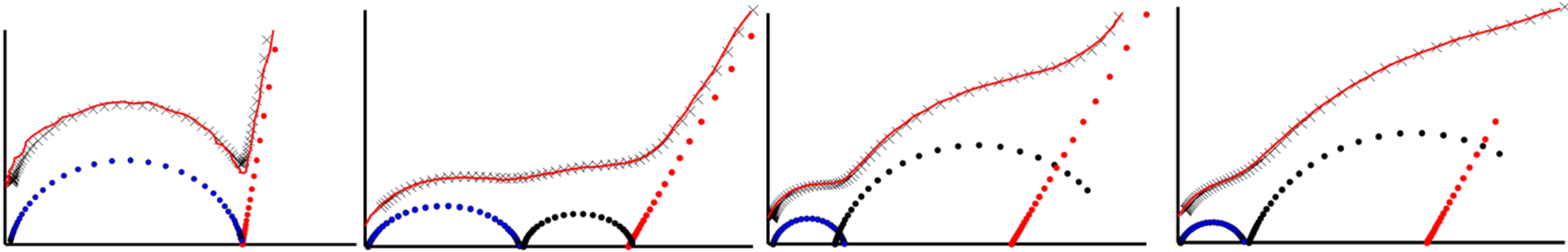


Silicon lithiation states held at a constant potential

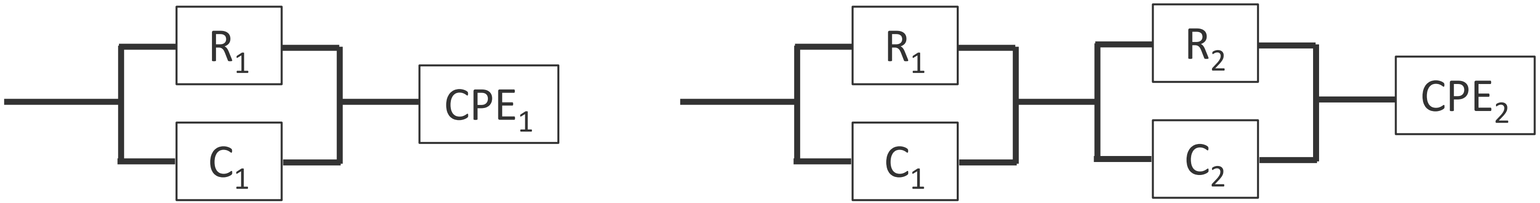
Potentiostatic EIS performed at end of V-hold every 4 hours.

Delithiation sweep investigated specifically

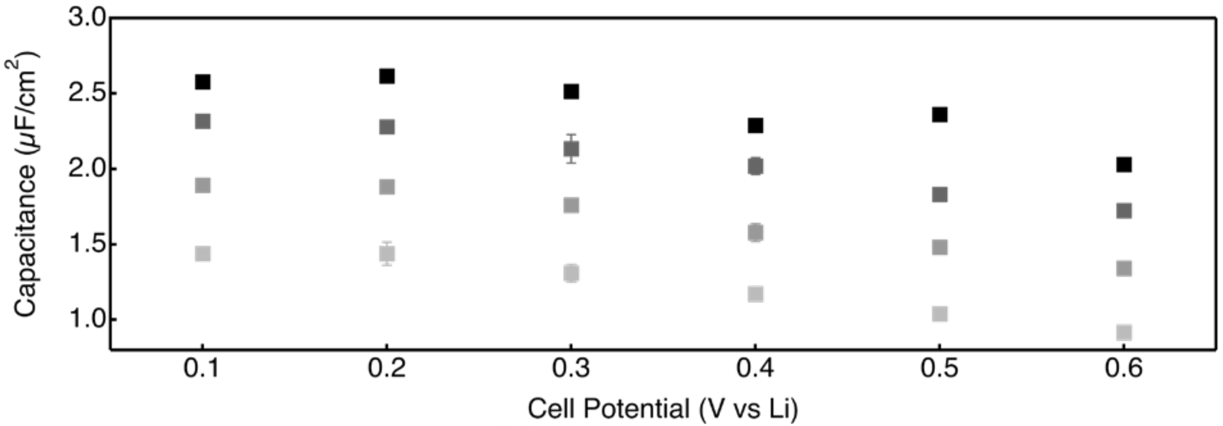
Impedance Evolution on Delithiation

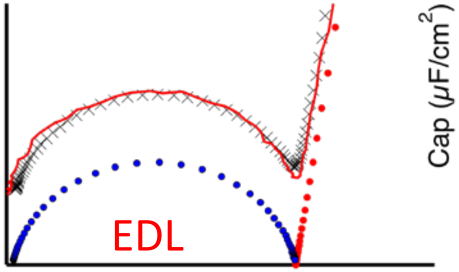


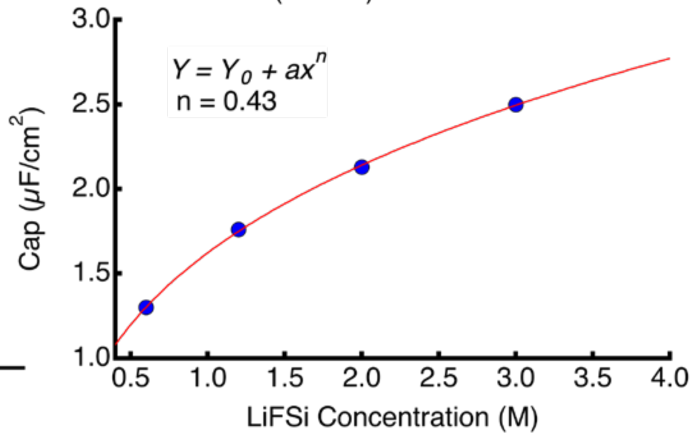
$E_W \leq 0.7$ vs Li	$E_W = 0.8$V vs Li	$E_W = 0.9$V vs Li	$E_W \geq 1$ V vs Li
SOC > 20%	SOC ~ 20%	SOC ~ 10%	SOC < 5%



Capacitive Feature Assignment







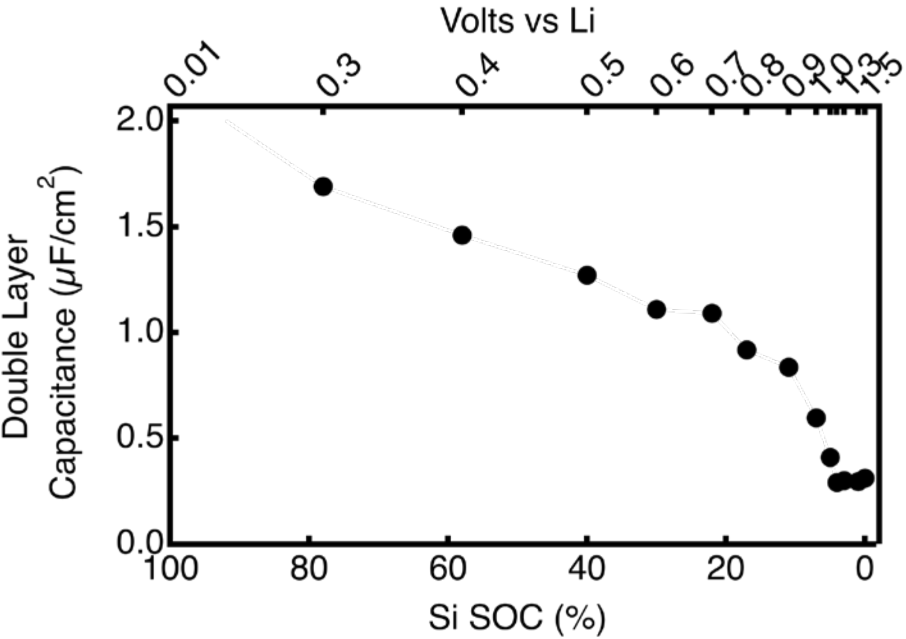
Double layer capacitance:

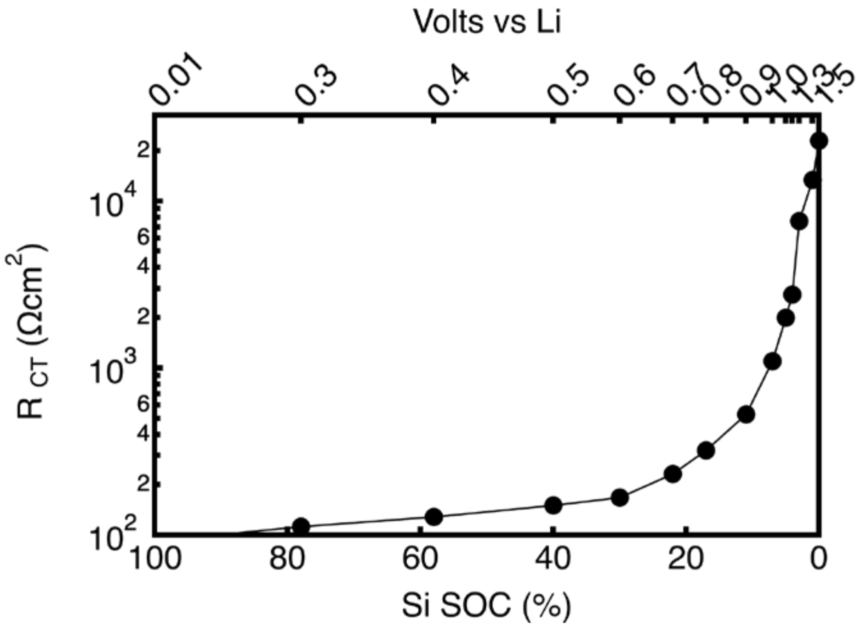
Differential capacitance is not zero

Capacitance is proportional to sq. root of ion activity (~ concentration$^{1/2}$)

First semi circle is capacitance of EDL.

