

# **UC San Diego**

## **UC San Diego Previously Published Works**

### **Title**

Lithium Metal Anode – Advanced Characterization, Slides from the Web Seminar by Dr. Y. Shirley Meng

### **Permalink**

<https://escholarship.org/uc/item/7dj377k7>

### **Author**

Meng, Ying Shirley

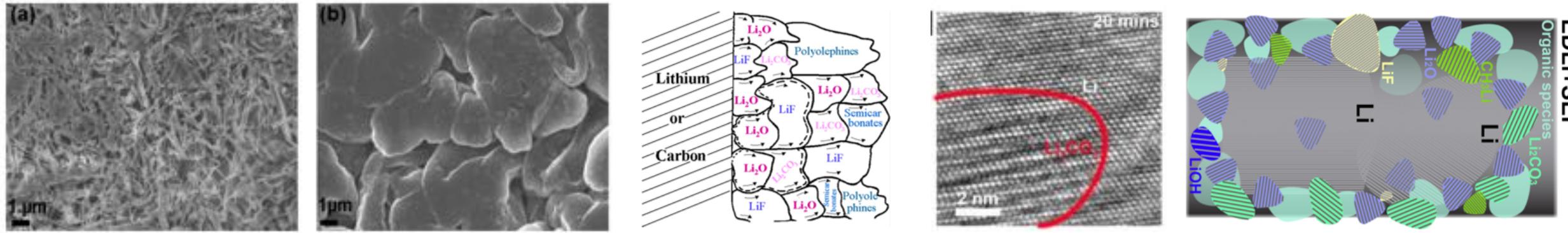
### **Publication Date**

2020-05-27

### **DOI**

10.1149/osf.io/6fr7c

Peer reviewed



# Lithium Metal Anode – Advanced Characterization

**Y. Shirley Meng**  
[shmeng@ucsd.edu](mailto:shmeng@ucsd.edu)

Sustainable Power and Energy Center (SPEC)

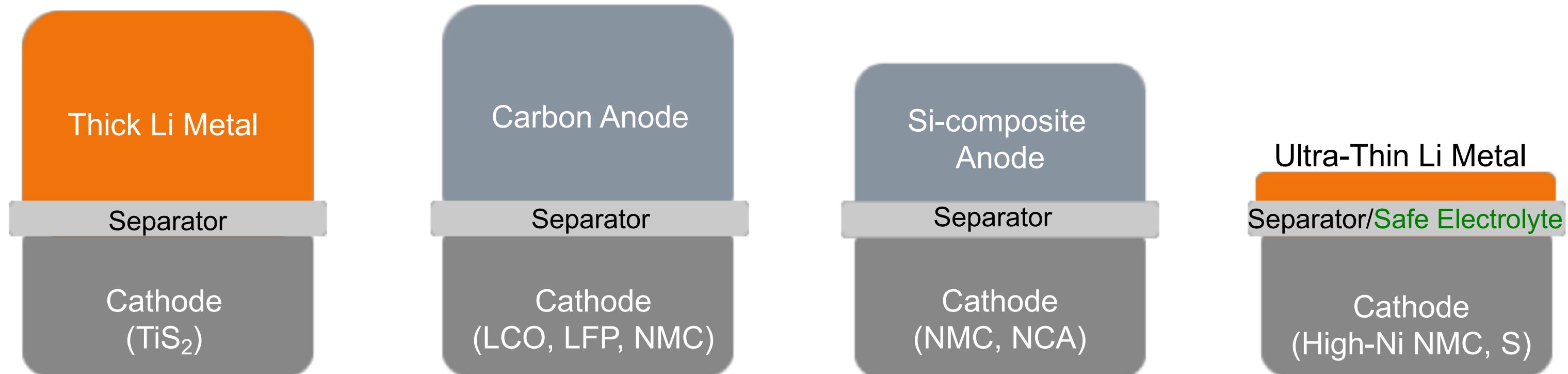
Department of NanoEngineering

**University of California San Diego**

<http://smeng.ucsd.edu/>

*SF Section of ECS, May 18<sup>th</sup> 2020*

# Development of Li Metal Battery



**Gen 0  
Li-Metal**  
100-200 Wh/kg  
200-300 Wh/L  
Dangerous

**Gen 1  
Li-ion**  
200-250 Wh/kg  
600 Wh/L  
Safe

**Gen 2  
Li-ion**  
250-300 Wh/kg  
700 Wh/L  
Safe

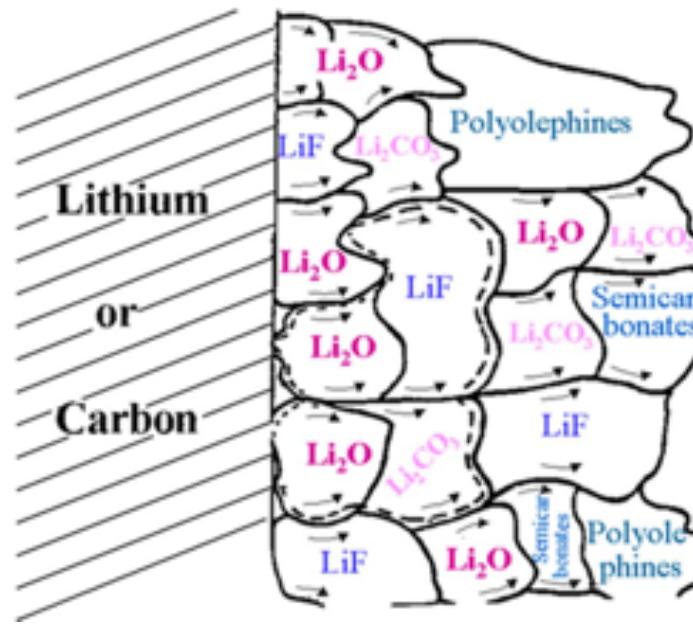
**Gen 3  
Li-Metal**  
400-500 Wh/kg  
1200 Wh/L  
Safe

# Grand Challenge - Li Metal Anode

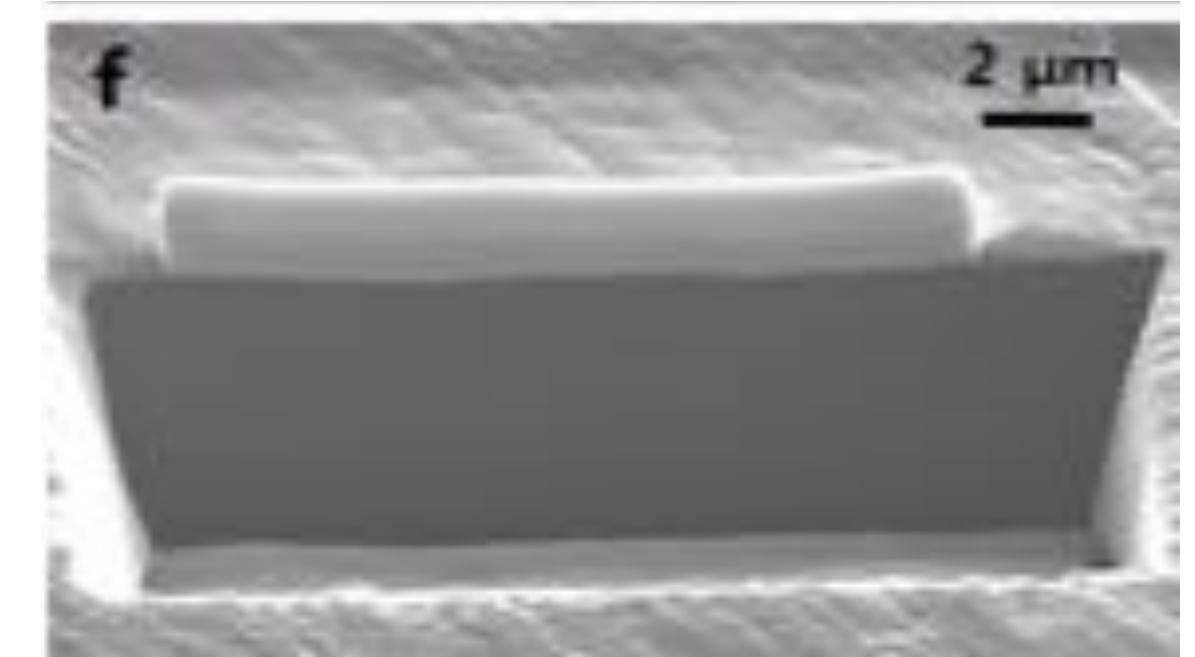
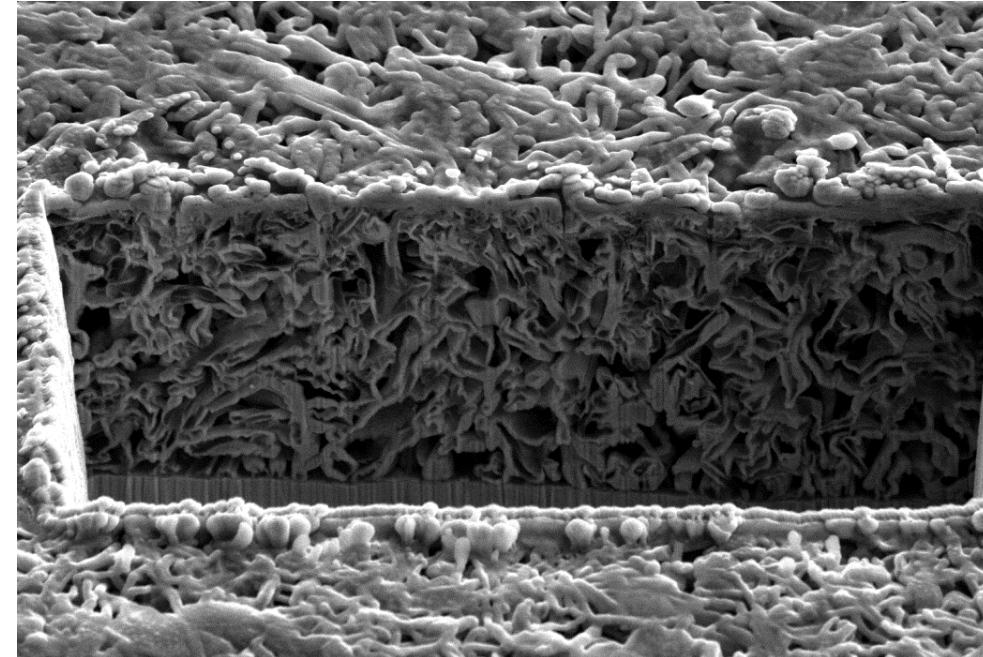
BATTERY  
CONSORTIUM 500

## Scientific Gaps:

1. What is the true CE ??? Depositing Li, Li<sub>2</sub>O, Li<sub>2</sub>CO<sub>3</sub>, LiOH, LiF
2. Not all Li are the same - Li Foil, Vapor Deposited Li (VDLi) and Electrochemically Deposited Li (EDLi)
3. Substrate/Separator/Electrolyte (system level electrochemical engineering )



E. Peled 1998

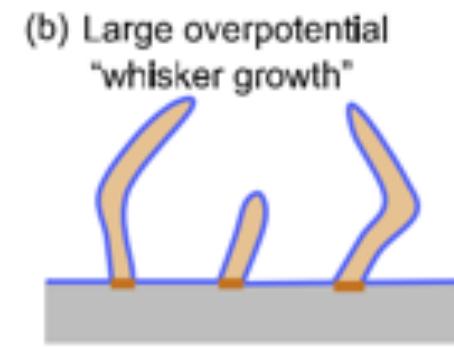
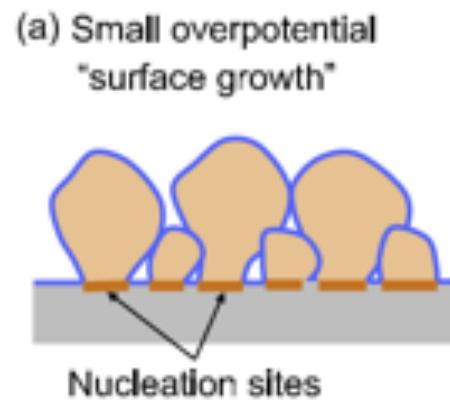


# Imaging Tools for Li Metal Plating

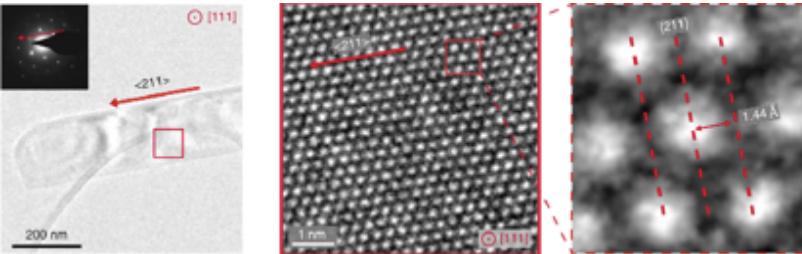


## Challenges for Li metal characterization:

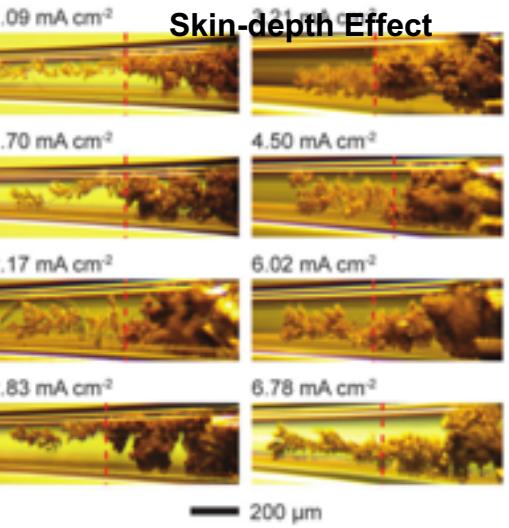
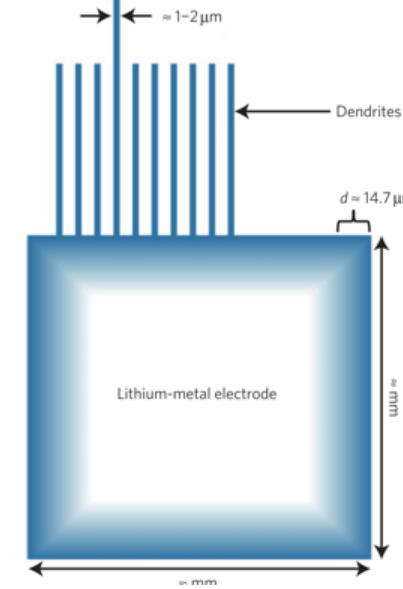
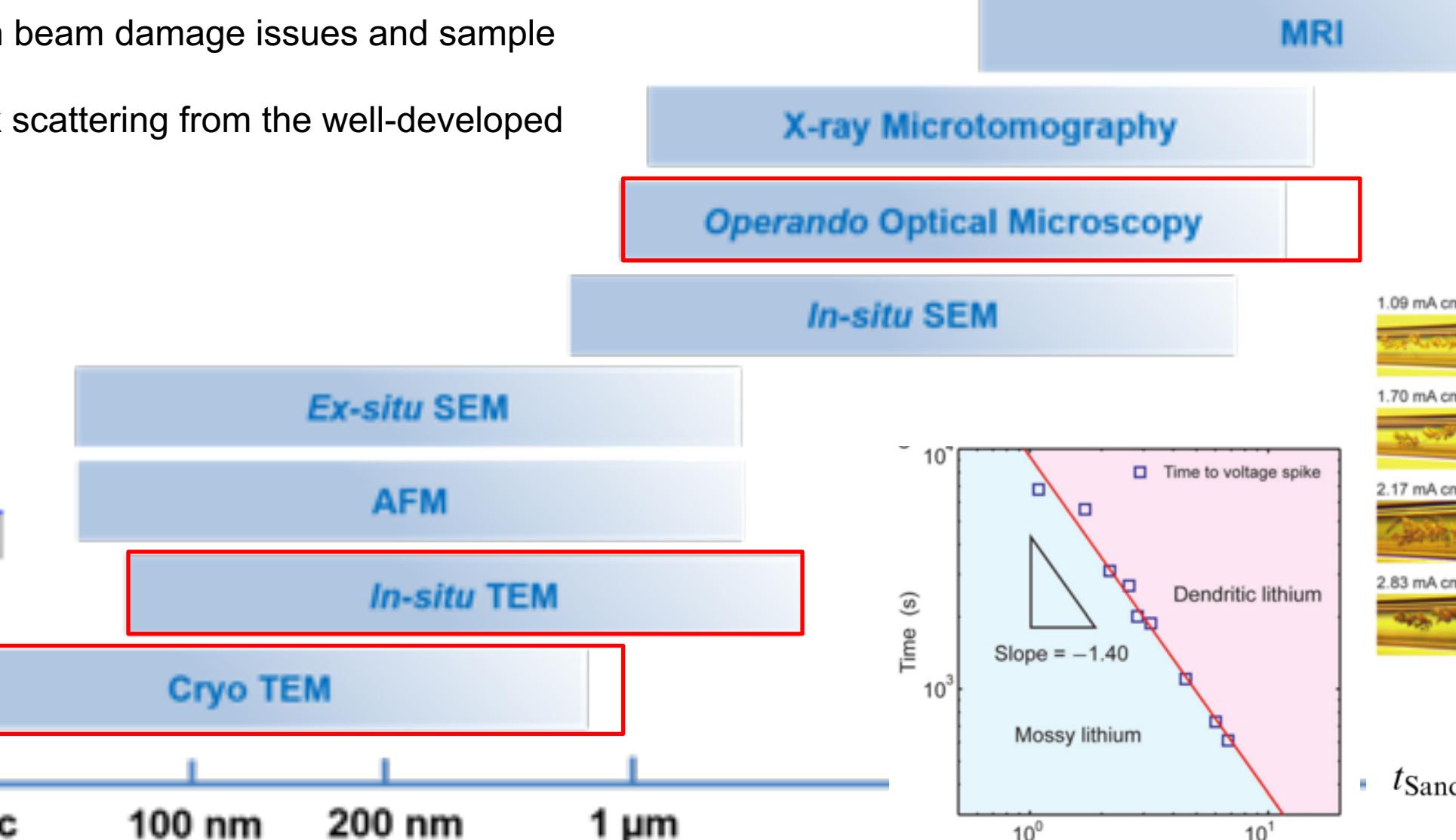
- **High reactivity**, leading to difficulties in beam damage issues and sample protection
- **Low atomic number**, resulting in weak scattering from the well-developed electron and X-ray techniques



Kushima et al., *Nano Energy*, 2017, 32, 271



Li et al., *Science*, 2017, 358, 506



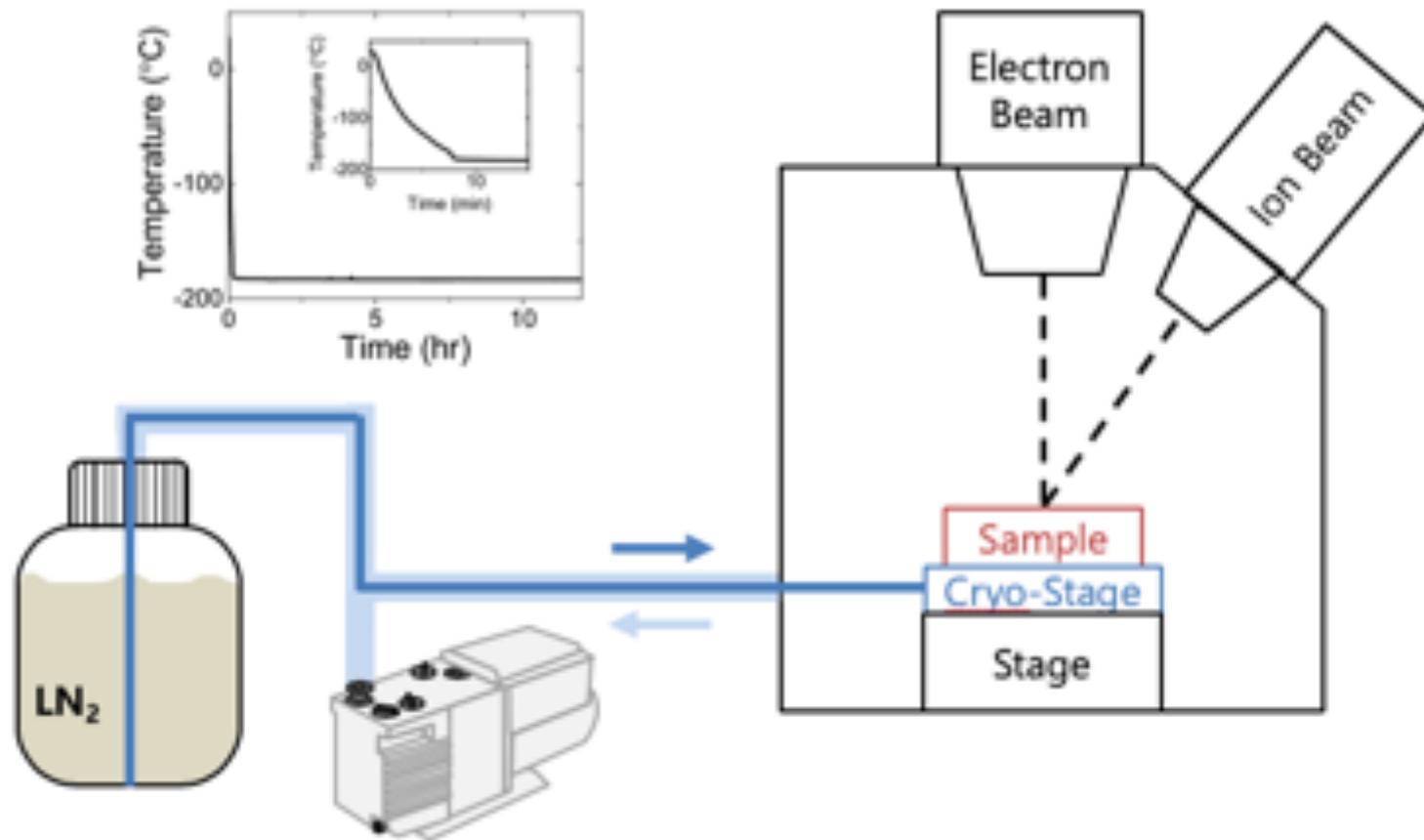
$$t_{\text{Sand}} = \pi D_{\text{app}} \frac{(z_c c_0 F)^2}{4(J t_a)^2}$$

