The Solid Electrolyte Interphase Dispersion Can Predict Cycle and Calendar Lifetimes in Silicon Anodes for Lithium-Ion Batteries

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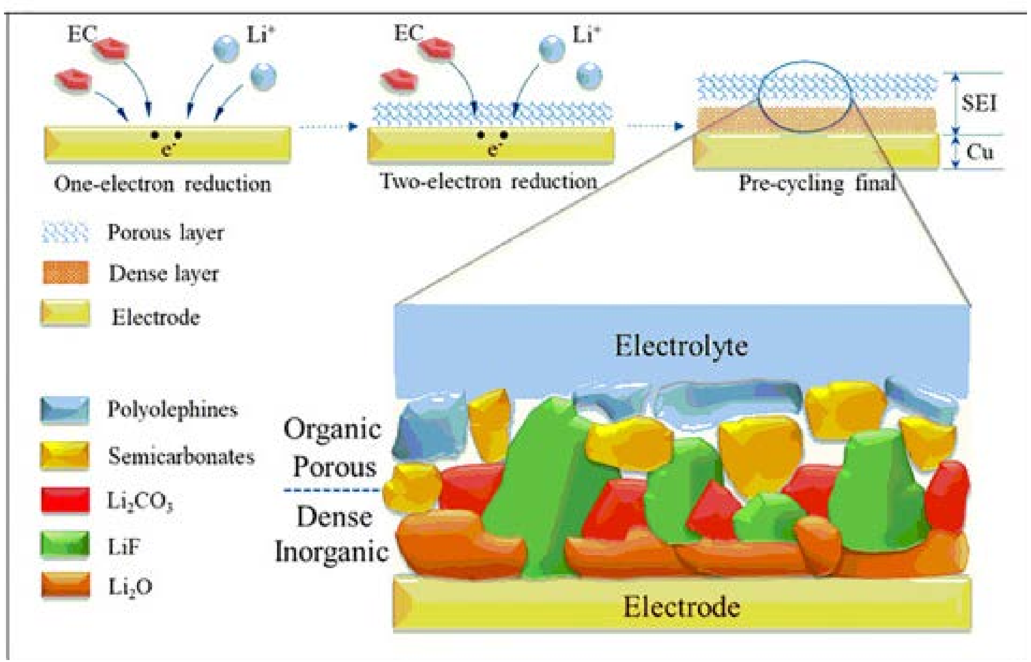
ECS PRIME 2024

Presentation: A07-0888

SEI heterogeneity and calendar aging

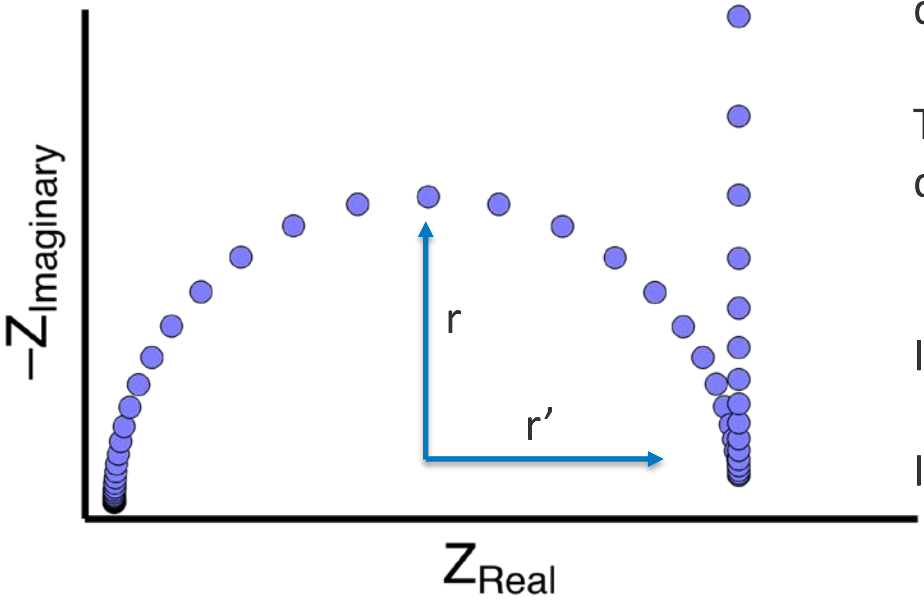


SEI passivity is likely related to calendar aging → better passivity, longer calendar life

SEI is highly heterogeneous → dozens of inorganic and organic species constitute SEI

SEI Dispersion Hypothesis

Hypothesis: Calendar aging and coulombic efficiency is related to the uniformity of the SEI. Higher dispersion allows more access to LixSi which reduces calendar life in reactive electrolytes.