EDLC and Charge Transfer Resistance

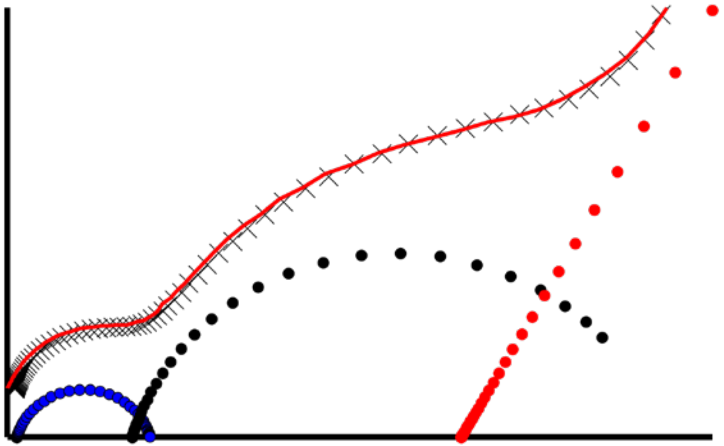


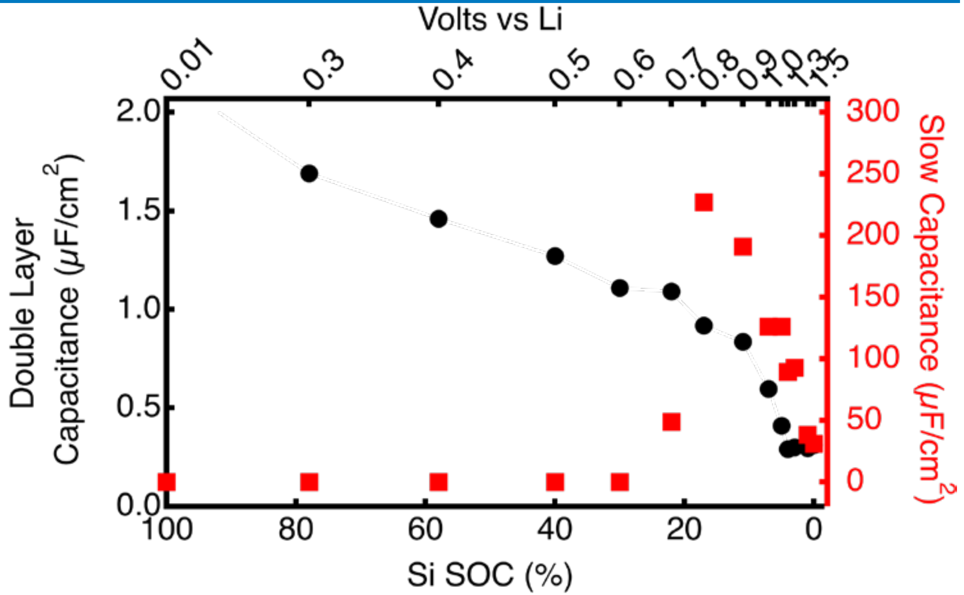


Inverse relationship between R_{CT} and C_{DL}

Indicates change in limiting step in charge transfer

Slow Process Capacitance



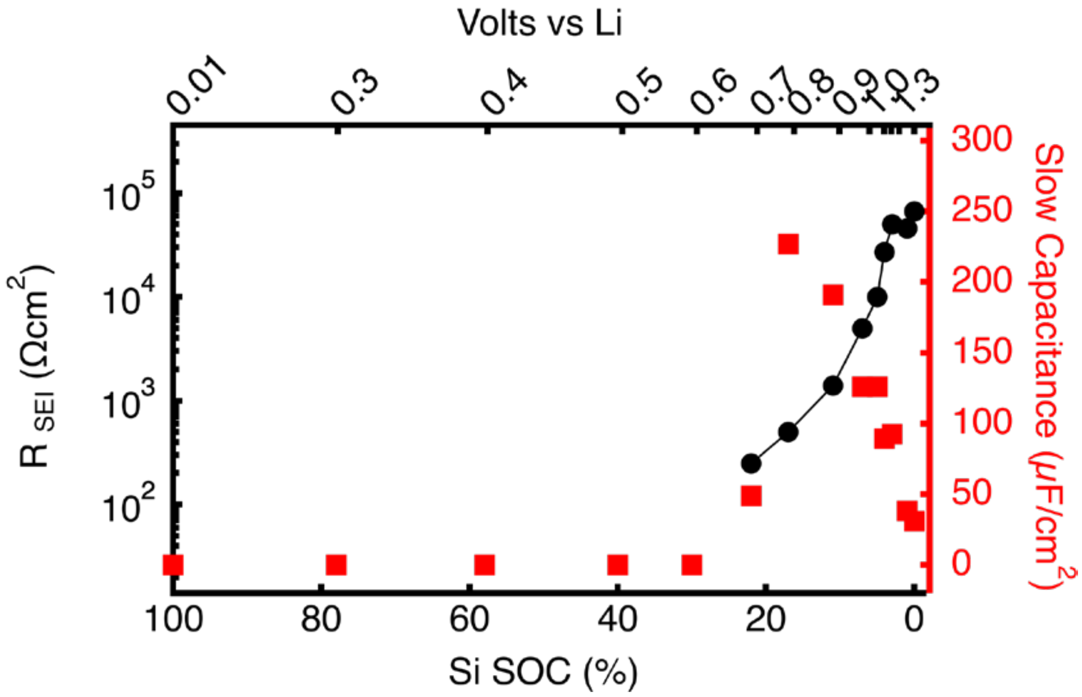


Capacitance of slow process has sharp increase at EDL drop

Slow capacitance is > 100 greater than EDL capacitance

Slow semicircle is likely SEI capacitance and resistance

Resistance of the SEI

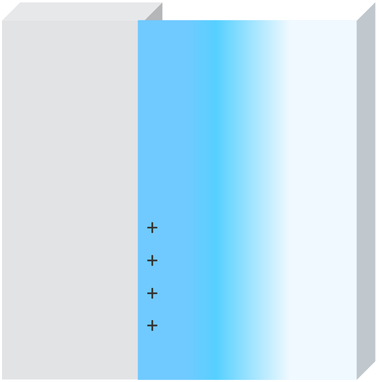


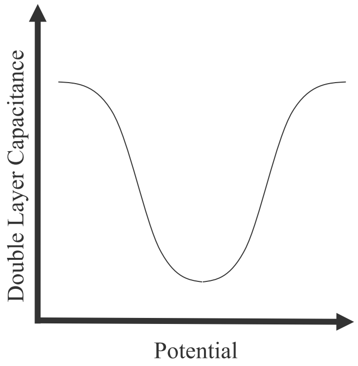
Resistance values keep climbing despite decreasing differential capacitance

Suggests SEI continues to grow

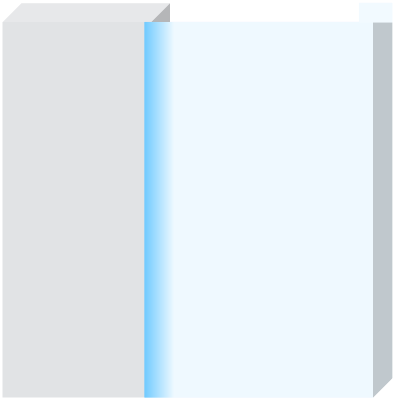
SOC-dependent EDLC

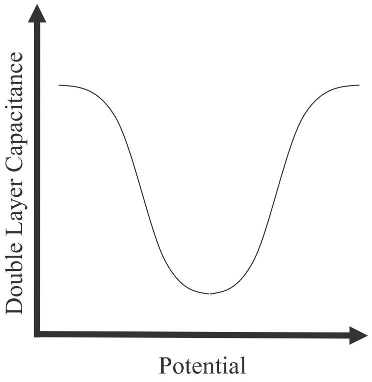
~90% > SOC > ~20%





SOC < ~20%





Calendar Aging in Symmetric Cells

Si@PEO || Si@PEO

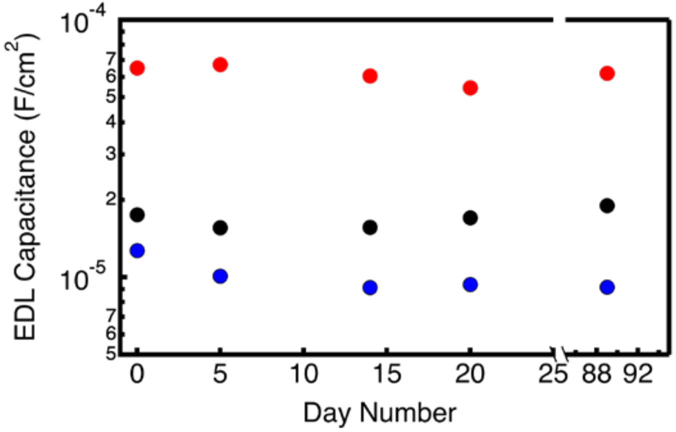
Gen2 electrolyte

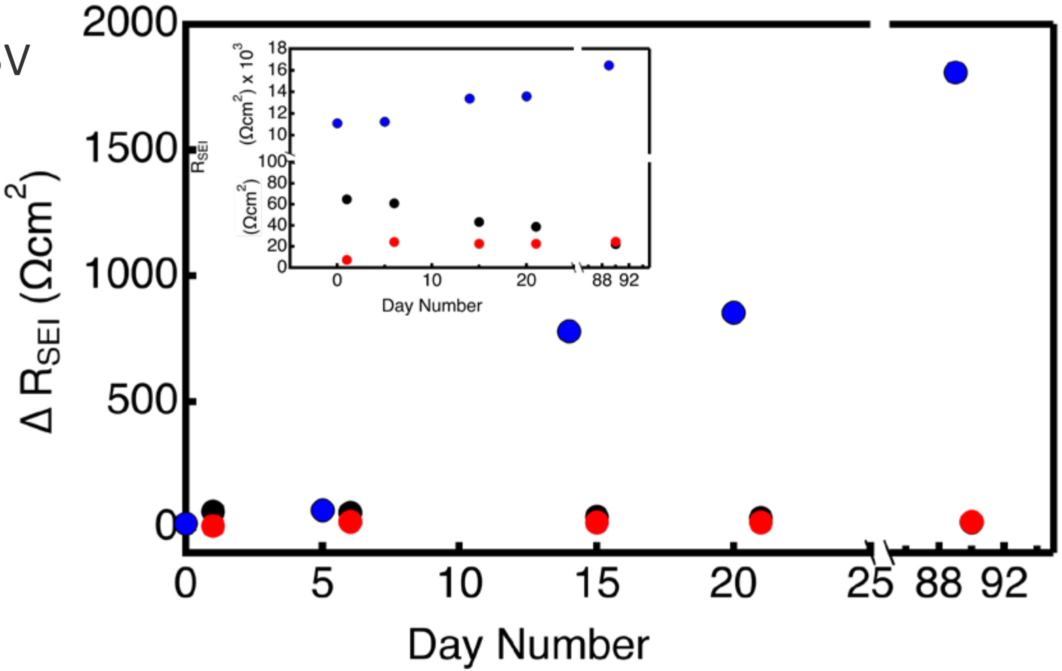
Formed at C/10 between 0.01 and 1.5V

Delithiated to: 0.01 V, 0.4 V, 1 V

48 hr V-hold @ desired potential

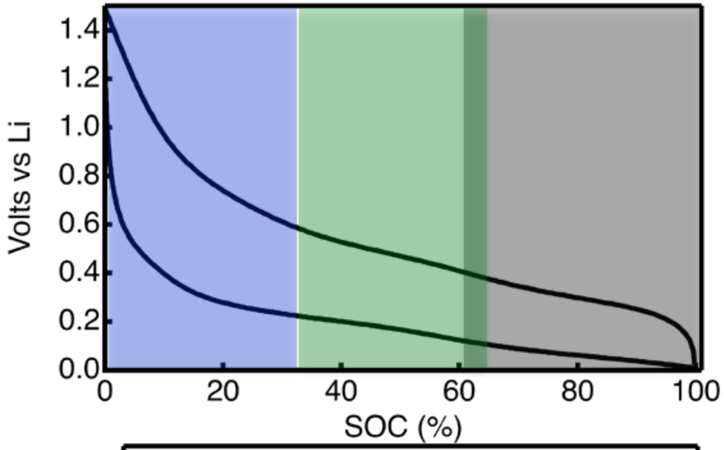
Aged at 45 C at 0V vs Li_xSi

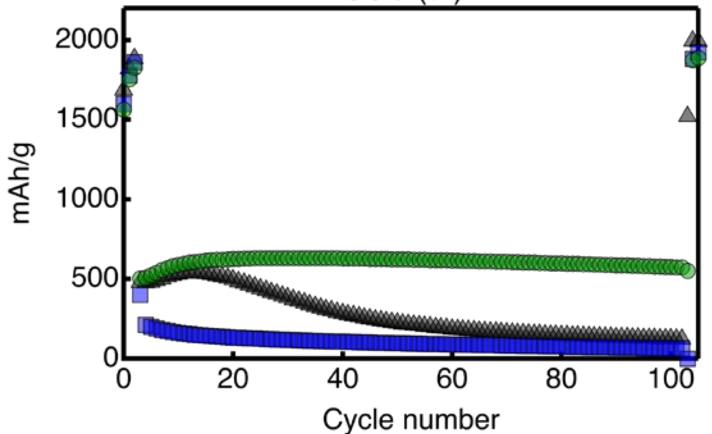


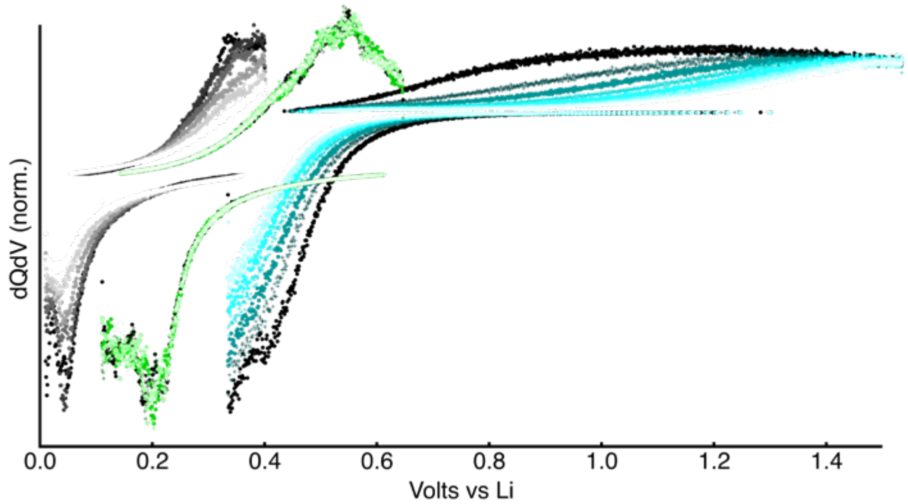


Increasing impedance at low SOCs is consistent with PZC-like regime

Cycle Lifetime (Composite Half cells)





