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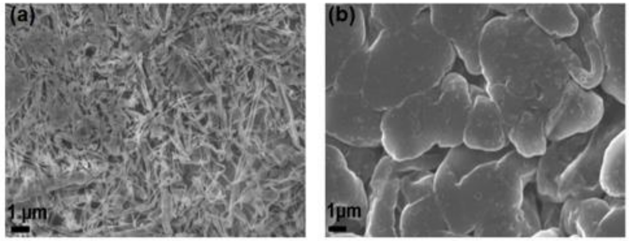
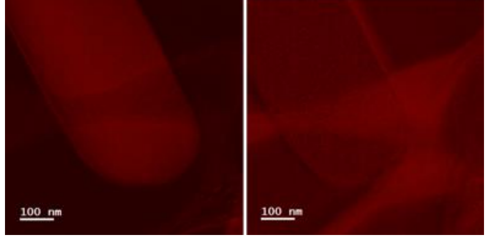
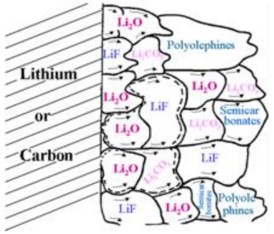
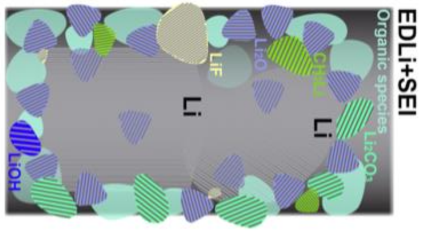








Advanced Imaging and Quantitative Characterization of Lithium Metal Anode and Its SEI

P.I. Y. Shirley Meng

Department of NanoEngineering
University of California San Diego
June 2021

Project ID# bat 366

2021 DOE Vehicle Technologies Office Annual Merit Review

Overview

Timeline

- Project start date: 10/01/2016
- Project end data: 9/30/2021
- Percent complete: 90%

Budget

- Total project funding
  - DOE share:$50M
- FY2019 funding: $10M
- FY2020 funding: $10M

Barriers

- **Abuse Tolerance**: Li-metal based batteries have a long history of problematic dendrite growth
- **Life**: Cells containing Li metal anode suffer from major cycling and calendar life issues.

Partners

- Battery500 and BMR
- PNNL, INL, ARL
- UCLA, SDSU
- General Motors, South 8 Technologies

Relevance

❖Overall objective

--Develop commercially viable lithium (Li) battery technologies with a cell level specific energy of 500 Wh/kg

-- Achieve 1000 cycles for the developed technologies

❖Objectives this period

-- Develop large-scale co-precipitation high-Ni synthesis method

-- Optimize electrolytes and electrodes

-- Fabricate and test 350/400 Wh/kg Li-NMC pouch cells

-- Develop advanced tools to characterize thick electrodes, Li dendrite formation and pressure effect to extend pouch cell cycling life

-- Understand the degradation mechanisms of Li-S pouch cells and reveal new materials and cell design strategies

❖Impact

-- Significantly increase the energy density, cycle life and reduce the cost of rechargeable batteries for electric vehicles

Milestones UCSD FY20

Date	Milestones and Go/No-Go Decisions	Status
December 2020	Milestones: Structural characterization of coated NMC with benchmark NMC using protocols for 350 Wh/kg cells.	Complete
March 2021	Milestones: Develop understanding of SPAN structure and reaction mechanisms.	Complete
June 2021	Milestones: Compare SPAN cathode with benchmark S cathode using protocols for 300 Wh/kg cells with 50 cycles.	On Track
September 2021	Milestones: Propose strategies to incorporate Li anode, Li protection for practically implementing into pouch cells.	On Track

