Corrosion of Lithium Metal Anodes during Calendar Aging and its Microscopic Origins

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Solid Power Workshop

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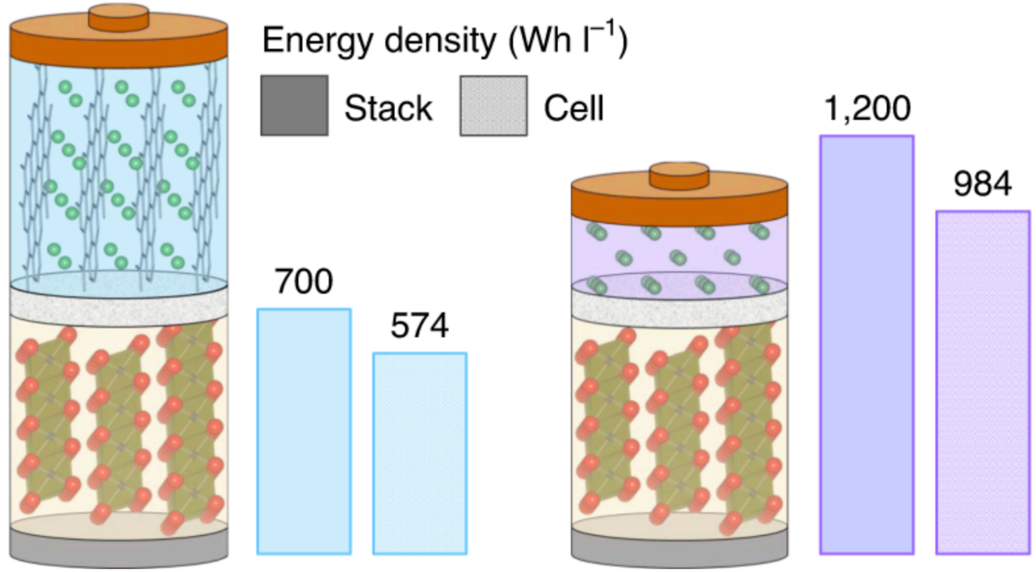
Li Metal Battery Chemistry

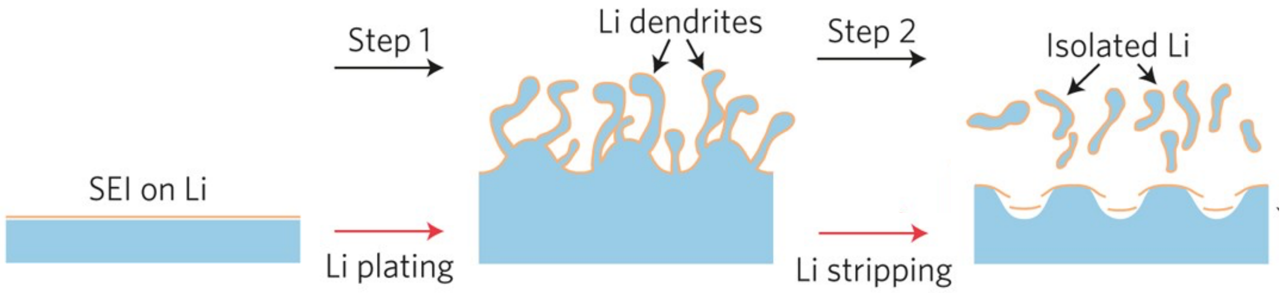
'Anode-free' Cells: Major boost to Energy Density



J. Dahn & co-workers *Nature Energy* **2020**, *5,* 693–702

Li metal generally has poor rechargeability

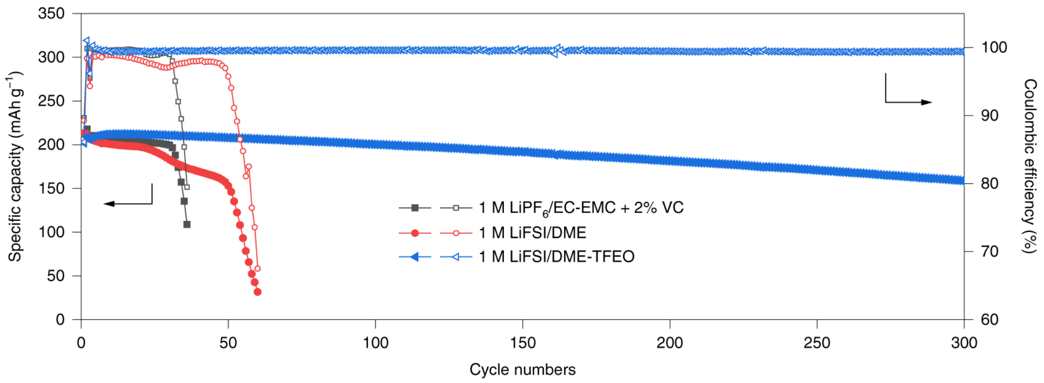
- high surface area – side reactions with electrolyte
- Isolated ('dead') Li



Lin, D.; Liu, Y.; Cui, Y. *Nature Nano.* **2017**

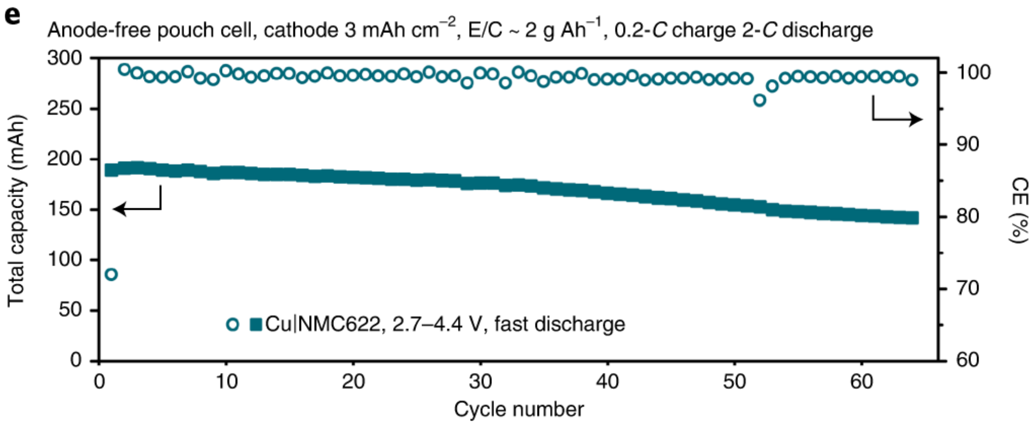
Electrolyte Engineering: Cycle Life of Li metal

Localized high-concentration (LCHE)



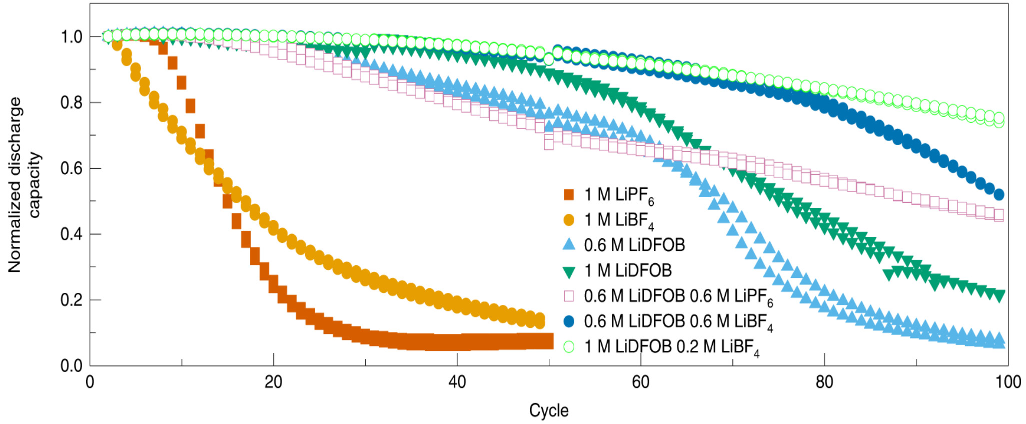
J. Zhang, W. Xu & coworkers *Nature Energy* **2019**, *4*, 796-805

LiFSI and fluorodimethoxybutane (FDMB)



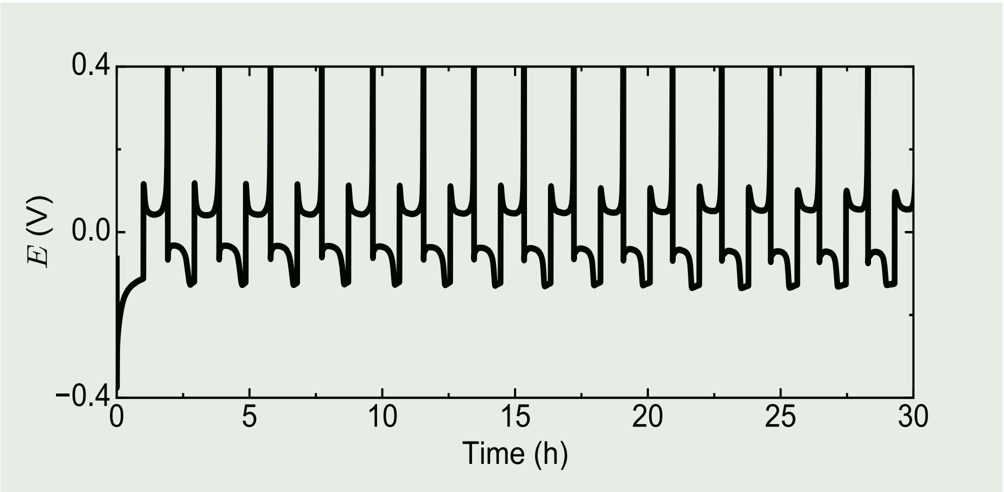
Z. Yu, Z. Bao, Y. Cui & coworkers *Nature Energy* **2020**, *5*, 526-533