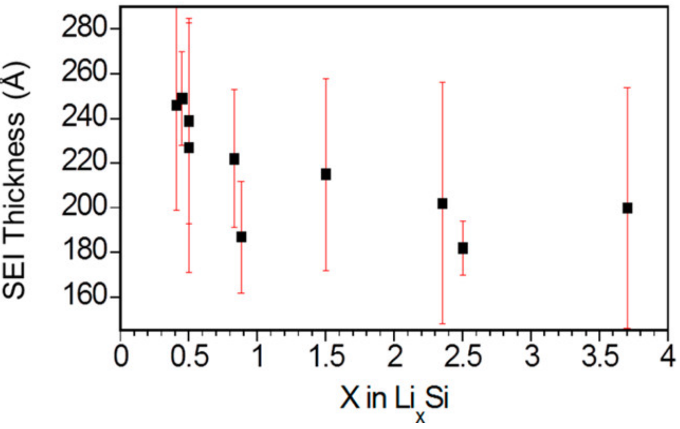


Large impedance gain in High SOC and Low SOC cycle domains

No apparent loss of active material

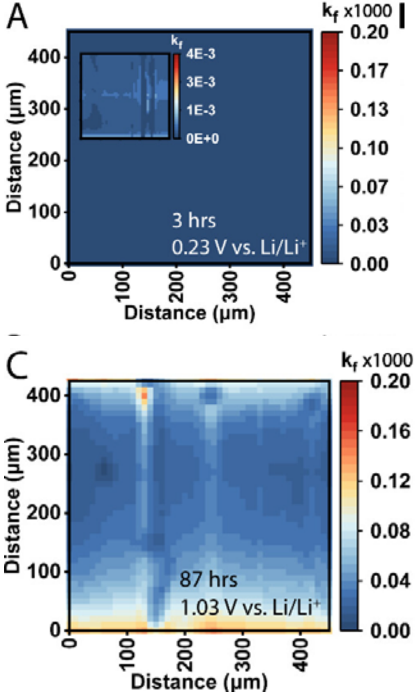
SOC-Dependent SEI Electrostatic Picture

Neutron Reflectometry Measurements of SEI thickness



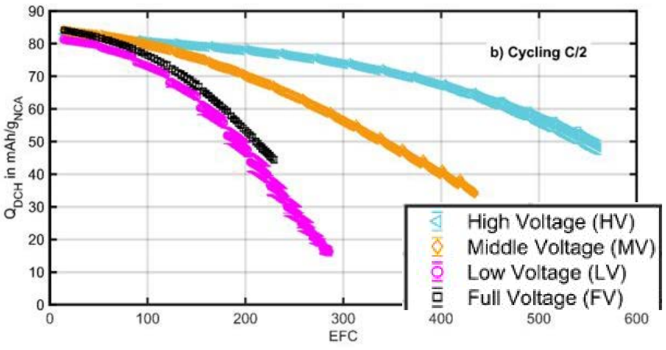
Veith, et al; *JPCC* **2019**

Scanning Electrochemical Microscopy Measurements on SEI Passivation



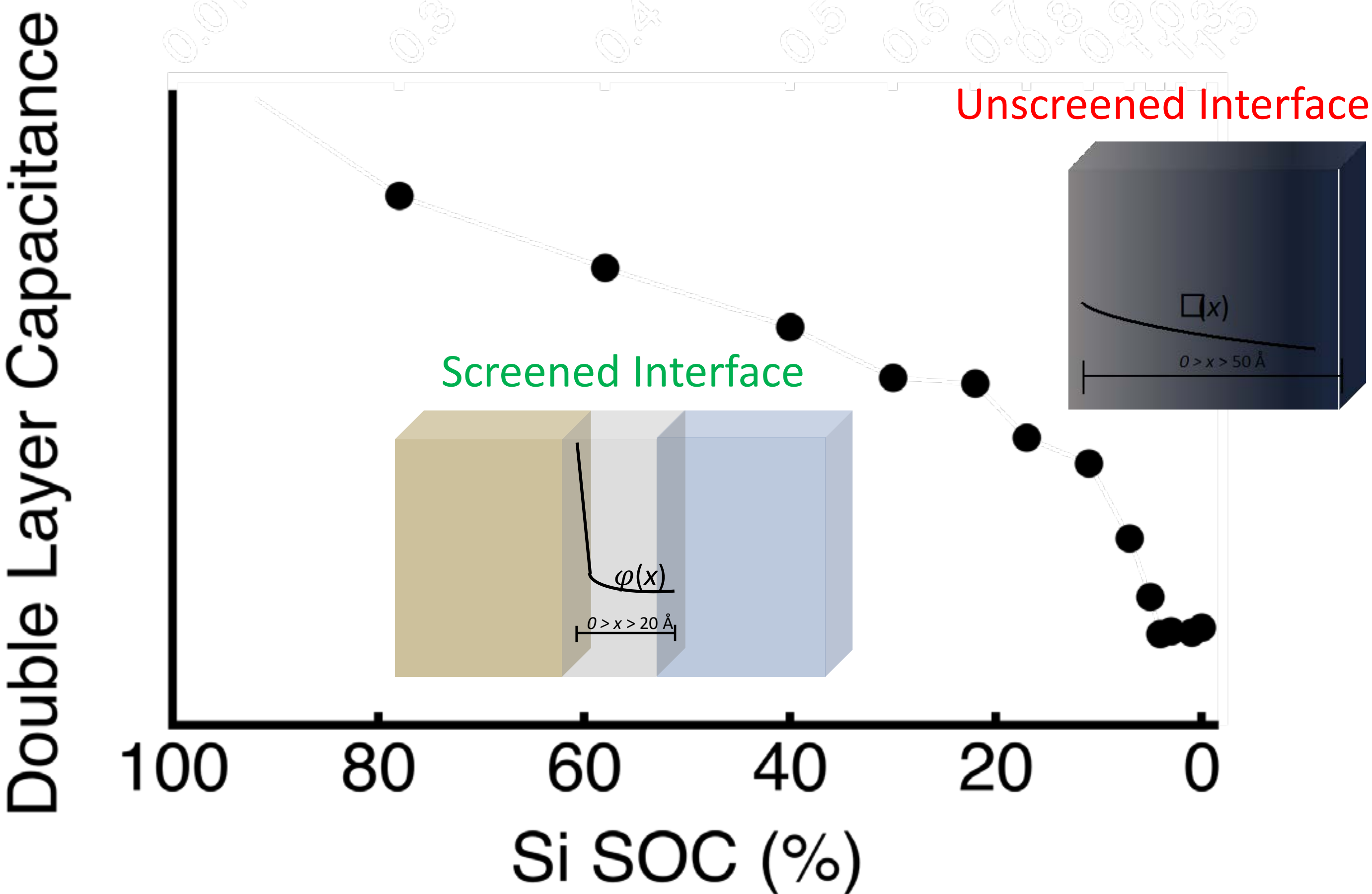
McBrayer, et al; *J. Appl. Mater. Interfaces* **2024**

Battery Cycling



Sven Friedrich, *245th ECS A02-0240* **2024**

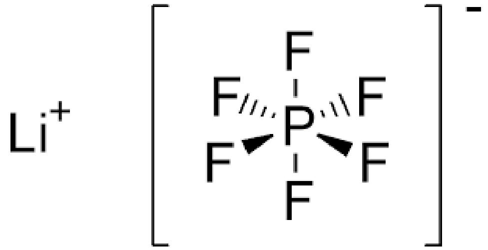
SOC-Dependent SEI Electrostatic Picture



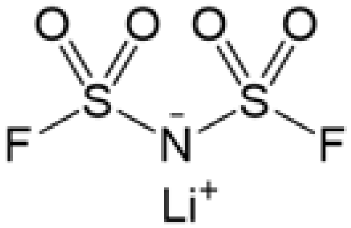
Anion Variation

1.2M Li*X* dissolved in 3:7 EC:EMC

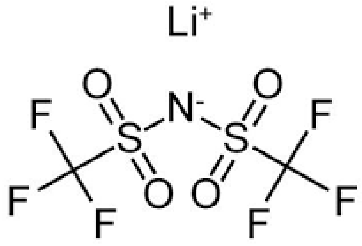
$LiPF_6$



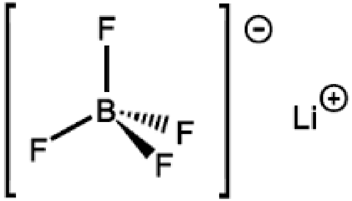
LiFSI



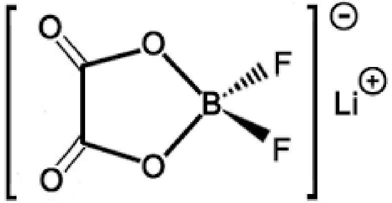
LiTFSI



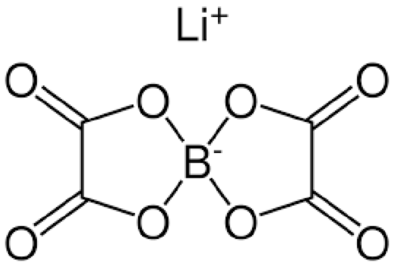
$LiBF_4$



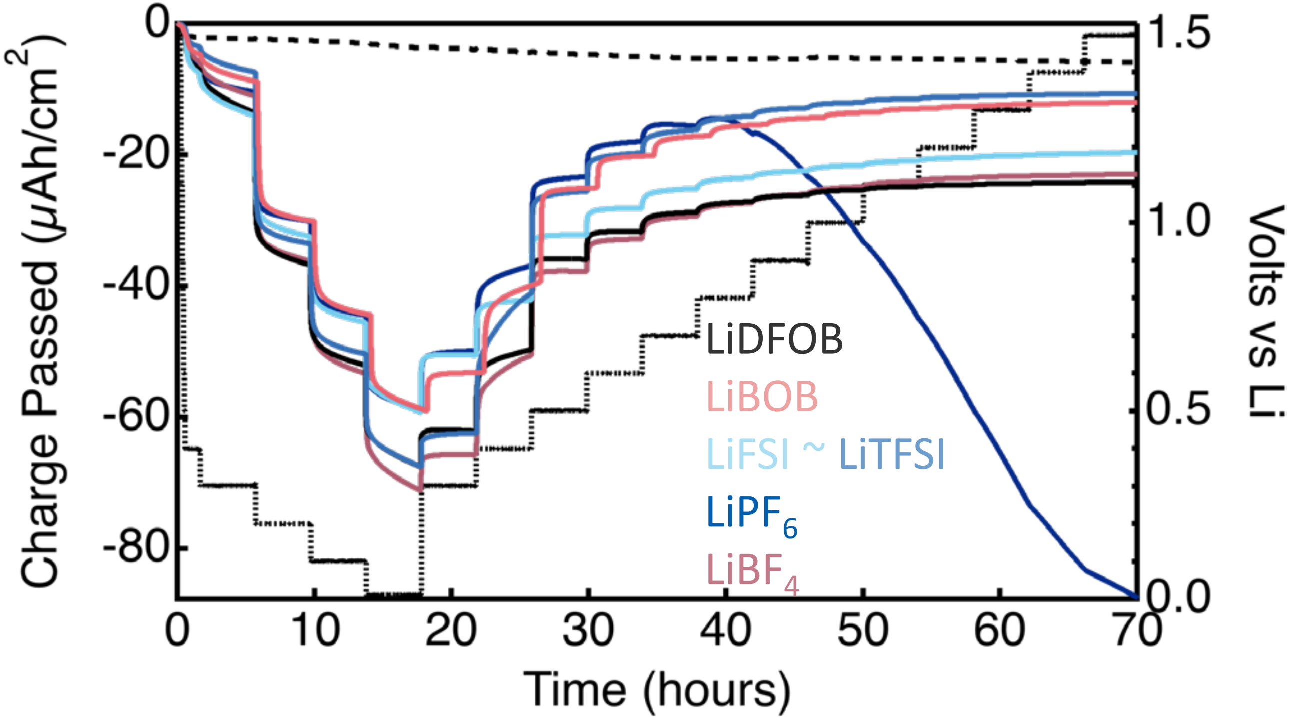
LiDFOB



LiBOB

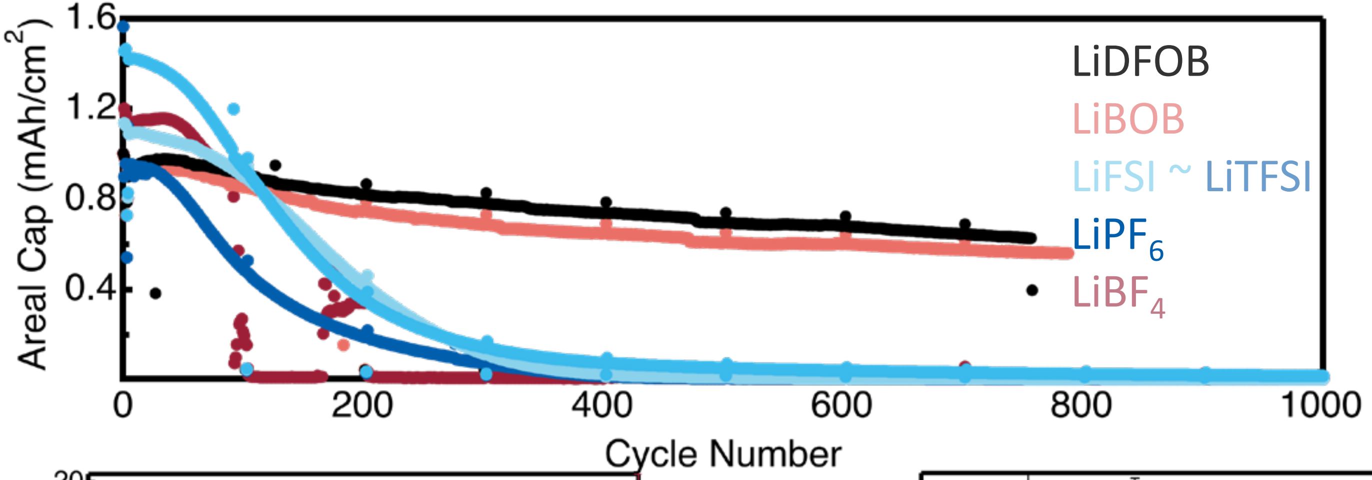


Charge Accumulation

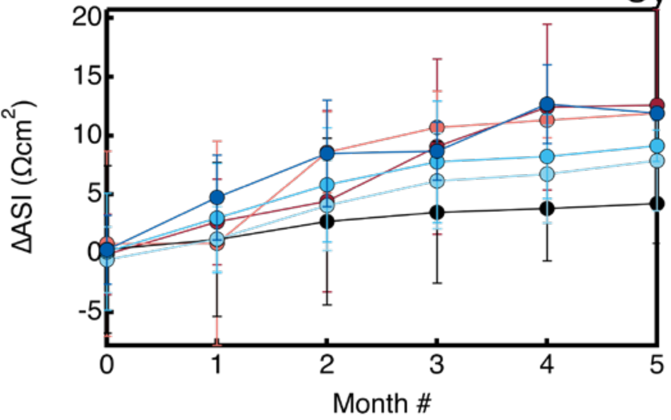


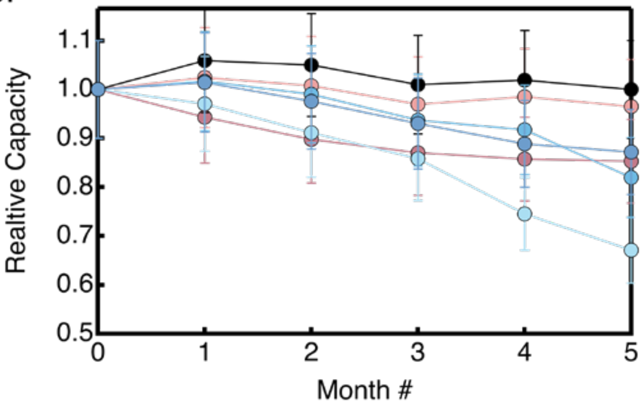
$LiPF_6$ coupled with EC shows continuous current at low SOC's
All other electrolytes are stable at low SOC's