Approach

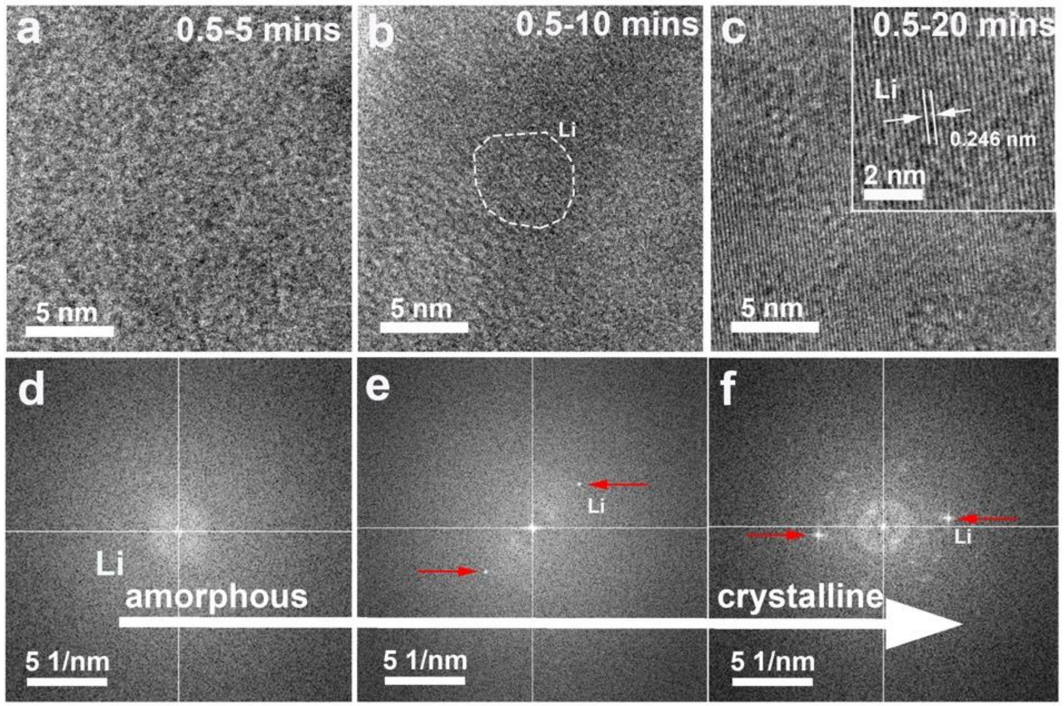
Advanced imaging tools and quantitative tools (chemically, morphologically and computationally) have been developed to understand the electrochemical behavior and SEI properties of Li metal anode:

- **Developed cryogenic electron microscopy (Cryo-EM) and cryogenic focused ion beam (Cryo-FIB) to image and diagnose the Li metal**
- **Combined cryo-EM with MD simulation to understand Li nucleation process**
- **Developed a new analytical tool Titration Gas Chromatography (TGC) to quantify SEI components and inactive metallic Li (“dead” Li)**
- **Developed micro Computed Tomography (CT) for 3D current collector structures quantification**

Technical Accomplishments and Progress

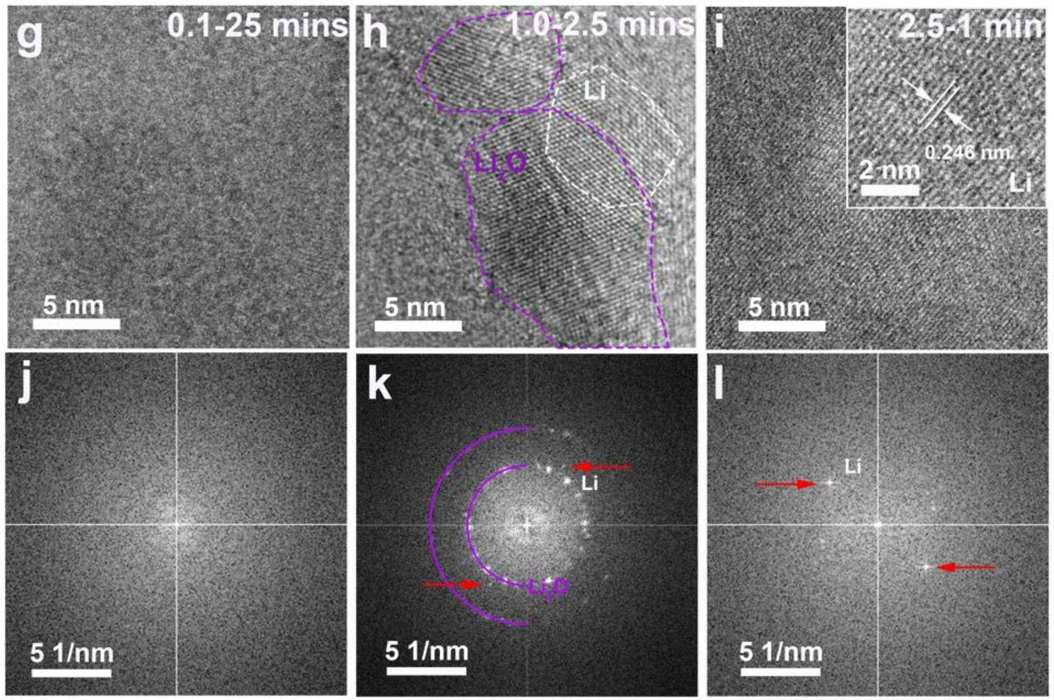
1. Nanostructure Evolution of Li Nucleation