Interface homogeneity can be measured by dispersion of redox processes

The symmetry of the semicircle reports on the distribution of electron transfer kinetics

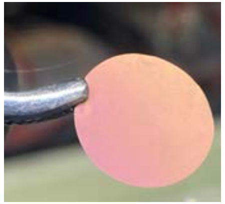
-proxy for interface homogeneity

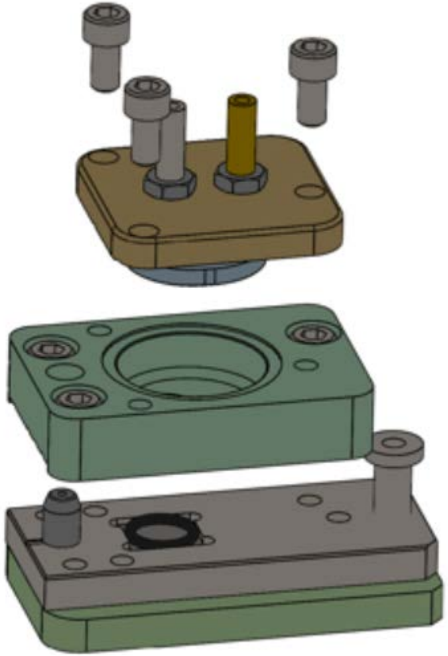
If r = r’, interface dispersion is low and α = 1