Cycle/Calendar Lifetime vs LFP (n-limited)

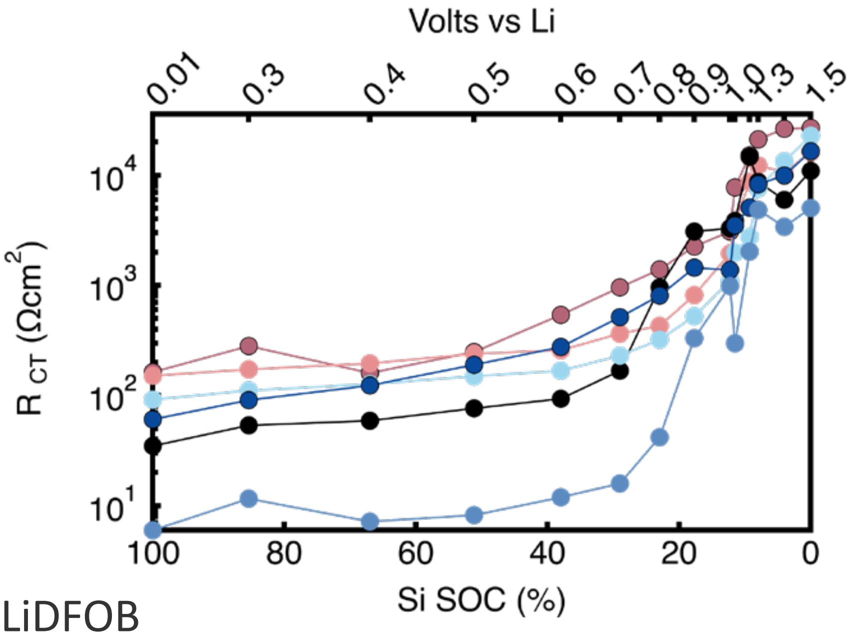


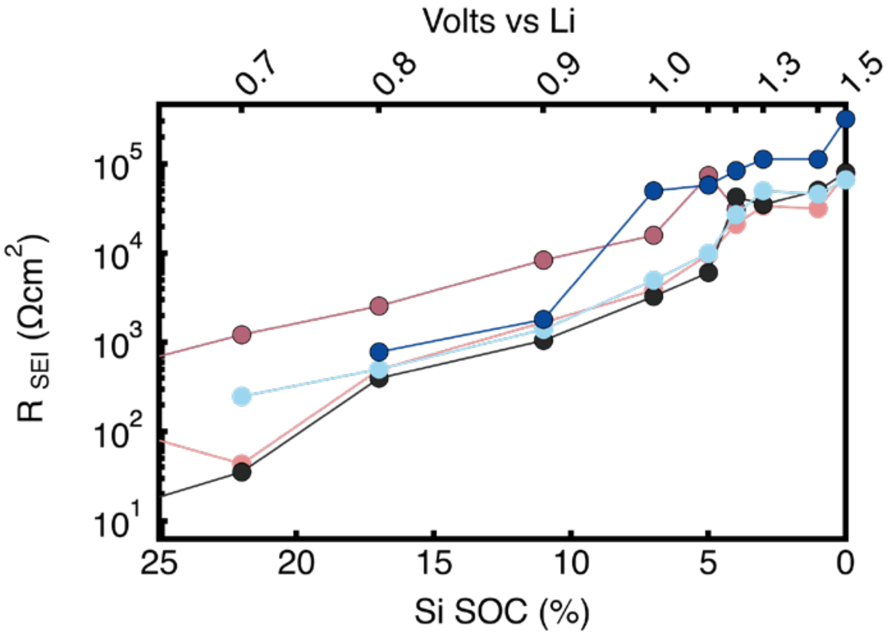
Si@PEO|| LFP
1.2 M salt
3:7 EC:EMC
coin cell
non-prelithiated





Resistances

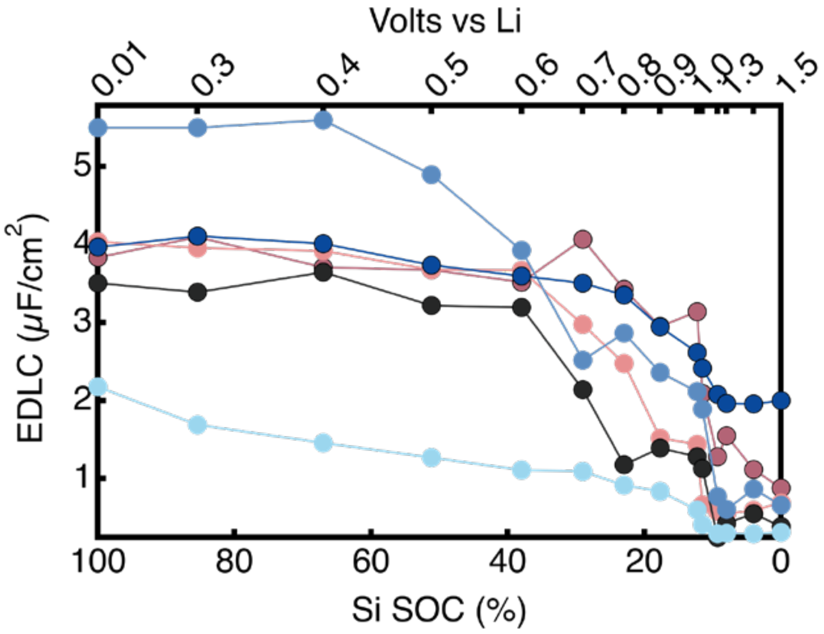


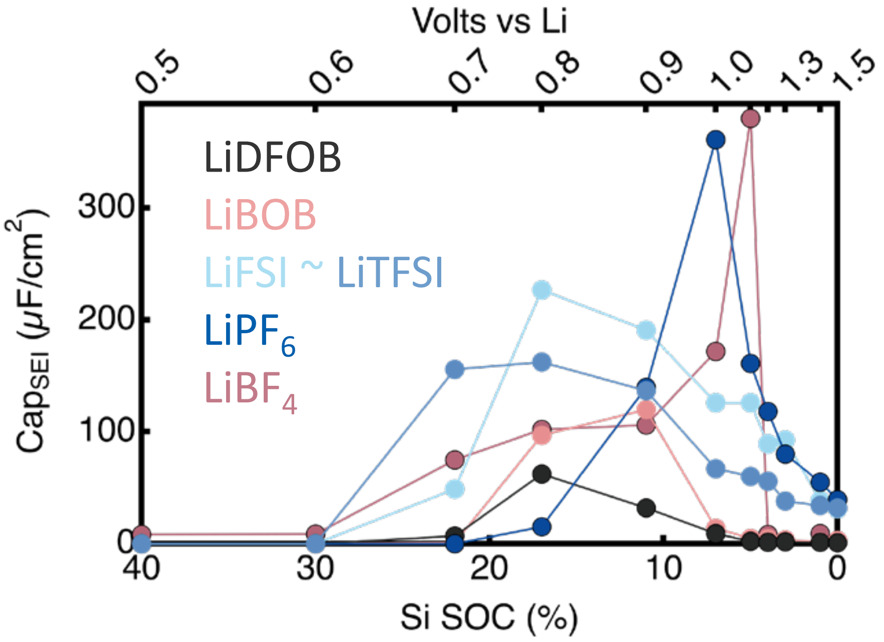


LiDFOB
LiBOB
LiFSI ~ LiTFSI
$LiPF_6$
$LiBF_4$

R_{CT} and R_{SEI} follow the same trajectory for all salts
R_{CT} values vary significantly
R_{SEI} are generally the same

Capacitance and Passivation





Onset for SEI capacitance gain tracks with the drop in EDLC (except $LiBF_4$)

→Expected as PZC is set by electrode *and* electrolyte

Capacitance in SEI roughly follows performance→ lower SEI capacitance is signature of more passivated surface

Conclusions

1. Lithium silicide interface and SEI can be understood through the classical model of electrochemical interfaces

- EIS enables measurements of relevant properties at a very non-ideal electrochemical interface

2. EDLC measurements reveal that Li_xSi have very dynamic surface electrostatics:

- At SOC < ~20% the electrode surface resembles a structure analogous to the PZC
- The PZC regime is least passivated--> fasted impedance gain in calendar life cells
- The PZC regime may be appropriate for accelerating calendar life measurements and assessing the passivation of the SEI with different electrolytes

3. Measurements of different anions:

1. The onset of PZC regime depends on anions
2. Anions play a large role in passivation
3. The degree of passivation (C_{SEI}) strongly correlates with cycle and calendar life

Conclusions

1. Cycle life in majority Si anodes is less relevant than calendar life

2. Lithium silicide interface and SEI can be understood through the classical model of electrochemical interfaces
    - EIS enables measurements of fundamental electrochemical interface properties of a highly non-ideal electrochemical interface

3. The interface structure and mass transport properties are strongly dependent on the electrode state of charge

If your battery has silicon in it, don't store it fully charged or discharged

The Silicon Consortium Project

Baris Key
Sohyun Park
Zhengcheng Zhang
Joseph Kubal
Devashish Salpekar
Brian Ingram
Steve Trask
Avi Gargye
Zhenzhen Yang
Glenn Teeter
Jaclyn Coyle
Juliane Preimesberger

Rachel Korkosz
Eric Dufek
Jack Deppe
Kevin Gering
Bumjun Park
Mauresh Savargaonkar
Robert Kostecki
Tony Burrell
Eric Allcorn
Megan Diaz

Ankit Verma
Petter Weddle
Bertrand Tremolet de Villers
Kae Fink
Ryan Tancin
Mike Carroll
Jae Ho Kim
Zoey Huey
Chun-Sheng Jiang
Jasmine Tabatabai
John Westgard
Qian Huang
Josey McBrayer

Francois Usseglio-Viretta
Donal Finegan
Max Schulze
Matt Keyser
Pashupati Adhikari
Pallavi Sundaram
John Farrell
Nina Prakash
Trevor Martin
Jackson Pope
Erika Hunting
Lydia Meyer

Anton Tomich
Alison Dunlop
Marco Tulio Fonseca Rodrigues
Wenquan Lu
Evelyna Wang
Fulya Dogan Key
Lily Robertson
Daniel Abraham
Andrew Jansen
Nate Neale
Katie Harrison
Andrew Colclasure

Jack Vaughey
Chris Johnson
Tyler Sweet
Gabe Veith
Beth Armstrong
Khryslyn Arano
Amanda Musgrove
Robert Sacci
Steven Lam
Jie Xiao
Chongmin Wang
Joseph Quinn

NREL Transforming ENERGY | Sandia National Laboratories | Berkeley Lab | Oak Ridge National Laboratory | Argonne National Laboratory | Pacific Northwest National Laboratory

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

VEHICLE TECHNOLOGIES OFFICE

Questions?

www.nrel.gov

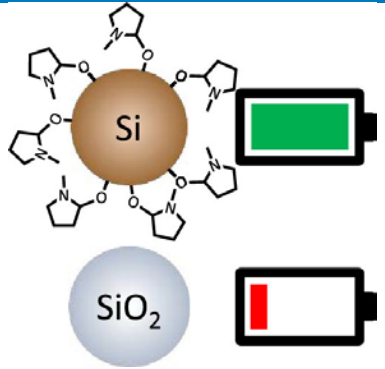
Mike Carroll
mike.carroll@nrel.gov

NREL/PR-5900-90535

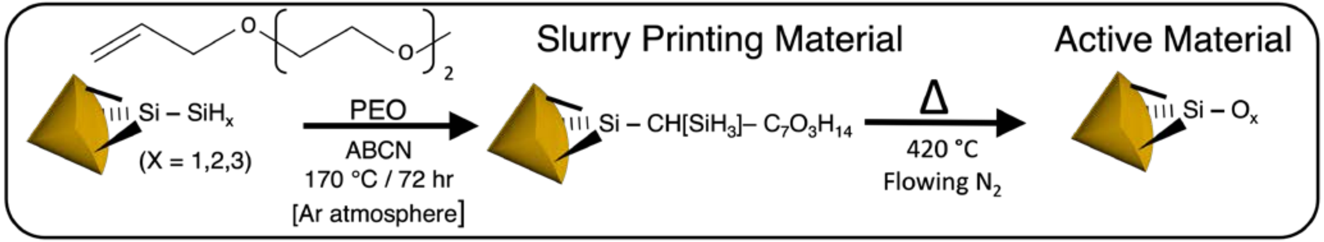
This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Vehicle Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

NREL Transforming ENERGY

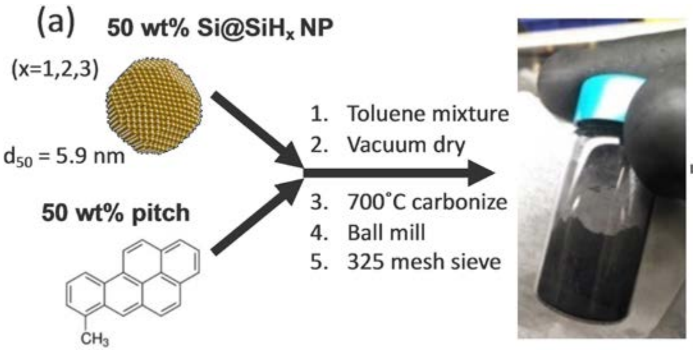
Controlling the Surface Chemistry of Si Electrodes



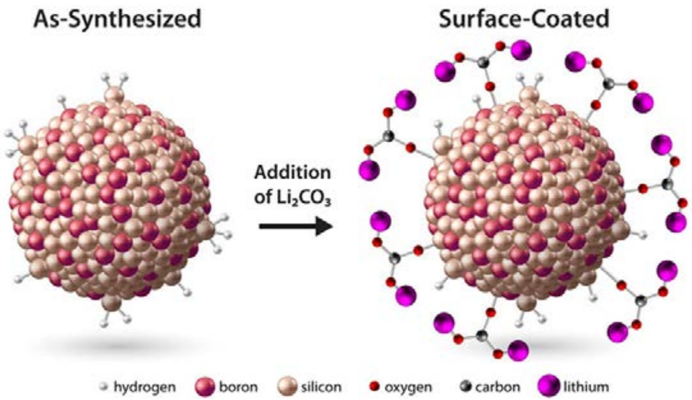
Carroll, … Neale; *ACS Appl. Energy Mater.* **2020**



Schulze, … Carroll; *J. Mater. Chem. A* **2023**



Schulze, et al.; *Batteries and Supercaps* **2023**



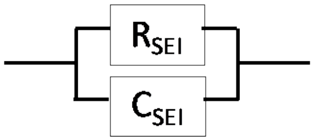
Pach, … Carroll; *ACS Energy Letters* **2024**

EIS of a Redox Active Thin Film (SEI) at a Reflective Boundary.