Deposition time



0.5 mA cm^{-2} for 5 min, 10 min and 20 min

Current density



0.1 mA cm^{-2} for 25 min, 1.0 mA cm^{-2} for 2.5 min and 2.5 mA cm^{-2} for 1.0 min

Time and current density change the crystallinity of Li metal and SEI properties

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X. Wang, G. Pawar, B.Y. Liaw and Y.S. Meng et al, Nature Materials, (2020) 19, 1339–1345

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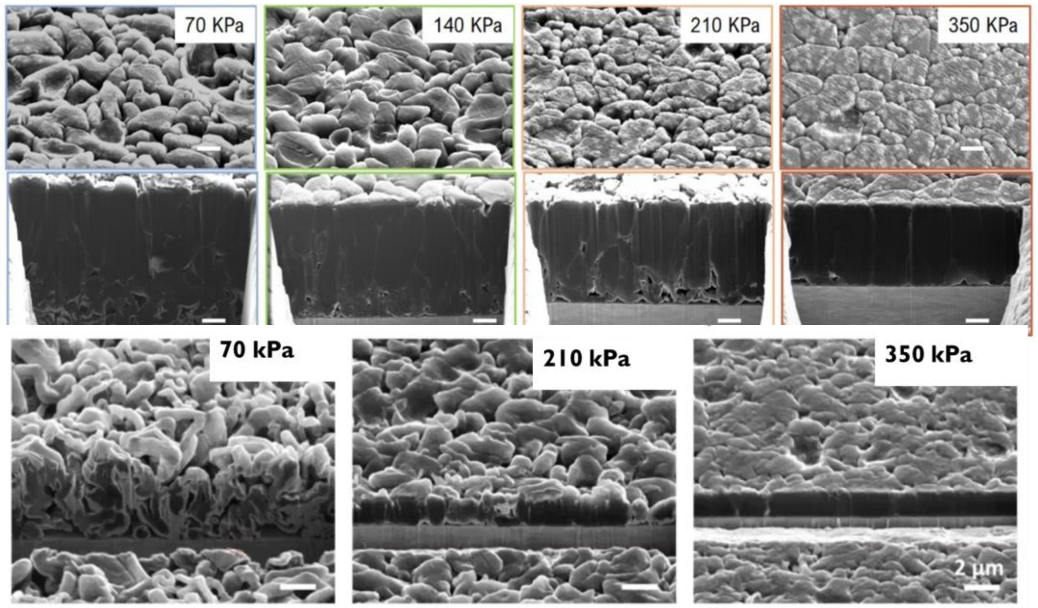
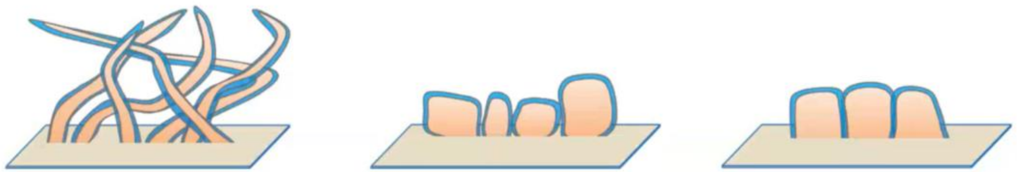
Technical Accomplishments and Progress