Bai et al., *Energy Environ. Sci.*, 2016, 9, 3221

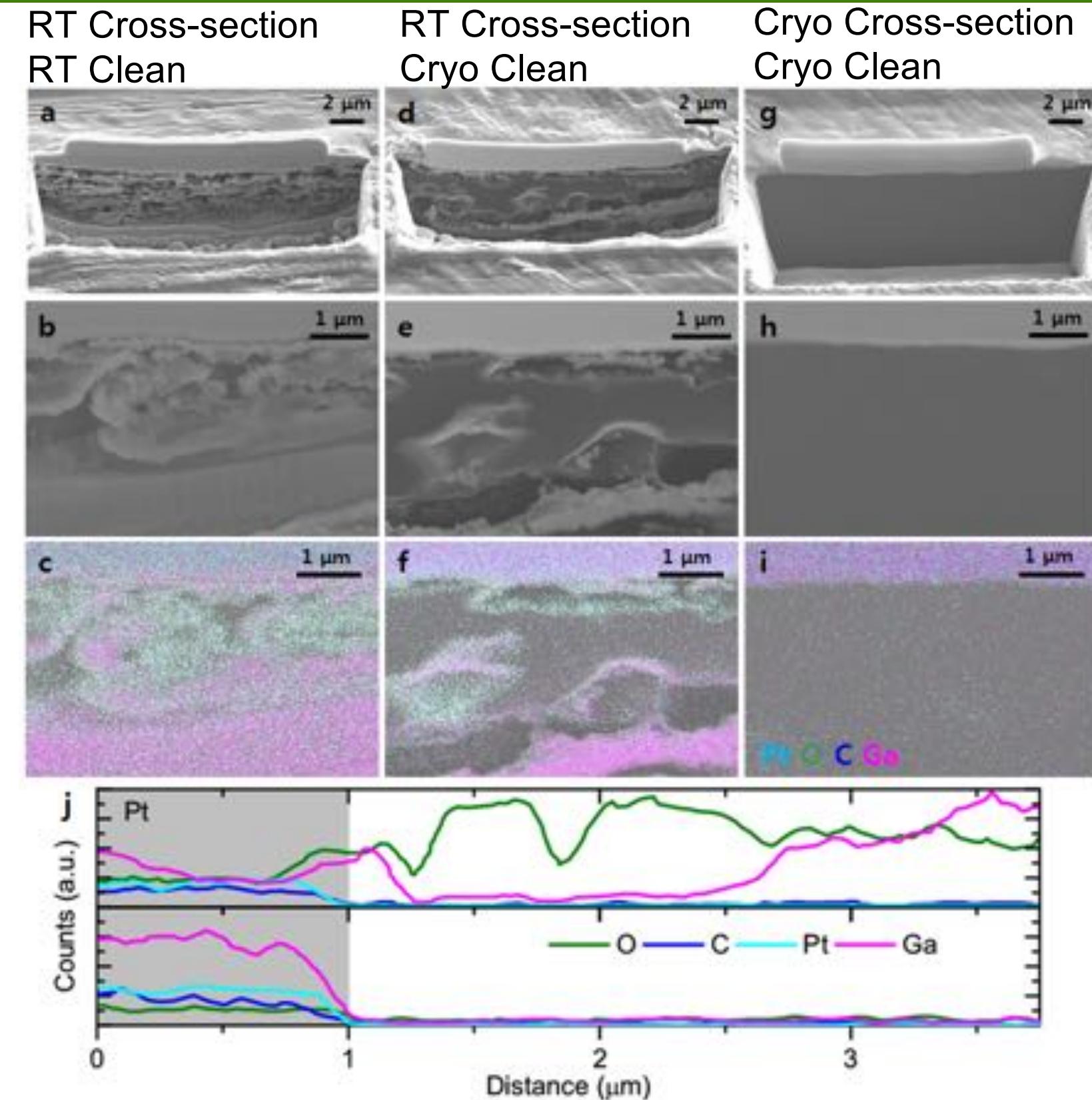
# Cryo-FIB: Enabling Beam Sensitive Materials

J.Z. Lee, T.A. Wynn, Y.S. Meng, et al, ACS Energy Letters , 2019

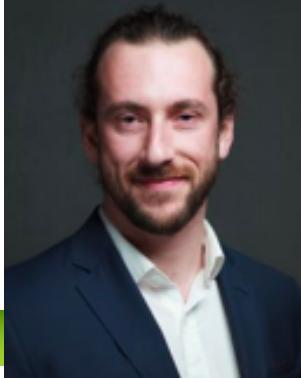
U.S. Department of Energy, Office of Basic Energy Sciences,  
under Award Number DE-SC0002357  
(Program Manager: Dr. Jane Zhu)



Cryogenic focused ion beam ( $-170^{\circ}\text{C}$ ) shows notably reduced morphology change as well as reduced  $\text{Ga}^+$  implantation via EDS. Permits lift-out of lithium metal anode-based batteries.



# Cryogenic Microscopy - FIB/SEM and TEM/STEM

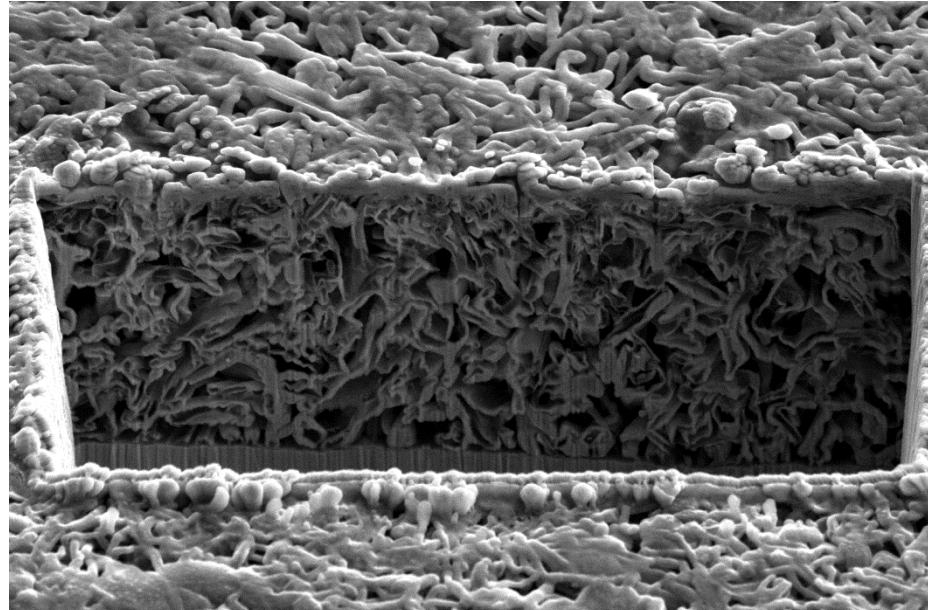


J.Z. Lee, T.A. Wynn, Y.S. Meng, et al, ACS Energy Letters , 2019

## Electrochemically Deposited Li (EDLi)

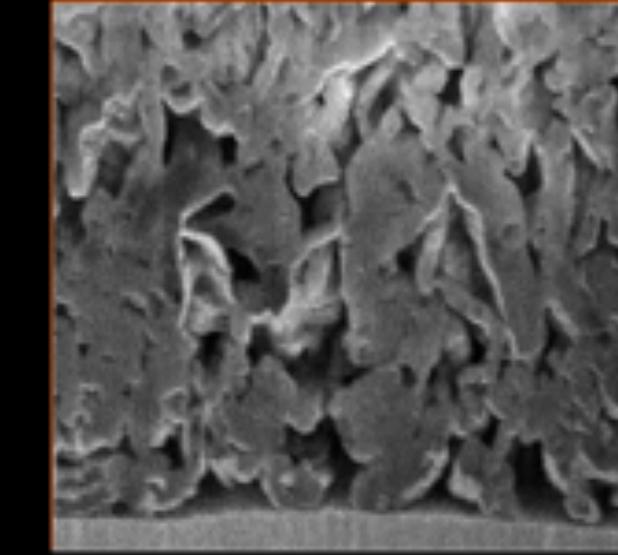
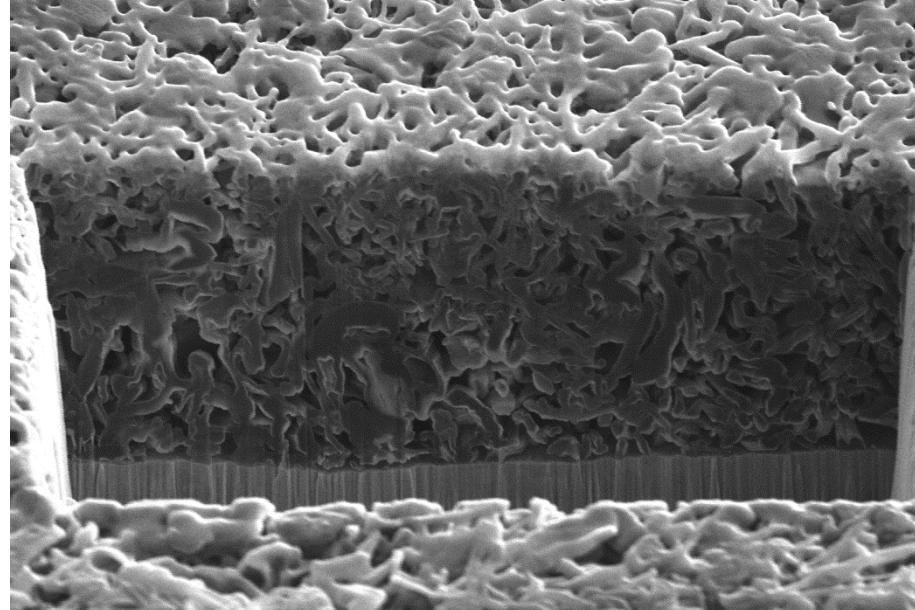
- 1.2M LiPF<sub>6</sub> (3:7) EC:EMC, 0.5 mA/ cm<sup>2</sup>

Room Temp (22 °C)



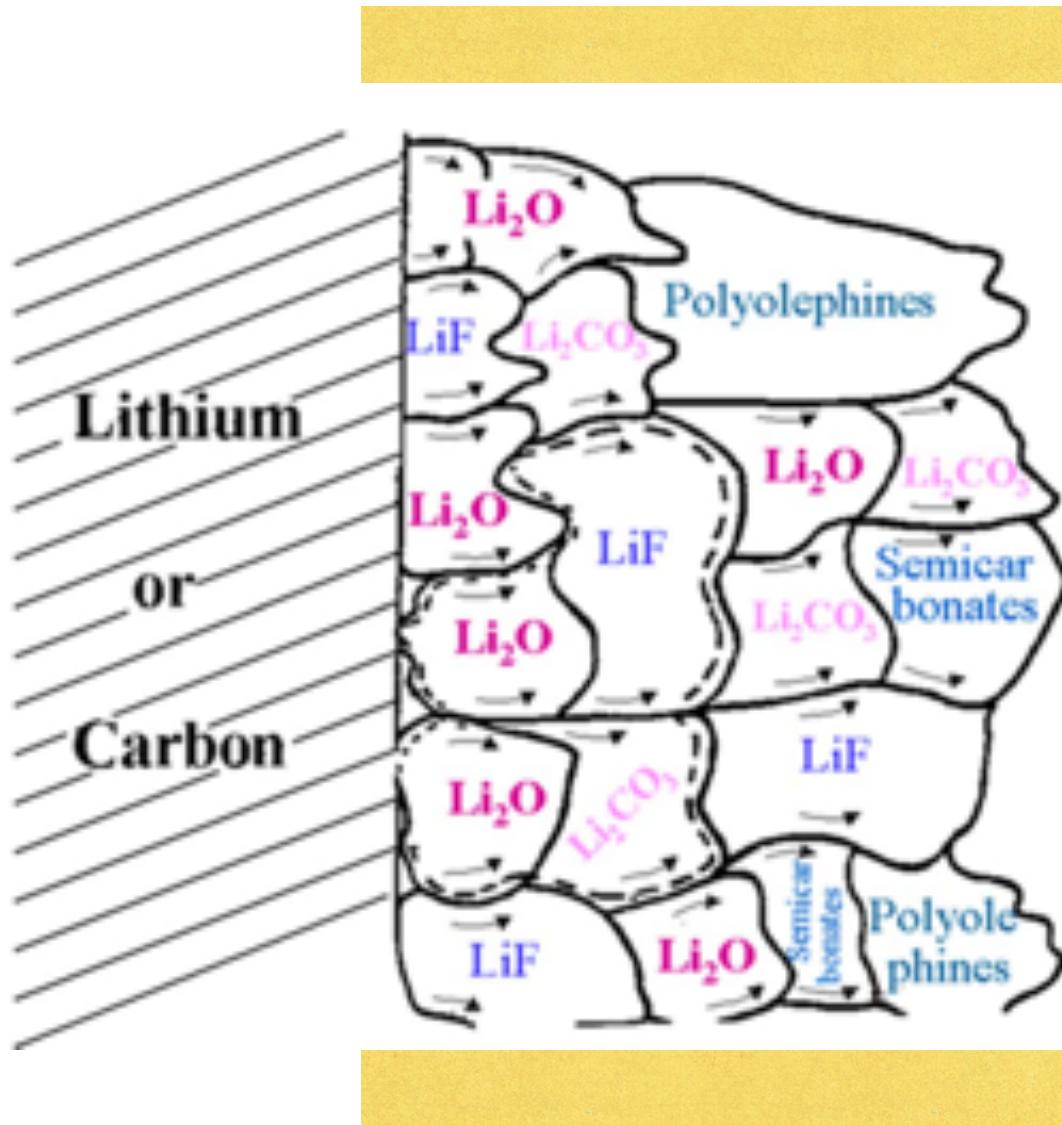
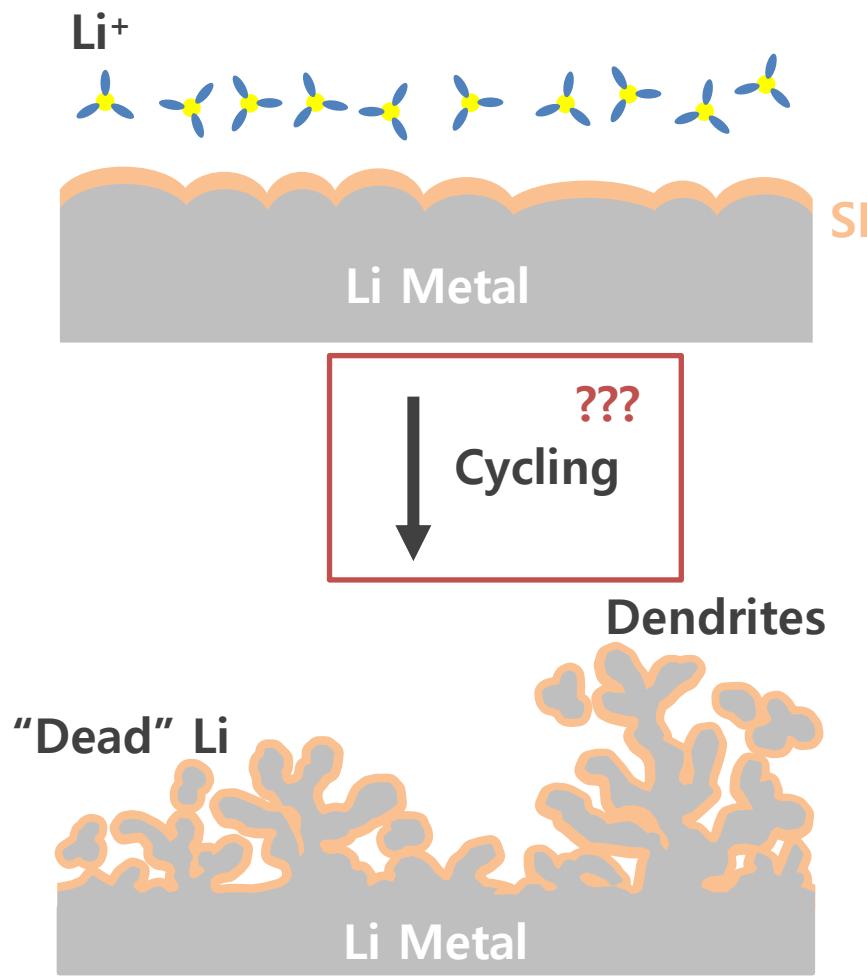
5 μm

Cryo (-170 °C)



Void space  
Substrate

# Electrochemically Deposited Li



Electrolytes/Salt : Ether, Carbonate, Sulfone, Polymer, LiPON, LLZO, LPS

- To pair with NMC

Stack pressure

- 1psi, 10 psi, 100 psi or more?

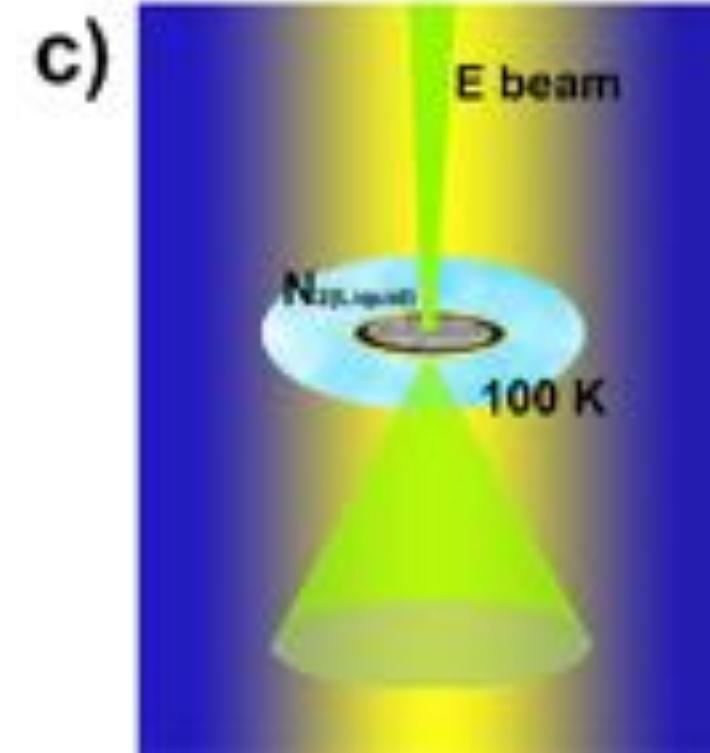
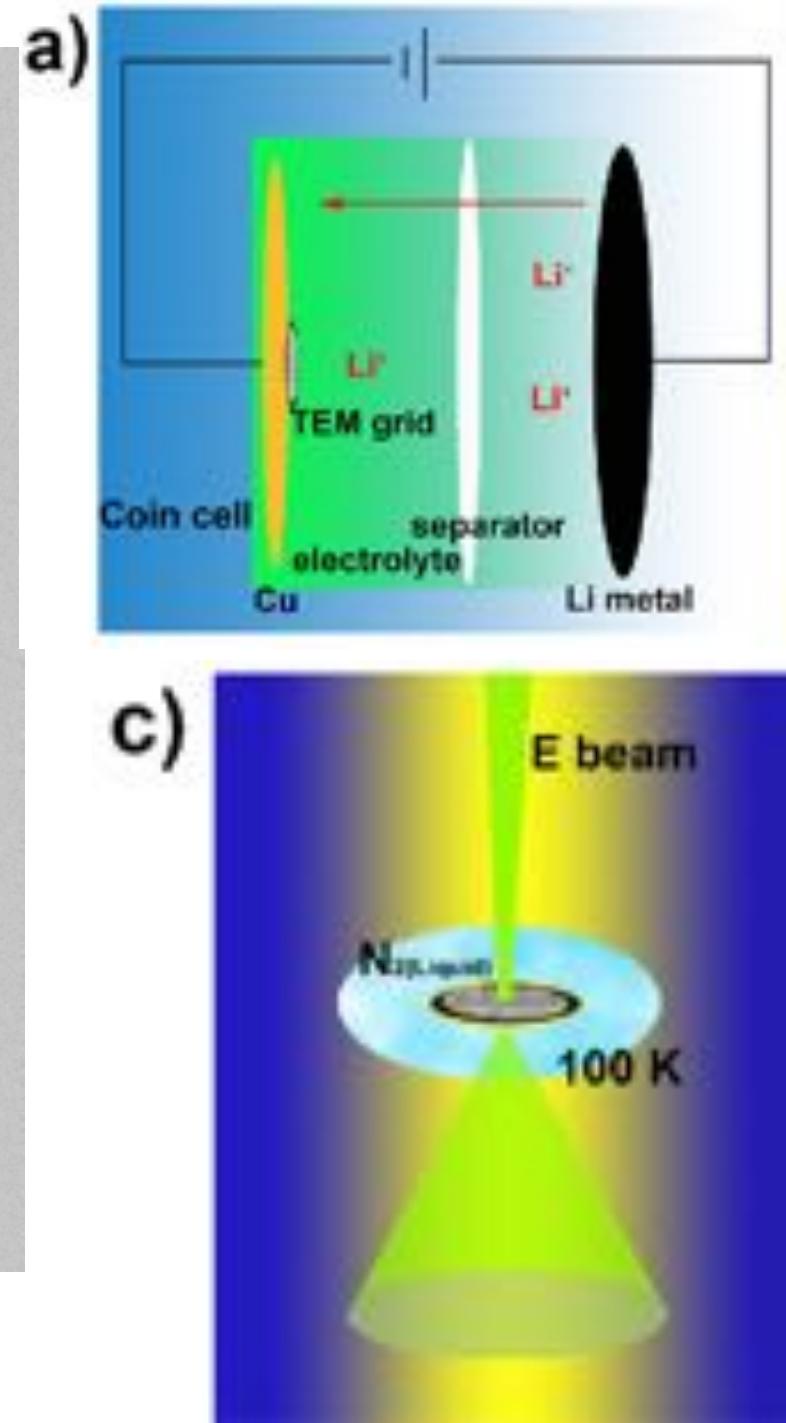
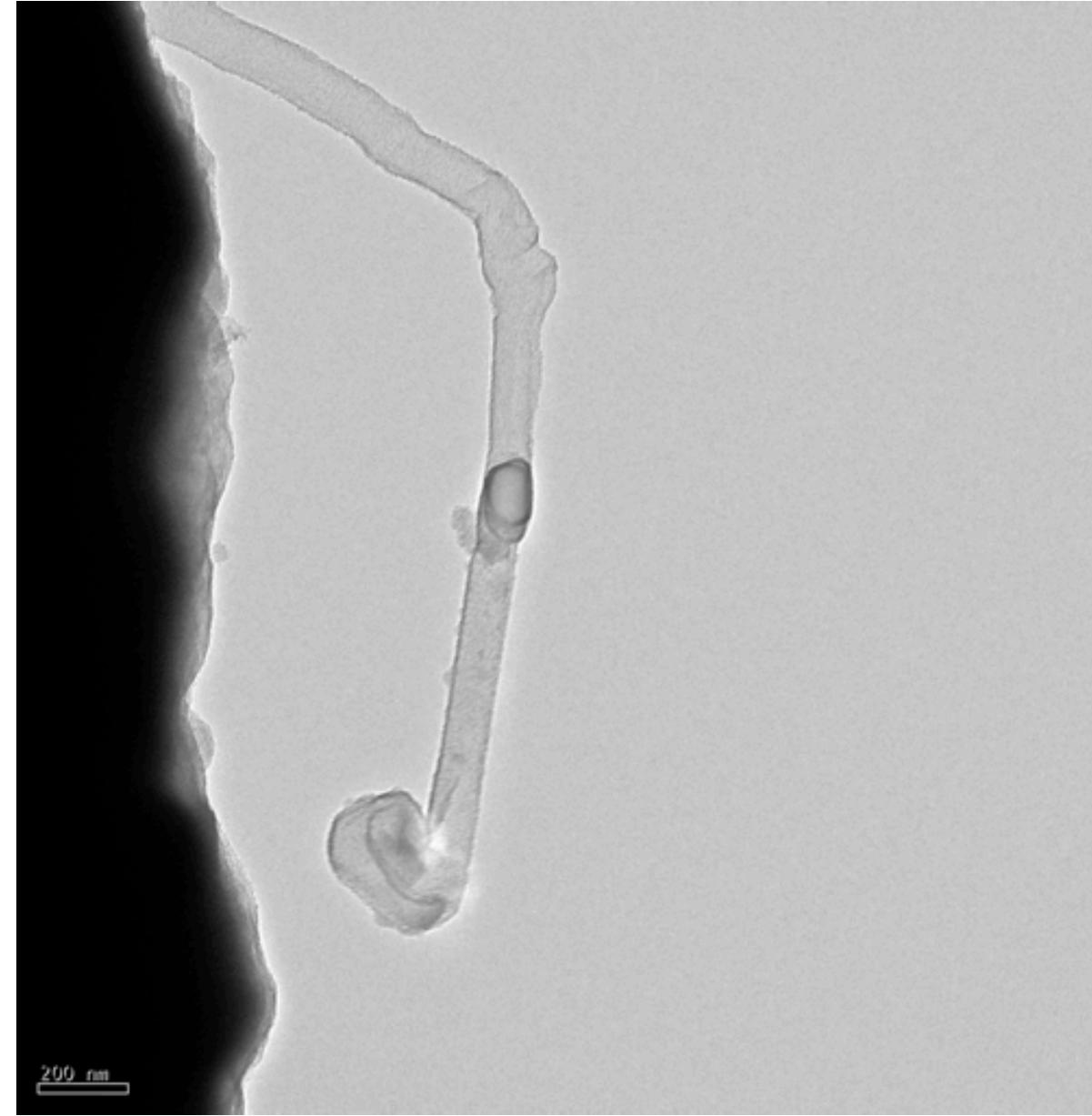
Ensemble average of  
 $\text{LiF}/\text{Li}_2\text{O}/\text{Li}_2\text{CO}_3/\text{LiOH}/\text{and others}$