FEC:DEC LiDFOB and $LiBF_4$



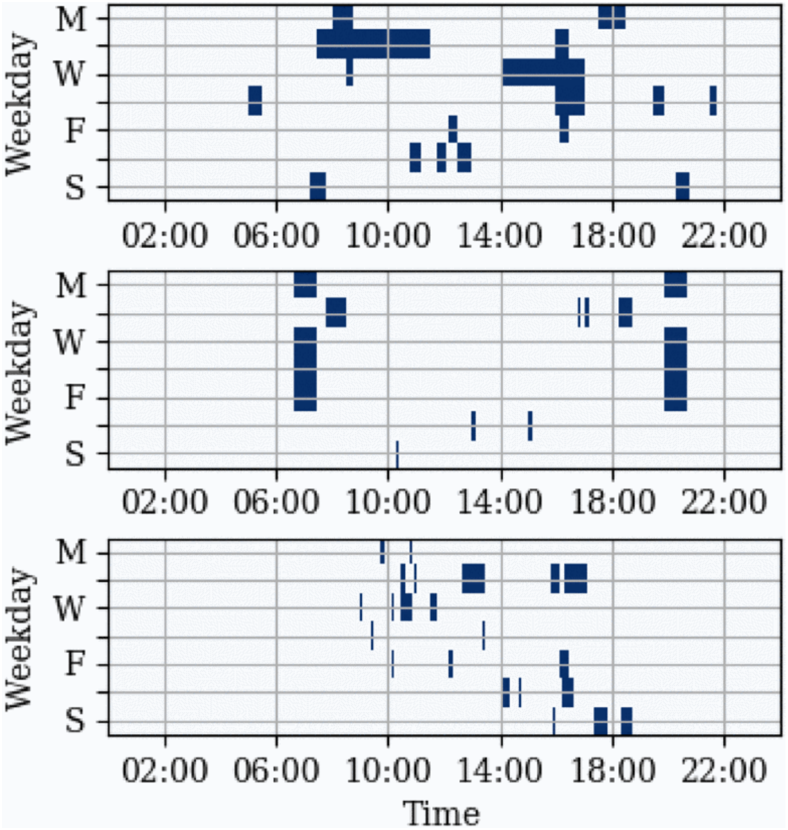
A. Louli, J. Dahn & coworkers. *Nature Energy* **2019**, *4*, 683

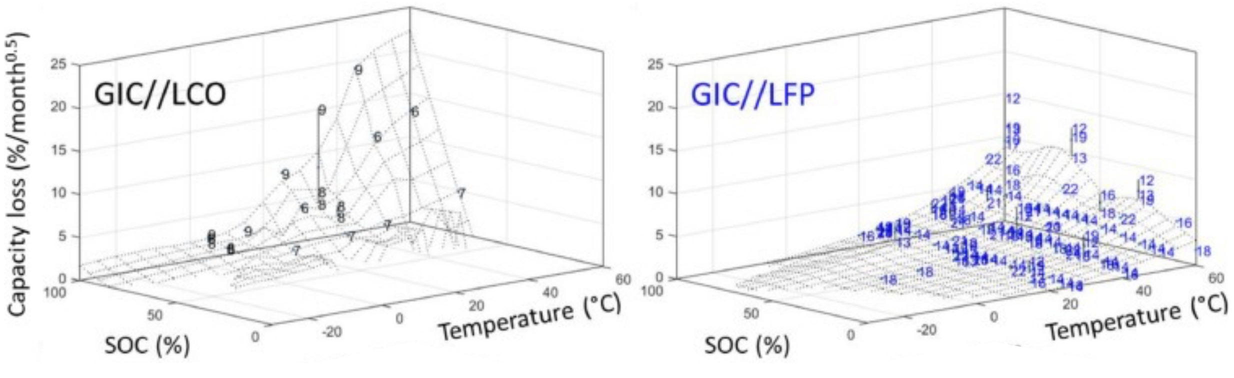
Standard testing: constant cycling



Storage of Li-ion batteries and key differences for Li metal

Electric vehicle usage





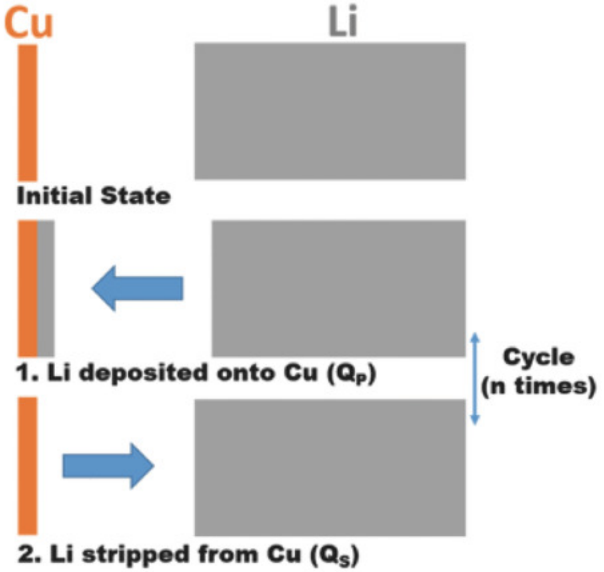
- Loss of capacity during storage is highest at 100% SOC and high temperature
- SEI growth from electrolyte reduction at the anode at low anode potentials
- In lithium metal batteries, the anode potential is ≈ 0 V vs. Li/Li^+ at all SOC

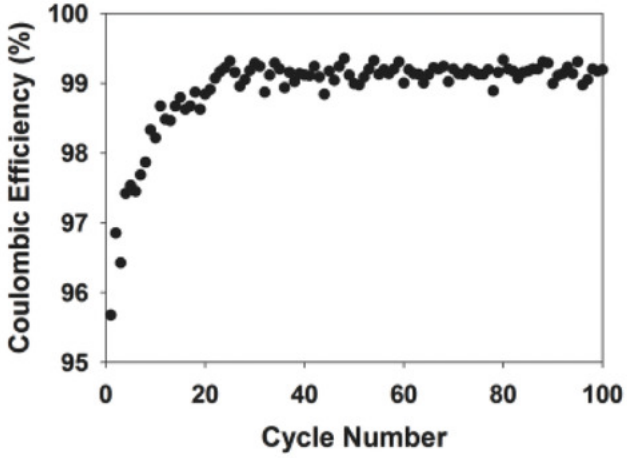
Central Questions: How does storage affect rechargeability of Li metal? What causes any loss of capacity? How can losses be prevented?

"Clustering of Usage Profiles for Electric Vehicle Behaviour Analysis," **2018** *IEEE PES Innovative Smart Grid Technologies Conference Europe (ISGT-Europe)*, Sarajevo, 2018, pp. 1-6.

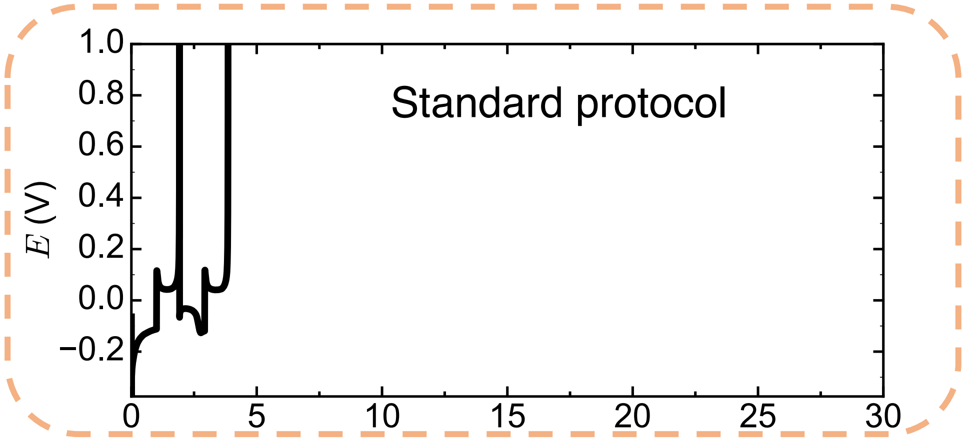
Current Opinion in Electrochemistry **2018**, *9,* 106–113

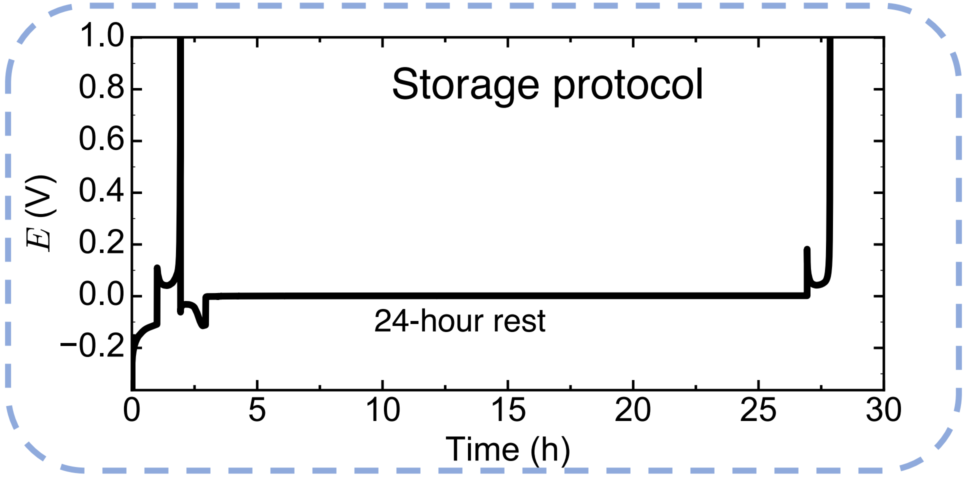
Measuring Rechargeability of Lithium Anodes