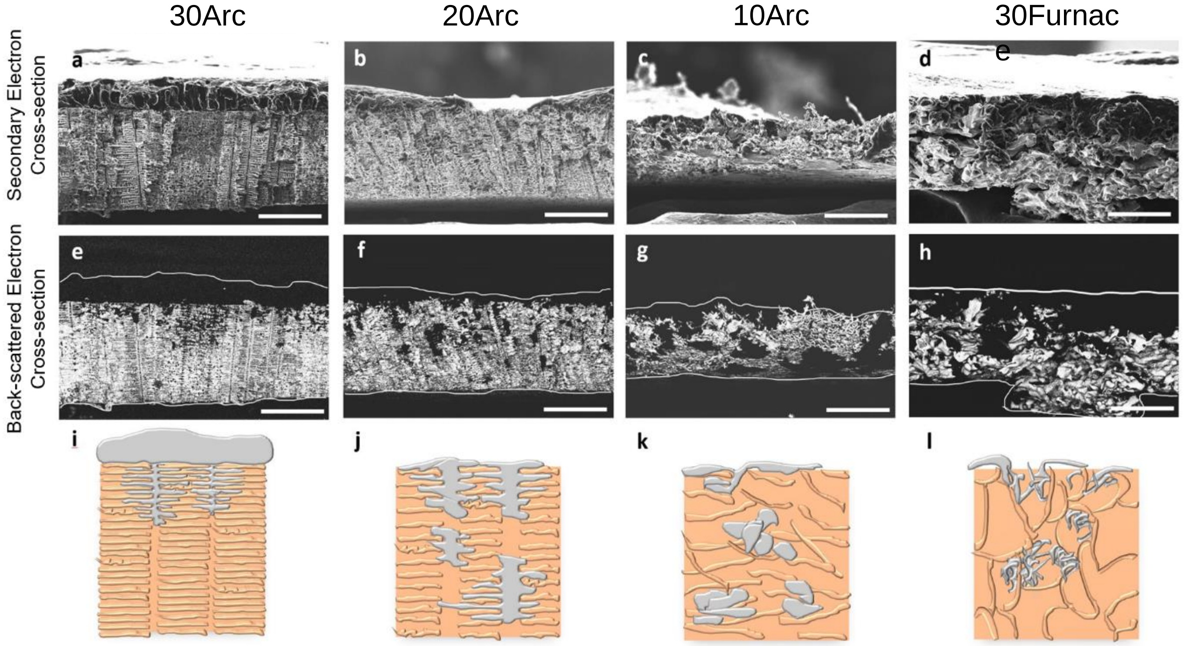
2. Pressure Tailored Li Metal Growth



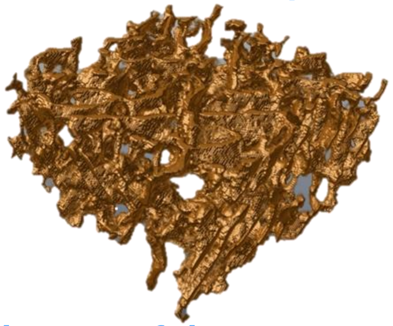


The stacking pressure plays a significant role in the nucleation of Li, which will determine the morphology of the deposited Li.