How much Metallic Li?

Substrate : Li on Li , Li on Cu, Li on other substrates

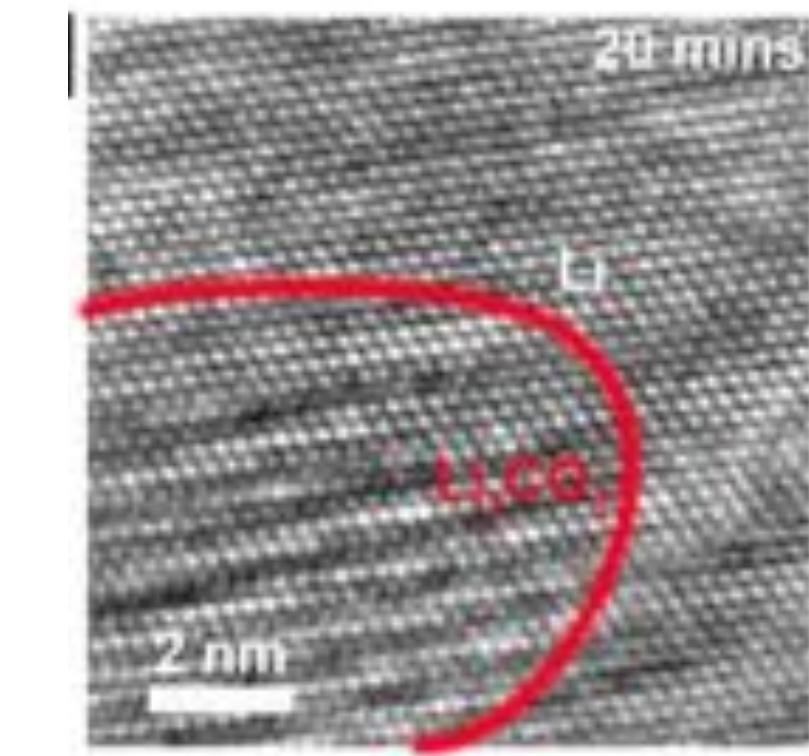
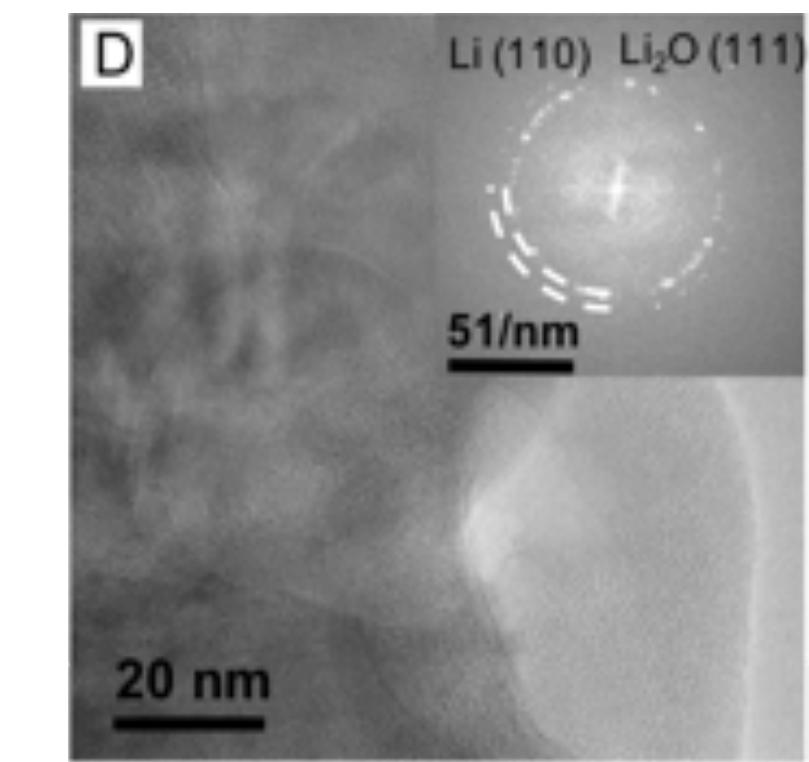
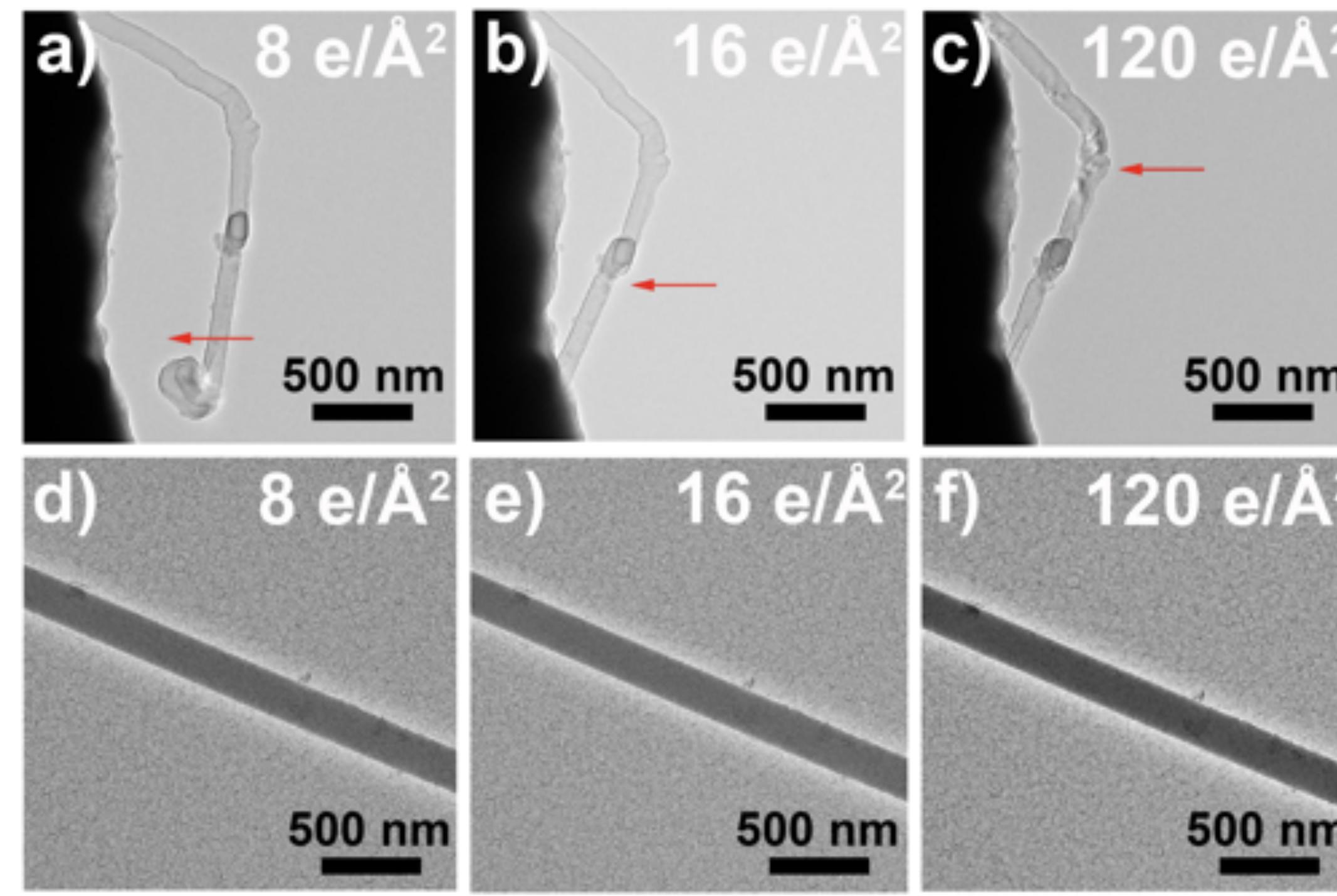
- Ultimate test is anode free

# Why Cryo TEM?

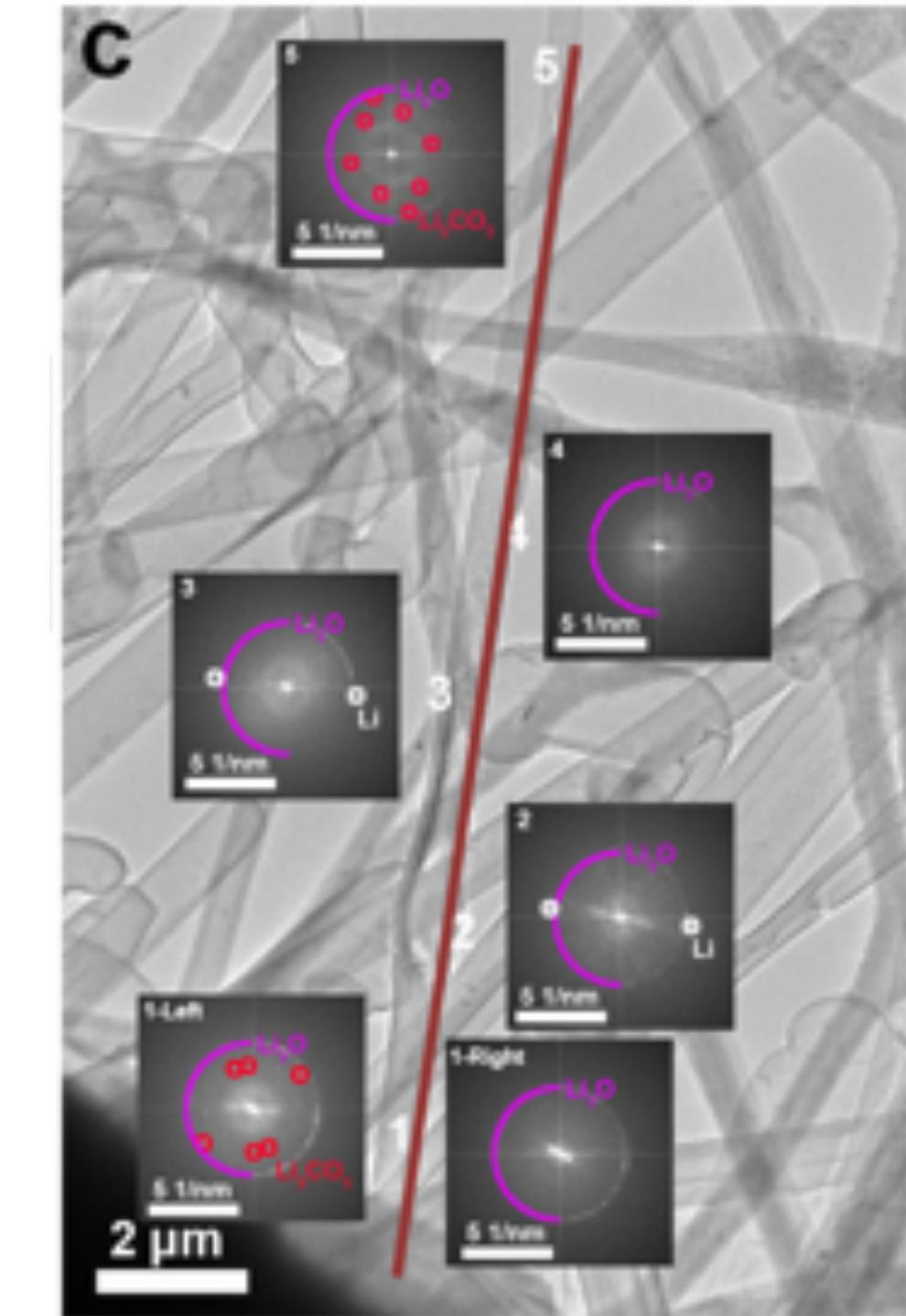
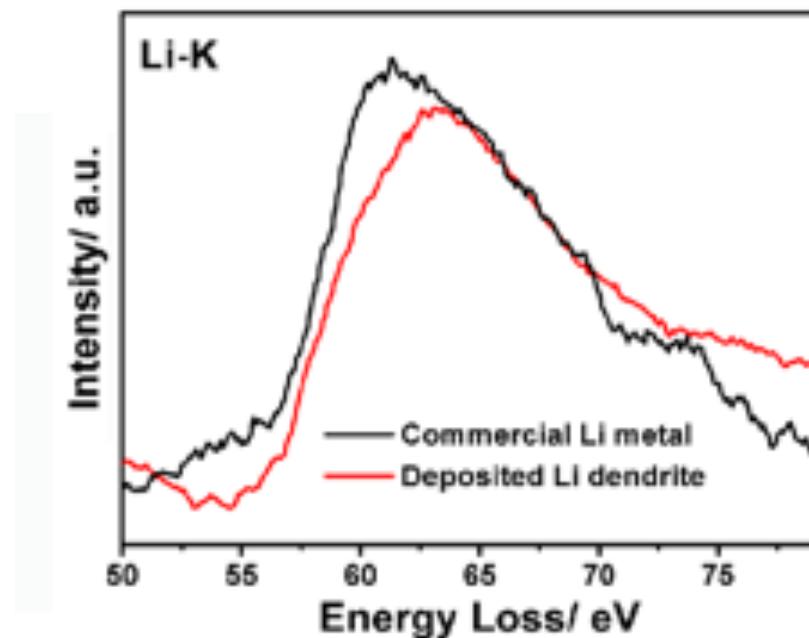
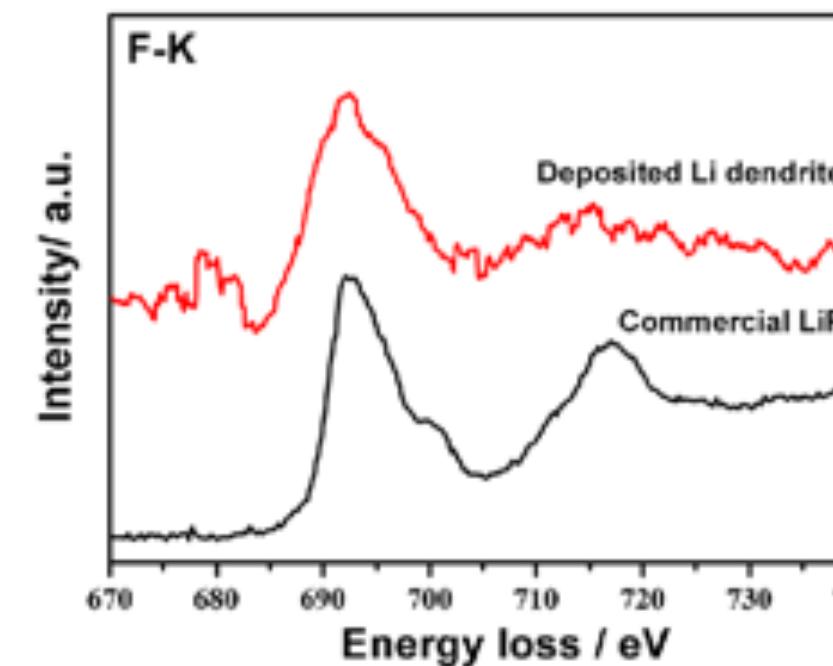
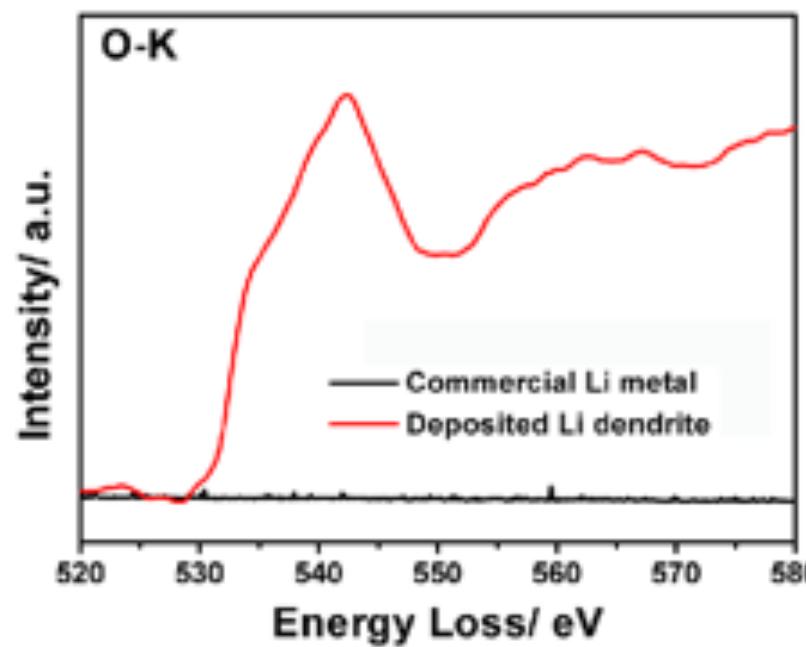
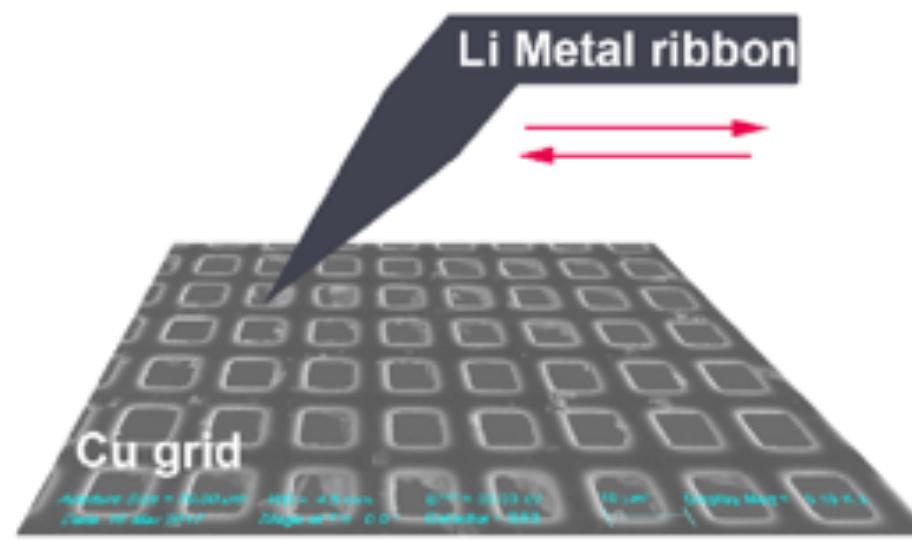