If r < r’, interface dispersion is high and 0< α < 1

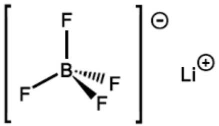
Study Parameters

Electrolyte variation to correlate dispersion and performance metrics

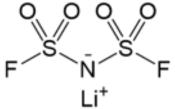




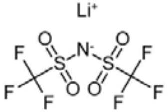
Anion Study with EC:EMC



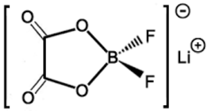
LiFSI



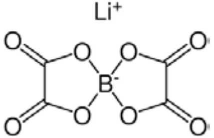
LiTFSI



LiDFOB



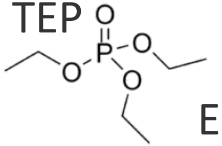
LiBOB



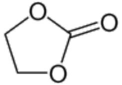
Solvent Study with 1.2M LiFSi

High dielectrics

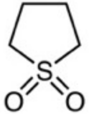
TEP



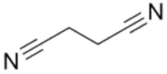
EC



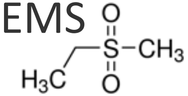
TMS



SN

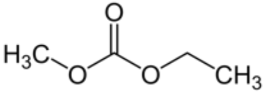


EMS

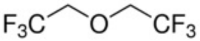


Low dielectrics

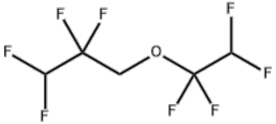
EMC



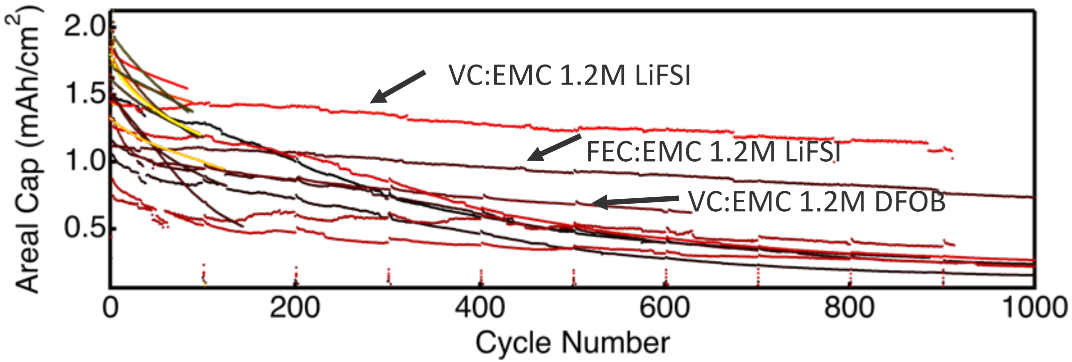
BTFE

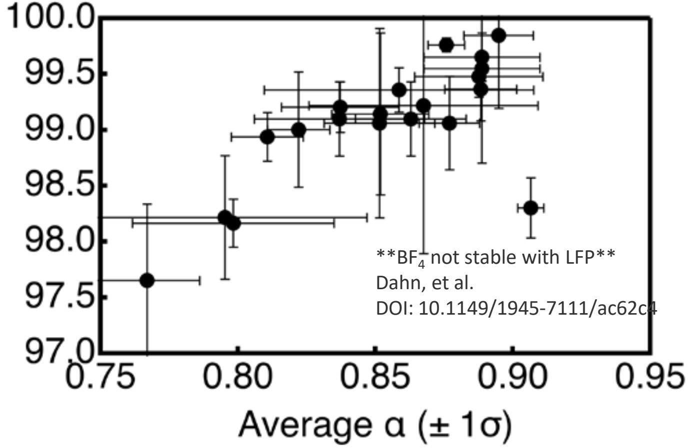


TTE

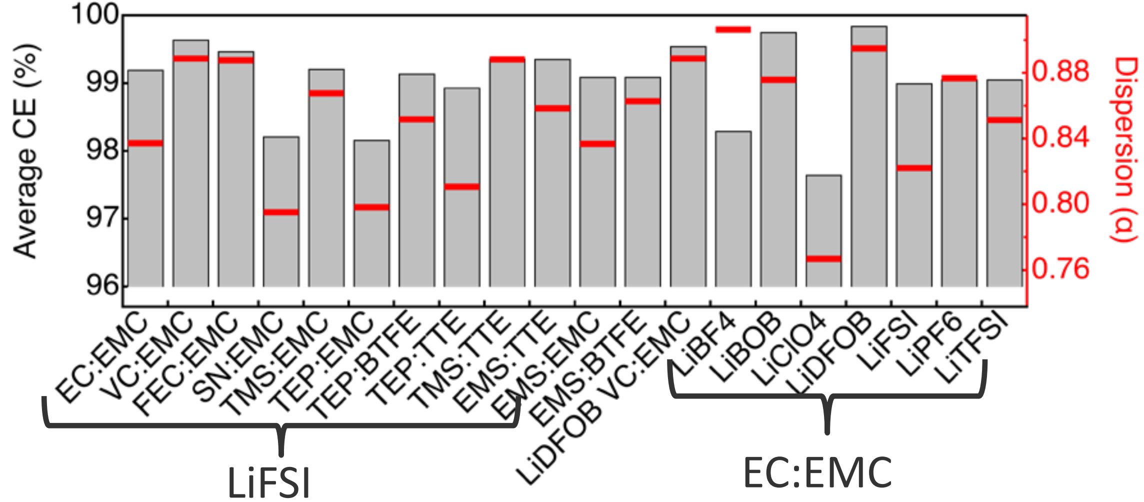


Electrolyte Screen: Cycling





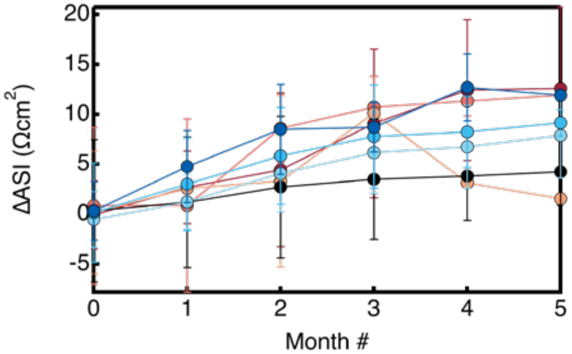
BF$_4$ not stable with LFP
Dahn, et al.
DOI: 10.1149/1945-7111/ac62c4