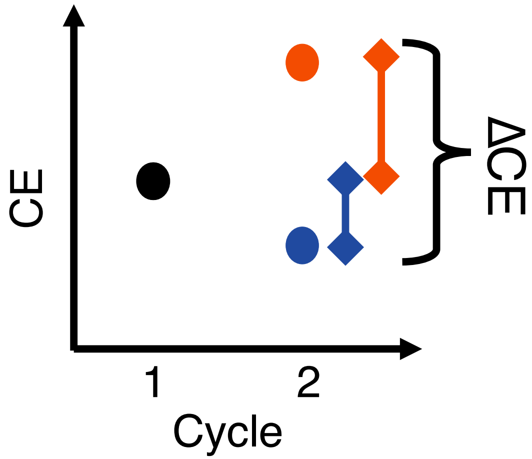


- Incorporate storage into the CE protocol





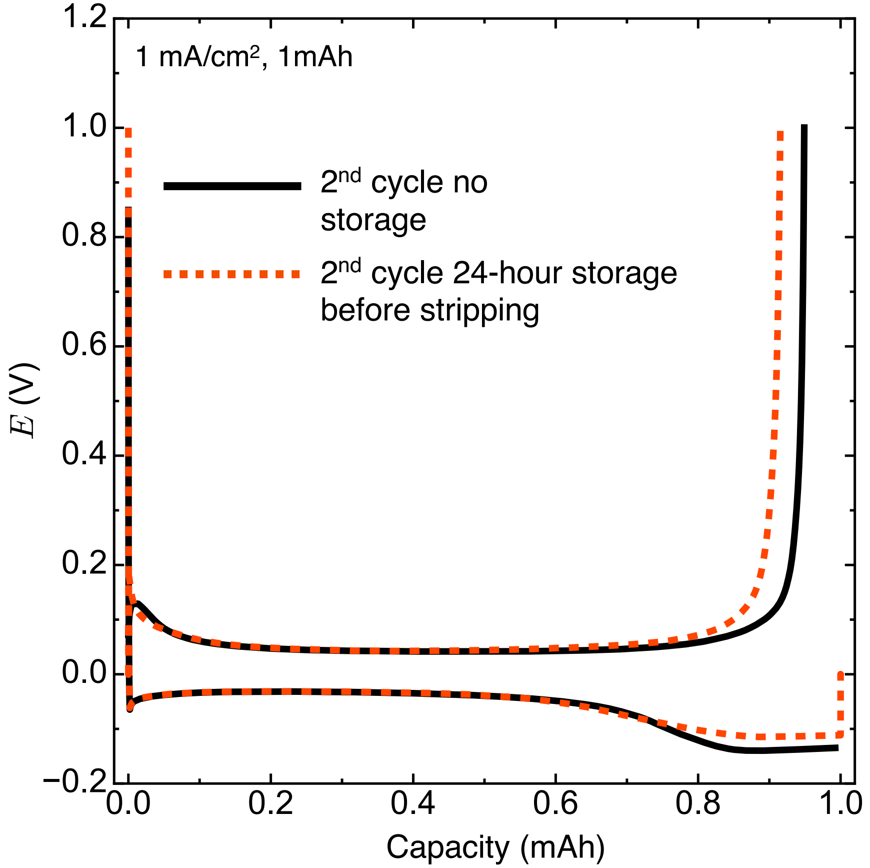
Extra Lithium Loss



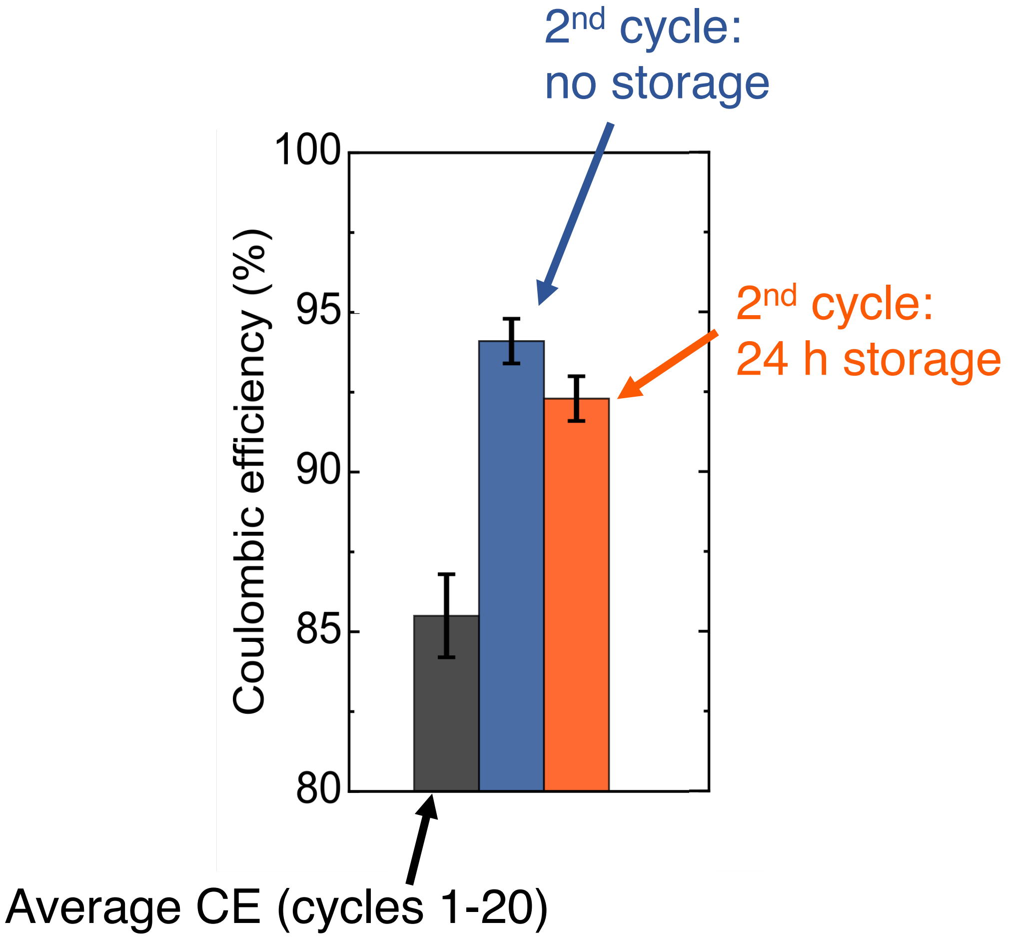
J. Guang and co workers *Adv. Energy Mater.* **2017**, 1702097

Effect of Aging on Li metal Rechargeability

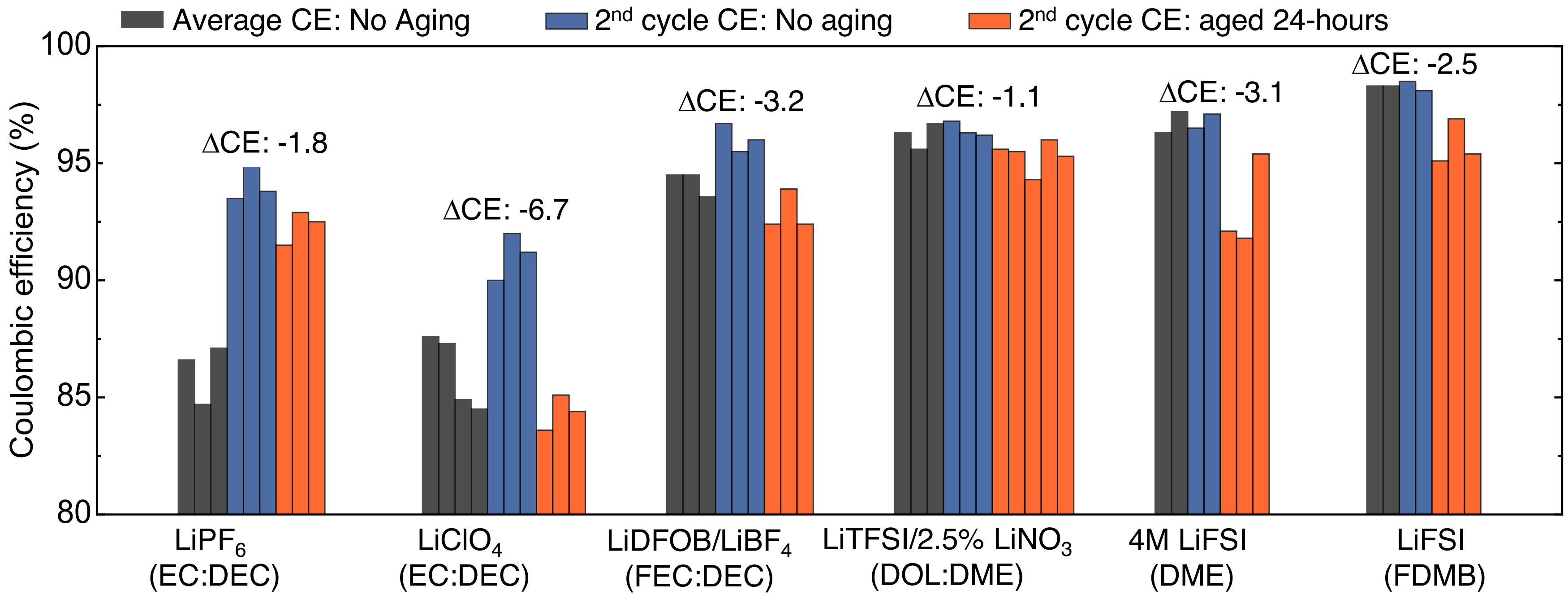
Commercial carbonate electrolyte
$LiPF_6$ (EC:DEC)