3. Quantitative Design of 3D Current Collector



Li Metal Deposition Behavior in the Porous Coppers



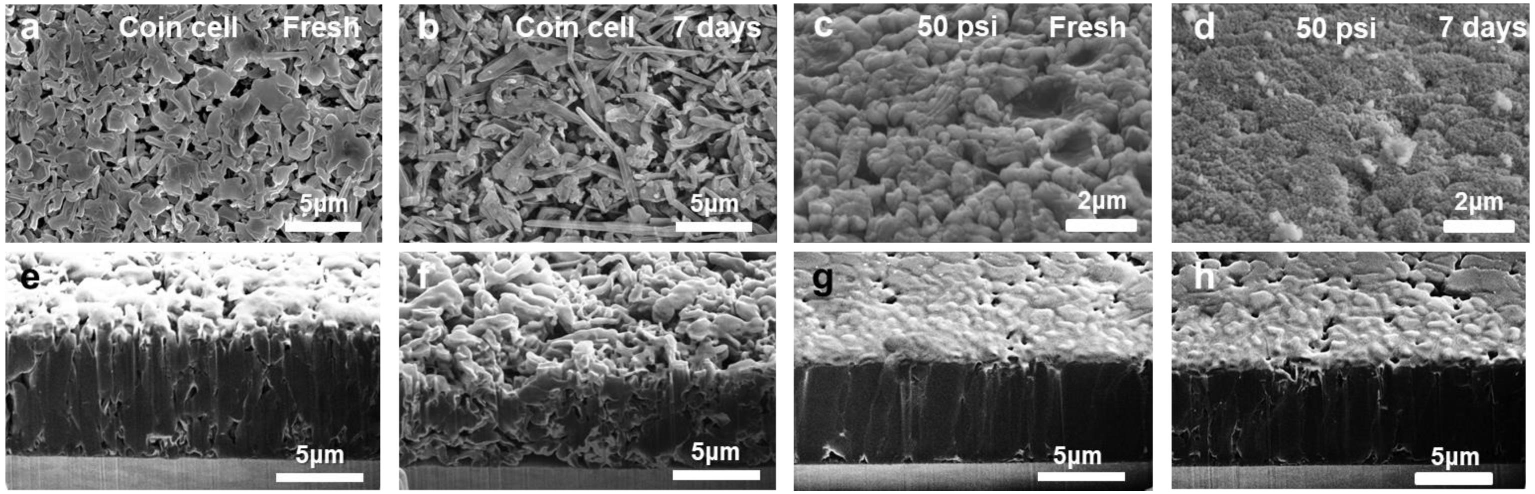
MicroCT of the Porous Copper

- The key physical parameters, pore size, surface area and tortuosity of the porous copper 3D current collector is quantified by MicroCT.
- The effect of the key physical parameters is quantitatively studied.

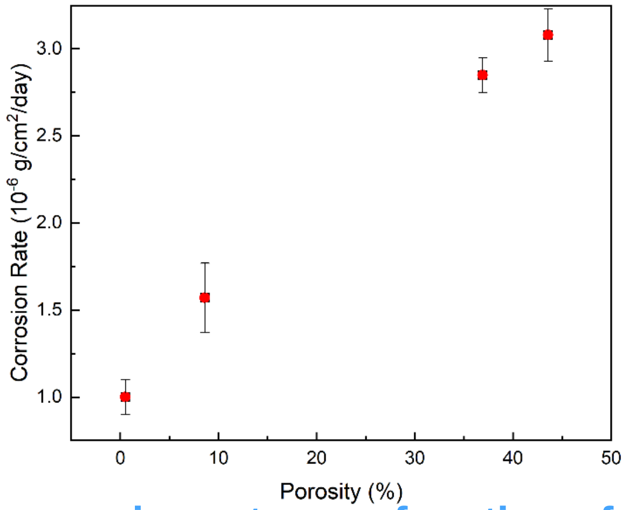
C. Fang, B. Lu, Y. S. Meng, et al under review
B. Lu, Y. S. Meng, et al under review
Porous copper work is in collaboration with Prof. Sarah Tolbert's group at UCLA

Technical Accomplishments and Progress

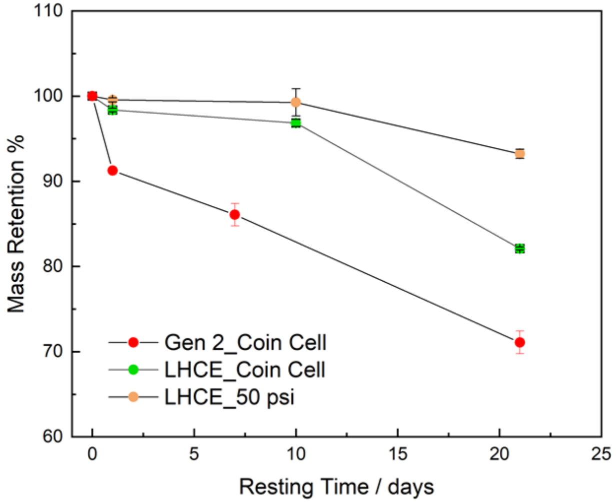
4. Suppressing the Corrosion of Li Metal



Li plated in Gen2 electrolyte under different pressures and its morphology before and after corrosion



Li corrosion rate as a function of porosity



Li corrosion trend in LHCE

- TGC method and Cryo-FIB are used to study the corrosion process of Li in liquid electrolytes.
- The porosity/surface area of the Li is identified as the key factor in controlling the corrosion in Li metal anode in liquid electrolytes.
- The corrosion of Li metal can be limited to **only 0.5% after 10 days of resting** under optimized conditions (LHCE and high pressure).

Gen2: 1M $LiPF_6$ in EC:EMC; LHCE: LiFSI:DME:TTE (1:1.2:3 molar ratio)

B. Lu, Y.S. Meng et al, to be submitted 2021

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Responses to Previous Year Reviewers' Comments

We thank the reviewers from last year for providing comments. The majority of the comments were highly positive. There was one question from the reviewer that needs to be addressed.