- **Low dosage Imaging**
- **Cryo Sample Prep**
- **Superfast Detector (2000frames/sec)**

# Cryo-TEM: Beam Sensitive Materials at Atomic Scale



# EELS – Metallic Li and Many Other Forms of Li +

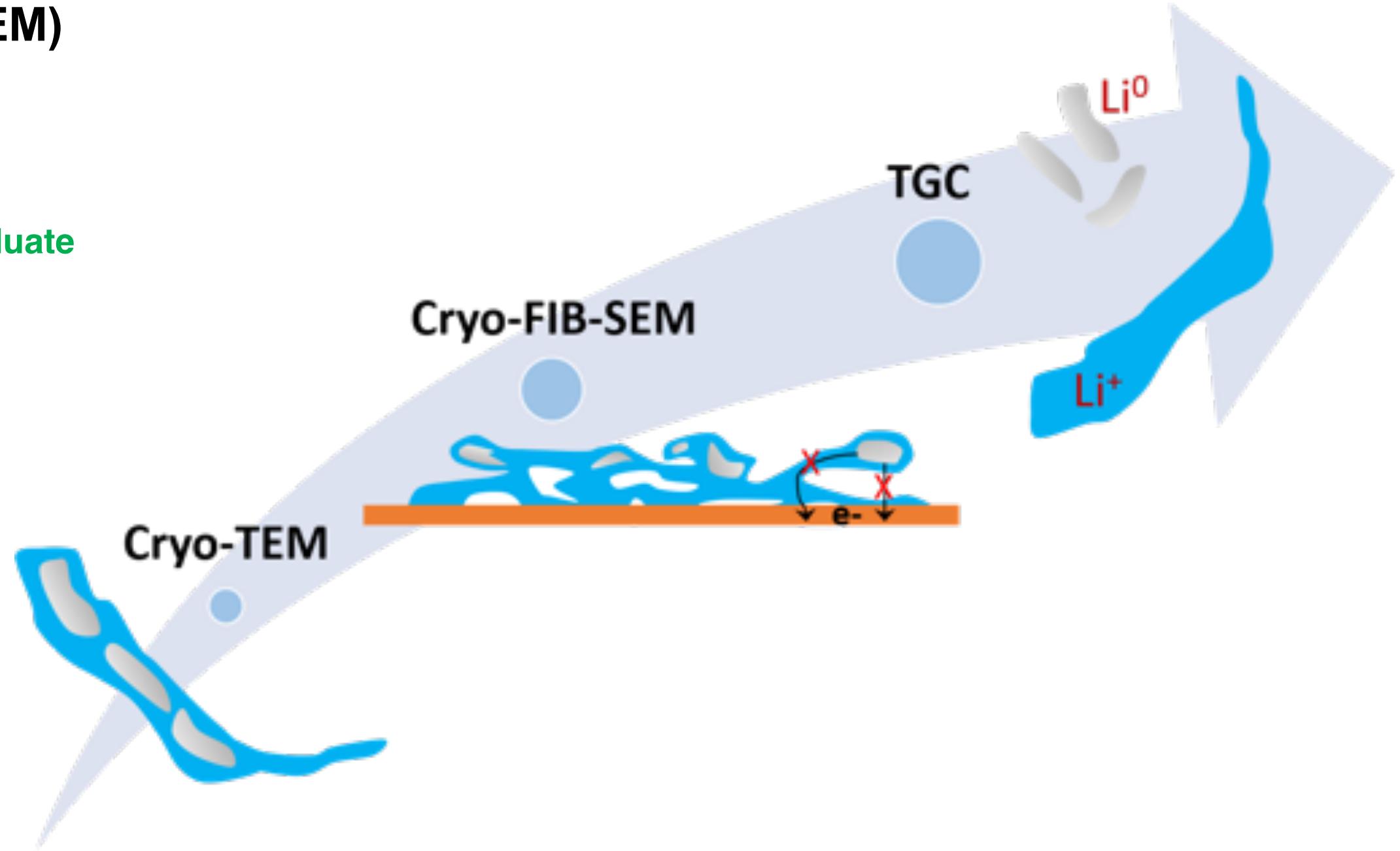


# Multi-scale Investigation of Inactive Li

1. Macro quantification of SEI  $\text{Li}^+$  and metallic  $\text{Li}^0$  (A new analytic method, TGC)
2. Microstructure (Cryo-FIB SEM)
3. Nanostructure (Cryo-TEM)

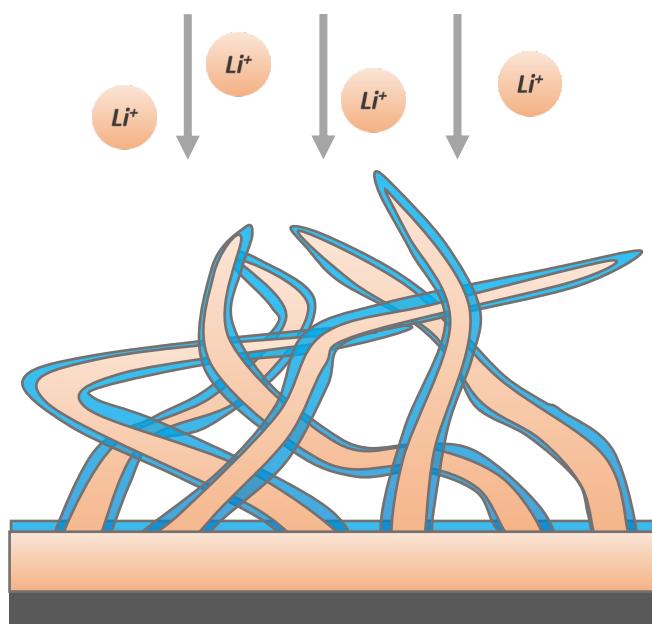


2019 MRS Graduate  
Student Award

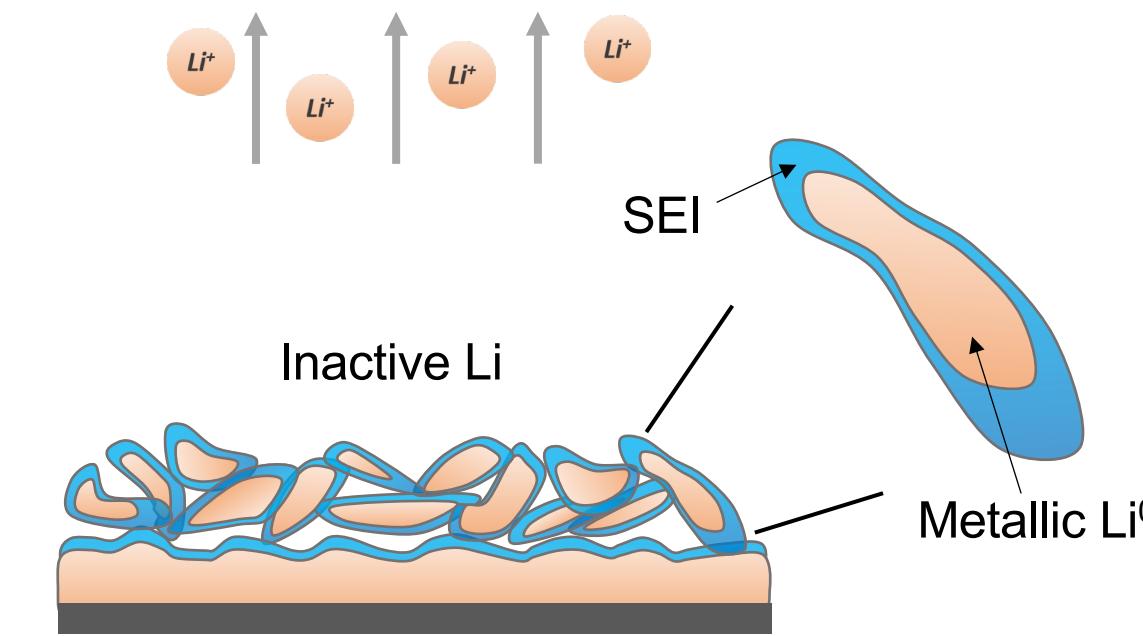


# Inactive (dead) Lithium Formation

$$\text{Inactive Li} = \text{SEI Li}^+ + \text{Metallic Li}^0$$



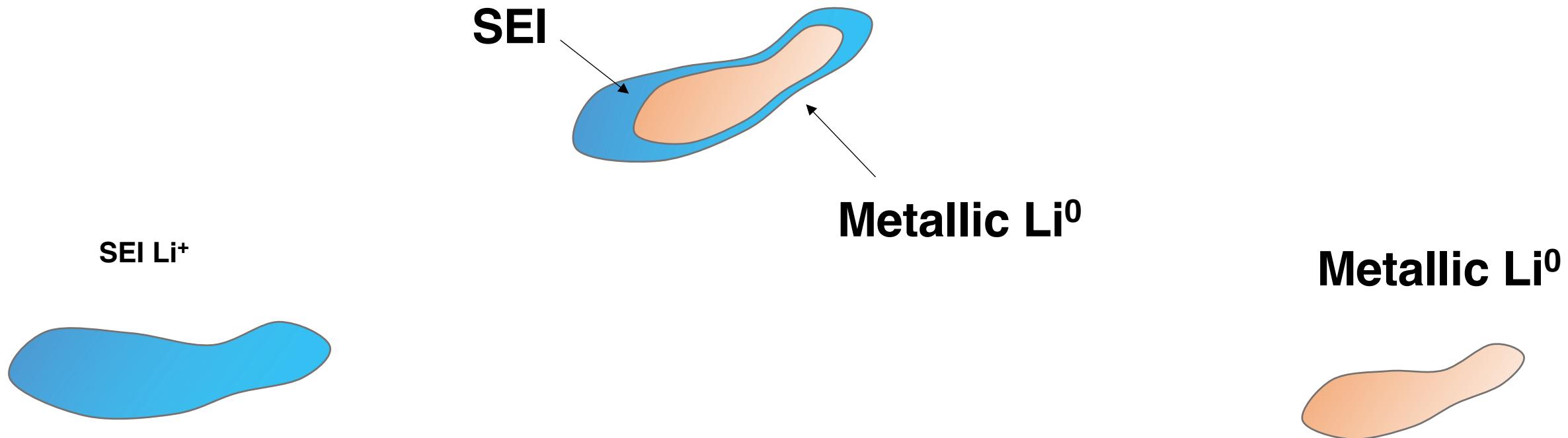
Li plating



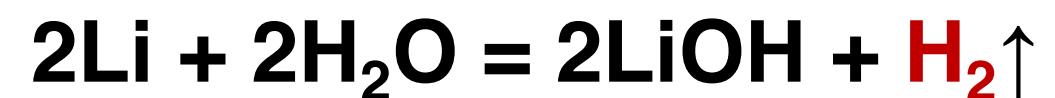
Li stripping

- What are the contents of SEI  $Li^+$  and metallic  $Li^0$ ?
- What is the underlying cause?

# Differentiating Inactive Li

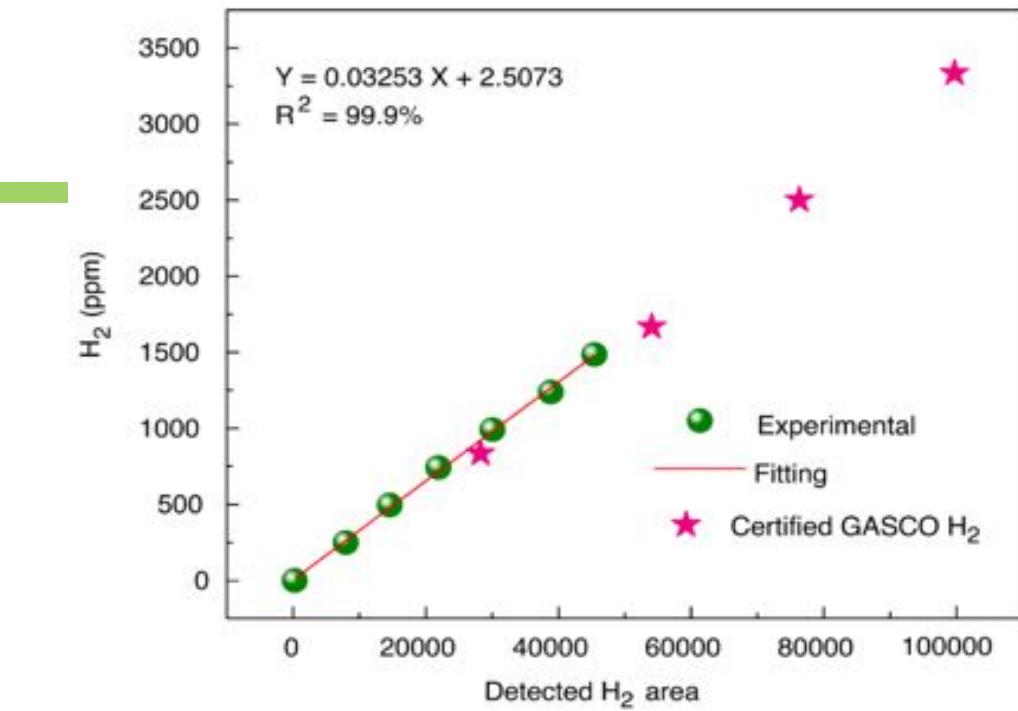
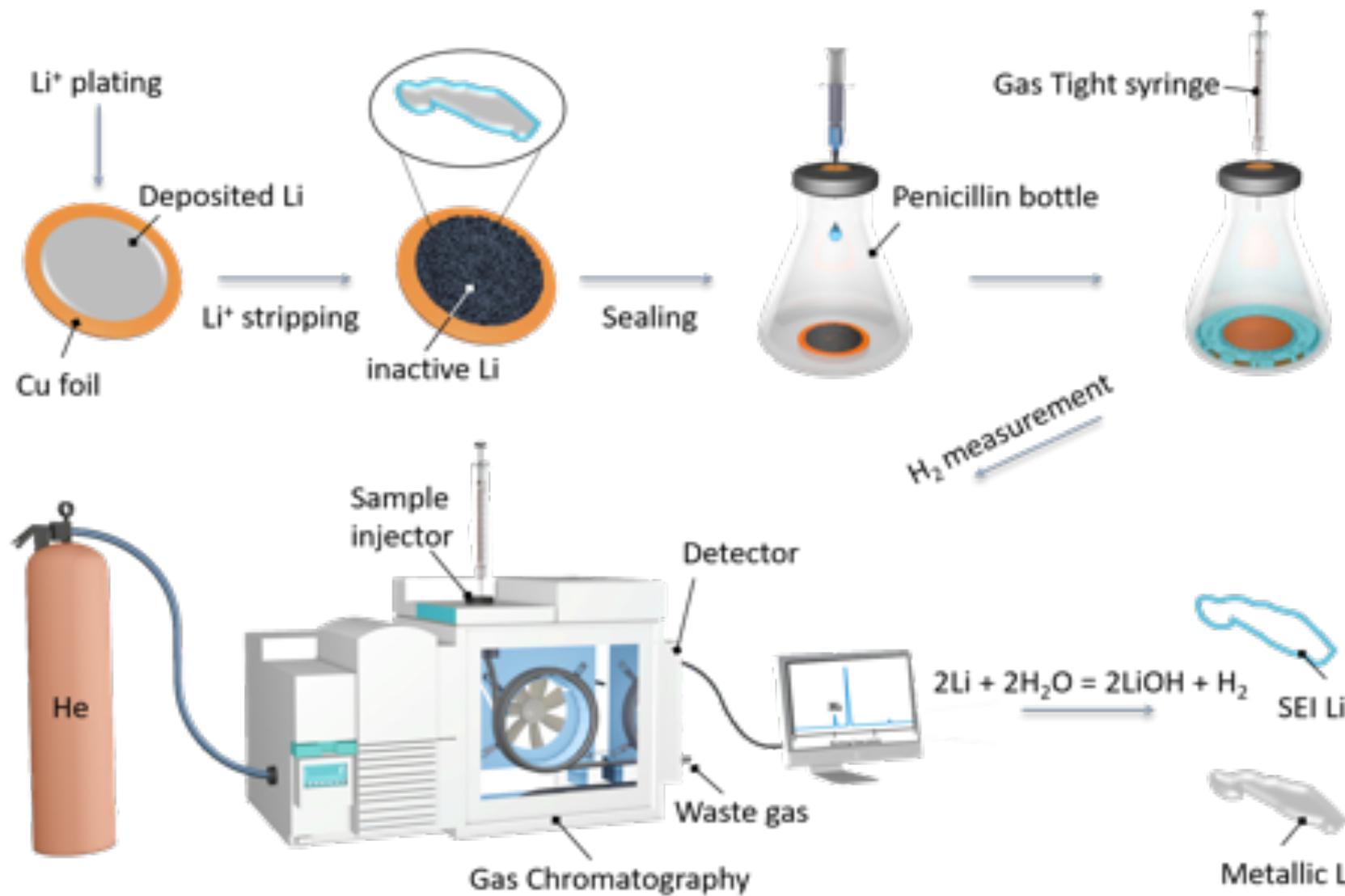


SEI component	Solubility in 100 mL H <sub>2</sub> O
LiF	0.134 g (0.67 mg in 0.5 mL H <sub>2</sub> O)
LiOH	12.8 g
Li <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	8 g
Li <sub>2</sub> CO <sub>3</sub>	1.29 g
Li <sub>2</sub> O	Li <sub>2</sub> O + H <sub>2</sub> O = LiOH
CH <sub>3</sub> Li	CH <sub>3</sub> Li + H <sub>2</sub> O = LiOH + CH <sub>4</sub> ↑
ROLi	ROLi + H <sub>2</sub> O = LiOH + ROH
(CH <sub>2</sub> OCO <sub>2</sub> Li) <sub>2</sub>	(CH <sub>2</sub> OCO <sub>2</sub> Li) <sub>2</sub> + H <sub>2</sub> O = Li <sub>2</sub> CO <sub>3</sub> + (CH <sub>2</sub> OH) <sub>2</sub> + CO <sub>2</sub> ↑
LiOCO <sub>2</sub> R	2LiOCO <sub>2</sub> R + H <sub>2</sub> O = Li <sub>2</sub> CO <sub>3</sub> + 2ROH + CO <sub>2</sub> ↑