- Storage for 24 hours causes a ΔCE = -1.8%



Effect of Electrolyte Chemistry



Low performance

- Commercial Carbonates

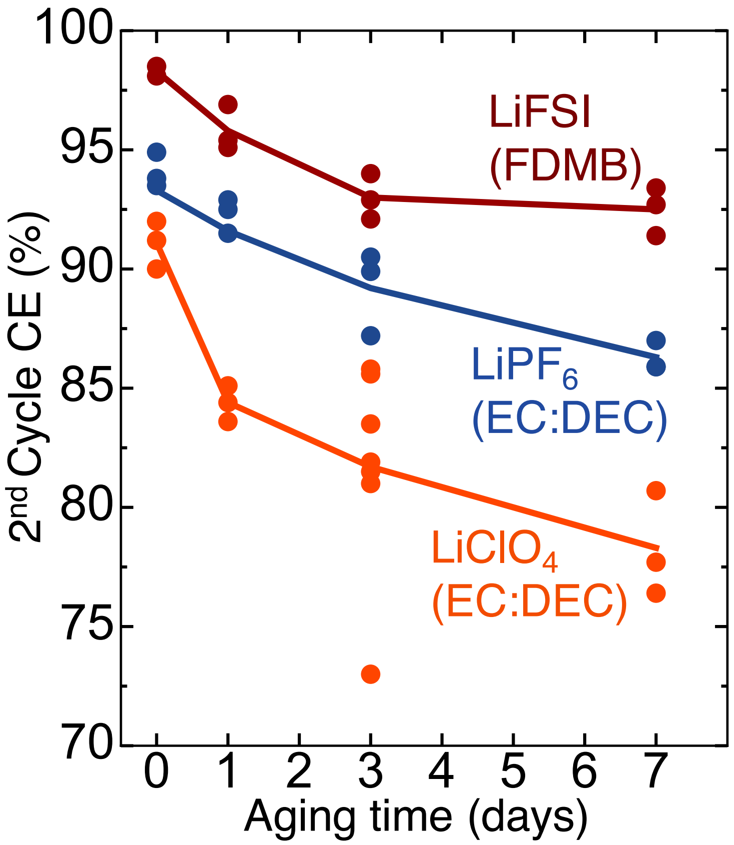
High performance

- Dual salt
- Additives
- High concentrations
- Ether and Fluorinated solvents

- Typically, ~2-3% of capacity is lost during 24 hours of storage
- Both high and low performance electrolytes show losses

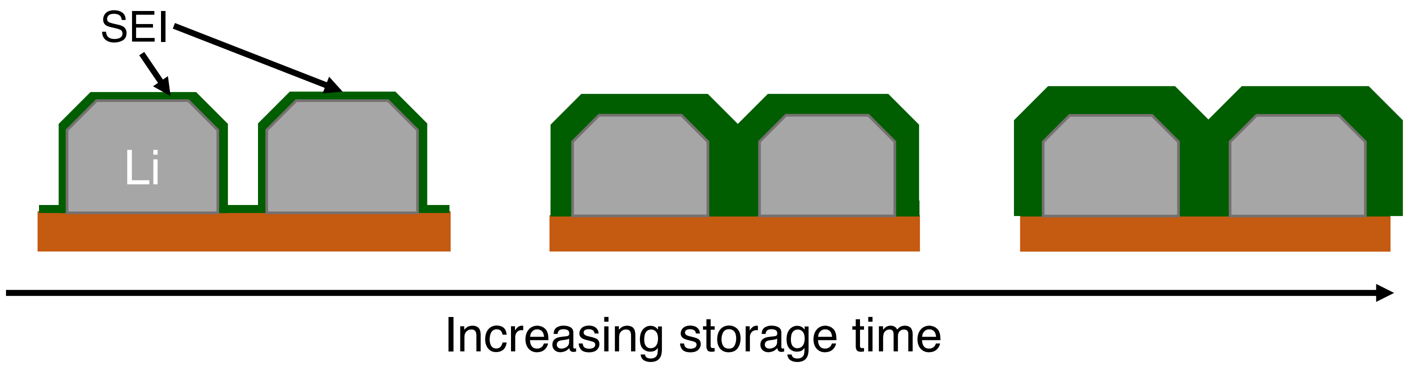
Can we identify the cause of these capacity losses?

SEI and Self-passivation over time



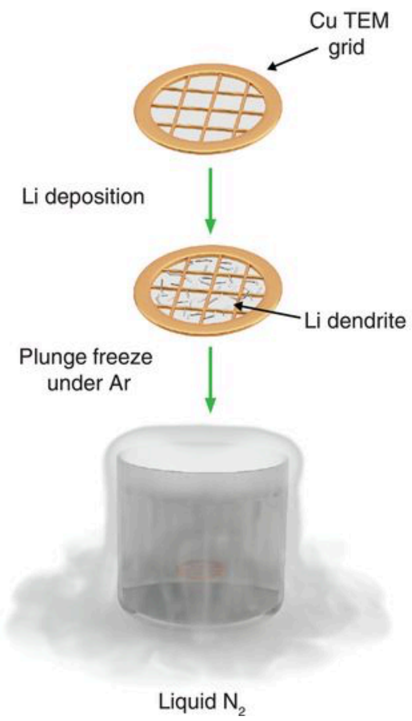
Storage time

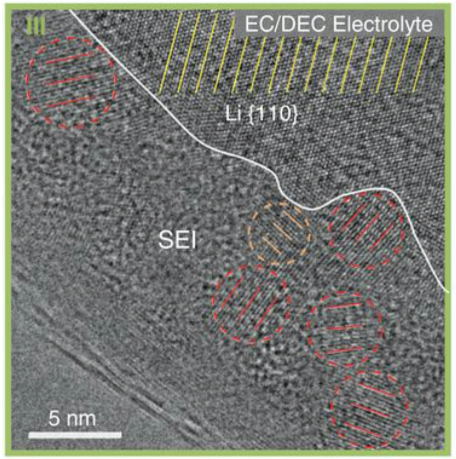
- Capacity loss smoothly increases with time – consistent with SEI growth

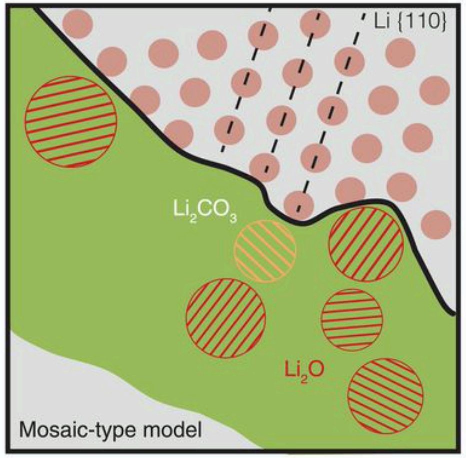


Visualizing SEI on Li with cryo-(S)TEM and EELS

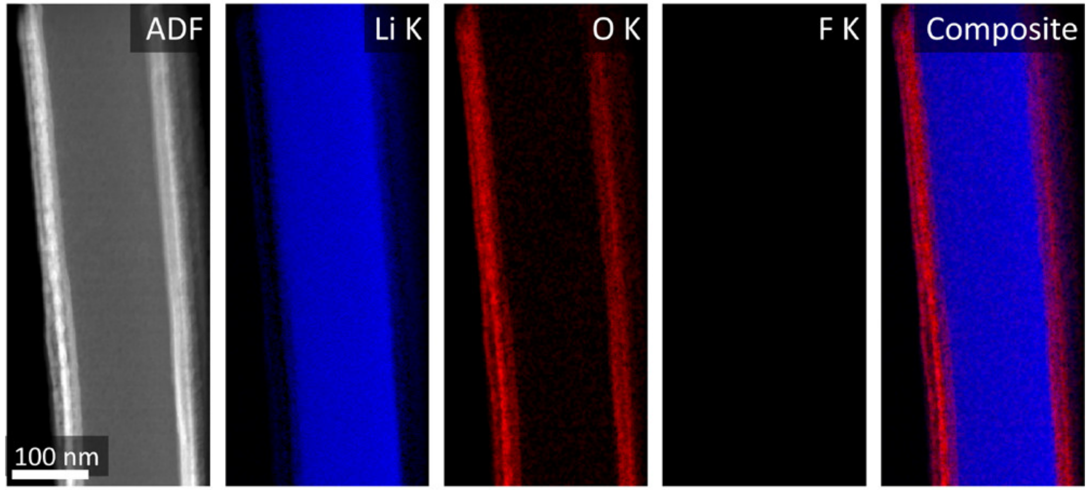
- Cryo-TEM maintains Li and its SEI in a pristine state for nano-scale imaging







- Cryo-STEM EELS simultaneously provides chemical and spatial information at the nanoscale