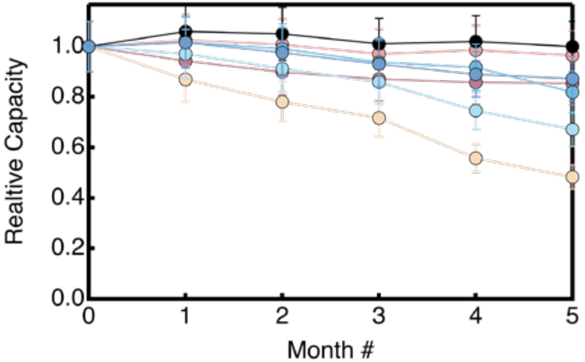


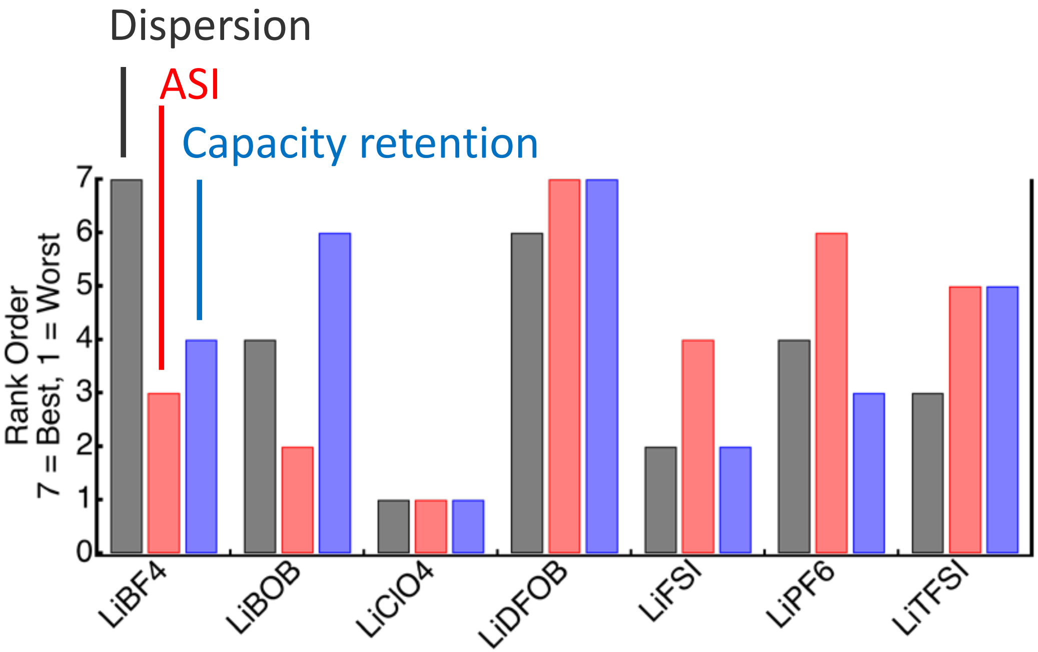
- -VC/EMC with 1.2M LiFSI has longest cycle life
- -Both salt and solvent impact CE
- -Strong correlation between α and average CE (cycle life predictor)