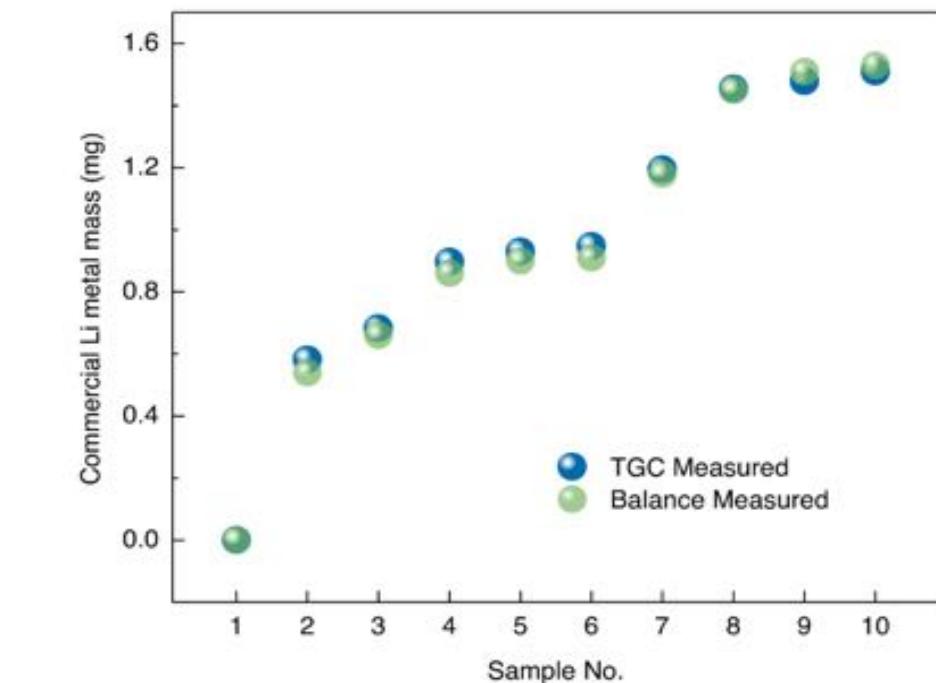


# TGC Method

A combination of H<sub>2</sub>O Titration and Gas Chromatography



1. H<sub>2</sub> measurement accuracy  
(Certified GASCO H<sub>2</sub>)



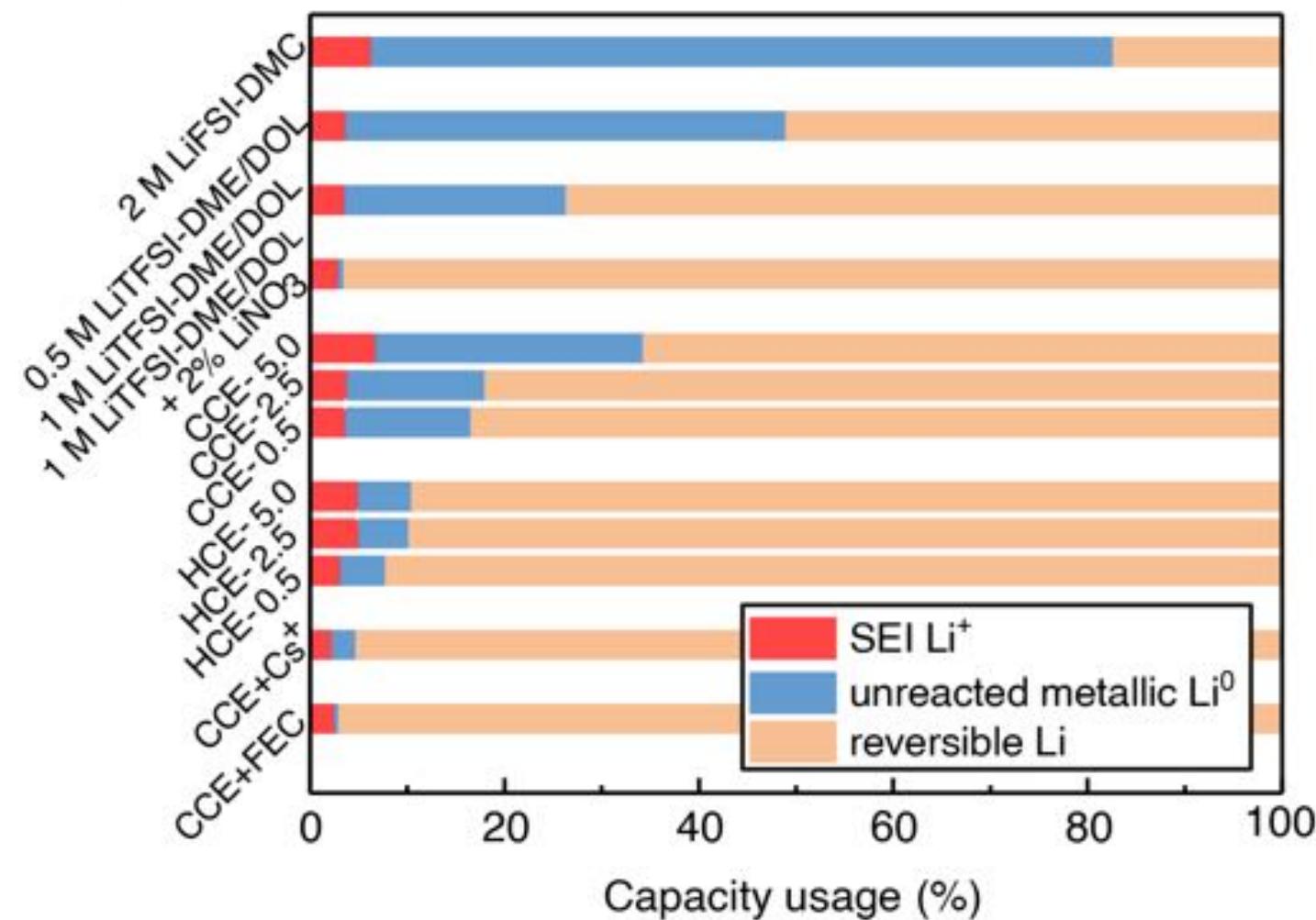
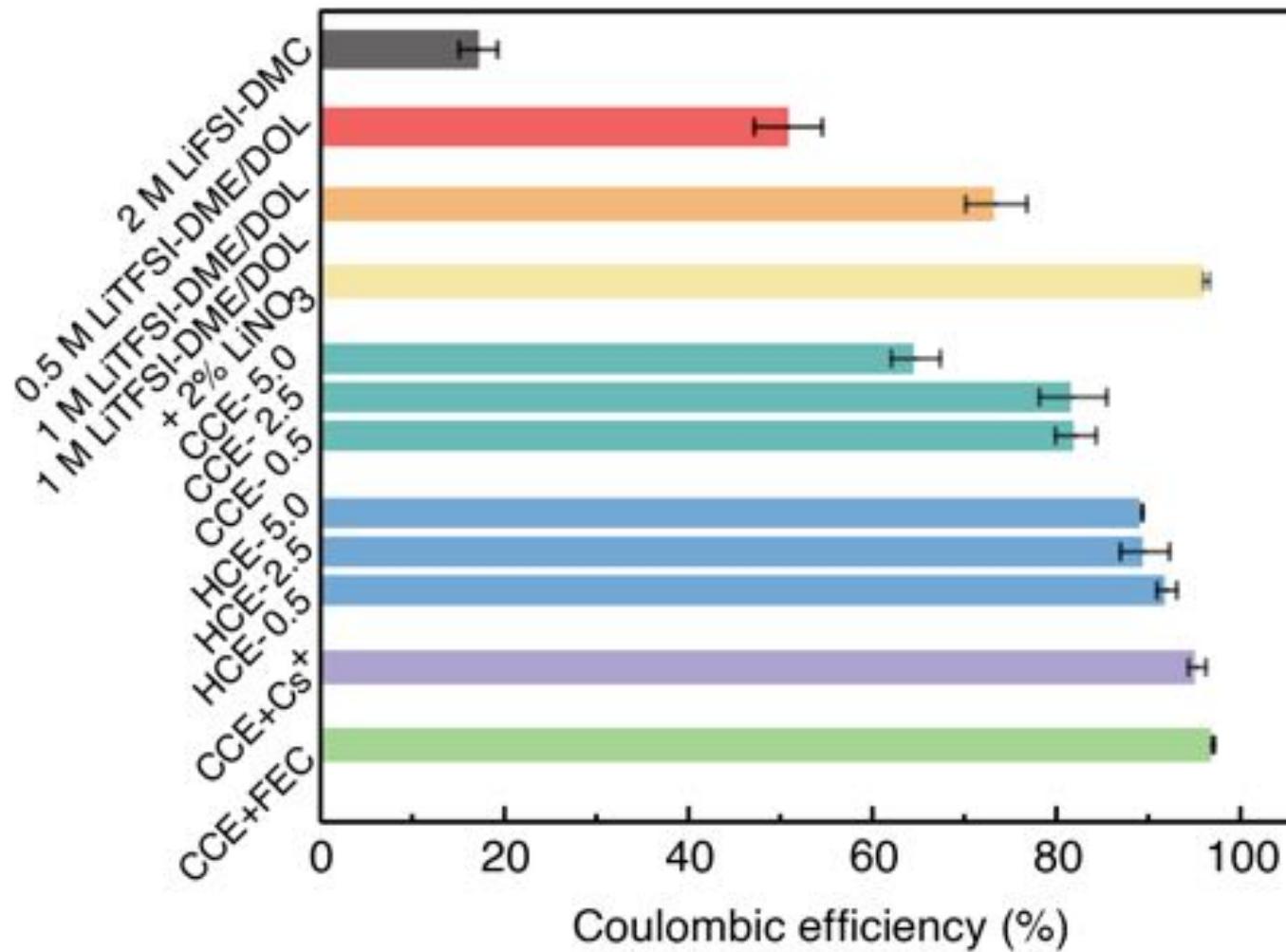
2. Li metal measurement accuracy  
(Commercial Li metal with known weight)



- C. Fang, Y.S. Meng et al., TGC Method and System for Metal Quantification, invention disclosure filed, 2018
- C. Fang, J. Li, Y.S. Meng et al., "Quantifying Inactive Lithium in Lithium Metal Batteries", *Nature* 572, 511–515 (2019)

# Capacity Usage Analysis

Inactive Li formed in **8 types of electrolytes**, and **3 different stripping rates** ( $0.5, 2.5$  and  $5 \text{ mA/cm}^2$ )



- First cycle Coulombic efficiencies range from 20% to 97% (plated at  $0.5 \text{ mA/cm}^2$ ,  $1 \text{ mAh/cm}^2$ )

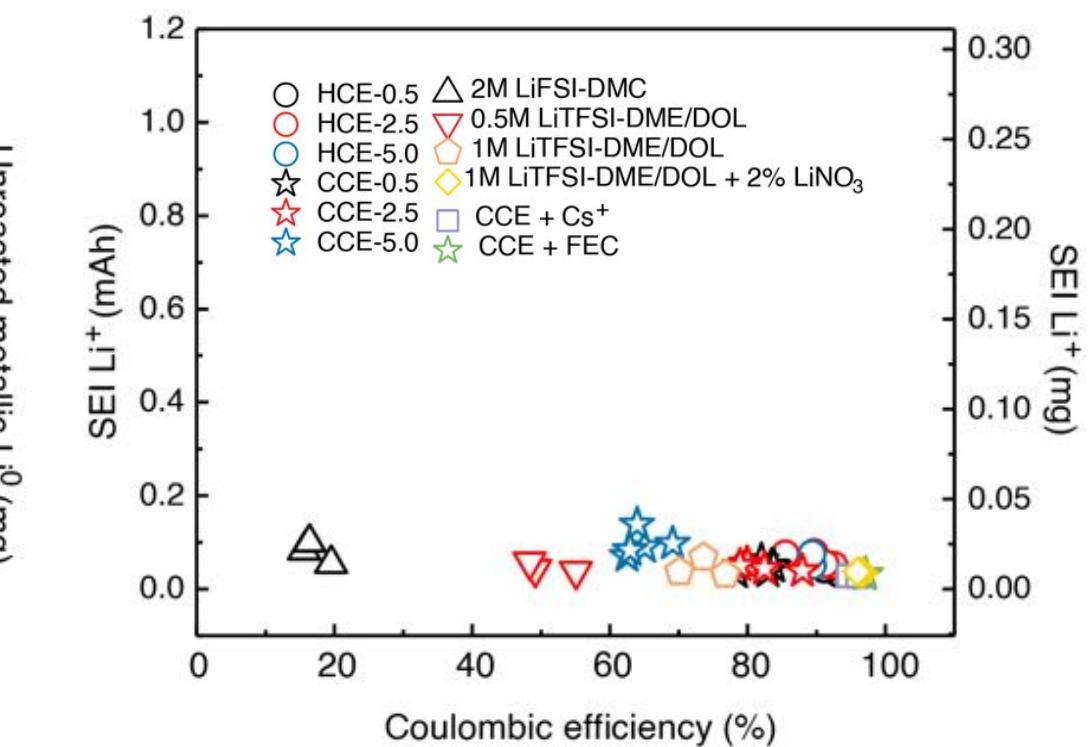
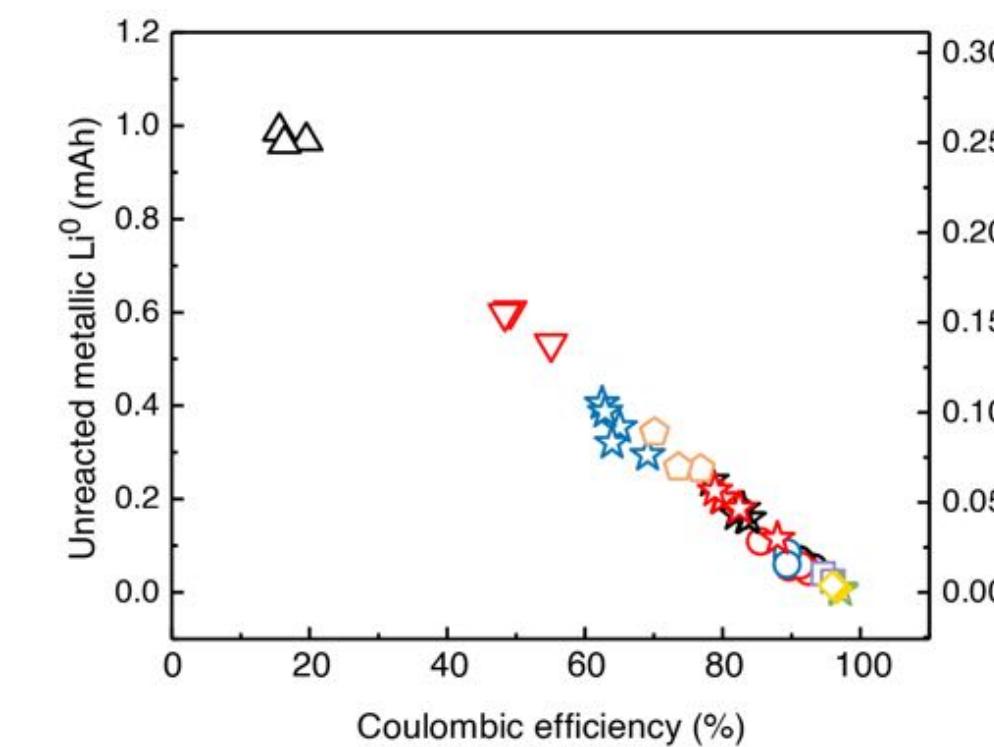
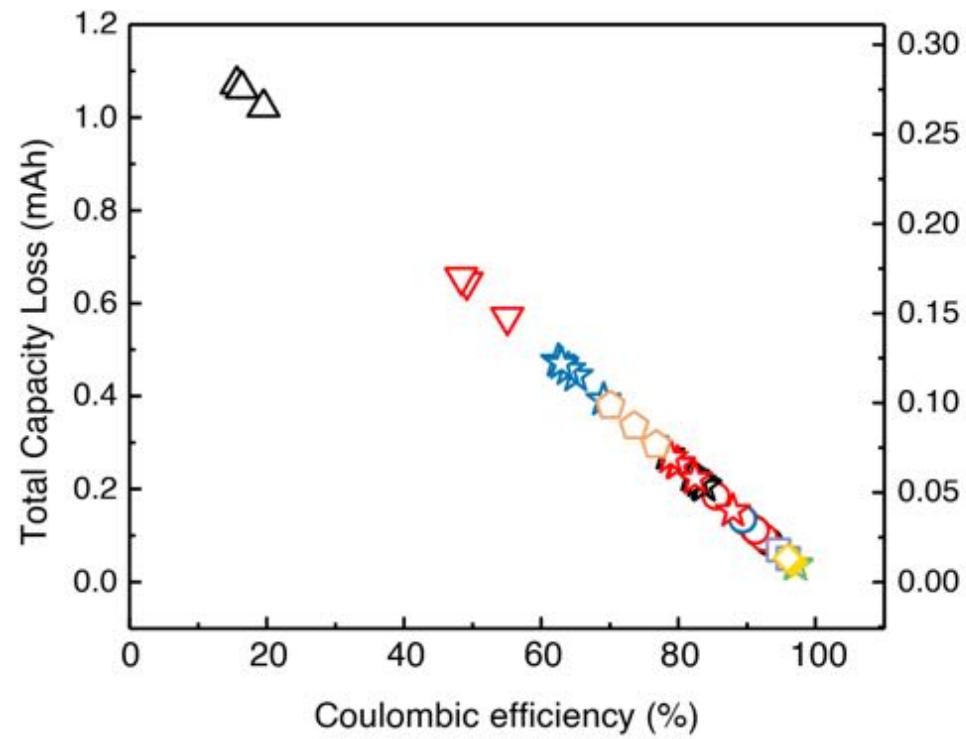
- Unreacted metallic Li measured by TGC
- An average of 3 – 5 samples at each condition

# Inactive Li Quantification

Total capacity loss

= Metallic Li<sup>0</sup>

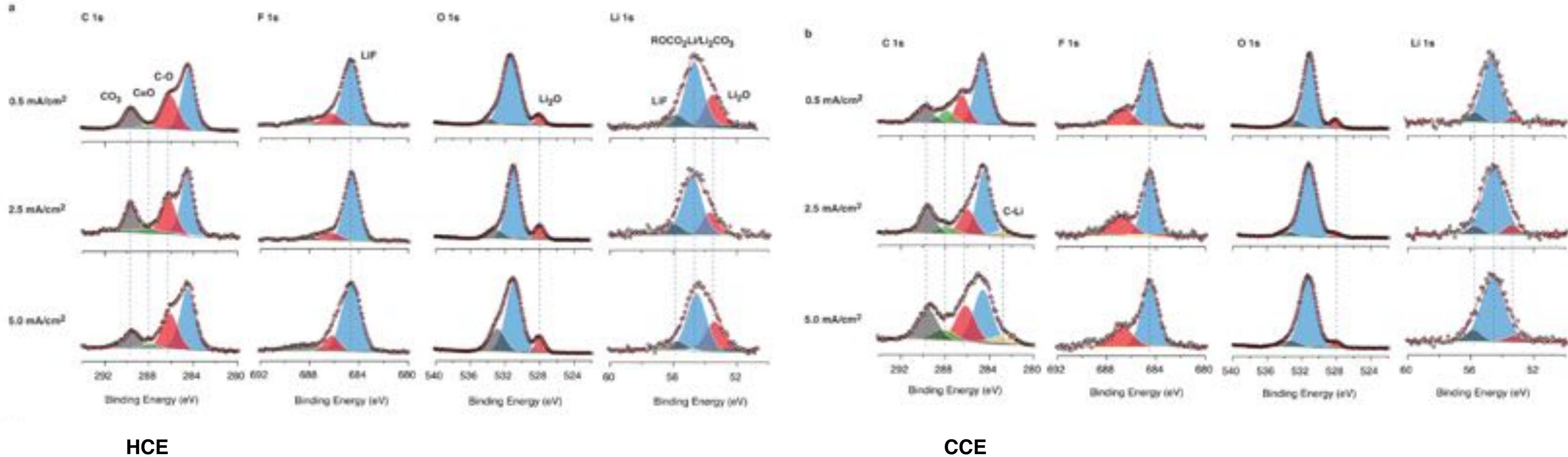
+ SEI Li<sup>+</sup>



- Metallic Li<sup>0</sup> dominates the capacity loss
- SEI Li<sup>+</sup> amount keeps almost identical under all testing conditions

SEI is not the main reason for low Coulombic efficiency in Li metal batteries

# XPS Analysis of Inactive Li



SEI components differences are minimal.

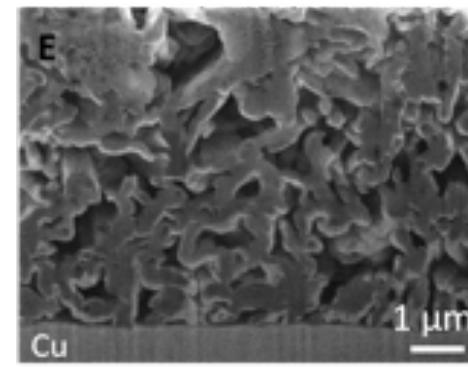
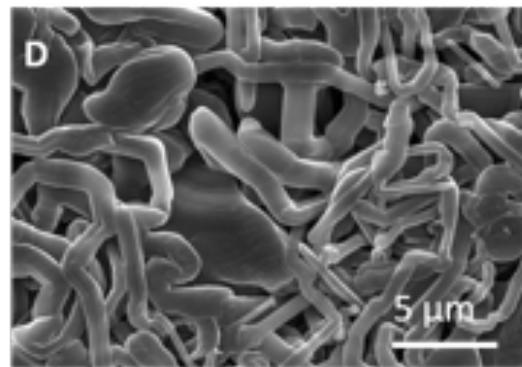
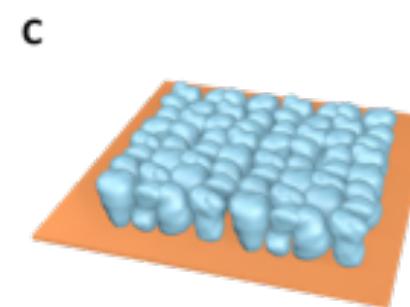
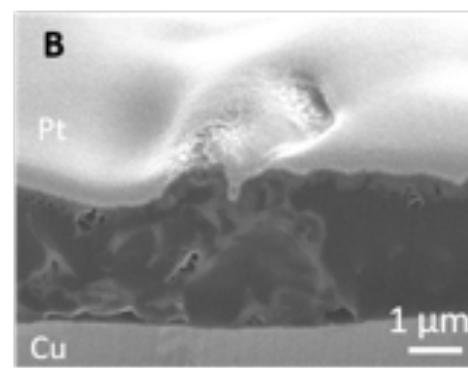
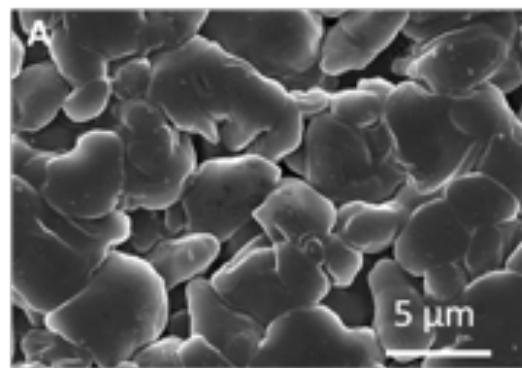
**HCE:** high concentration ether-based electrolyte  
(4M LiFSI + 2M LiTFSI in DME)

**CCE:** commercial carbonate electrolyte  
(1M LiPF<sub>6</sub> in EC/EMC, 3:7)



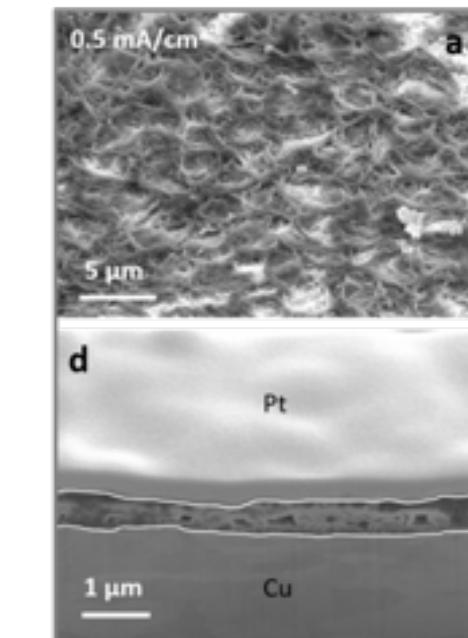
C. Fang, J. Li, Y.S. Meng *et al.*, “Quantifying Inactive Lithium in Lithium Metal Batteries”,  
**Nature** **572**, 511–515 (2019)