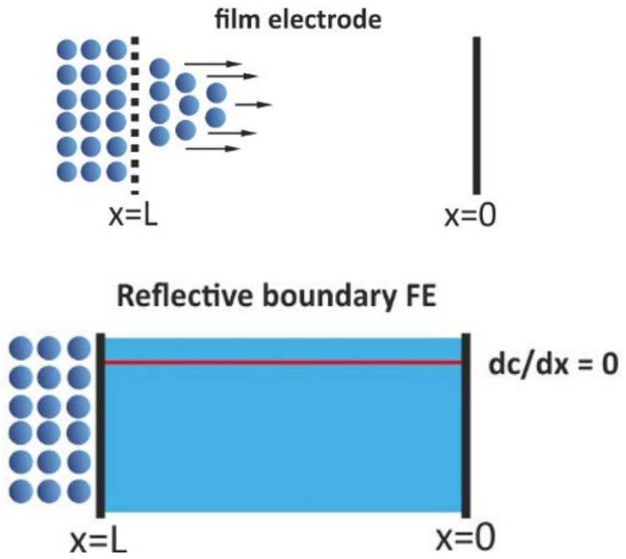
<u>(1) Faradaic</u>
<u>Redox Chemistry</u>

$SEI + e^{-} + Li^{+} \leftrightharpoons SEI(Li)$

Randles' Circuit

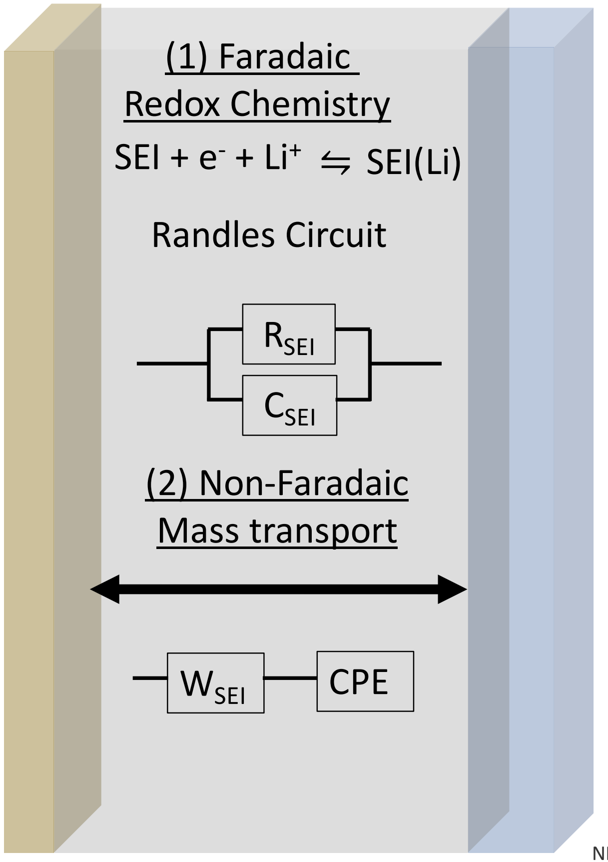


Mass Transport Through the SEI

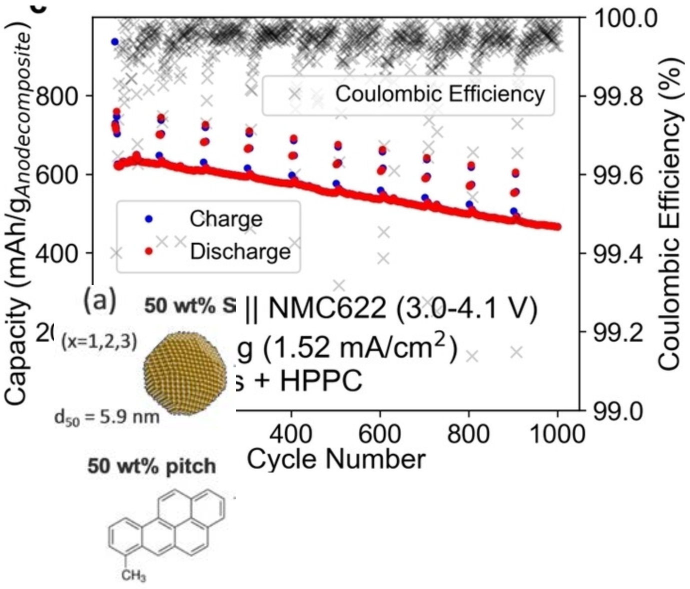


$$Z_t(\omega) = \frac{\coth(B\sqrt{j\omega})}{Y_0\sqrt{j\omega}}$$

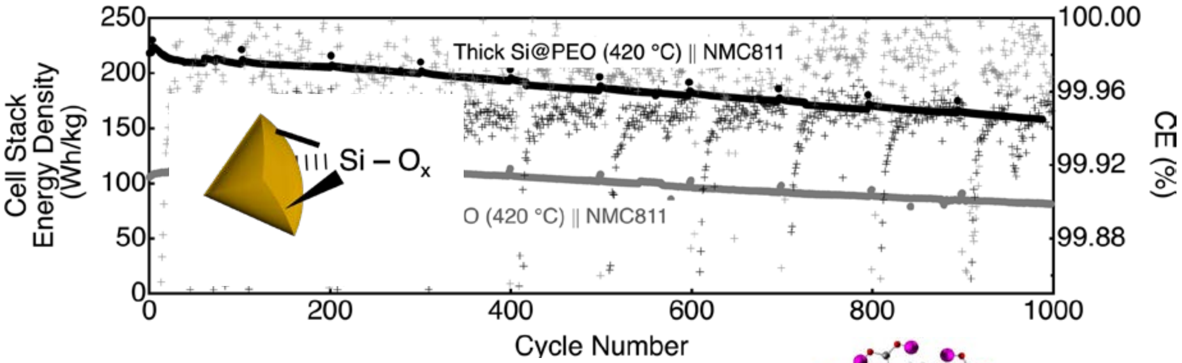
$$\beta = \frac{diffusion\ layer\ thickness}{diffusion\ coefficient^{\ 1/2}}$$



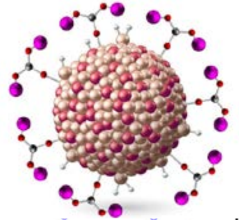
Cycle Life with Varied Surfaces

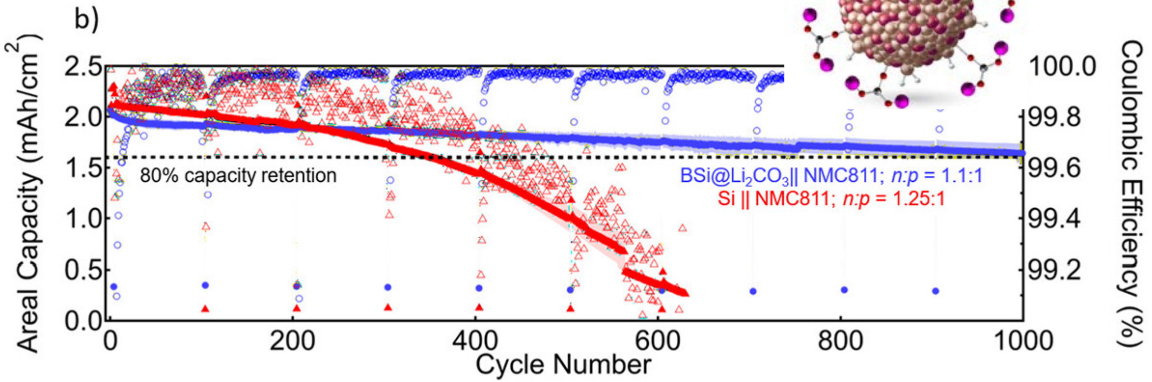


Schulze, et al.; *Batteries and Supercaps* **2023**



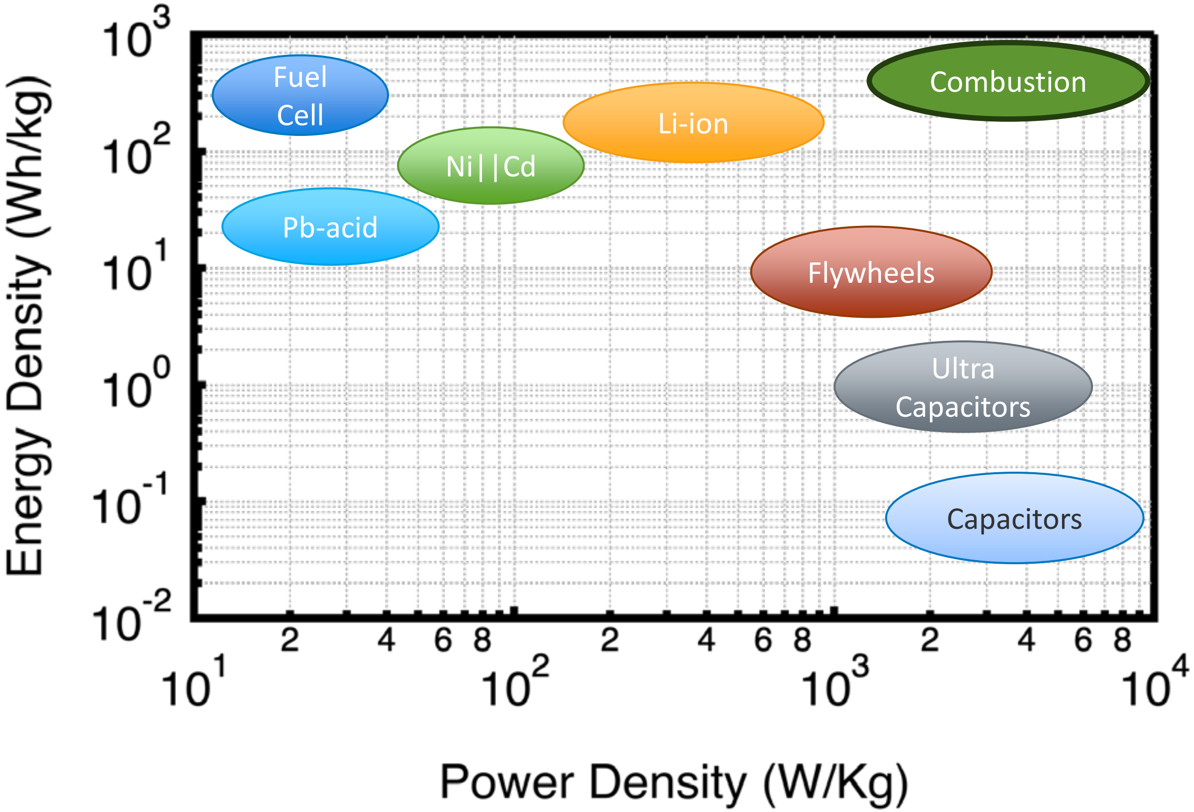
Carroll et al; *J. Mater. Chem. A* **2023**





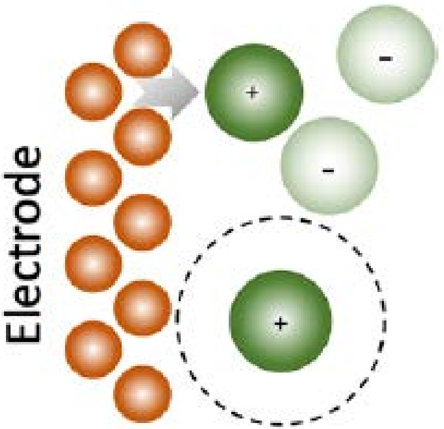
Pach, … Carroll; *ACS Energy Letters* **2024**