<u>Question 2: Technical Accomplishments and Progress toward overall project goals—the degree to which progress has been made and plan is on schedule.</u>

Reviewer 2: The reviewer was interested to know if the 3-D current collector approach can be scalable and, if so, what the fabrication methods are.

Response: The 3-D current collector was made by acid etching of Fe-Cu alloy. The Fe-Cu alloy was made by one step furnace melting of Fe and Cu powders. The overall process is very straightforward and easy to scale up.

Partners/Collaborators

- **Electrolyte provider and result discuss**

Dr. Jason Zhang, Dr. Wu Xu, Dr. Jie Xiao and Dr. Jun Liu (PNNL)

Dr. Kang Xu and Dr. Marshall Schroder (ARL)

Dr. Boryann Liaw (INL)

Dr. Mei Cai (GM)

- **Cryo TEM facility**

Dr. Xiaoing Pan (UC Irvine)

Dr. Jeff Wu (UC San Diego)

- Dr. Sarah Tolbert (UCLA)

Pacific Northwest NATIONAL LABORATORY

ARL

INL Idaho National Laboratory

UC San Diego BIOLOGICAL SCIENCES

Calit2 UNIVERSITY of CALIFORNIA · IRVINE

GM

UCLA

UC San Diego

Remaining Challenges and Barriers

- ❑ Evaluate the reactivity/safety of Li metal anode.
- ❑ Evaluate and develop S/polymer-based cathode materials.
- ❑ Automation of TEM data collection and analysis.
- ❑ *In situ* observe the plating and stripping process of Li metal by cryo-EM.

Proposed Future Research

Key Challenges

- Further stabilize Li metal anode in liquid electrolytes
- In situ observation by cryo-TEM
- Stabilize S-based cathodes.

Future work

- Comparing the reactivity/safety of Li in different conditions (electrolyte, additive, pressure)
- Develop new S-based cathode architectures.

Teamwork will continually be incorporated in the future work

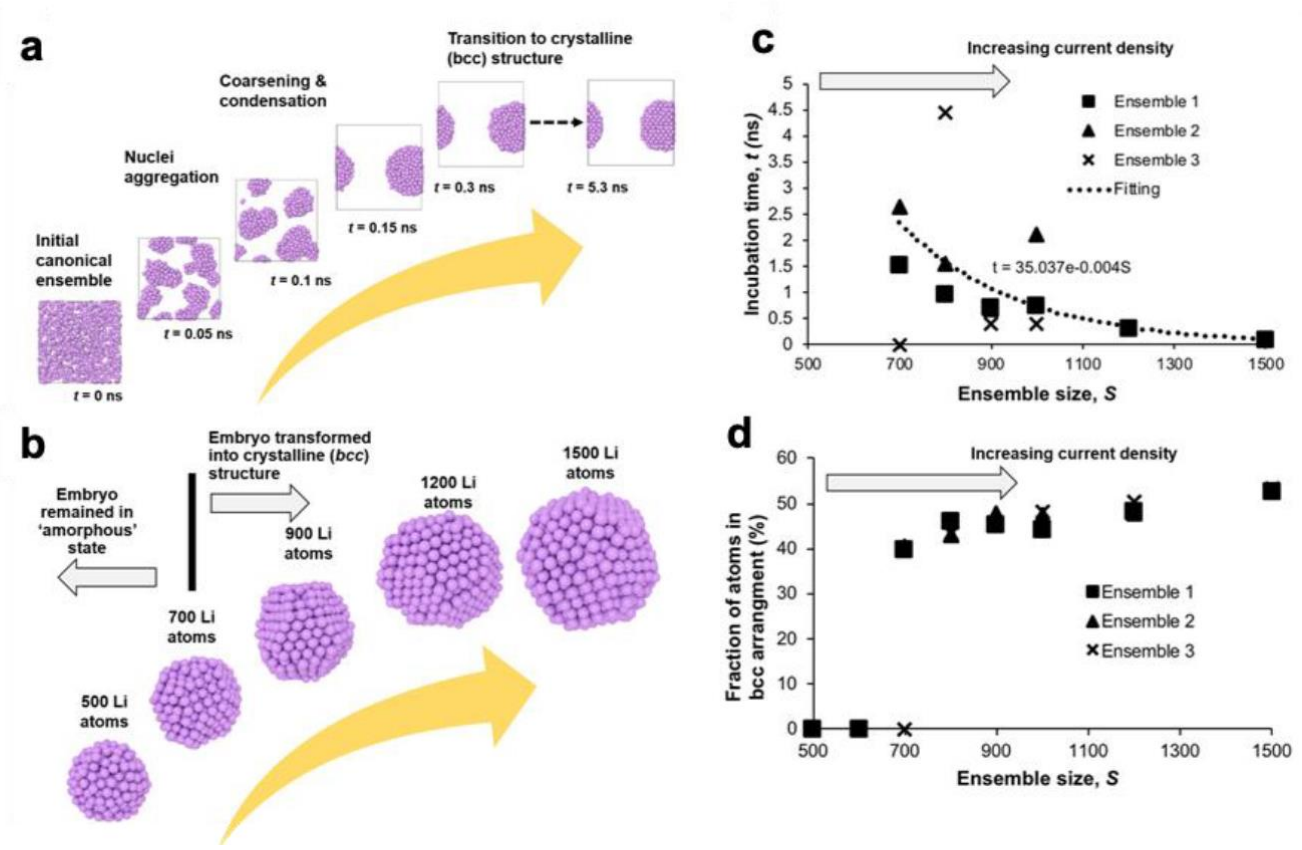
Any proposed future work is subject to change based on funding levels.