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

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



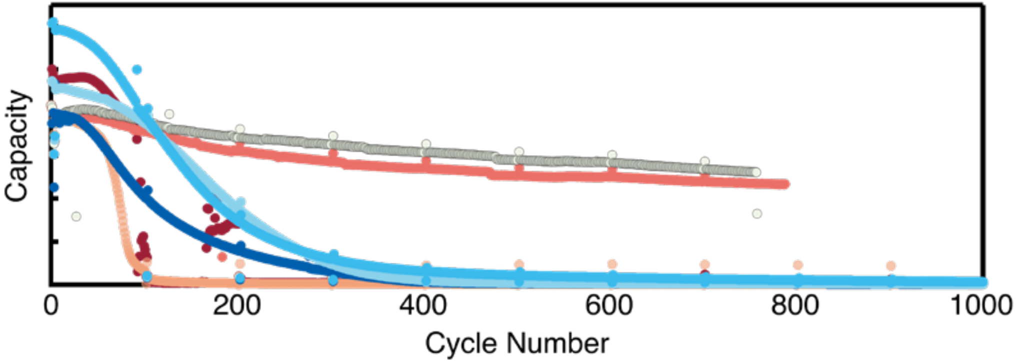


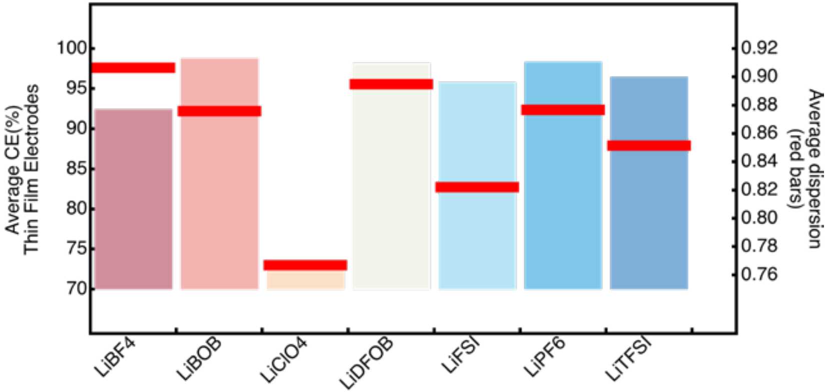


When ranked for ASI gain and capacity retention, α shows promise as a predictor for calendar-related degradation

Salts

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



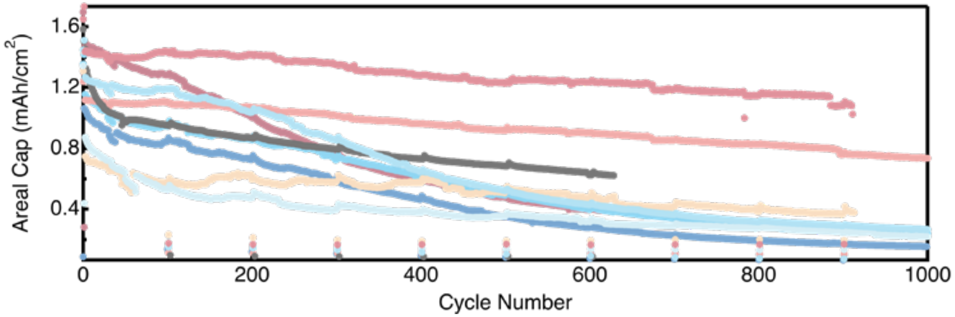


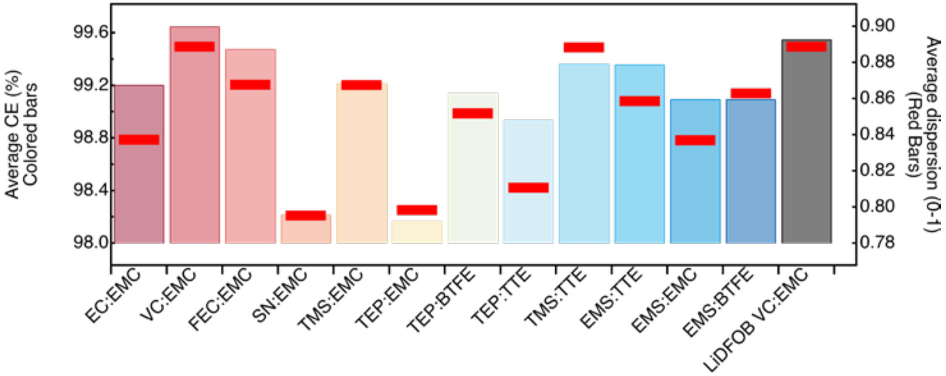
Both Si@PEO and Si thin film electrodes measured in varied salts for both cycle and calendar life.