# Microstructure of Inactive Li by Cryo-FIB-SEM



0.5 mA/cm<sup>2</sup>, 0.5 mAh/cm<sup>2</sup>

Stripping

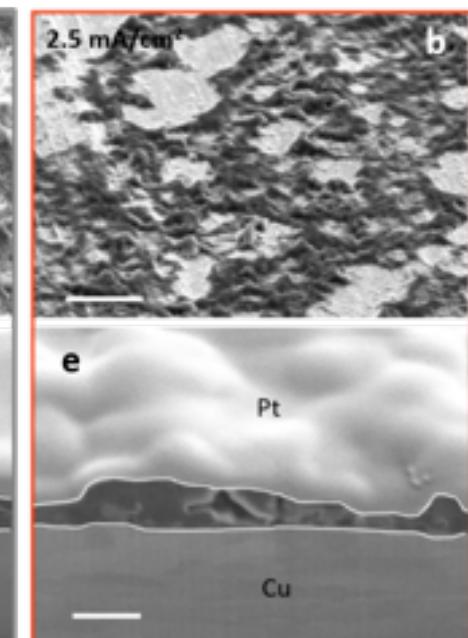


d

Pt

Cu

1 μm

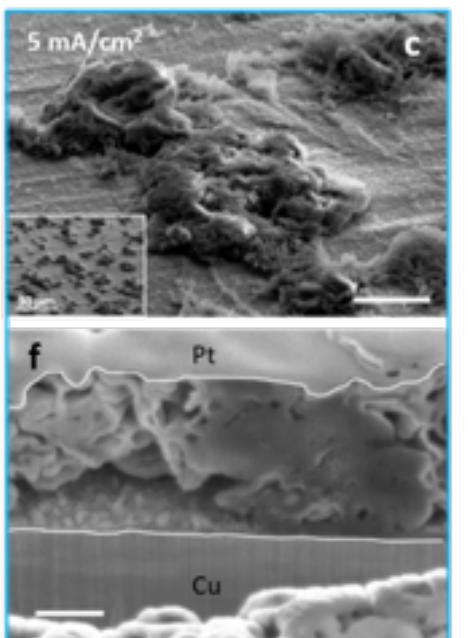


e

Pt

Cu

1 μm



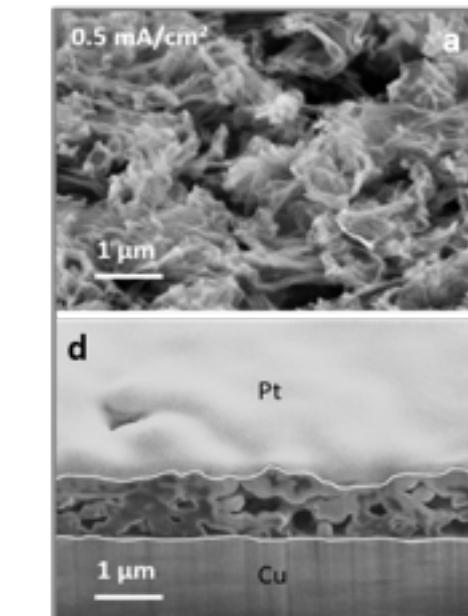
f

Pt

Cu

1 μm

HCE

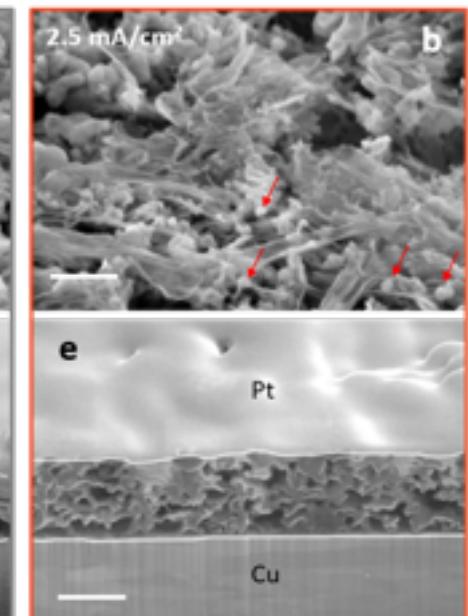


d

Pt

Cu

1 μm

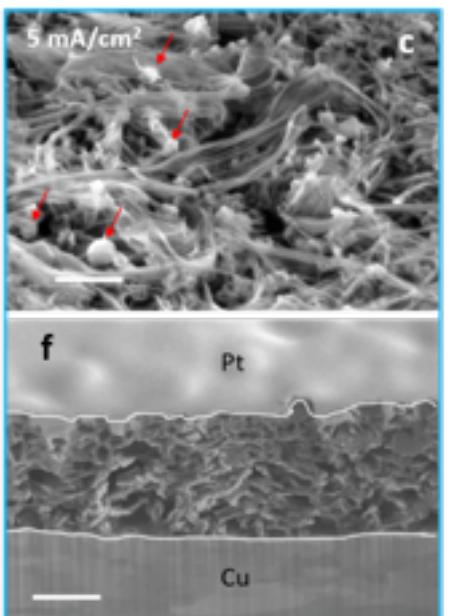


e

Pt

Cu

1 μm



f

Pt

Cu

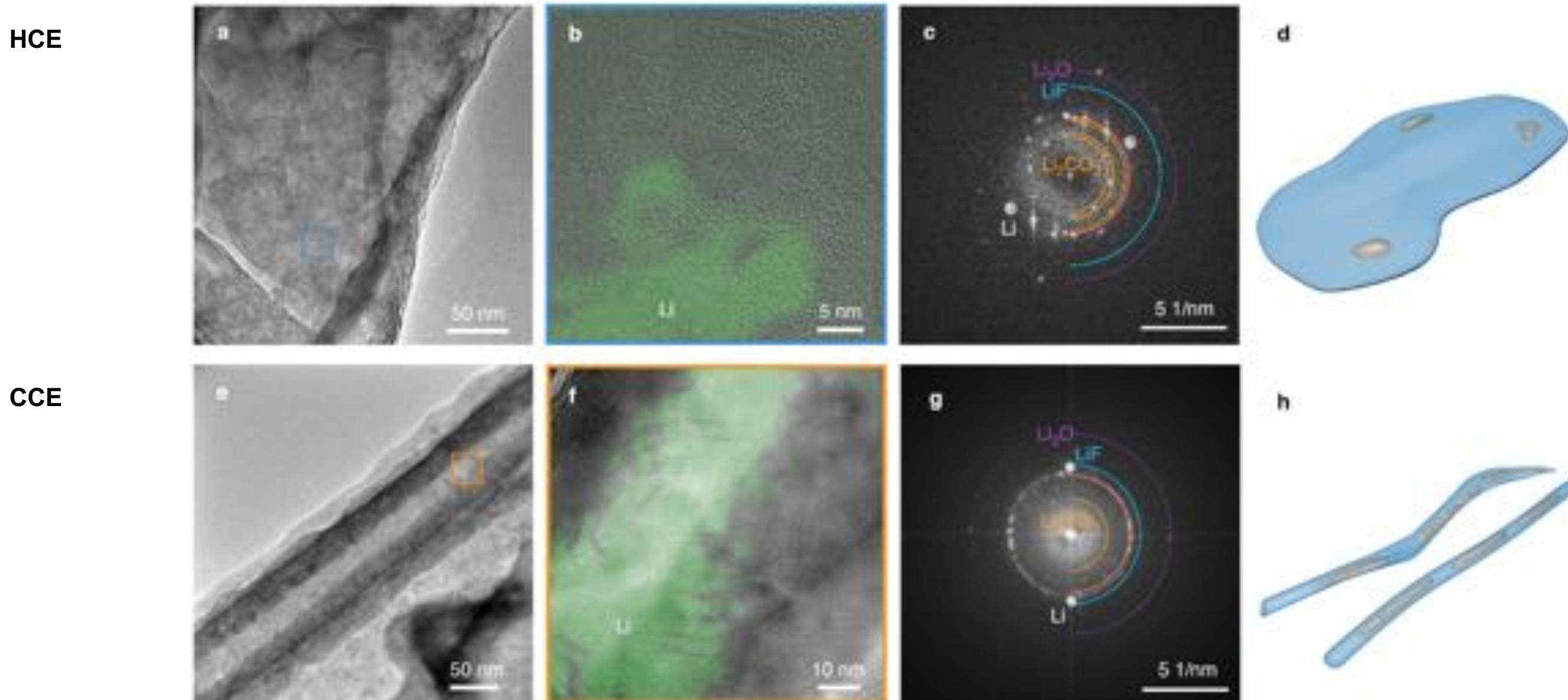
1 μm

CCE



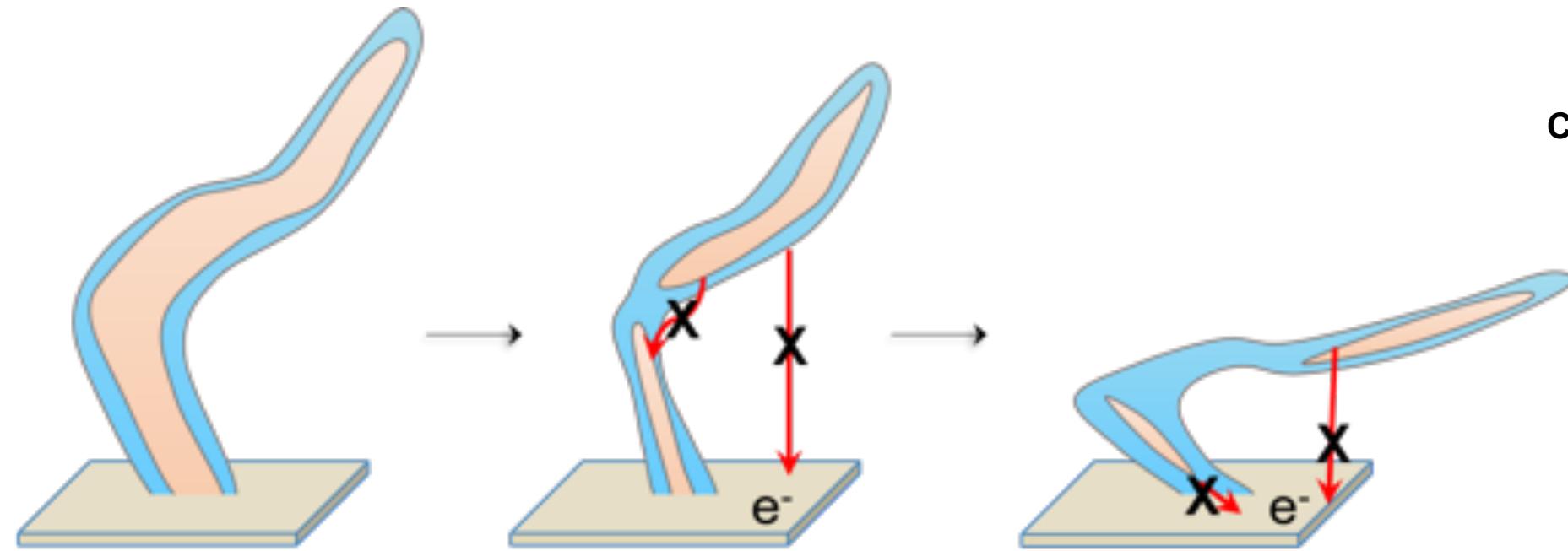
C. Fang, J. Li, Y.S. Meng *et al.*, "Quantifying Inactive Lithium in Lithium Metal Batteries", *Nature* 572, 511–515 (2019)

# Nanostructure of Inactive Li by Cryo-TEM



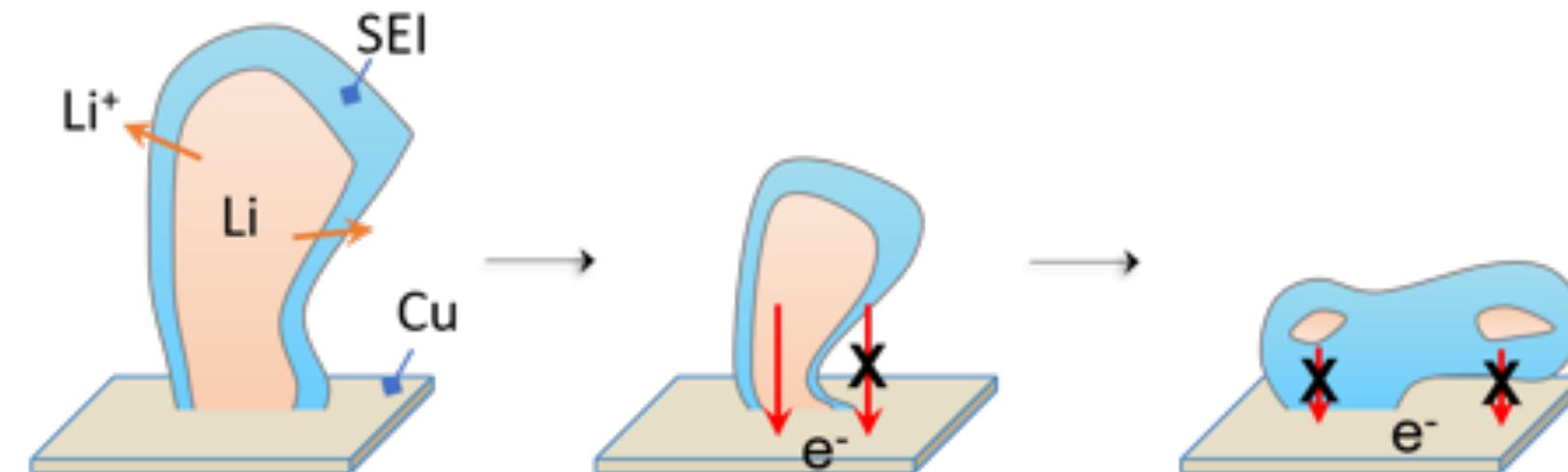
# Structural Connection

- ✗ Thin/ Ununiform in diameter
- ✗ **Large tortuosity**
- ✗ Bad structural connection



CCE

- ✓ Large granular size  
(thick in diameter)
- ✓ **Less tortuosity**
- ✓ Good structural connection

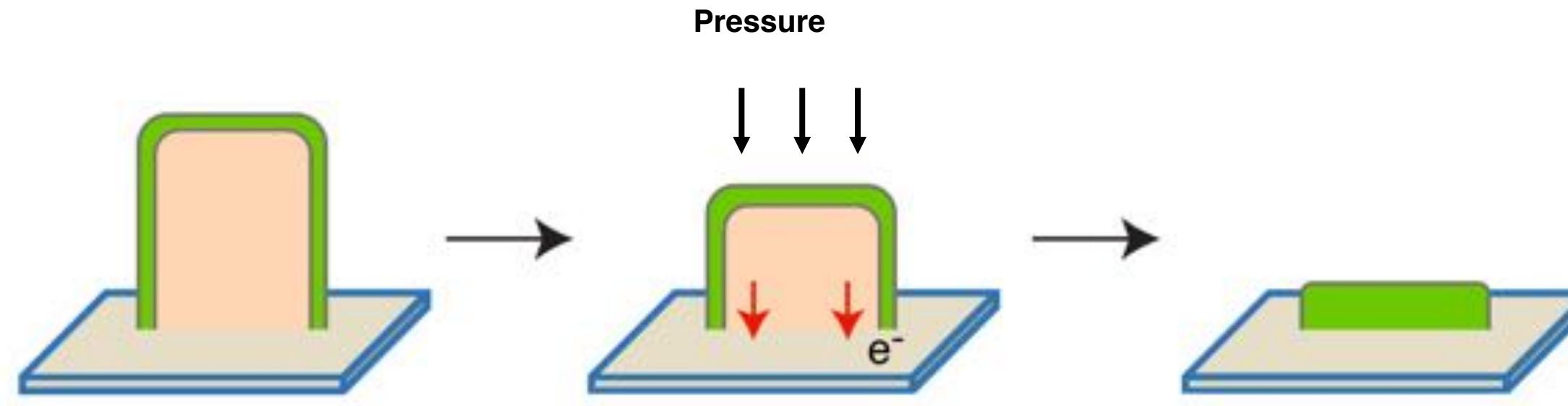


HCE

# Strategies to Mitigate Inactive Li Formation

The underlying cause of low Coulombic efficiency in Li Metal Batteries is

**Large amount of Li metal is trapped in SEI with tortuous microstructure**



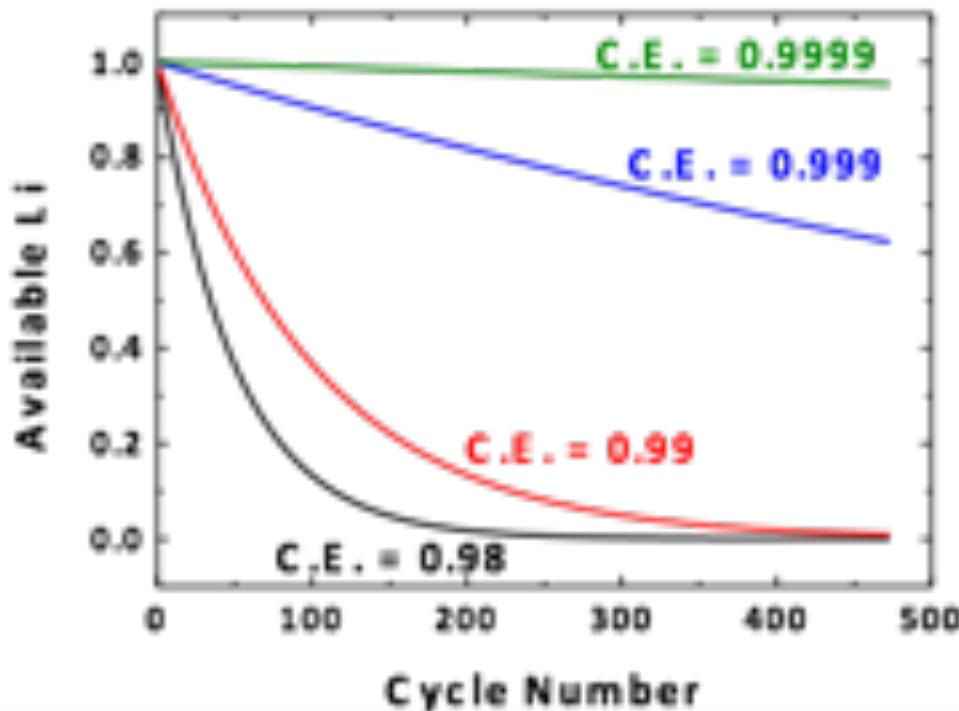
**Maintain a good structural electronic connection**

- Columnar Li deposits (advanced electrolytes, artificial SEI)
- 3D current collector
- Proper pressure

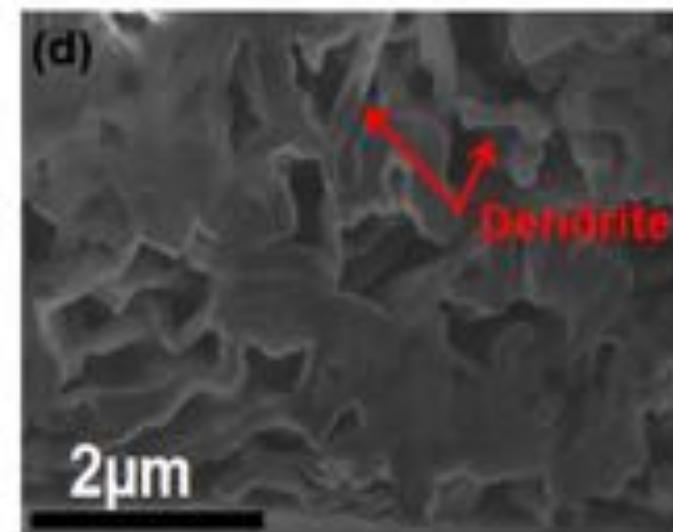
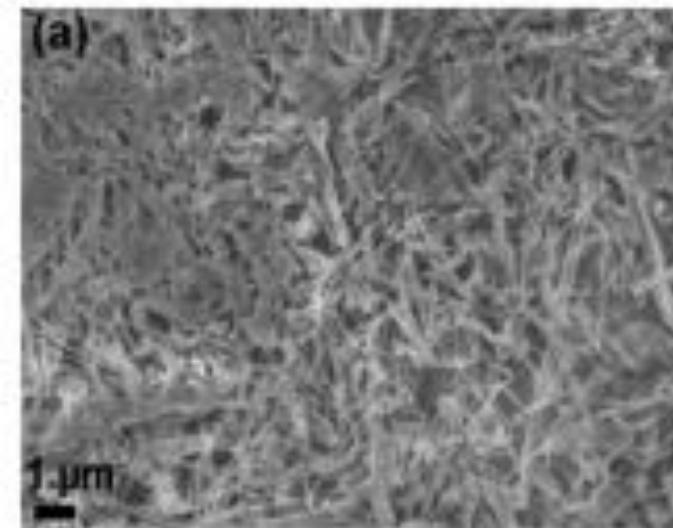
# Electrolyte! Electrolyte! Electrolyte!