Summary

- Established cryogenic techniques to explore the nucleation process of Li metal
- Identified pressure effects on Li morphologies under different conditions and their improvement to Li anode.
- Developed Micro/Nano-CT methodology for 3D current collector quantification (porosity, tortuosity, surface area, etc.)
- Studied the key factors in controlling the corrosion of Li metal anodes.

Technical Back-up Slides

Technical Back-up Slides: MD simulation of Li metal nucleation process



(a) Li nucleation, growth and kinetic pathway to an embryo with an ensemble of 700 Li atoms.

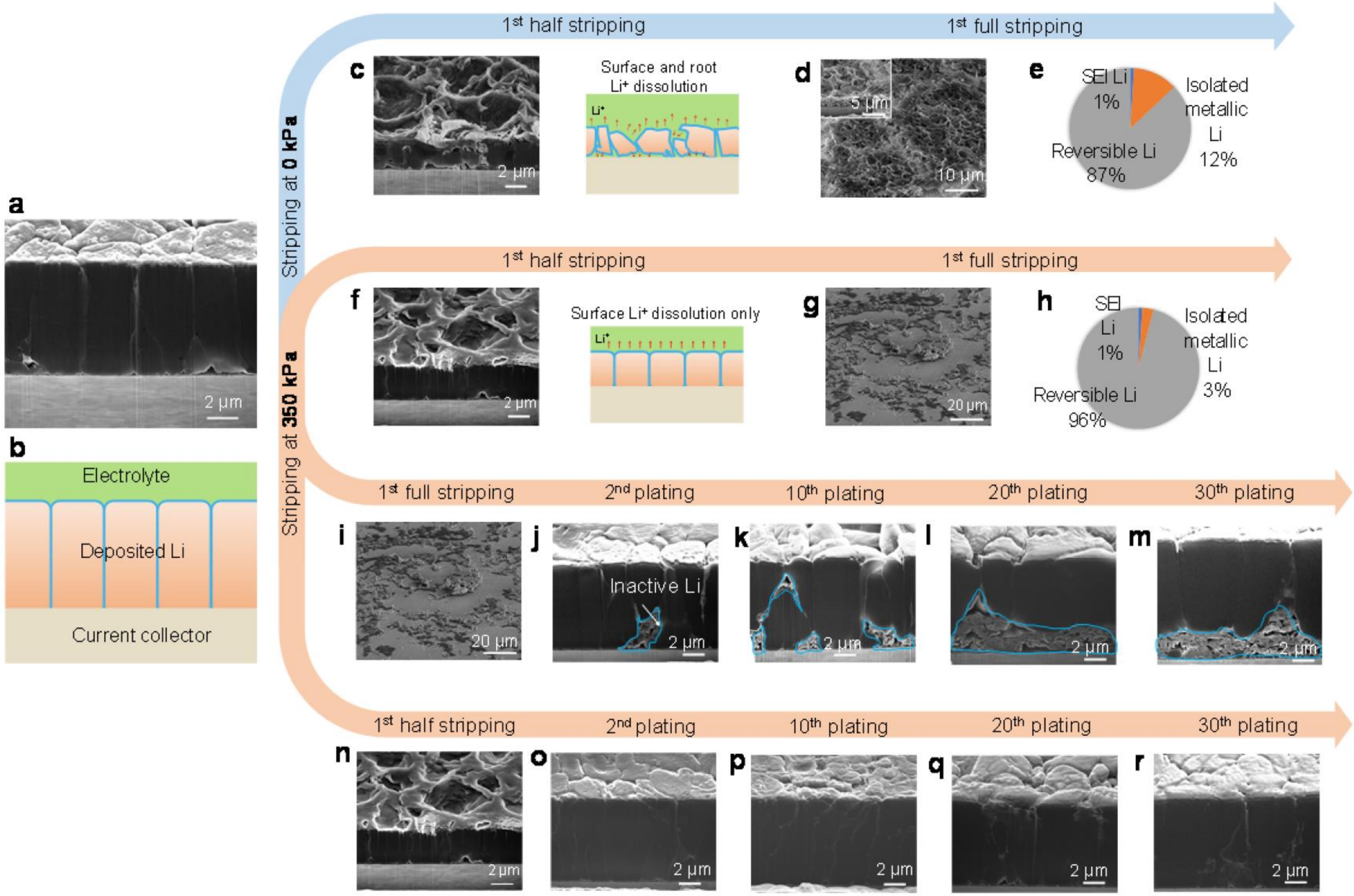
(b) The final state of various sizes of embryos at the end of the simulation (5.3 ns).