Relative cycle life of varied anions: LiDFOB> LiBOB > LiFSI = LiTFSI = $LiBF_4$ >$LiPF_6$> $LiClO_4$

Average CE shows reasonable correlation to dispersion

Solvents



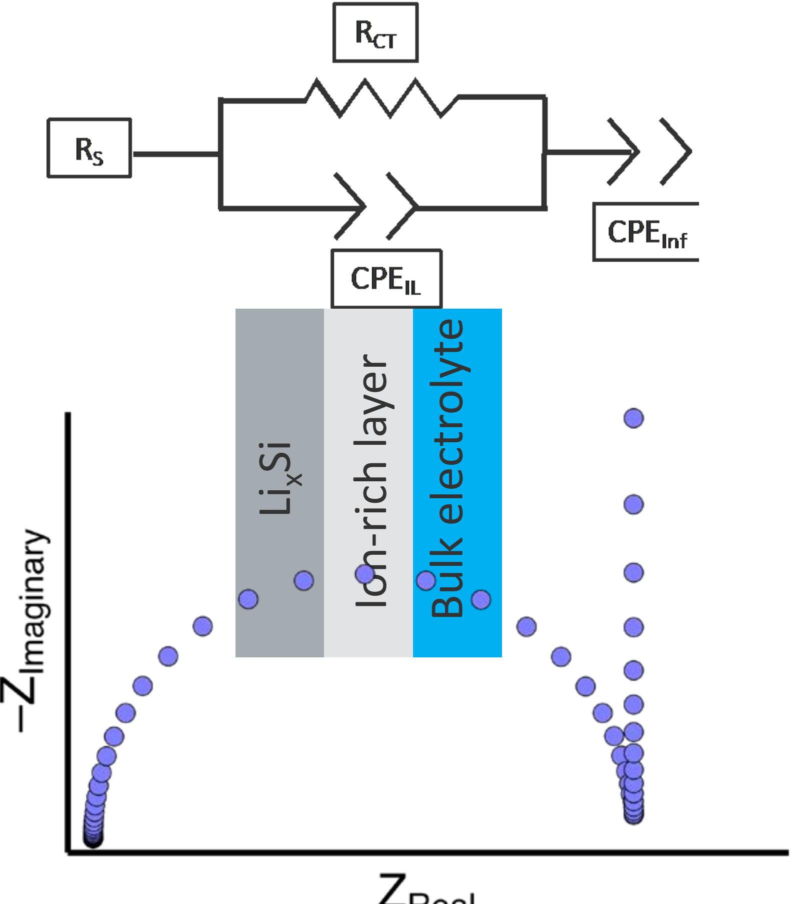


Si@PEO || LFP with 1.2M LiFSI

Solvent Rank for CE

1. VC:EMC
2. LiDFOB VC:EMC
3. FEC:EMC
4. TMS:TTE
5. EMS:TTE
6. TMS:EMC
7. EC:EMC
8. TEP:BTFE
9. EMS:EMC
10. EMS:BTFE
11. TEP:TTE
12. SN:EMC

Equivalent circuit fitting



R_{CT} = Charge transfer across the interface

$$\mathrm{CPE}_{\mathrm{Il,Inf}} = \hat{Z} = R_s + \frac{1}{Q(j\omega)^{\alpha}} = R_s + \frac{1}{Cj\omega} \text{ if } \alpha = 1$$

$$Capacitance = \frac{(Q \times R_{CT})^{1/\alpha}}{R_{CT}}$$

Constant Phase Element- Inner Layer

Cap_{Fast} = Capacitance (F/cm^2)

α_{Fast} = Dispersion parameter (0-1)