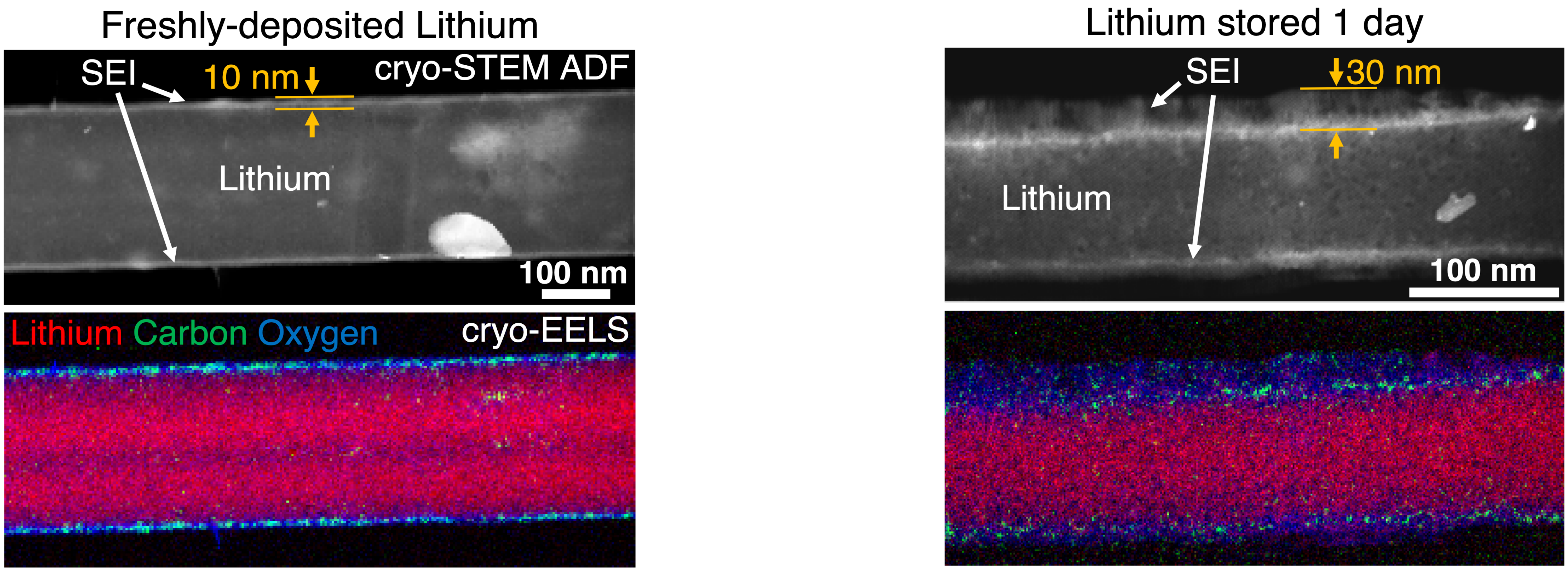


STEM-EELS image of Lithium and SEI

Li, Y.; Li, Y.; Cui, Y. et al. *Science* **2017**, *358*, 506

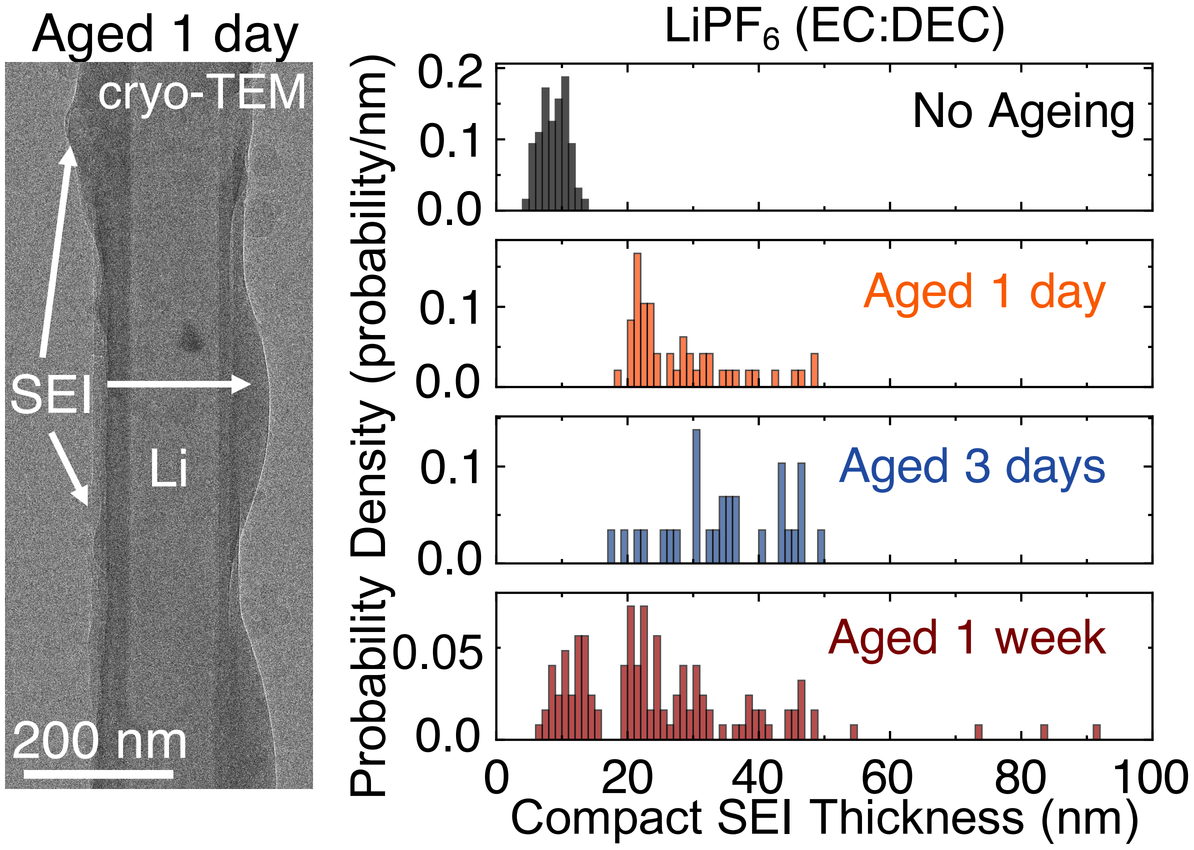
Huang, W.; Cui, Y. et al. *ACS Energy Lett.* **2020**

Growth of the SEI on Lithium

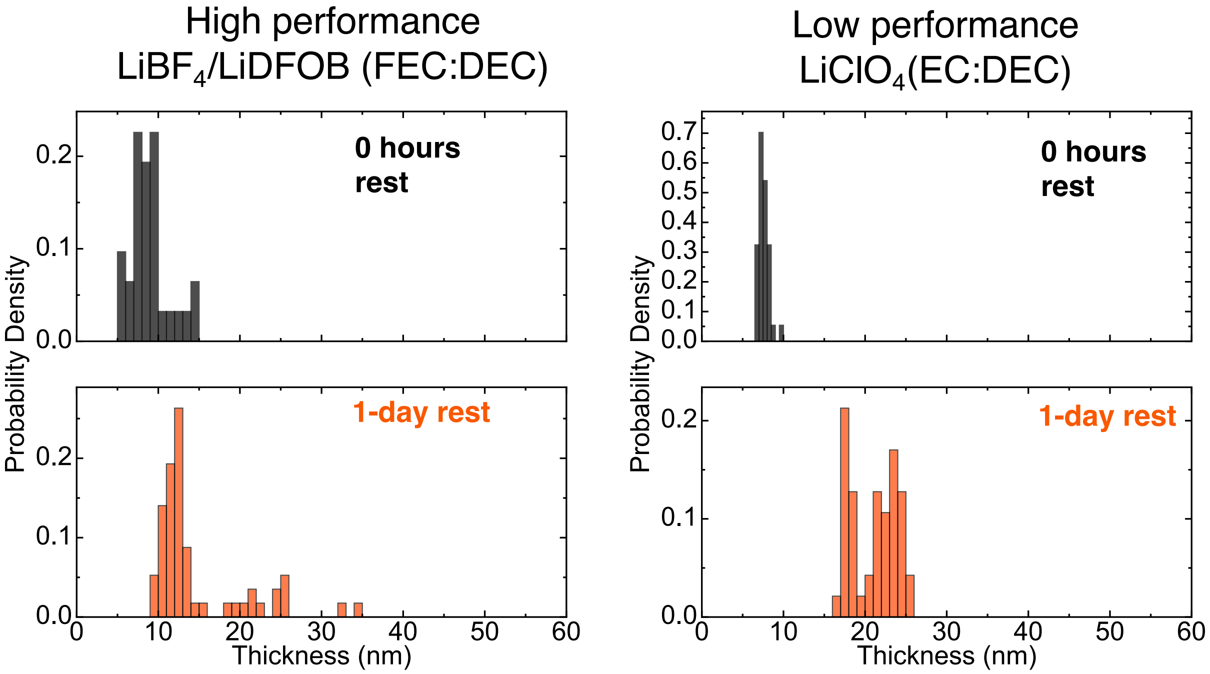


Heterogeneous growth of the SEI

- Thickness and heterogeneity of the compact SEI increases with longer storage times