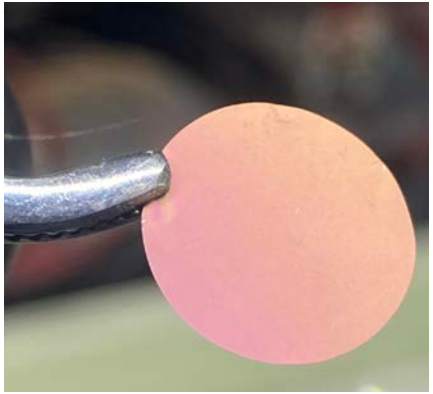
Energy Storage and Delivery Technology

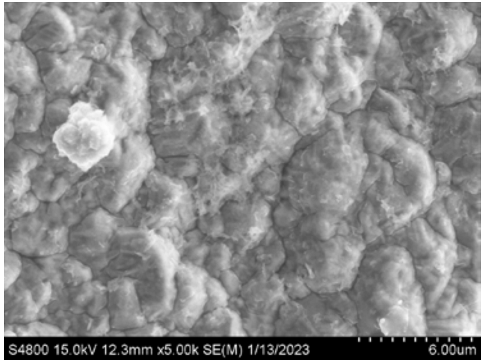


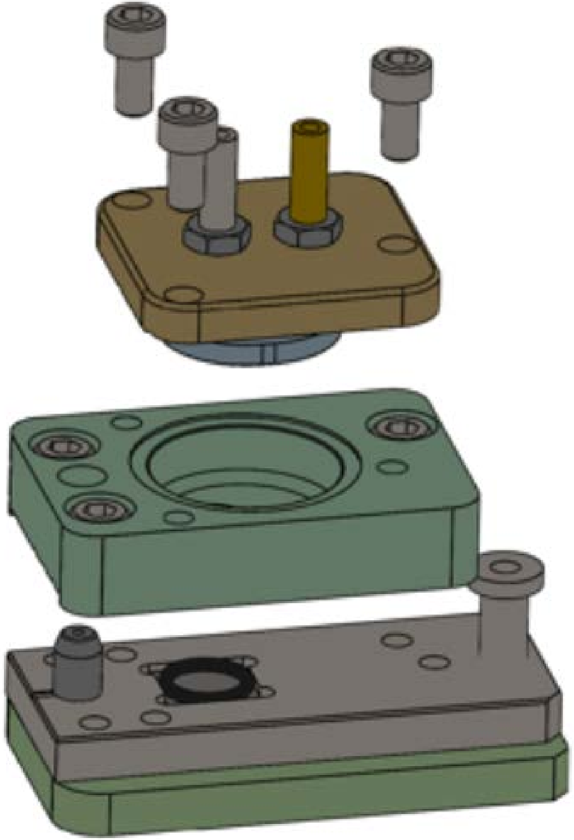
Thin Film Silicon Electrode

2D Planar electrode



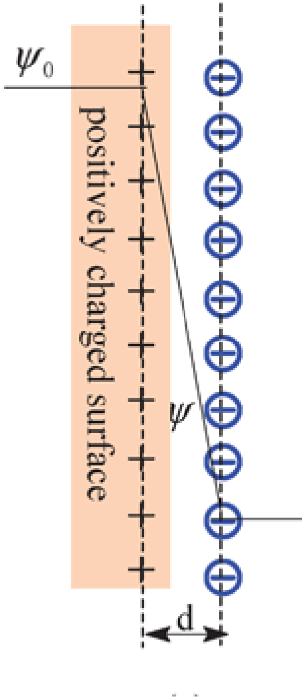




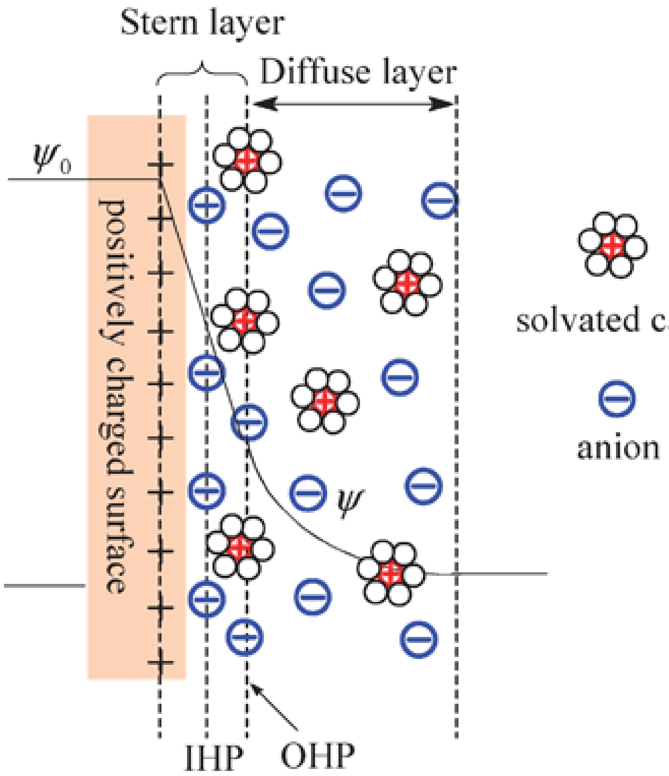


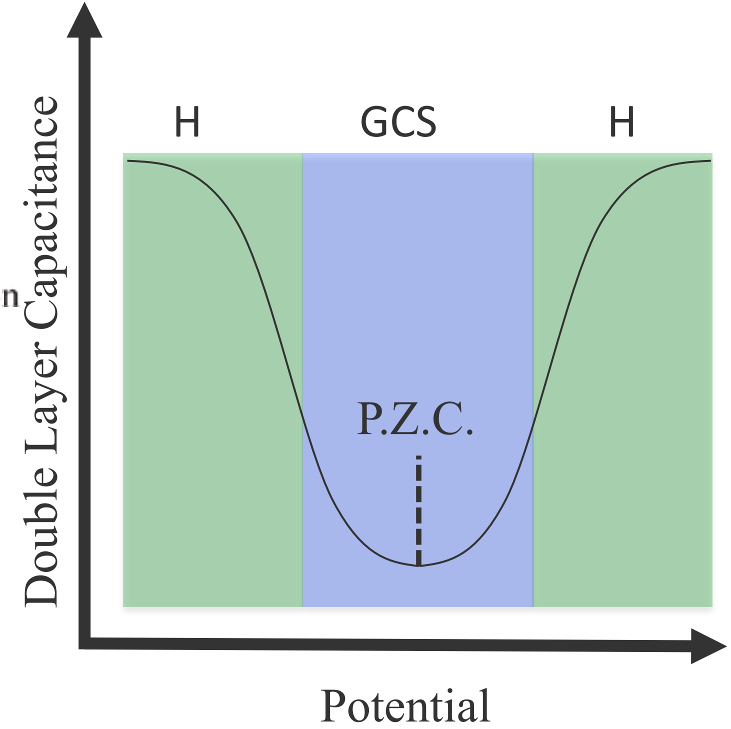
The Classical Model

Helmholtz Model



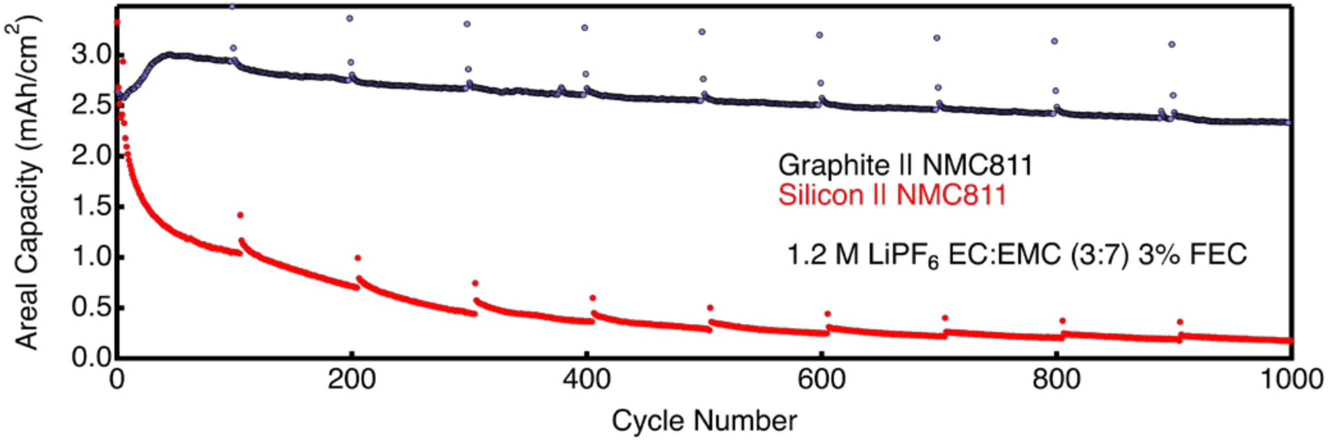
Gouy-Chapman-Stern Model

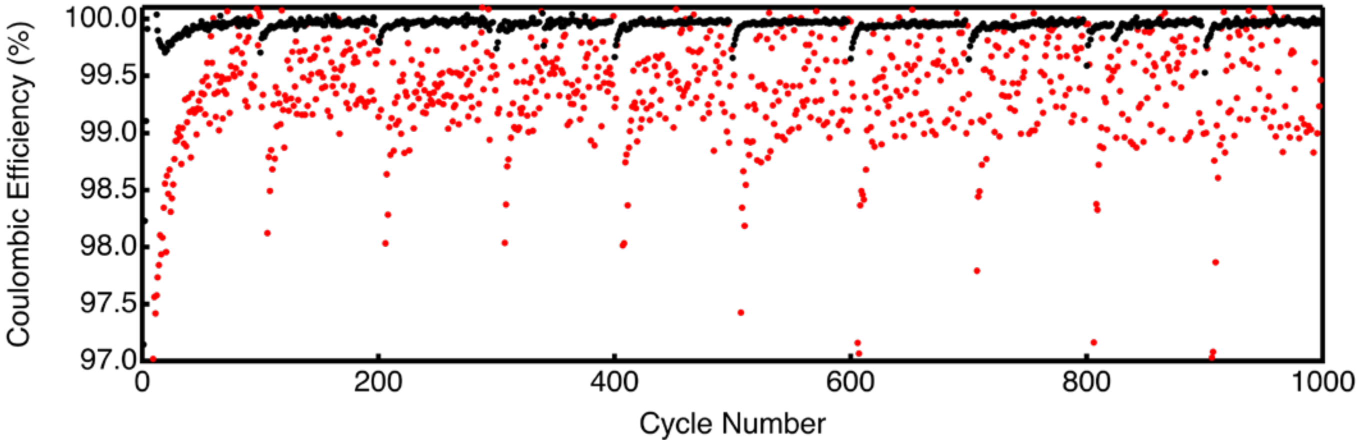




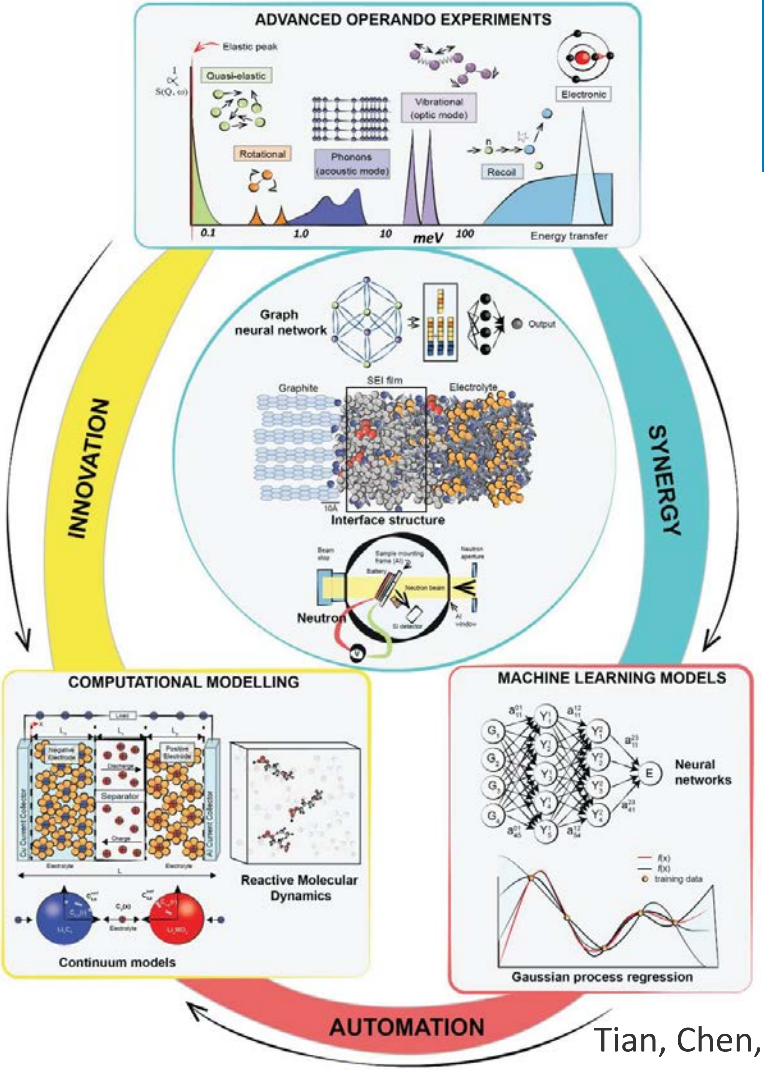
Zhang, L. L.; Zhao, X. S. *Chem. Soc. Rev.* **2009**