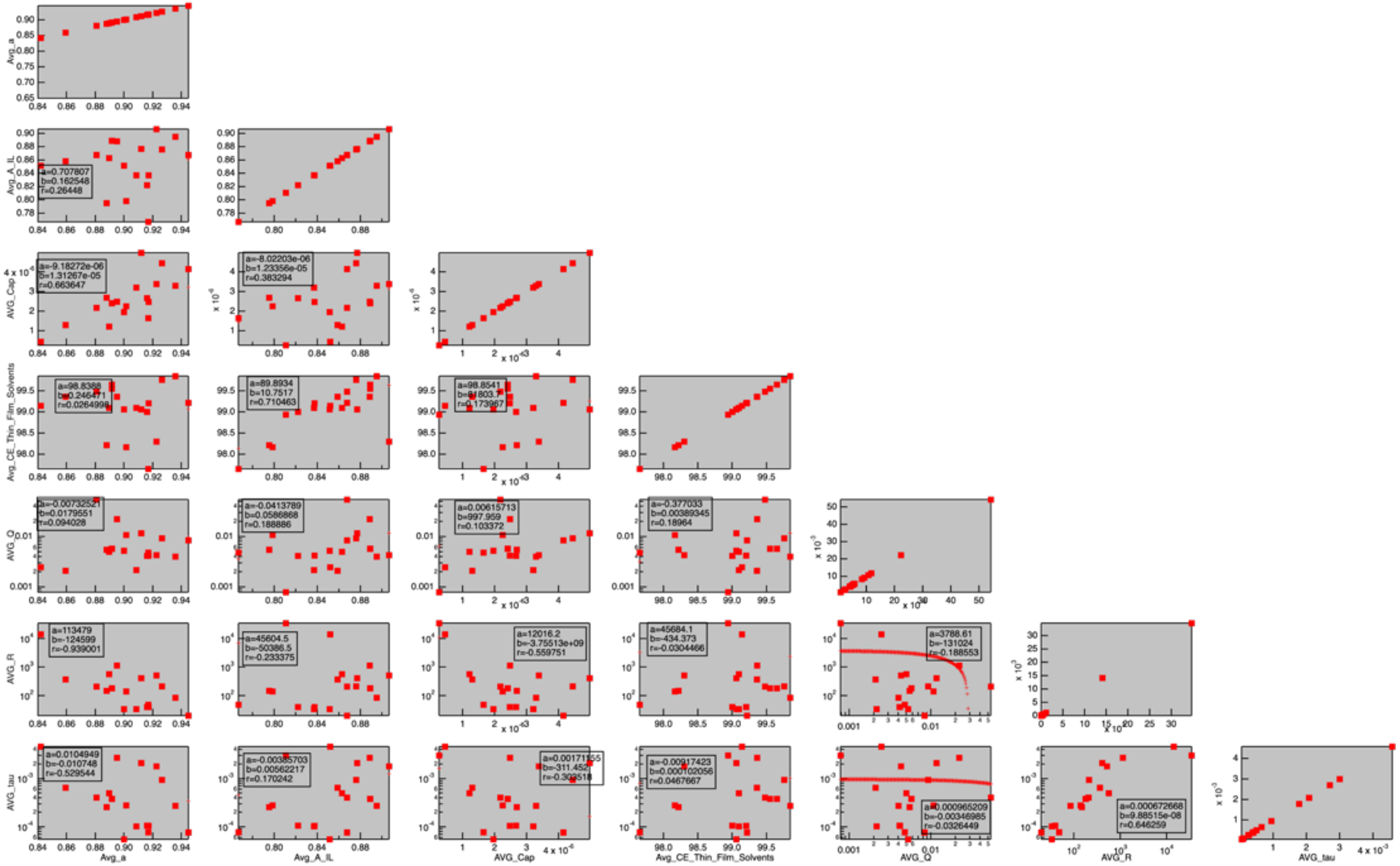
τ_{Fast}= time constant (seconds)

Constant Phase Element – INF

Q_{Slow} = $Fs^{\alpha-1}cm^{-1}$

α_{Slow} = Dispersion parameter (0-1)

Correlation Matrix



Calendar aging data (Tier 2, Li^+ limited)