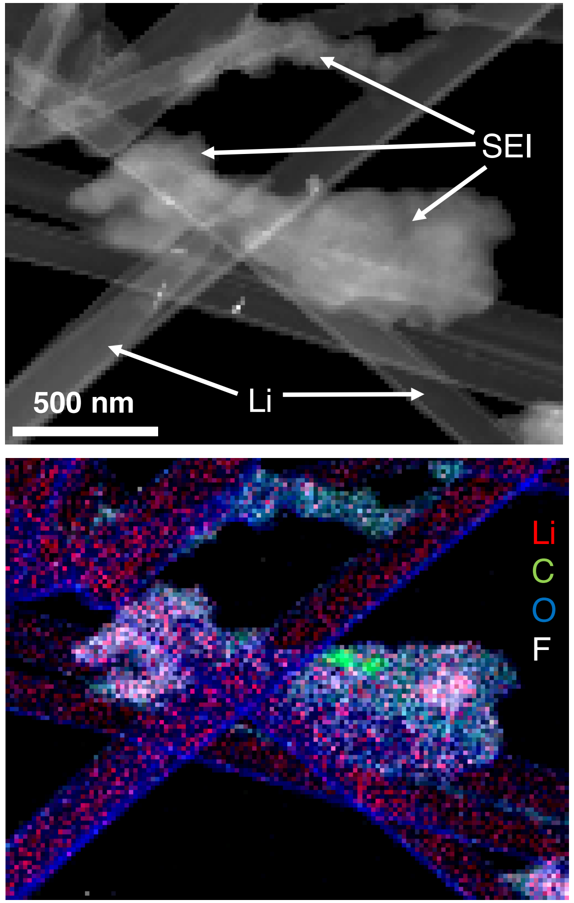


- Both low and high performance electrolytes have similar SEI growth

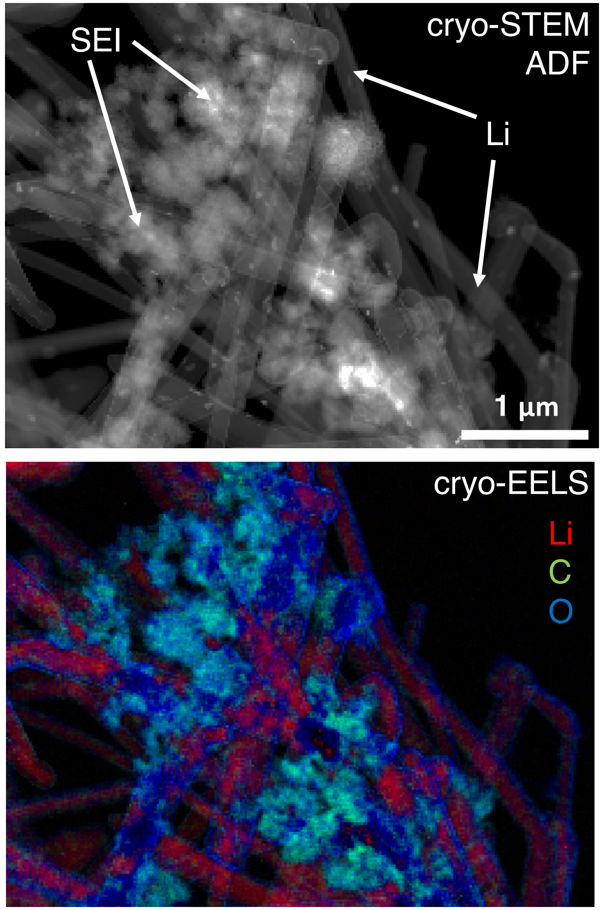


Growth of an Irregular & Extended SEI on Lithium

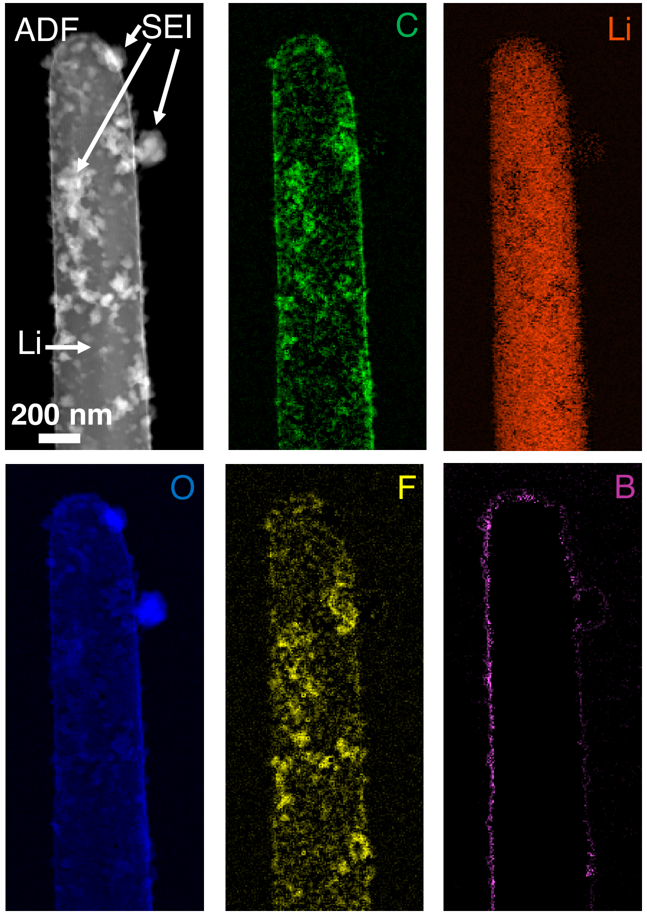
Stored 3 days
in $LiPF_6$ (EC:DEC)



Stored 1 day
in $LiClO_4$ (EC:DEC)

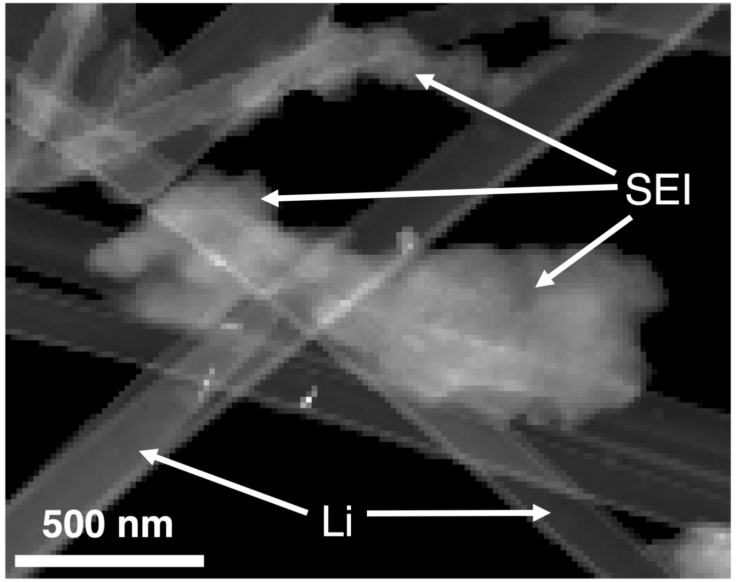


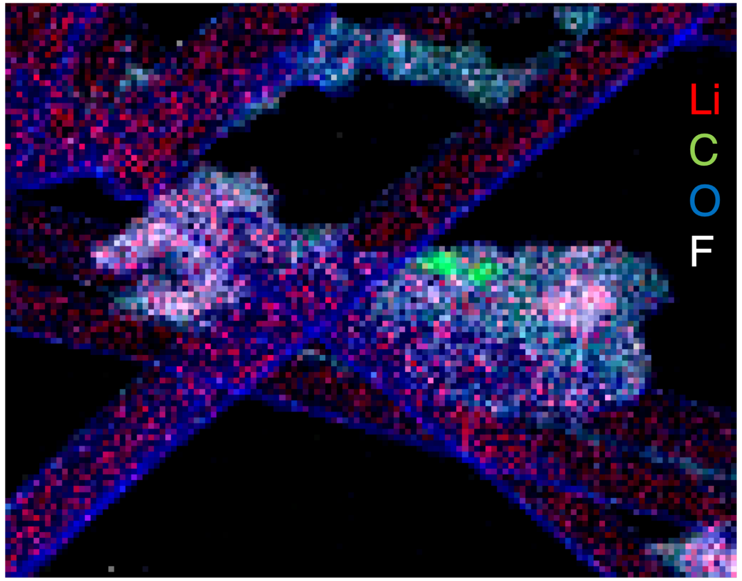
Stored 1 day
in $LiBF_4$/LiDFOB (EC:DEC)



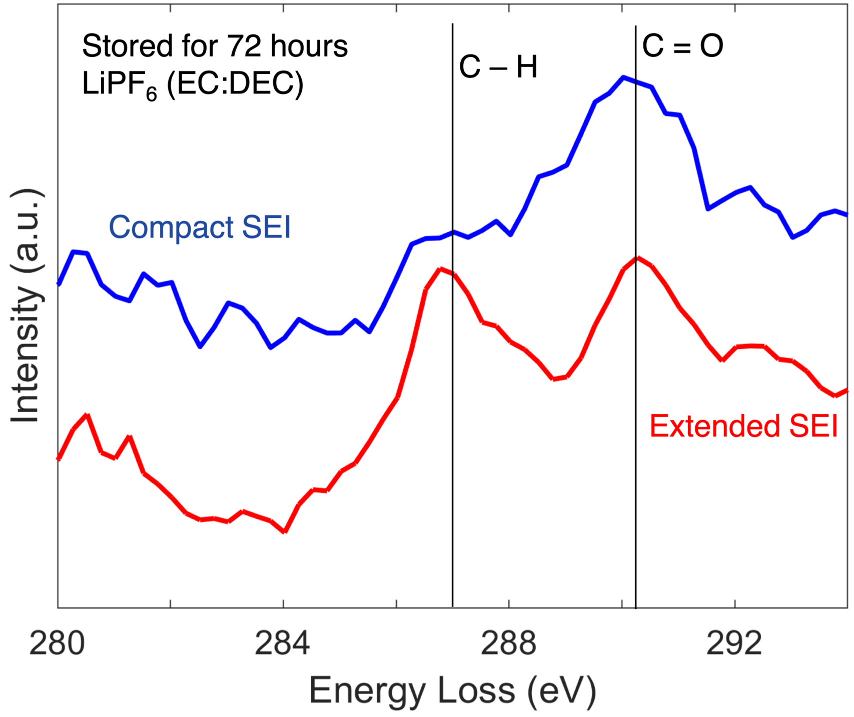
Dependence of extended SEI on Electrolyte

Stored 3 days in $LiPF_6$ (EC:DEC)



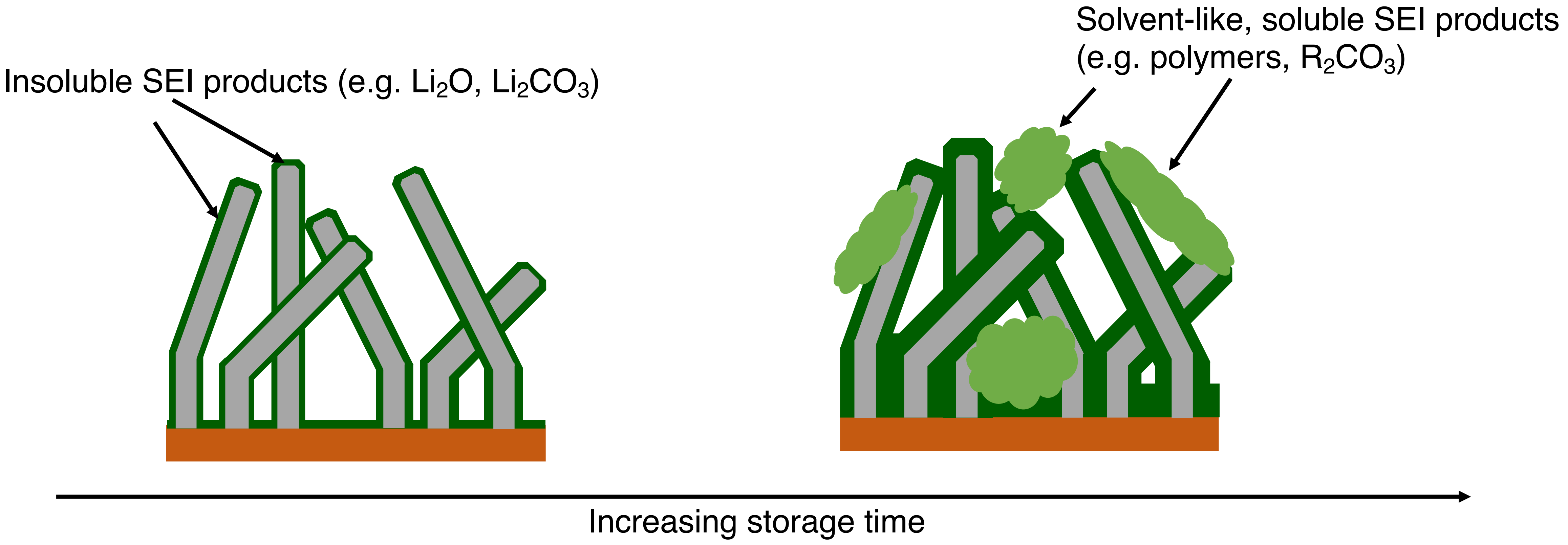


- Compact SEI is more inorganic
- Extended SEI is more solvent-like, suggesting that the SEI is precipitating out of the electrolyte