BATTERY  
CONSORTIUM 500

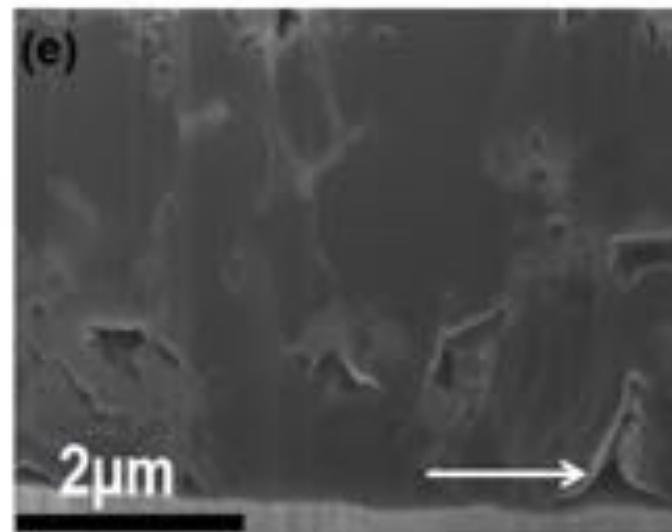
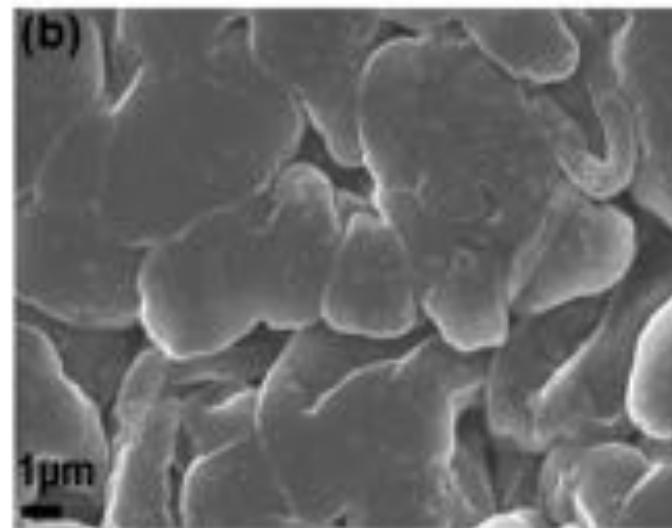
J. Alvarado , ...Y.S. Meng, et al, Energy & Environ Sciences, 2019



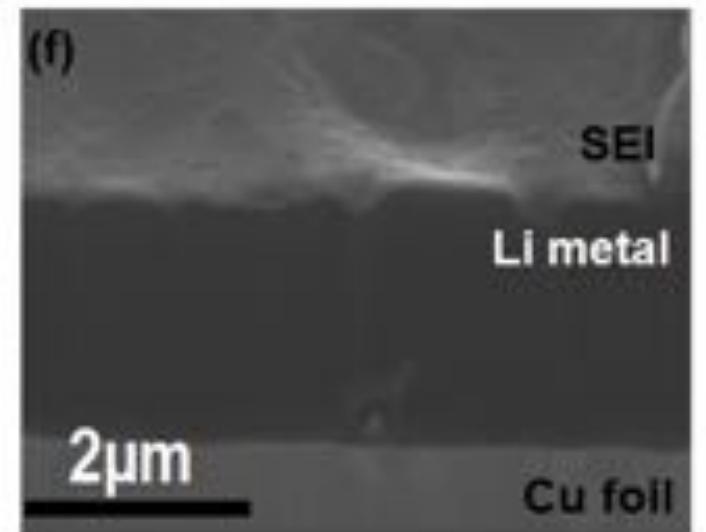
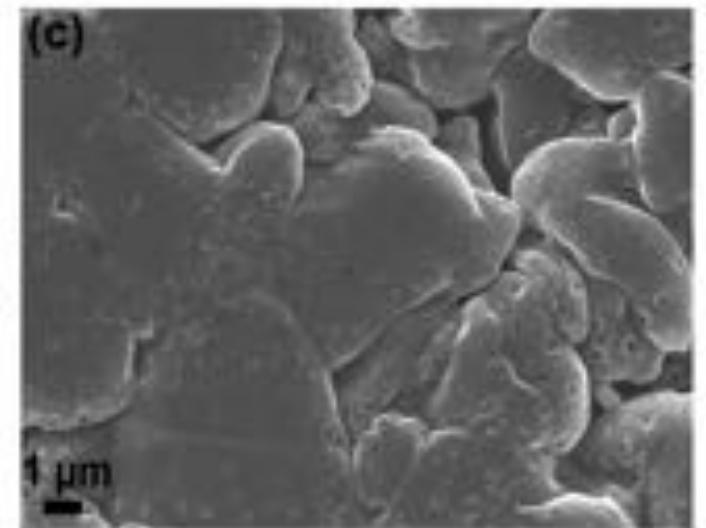
Gen II



New Salt



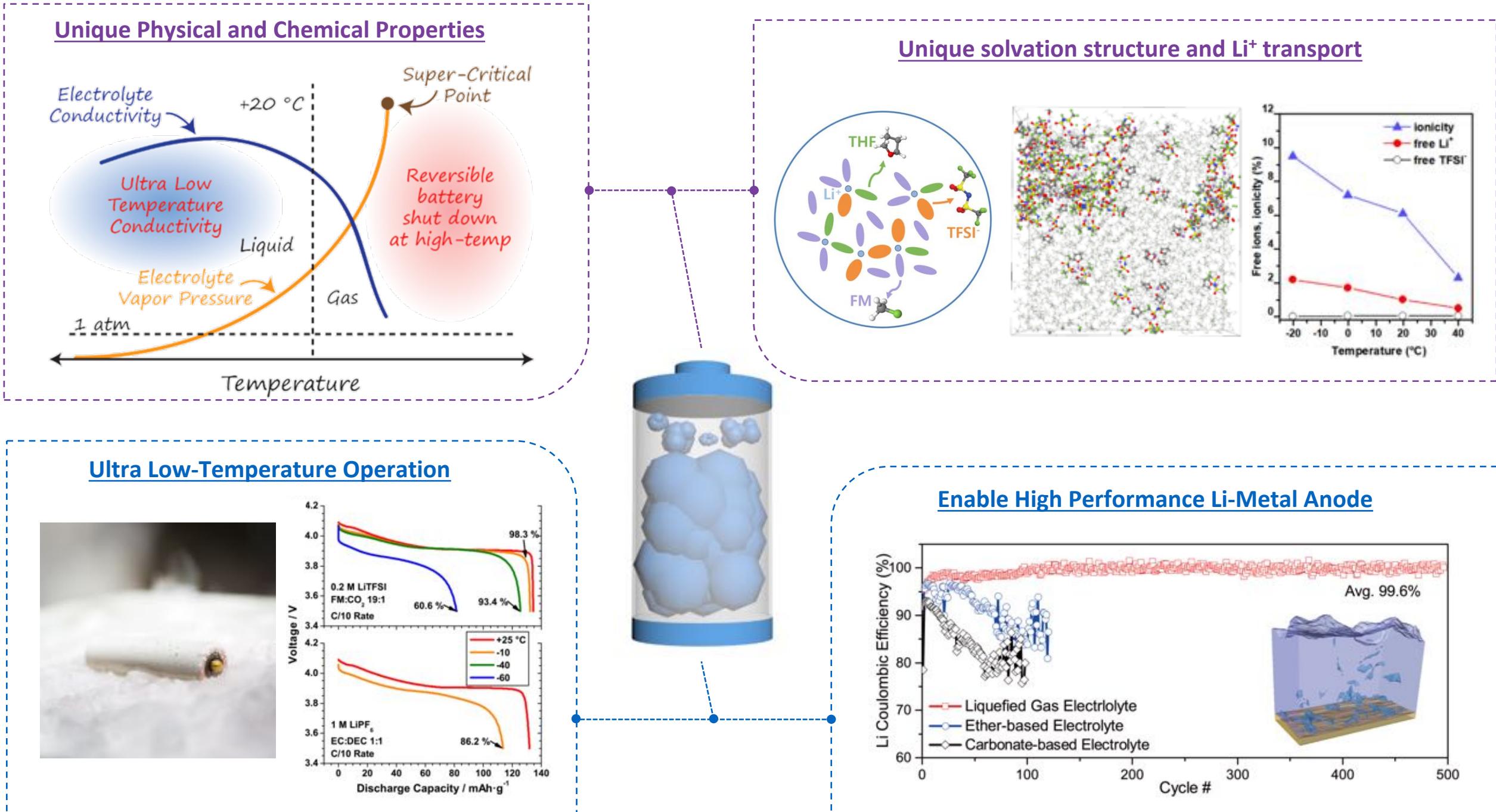
New Electrolyte



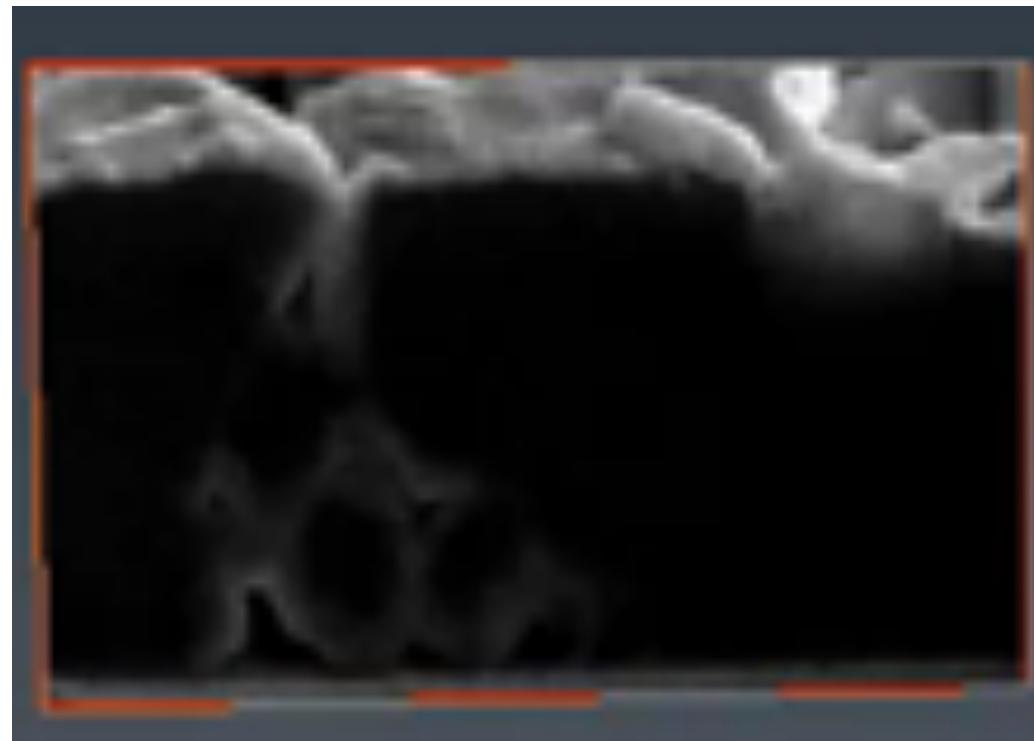
Scientific Gaps:

1. What is the true CE ??? Depositing Li, Li<sub>2</sub>O, Li<sub>2</sub>CO<sub>3</sub>, LiOH, LiF  
 $1\text{mAh/cm}^2 = 5\mu\text{m} / \text{cm}^2$ , so if you get 6 um? Porosity in EDLi

# Liquefied Gas Electrolytes Systems



# 3D Reconstruction: Plated Li in Non-Carbonate Electrolyte



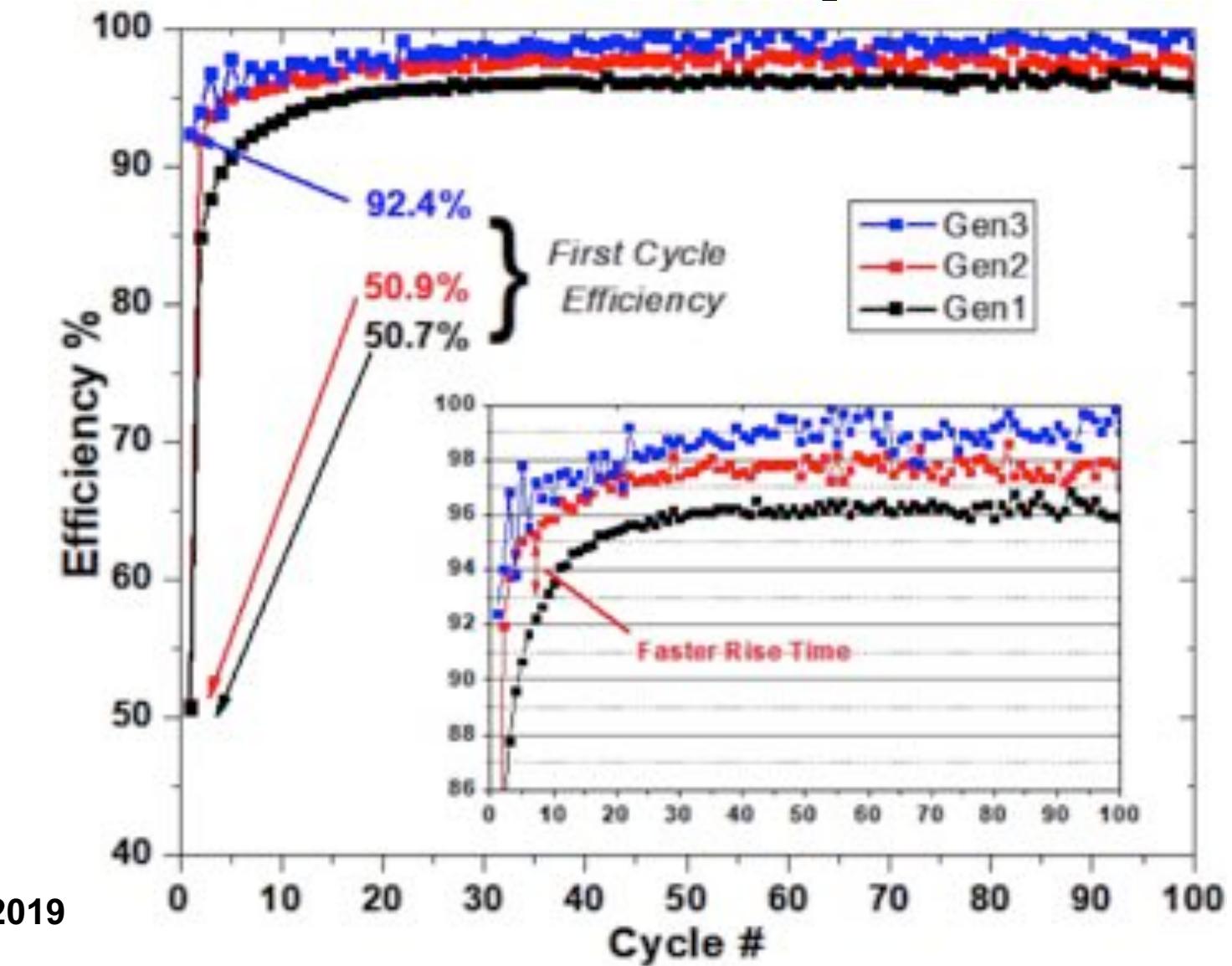
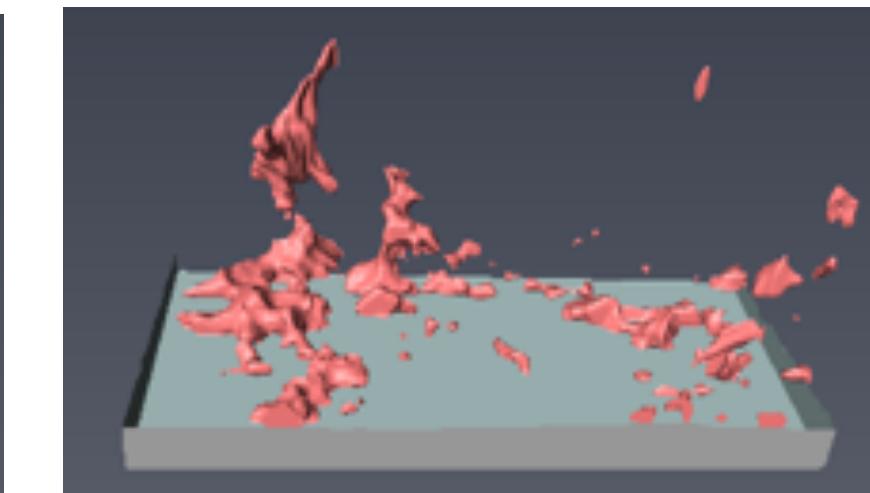
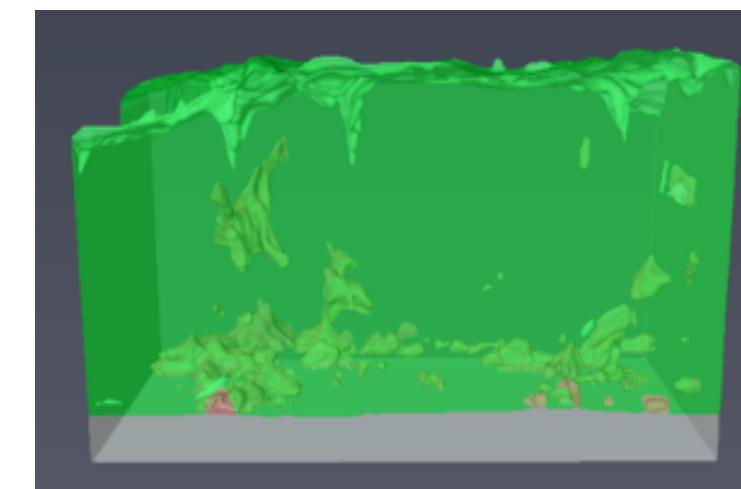
Liquified Gas Electrolyte!

5μm

Y. Yang...Y.S. Meng, et al, Joule, 2019

**Volume  
Analyzed:  
 $10^5 \times 5 \mu\text{m}^3$**

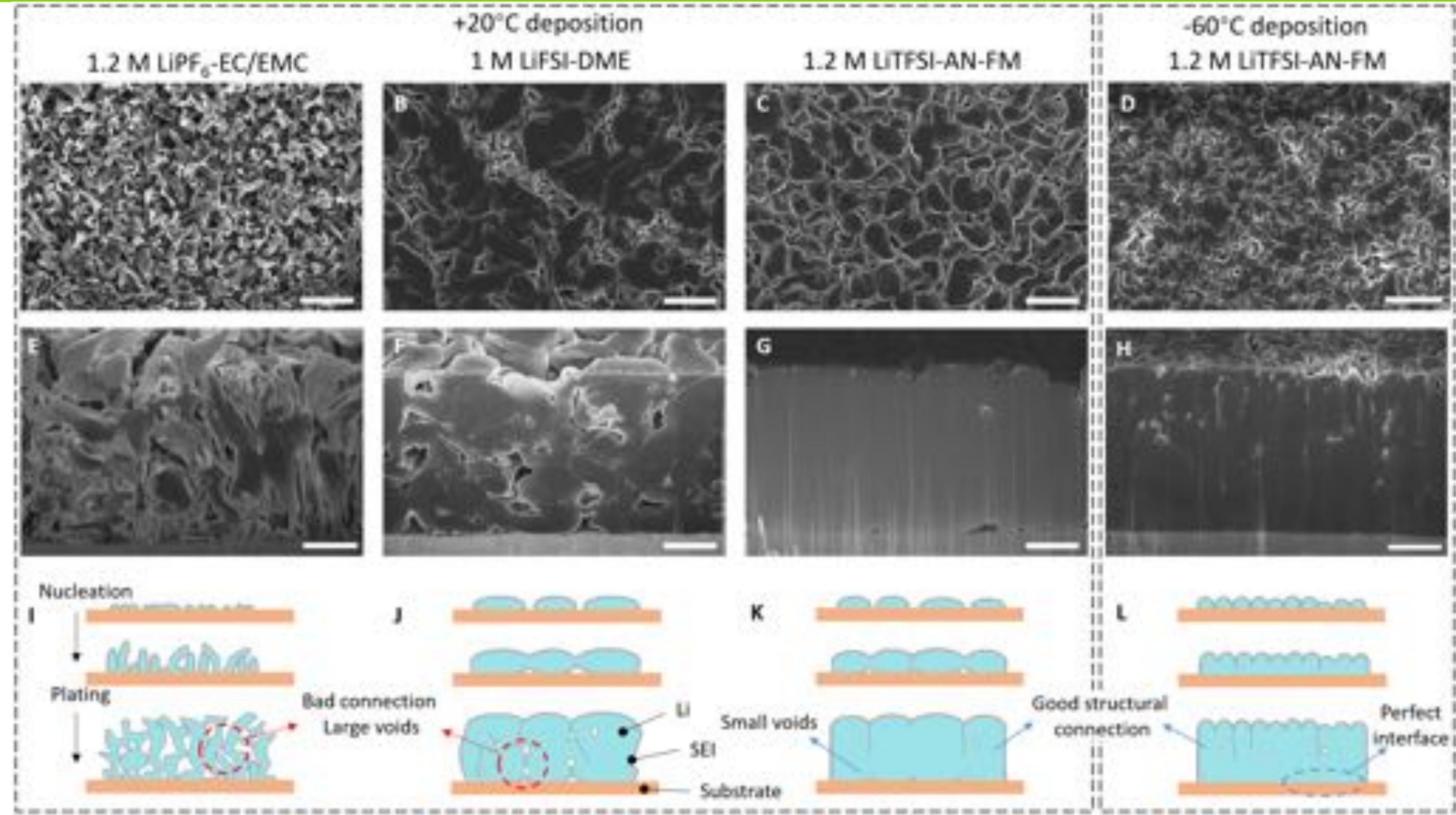
**Void fraction = 0.95%**



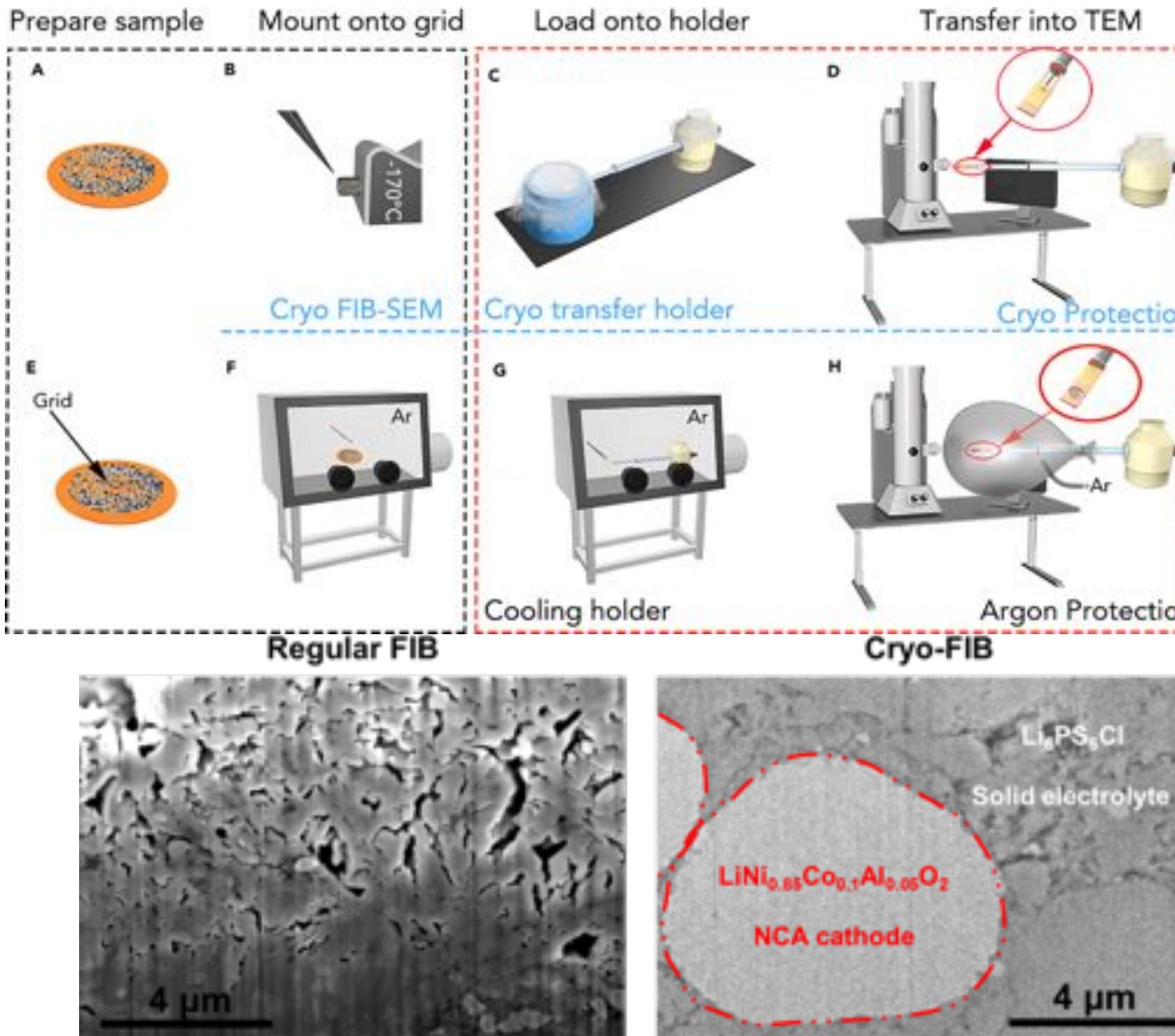
# Li-Metal Structure in Liquified Gas Electrolytes