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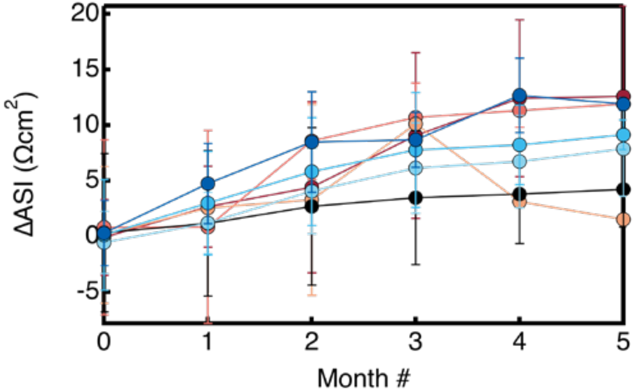
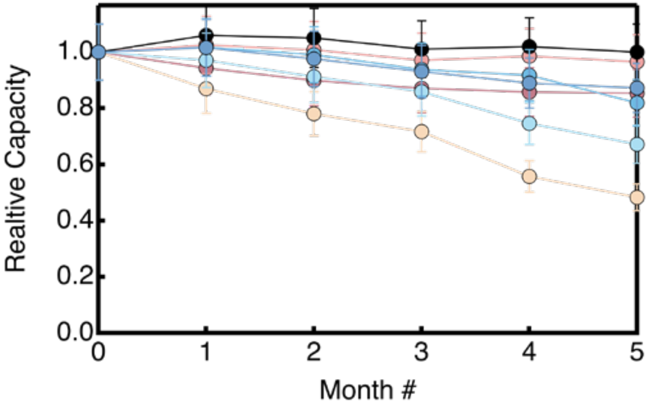
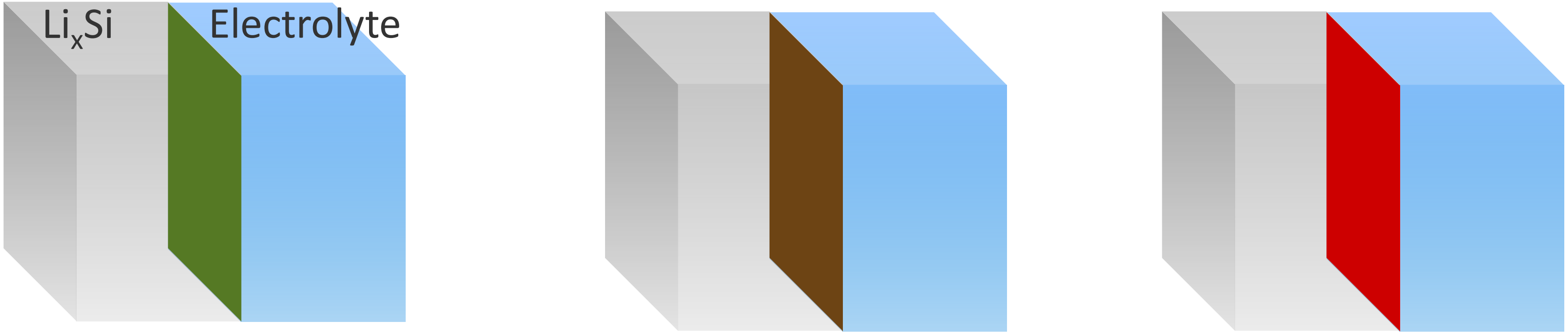




Lowest relative impedance gain from calendar aging:
LiDFOB> LiFSI > LiTFSI > LiBOB = $LiBF_4$ = $LiPF_6$ = $LiClO_4$

Relative Capacity retention from calendar aging:
LiDFOB> LiBOB > $LiPF_6$ = LiTFSI > $LiBF_4$ > LiFSI = $LiClO_4$

Dispersion at the Li_xSi surface



Ideal capacitive behavior	Ideal resistor behavior
Single time constant	Infinite distribution of time constants
Low dispersion	High dispersion
Single microscopic state	High # microscopic states
Low entropy differential with electrolyte	High entropy diff. with electrolyte

Ideal silicon surfaces and electrolytes are ones that minimize entropy differences at the interface

Conclusions

1. From electrolyte screening study:
    1. VC:EMC has highest average CE.
    2. FEC:EMC and TME:TTE are second and third
    3. Of the salts, LiDFOB has highest CE, lowest ASI gain, and highest capacity retention with EC:EMC as the solvent.

2. Interface dispersion analysis:
    1. Dispersion parameter is strongly correlated with CE for 20 electrolyte mixtures
        1. Nature of correlation may not be linear, but sigmoidal.
        2. At high α values, very accurate measurements are needed to determine differences in interface
    2. Initial calendar aging results show promise for assessing calendar life (ASI gain and cap. ret.) from α quantification

Questions?

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NREL/PR-5900-91292

This work was authored in part 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 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.

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