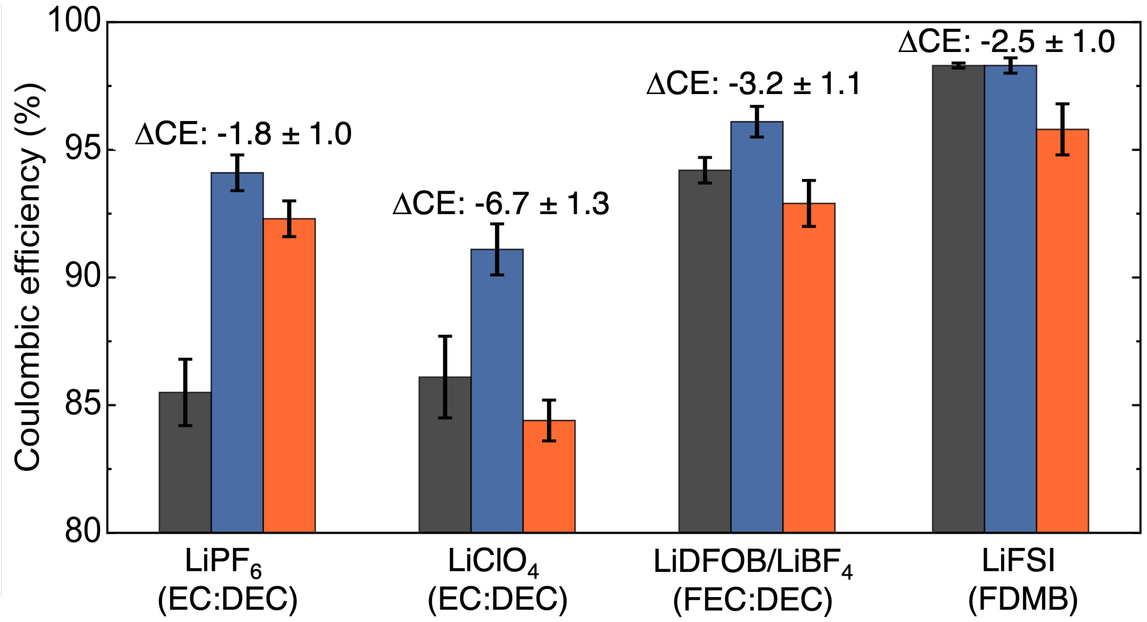


SEI growth during Storage

- Develop a time-dependent picture of SEI growth and capacity loss in LMBs

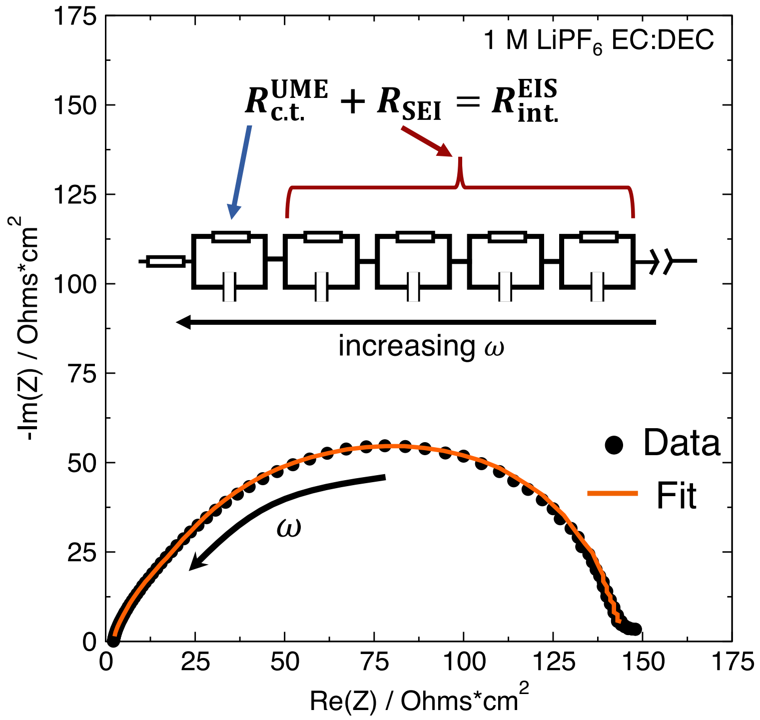


Why do electrolytes have unique ΔCE?



Why do high performance electrolytes have similar ΔCE to low performance electrolytes?

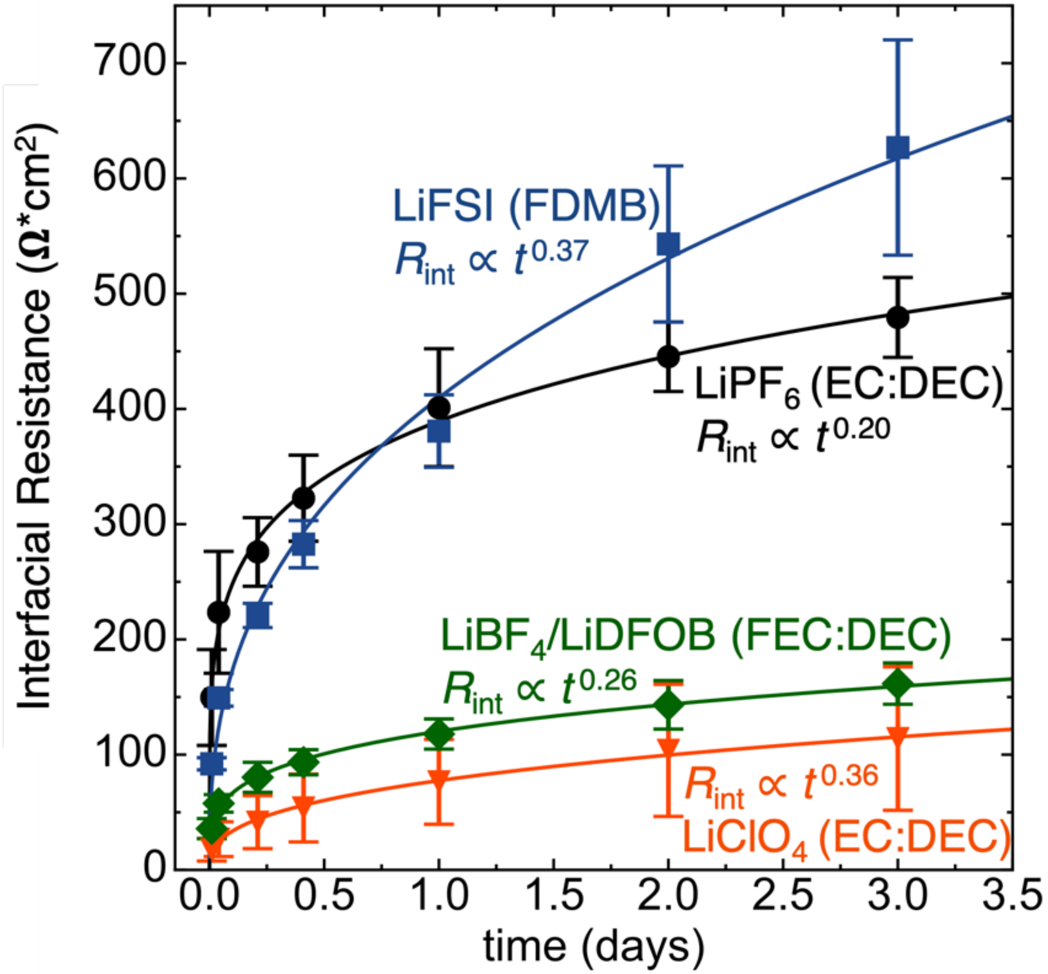
- Electrochemical impedance spectroscopy measures SEI growth



Boyle, D. T.; Cui, Y. *ACS Energy Lett.* **2020**, *5*, 701
Aurbach, D. et al. *J. Phys. Chem.* **1996**, *100*, 3089

Measuring SEI growth

EIS of Li ll Li symmetric cell with well controlled SA



$$R_{\text{int.}} \propto at^x$$

a – proportional to the resistivity of the SEI
t^x – proportional to the thickness of the SEI

Attia, P. M.; Cheuh, W. C.; Harris, S. J. *J. Electrochem. Soc.* **2020,** *167*

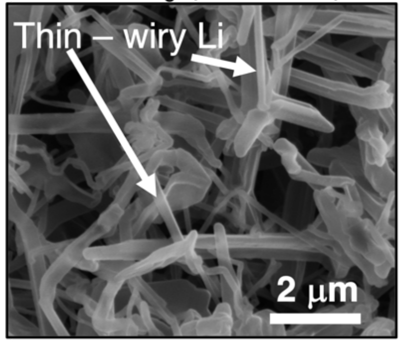
Electrolyte	Average CE	Rate of SEI growth
LiFSI (FDMB)	98.3	$t^{0.37}$
$LiBF_4$/LiDFOB (FEC:DEC)	94.2	$t^{0.26}$
$LiPF_6$ (EC:DEC)	85.5	$t^{0.20}$
$LiClO_4$ (EC:DEC)	86.1	$t^{0.36}$

- High CE electrolyte may not necessarily have strongly passivating SEI

$$\Delta CE \propto rate_{\text{SEI growth}} \times SA_{\text{Li}}$$

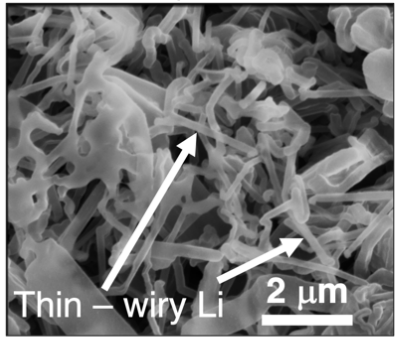
Rate of SEI Growth and Surface Area of Li