Electrochemical Cycling

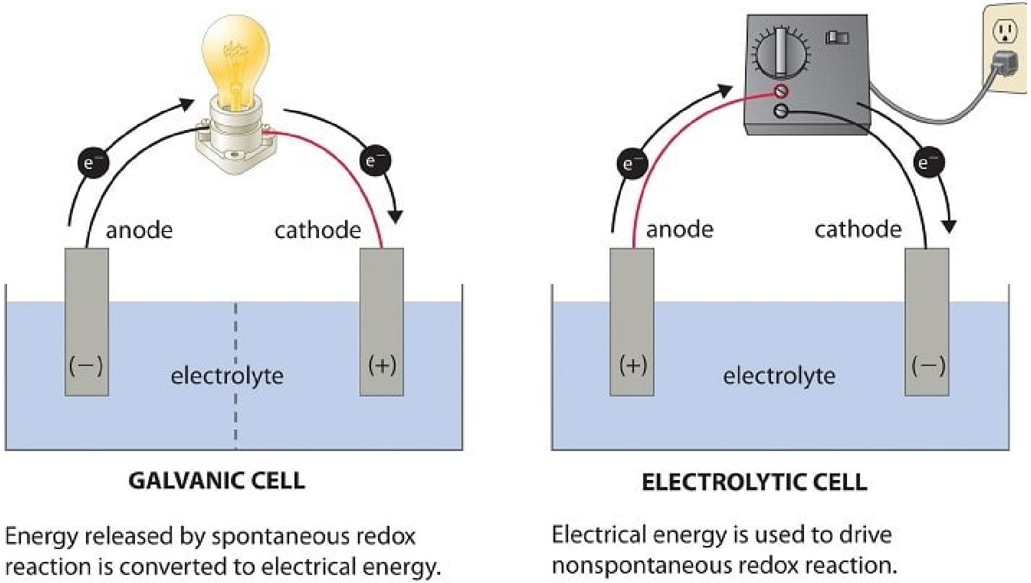




Understanding Calendar Life



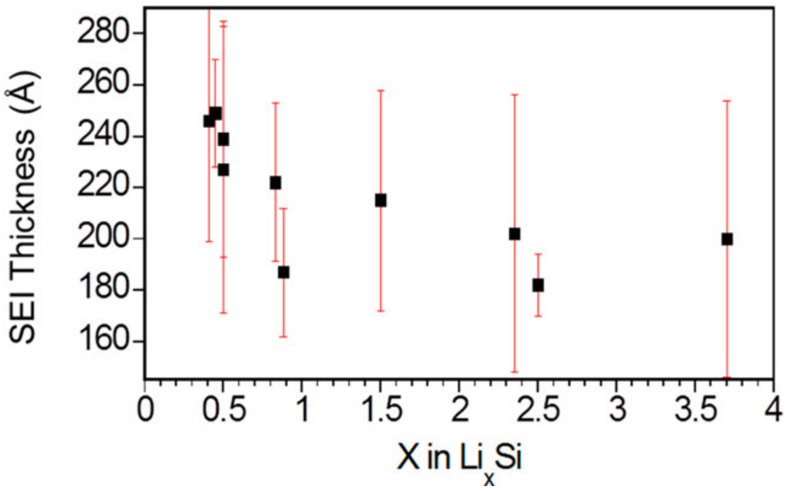
Tian, Chen, et al; *Adv. Energy Mater.* **2023**



Energy Education, Univ. of Calgary

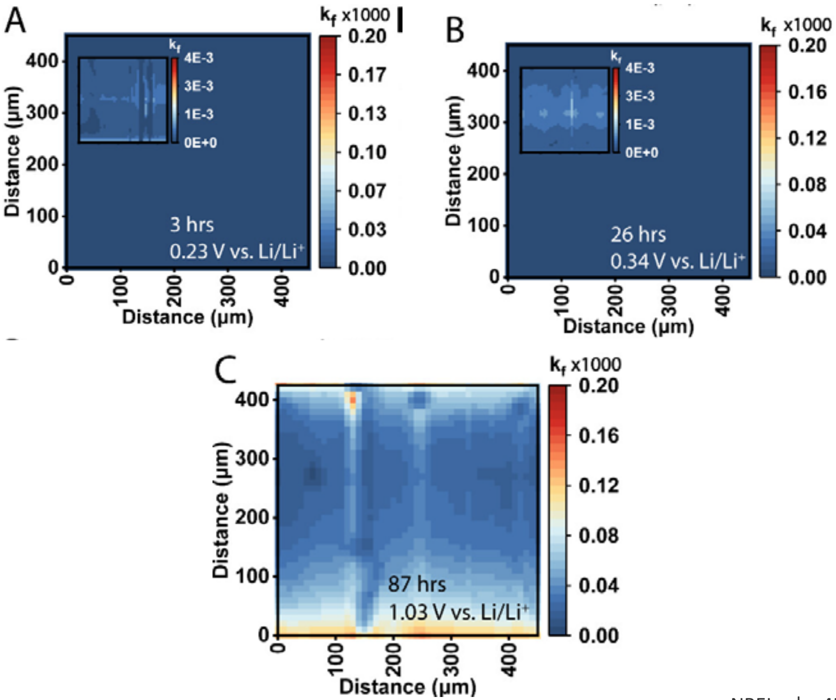
Corroborating Observations

Neutron Reflectometry Measurements of SEI thickness



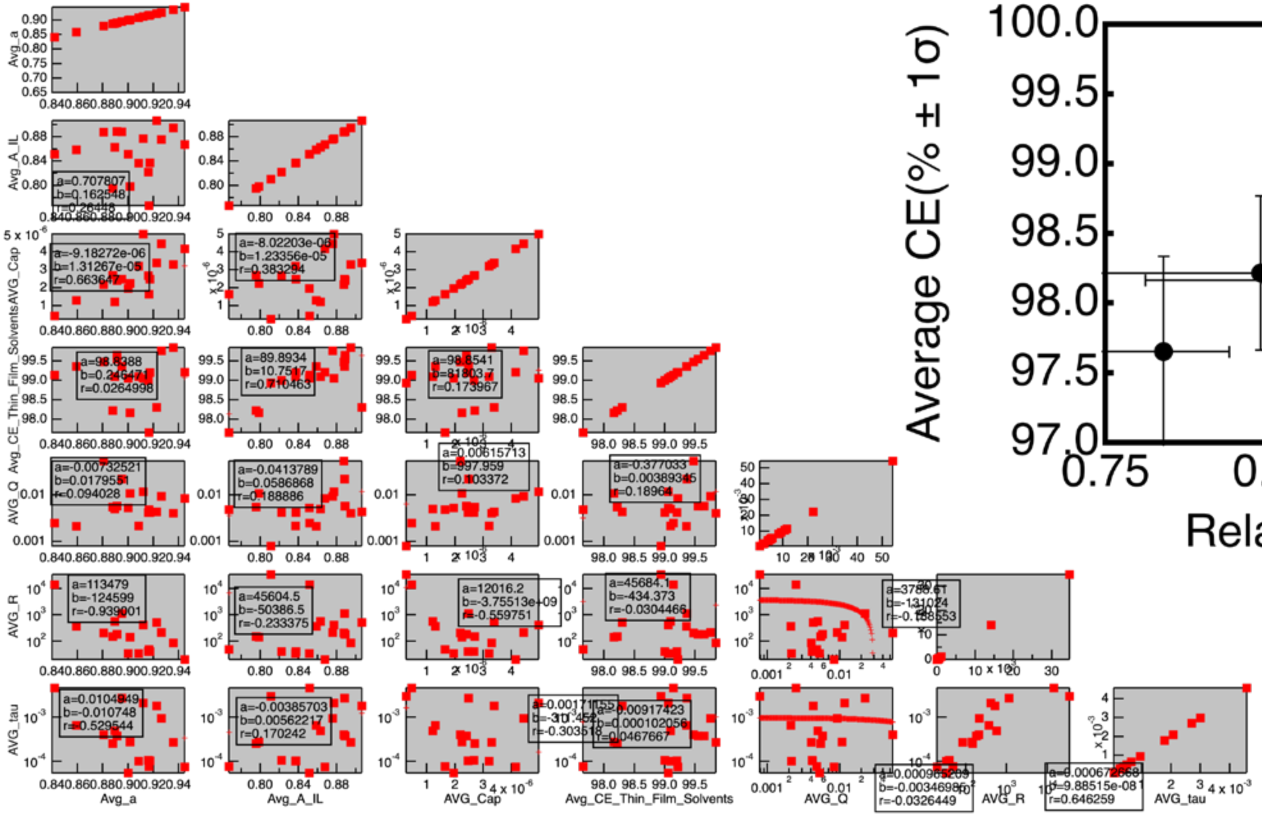
Veith, et al; *JPCC* **2019**

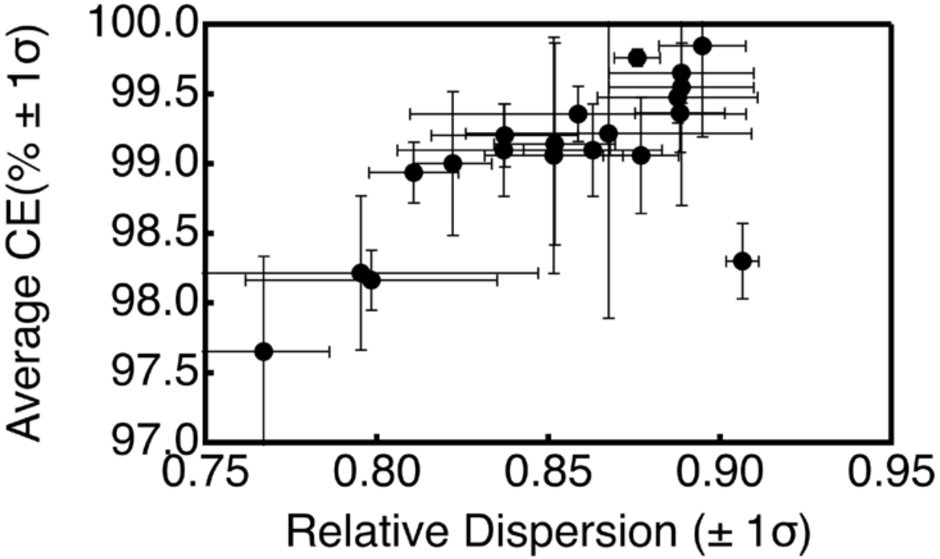
Scanning Electrochemical Microscopy Measurements on SEI Passivation



McBrayer, et al; *J. Appl. Mater. Interfaces* **2024**

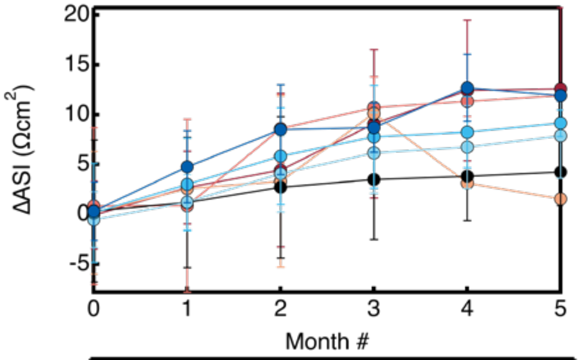
Predictive Parameters for Cycle and Calendar Life

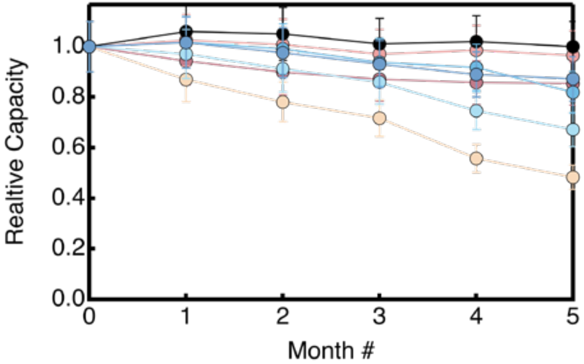


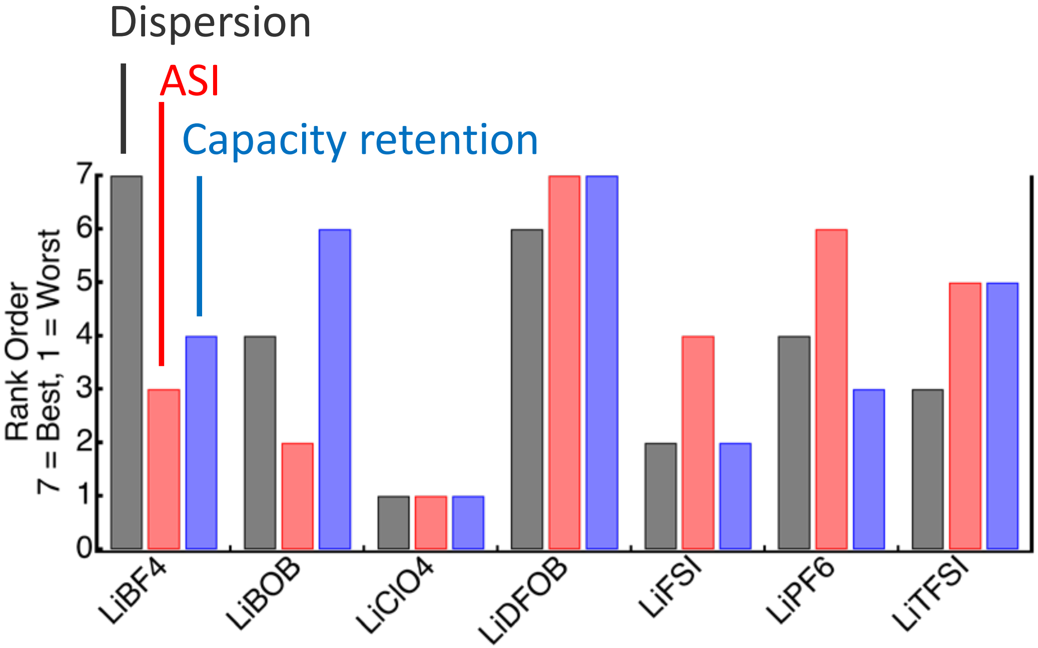


Calendar aging data in EC:EMC (Tier 2, Li^+ limited)