Y. Yang...Y.S. Meng, et al, Submitted, 2020

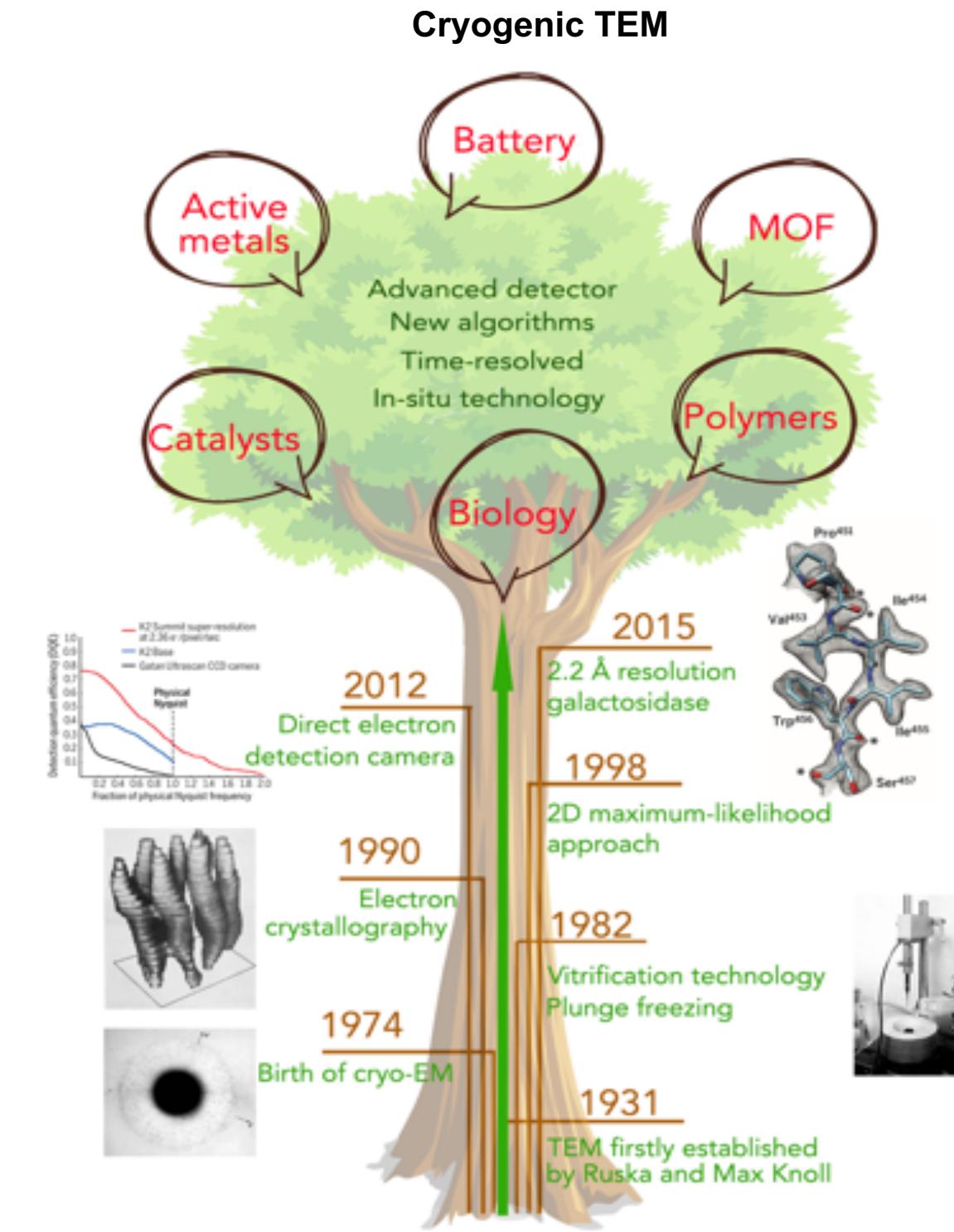
**0.5 mA/cm<sup>2</sup>,**  
**3 mAh/cm<sup>2</sup>**



# Cryo Imaging - New Paradigm for Materials Characterization



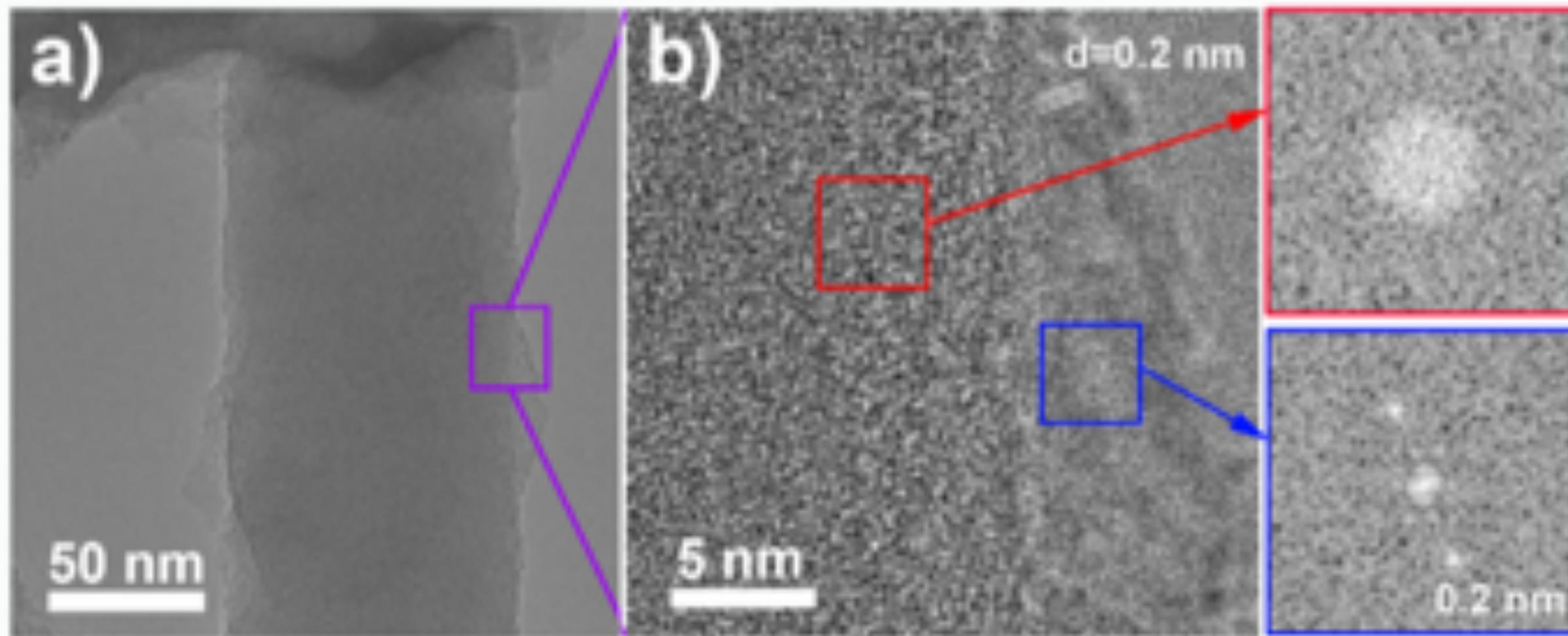
Cryo-FIB/TEM enables preparation of cross-sections and lift-outs while preserving morphology and crystallinity, demonstrated in blended NCA/LPS cross-sections and Li-metal anode lift-outs.



# Effect of Current Density and Electrolyte Additives

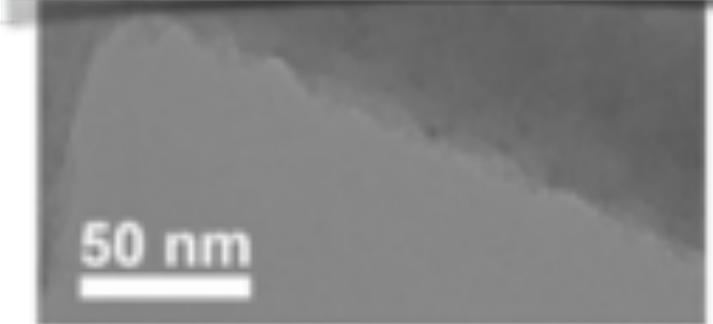
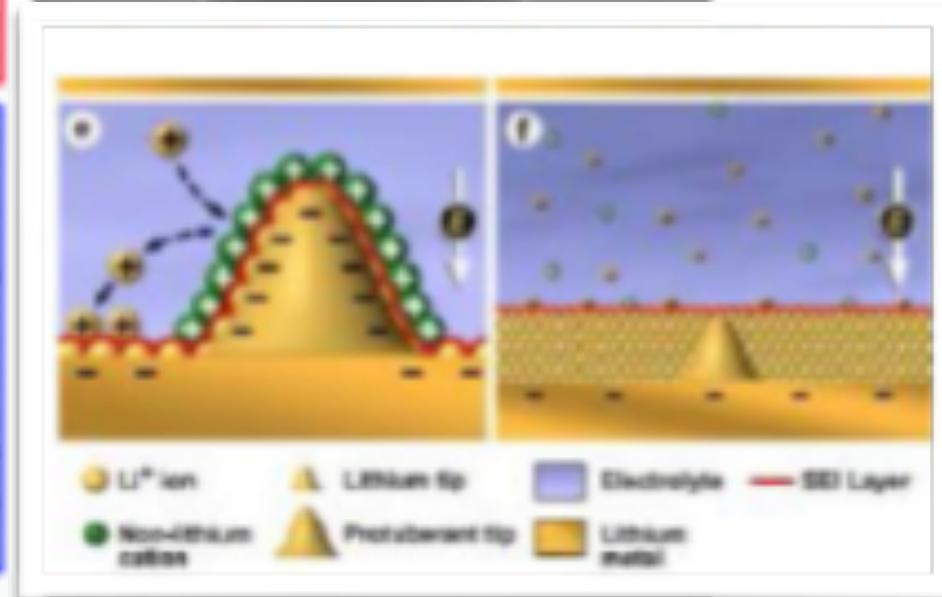
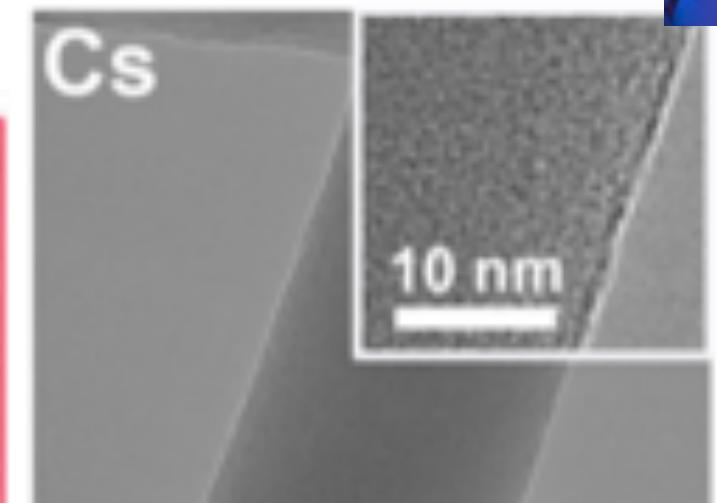


0.5mA/cm<sup>2</sup> for 5 minutes

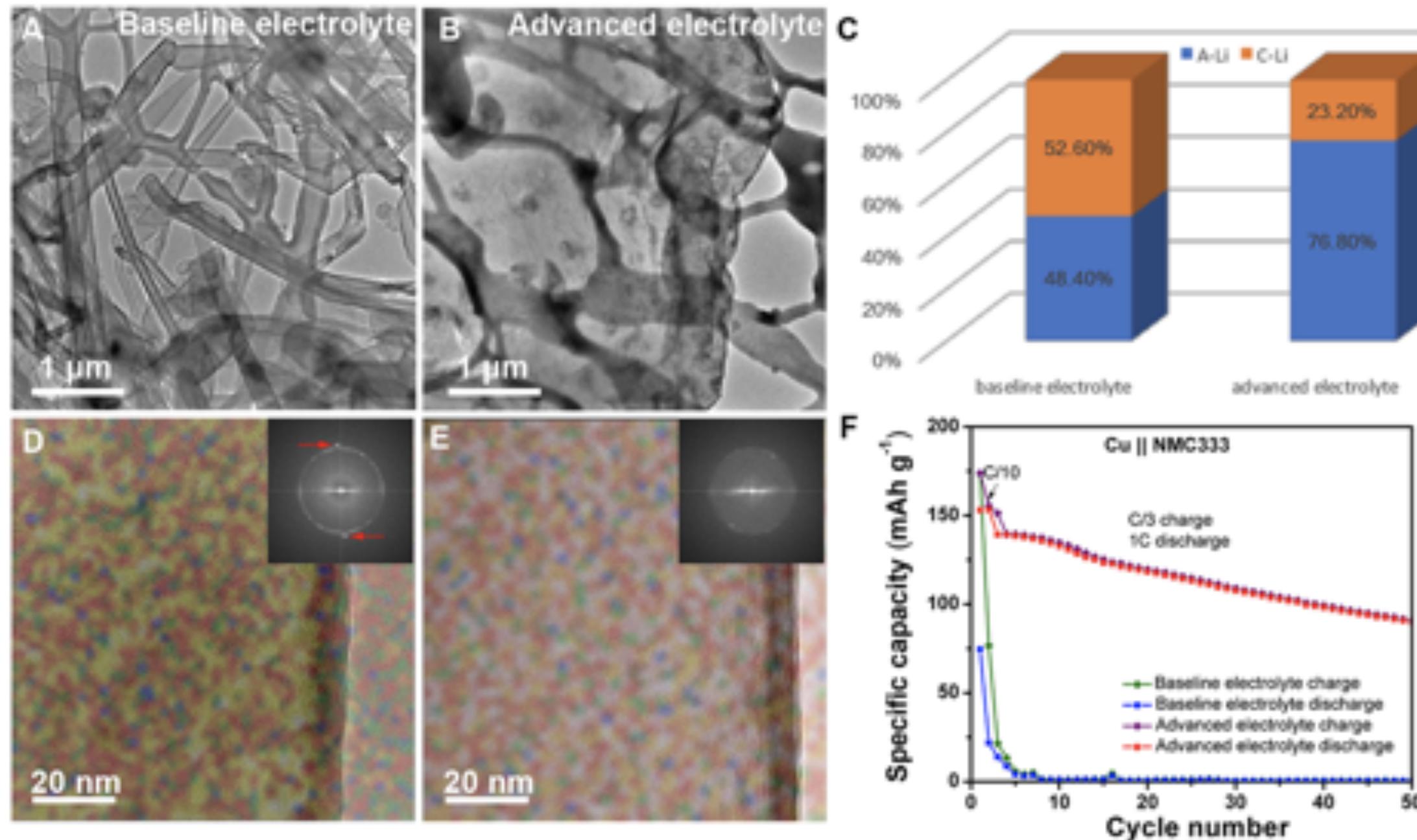


non-uniform SEI

Amorphous Li bulk and partial crystalline SEI



# Amorphous/Glassy Li ?



# Collaborators and Funding



## Students and Postdocs:

**Dr. Chengcheng Fang, Dr. Thomas Wynn, Dr. Xuefeng Wang,  
Bingyu Lu and Dylan Chen**



**Cryo-Imaging Tool Development:  
U.S. Department of Energy, Office of  
Basic Energy Sciences,**

**Lithium Metal Batteries :  
Vehicle Technology Office  
( Battery Materials Research BMR)**



## Collaborators:

**Dr. Jason Zhang and Dr. Wu Xu  
Dr. Jie Xiao and Dr. Jun Lu (PNNL)  
Dr. Kang Xu and Dr. Marshall Schroder (ARL)  
Dr. Xiaoqing Pan (UC Irvine/IMRI)  
Dr. Cyrus Rustmoji (South 8 Technology)  
Dr. Hieu Duong (Maxwell Technology)  
Dr. Boryann Liaw (Idaho National Lab)  
Dr. Mei Cai (General Motors)  
Dr. Jing Gu (San Diego State University)**



# THANK YOU



# Recommended Reading

- 1) Xu, K. Electrolytes and Interphases in Li-Ion Batteries and Beyond. *Chem. Rev.* **2014**, *114*, 11503-11618.
- 2) Cheng, X.-B.; Zhang, R.; Zhao, C.-Z.; Zhang, Q. Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review. *Chem. Rev.* **2017**, *117*, 10403-10473.
- 3) Fang, C.; Li, J.; Zhang, M.; Zhang, Y.; Yang, F.; Lee, J. Z.; Lee, M.-H.; Alvarado, J.; Schroeder, M. A.; Yang, Y. et al. Quantifying Inactive Lithium in Lithium Metal Batteries. *Nature* **2019**, *572*, 511-515.
- 4) Niu, C.; Lee, H.; Chen, S.; Li, Q.; Du, J.; Xu, W.; Zhang, J.-G.; Whittingham, M. S.; Xiao, J.; Liu, J. High-Energy Lithium Metal Pouch Cells with Limited Anode Swelling and Long Stable Cycles. *Nature Energy* **2019**, *4*, 551-559.
- 5) Peled, E.; Golodnitsky, D.; Ardel, G. Advanced Model for Solid Electrolyte Interphase Electrodes in Liquid and Polymer Electrolytes. *J. Electrochem. Soc.* **1997**, *144*, L208-L210.
- 6) Cao, X.; Ren, X.; Zou, L.; Engelhard, M. H.; Huang, W.; Wang, H.; Matthews, B. E.; Lee, H.; Niu, C.; Arey, B. W. et al. Monolithic Solid–Electrolyte Interphases Formed in Fluorinated Orthoformate-Based Electrolytes Minimize Li Depletion and Pulverization. *Nature Energy* **2019**, *4*, 796-805.
- 7) Li, N.-W.; Yin, Y.-X.; Yang, C.-P.; Guo, Y.-G. An Artificial Solid Electrolyte Interphase Layer for Stable Lithium Metal Anodes. *Adv. Mater.* **2016**, *28*, 1853-1858.
- 8) Xu, R.; Cheng, X.-B.; Yan, C.; Zhang, X.-Q.; Xiao, Y.; Zhao, C.-Z.; Huang, J.-Q.; Zhang, Q. Artificial Interphases for Highly Stable Lithium Metal Anode. *Matter* **2019**, *1*, 317-344.
- 9) Liu, Y.; Tzeng, Y.-K.; Lin, D.; Pei, A.; Lu, H.; Melosh, N. A.; Shen, Z.-X.; Chu, S.; Cui, Y. An Ultrastrong Double-Layer Nanodiamond Interface for Stable Lithium Metal Anodes. *Joule* **2018**, *2*, 1595-1609.
- 10) Gu, Y.; Wang, W.-W.; Li, Y.-J.; Wu, Q.-H.; Tang, S.; Yan, J.-W.; Zheng, M.-S.; Wu, D.-Y.; Fan, C.-H.; Hu, W.-Q. et al. Designable Ultra-Smooth Ultra-Thin Solid-Electrolyte Interphases of Three Alkali Metal Anodes. *Nat. Commun.* **2018**, *9*, 1339-1348.
- 11) Lu, D.; Shao, Y.; Lozano, T.; Bennett, W. D.; Graff, G. L.; Polzin, B.; Zhang, J.; Engelhard, M. H.; Saenz, N. T.; Henderson, W. A. et al. Failure Mechanism for Fast-Charged Lithium Metal Batteries with Liquid Electrolytes. *Adv. Energy Mater.* **2015**, *5*, 1400993-1401000.
- 12) Fang, C.; Wang, X.; Meng, Y. S. Key Issues Hindering a Practical Lithium-Metal Anode. *Trends in Chemistry* **2019**, *1*, 152-158.
- 13) Nagpure, S. C.; Tanim, T. R.; Dufek, E. J.; Viswanathan, V. V.; Crawford, A. J.; Wood, S. M.; Xiao, J.; Dickerson, C. C.; Liaw, B. Impacts of Lean Electrolyte on Cycle Life for Rechargeable Li Metal Batteries. *J. Power Sources* **2018**, *407*, 53-62.
- 14) Wang, J.; Huang, W.; Pei, A.; Li, Y.; Shi, F.; Yu, X.; Cui, Y. Improving Cyclability of Li Metal Batteries at Elevated Temperatures and Its Origin Revealed by Cryo-Electron Microscopy. *Nature Energy* **2019**, *4*, 664-670.
- 15) Weber, R.; Genovese, M.; Louli, A. J.; Hames, S.; Martin, C.; Hill, I. G.; Dahn, J. R. Long Cycle Life and Dendrite-Free Lithium Morphology in Anode-Free Lithium Pouch Cells Enabled by a Dual-Salt Liquid Electrolyte. *Nature Energy* **2019**, *4*, 683-689.