$LiPF_6$ (EC:DEC)



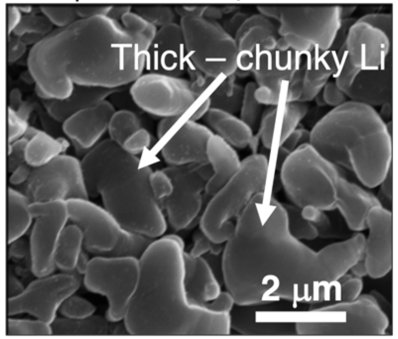
Slow SEI growth
High SA

$LiClO_4$ (EC:DEC)



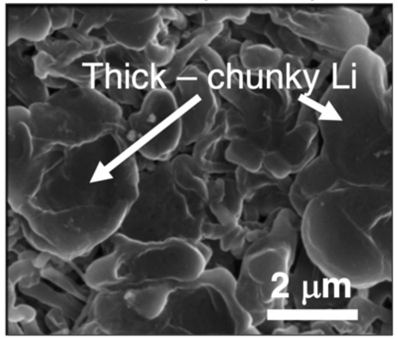
Fast SEI growth
High SA

$LiBF_4$/LiDFOB (FEC:DEC)



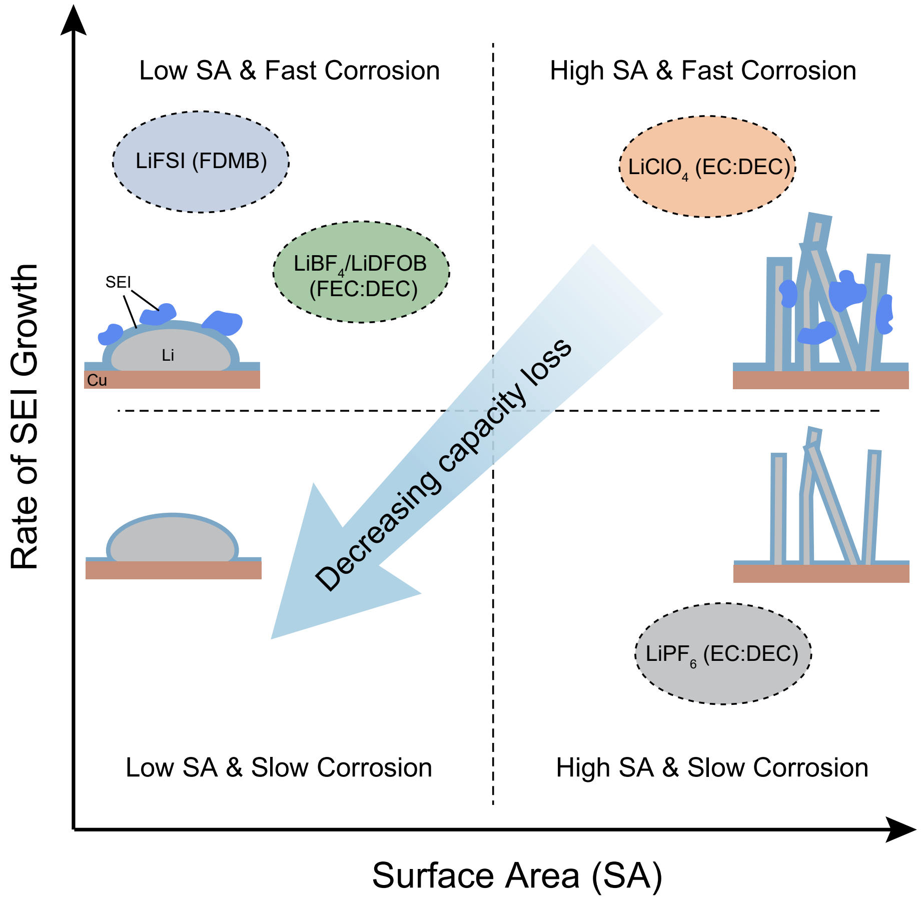
Fast SEI growth
Low SA

LiFSI (FDMB)



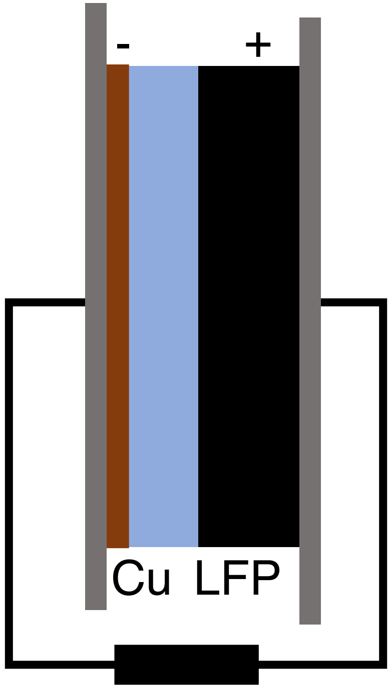
Fast SEI growth
Low SA

Electrolytes for anode-free Li metal batteries must simultaneously minimize surface area of Li and SEI growth

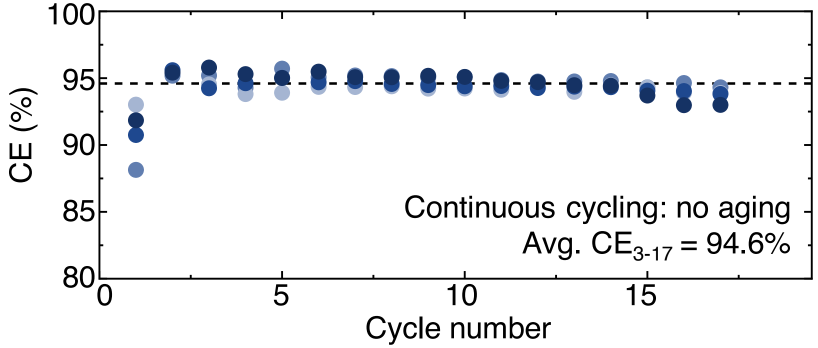


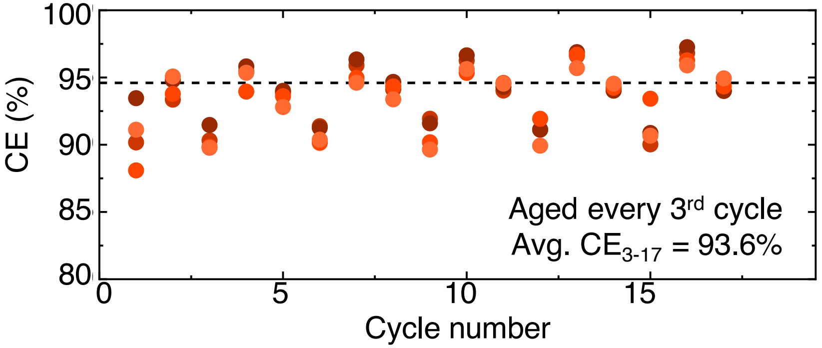
Potential Effects of Storage on Cycle Life

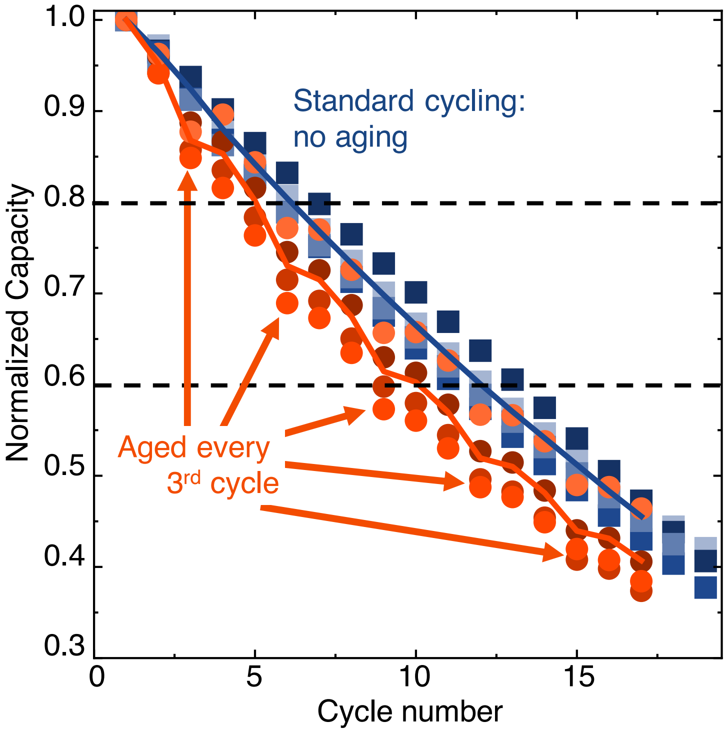
$LiFe(PO_4)$ (LFP) Full cells
(Anode-free)



Shortened cycle life with aging steps







Conclusions

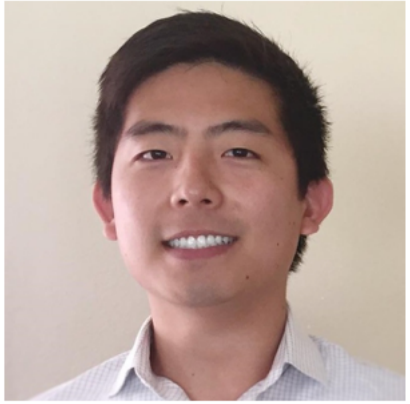
- Start testing out (anode-free) Li metal batteries with more realistic cycling protocol – relationships between cal. life/self-discharge and cycle life?
  - **Li metal batteries are still promising!** It’s another challenge to look in to.
- Electrolytes with long cycle life may not necessarily form the most passivating SEI – need very insoluble SEI components
- Strategies for reuse of existing SEI or assistance with passivation should be a key focus

Acknowledgements

Project Leader

Prof. Yi Cui
Stanford University

Collaborators and Co-authors



William Huang: Cryo-TEM
Now at Tesla

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- Hansen Wang
- Dr. Yuzhang Li
- Dr. Hao Chen
- Zhiao Yu