$LiPF_6$: LiTFSI : LiFSI : $LiClO_4$:
LiBOB : LiDFOB : $LiBF_4$

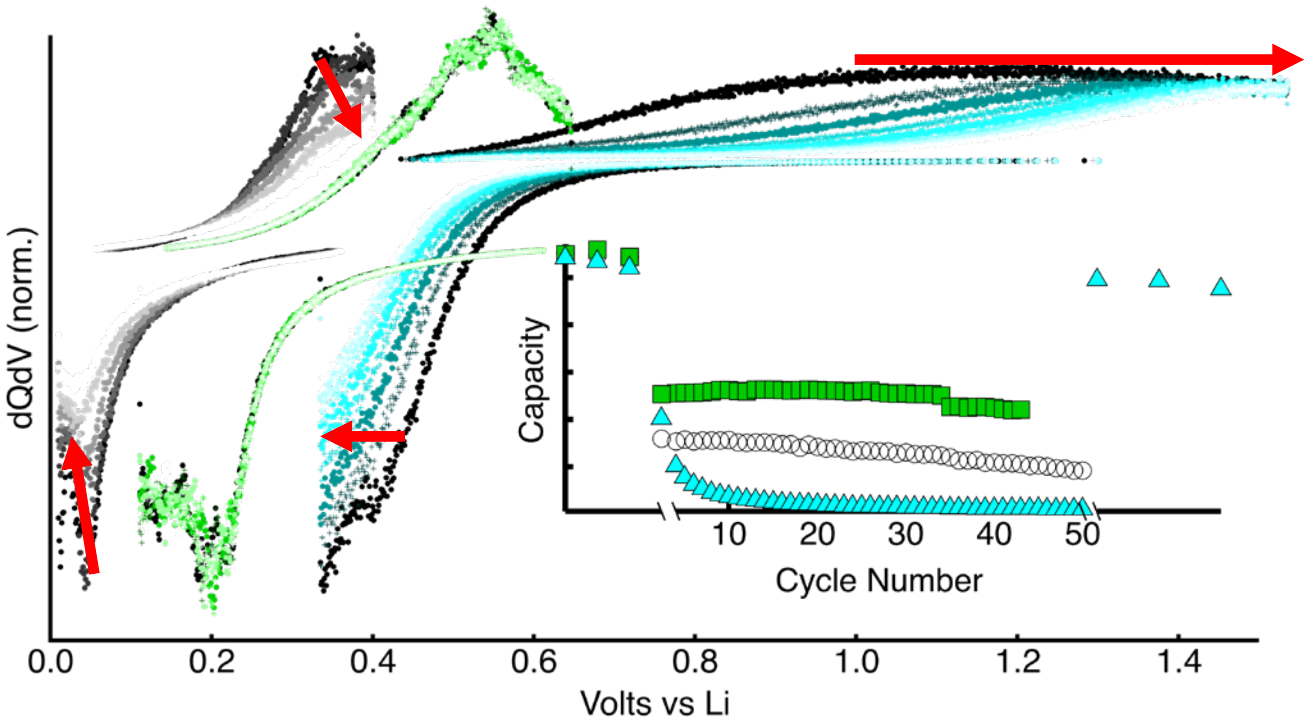






When ranked for ASI gain and capacity retention, α shows promise as a predictor for calendar-related degradation

Impact in Real System



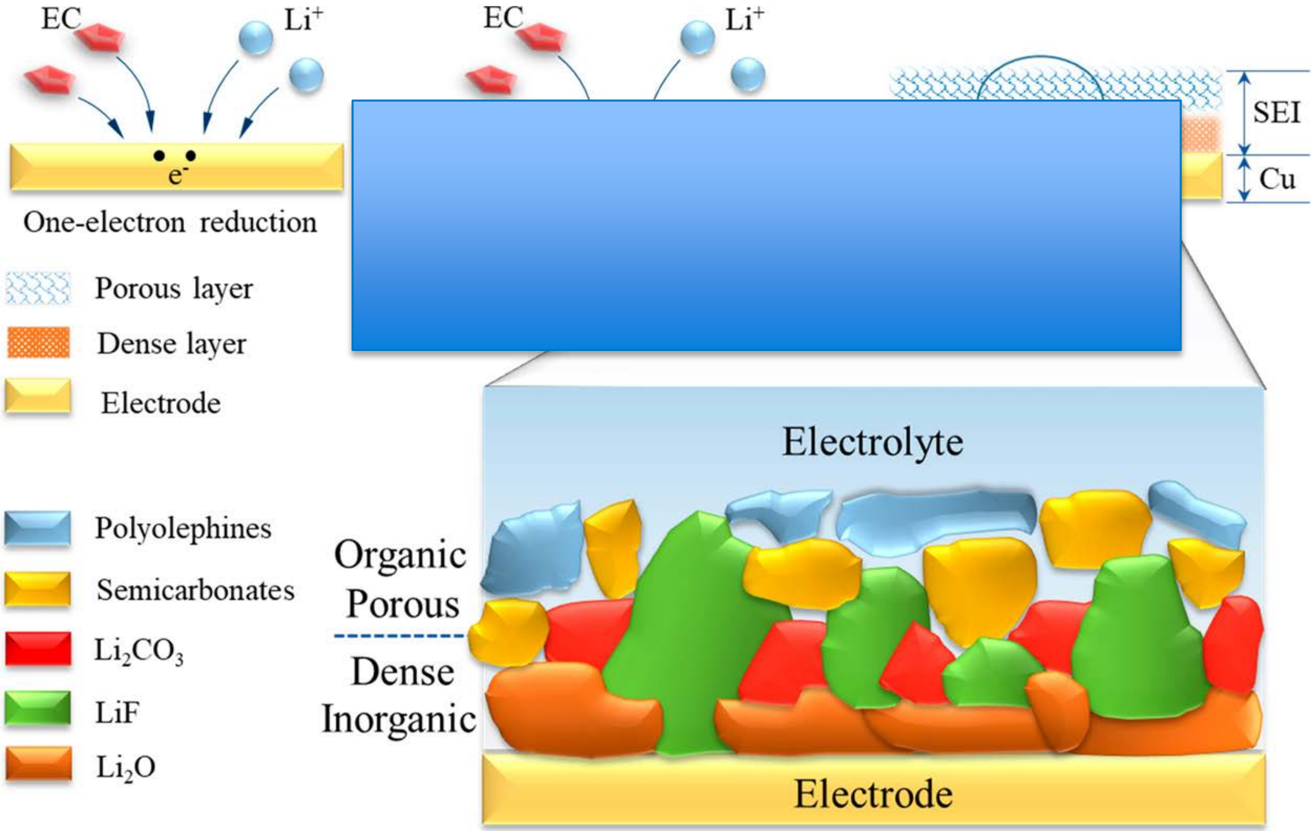
3 half cells formed between 0.01 – 1.5V

Then cycled in different voltage windows

Low voltage electrode shows increasing overpotential with cycling consistent with electrolyte reduction

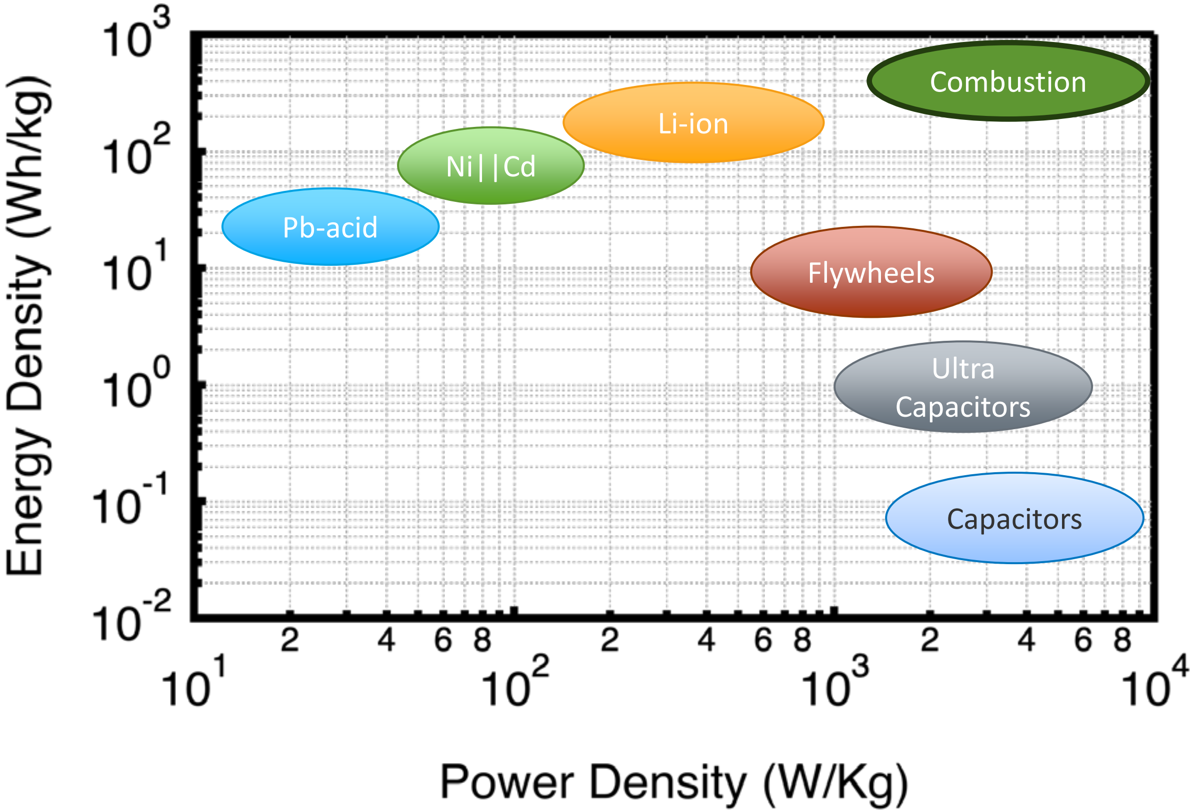
Recovers all capacity when cycled between 0.01 –1.5V

SEI on Copper

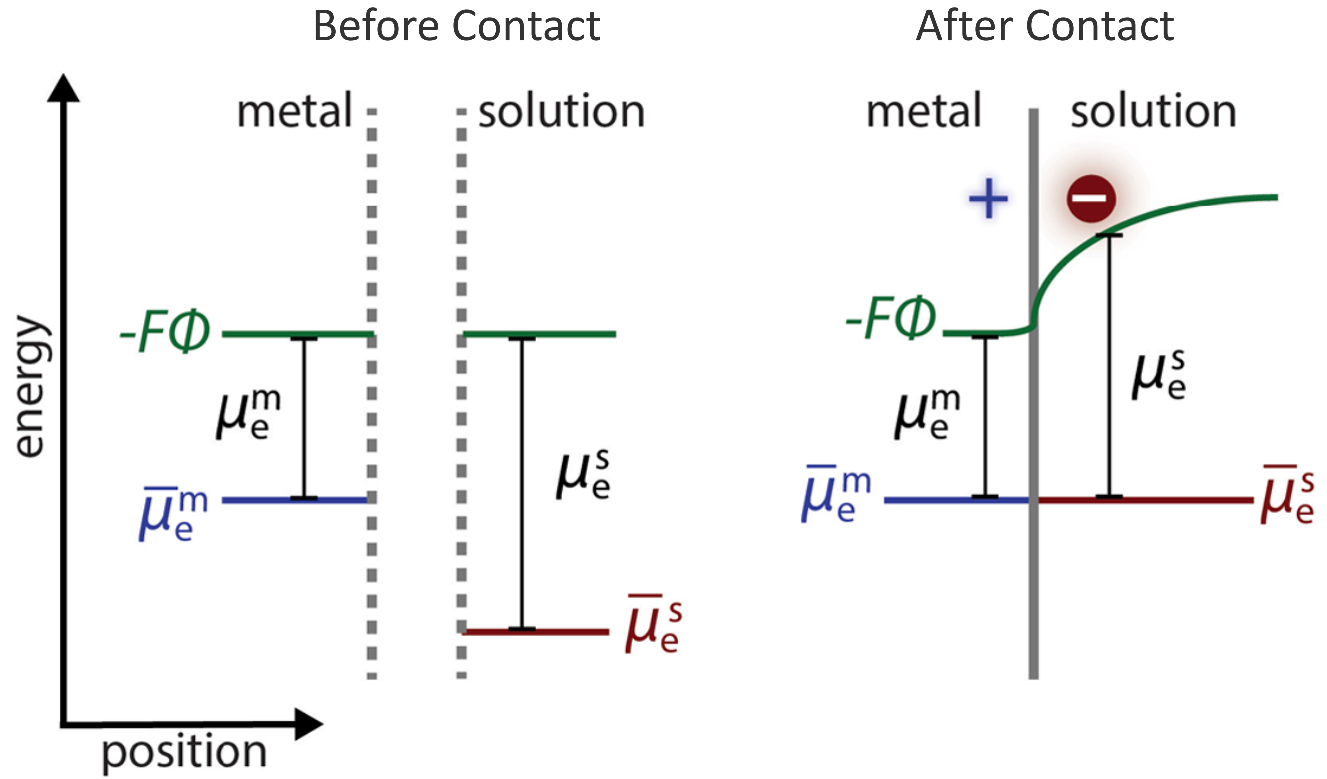


Zhang et al; *J. Phys. Chem Lett.* **2014**

Energy Storage and Delivery Technology



Electrode|Electrolyte Equilibration



Boettcher et. al., *ACS Energy Lett.*, **2021**