(c) Incubation time to second order phase transition as a function of ensemble size.

(d) A fraction of Li atoms in bcc lattice arrangement as a function of ensemble size.

X. Wang, G. Pawar, B.Y. Liaw and Y.S. Meng et al, Nature Materials, (2020) 19, 1339–1345

Technical Back-up Slides: Li reservoir effect study



Li reservoir effect study

- Plating and stripping under stack pressure of 350 kPa.
- Li deposition morphology evolution using full-stripping protocol (i-m) show the accumulation of inactive Li.
- Li deposition morphology evolution (n-r) using half-stripping protocol to retain Li reservoir for 30 cycles with no visible inactive Li accumulation.

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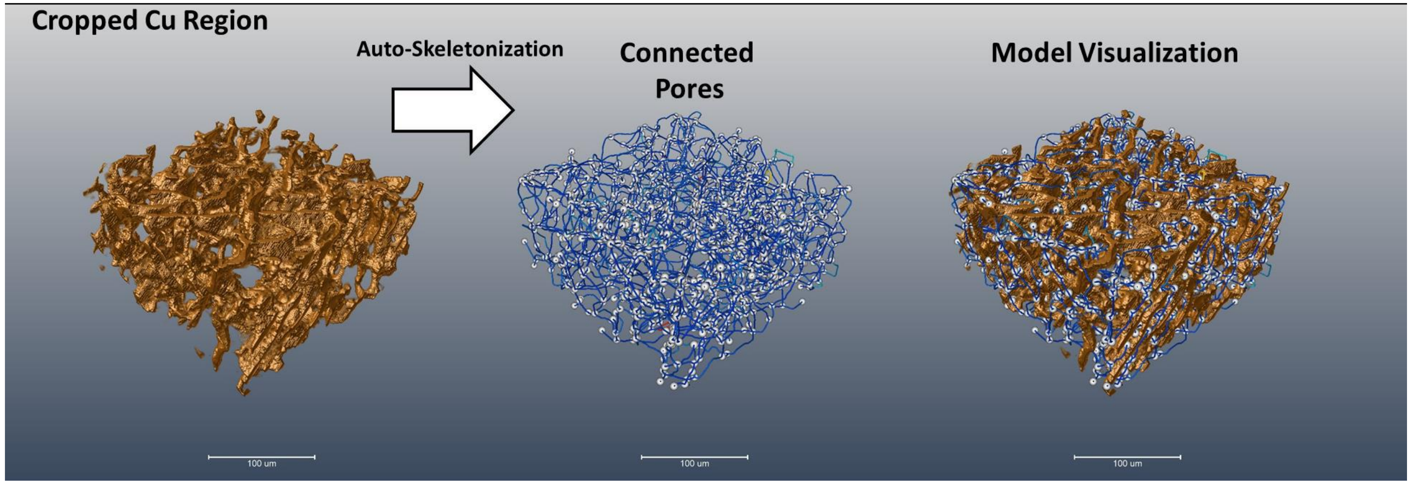
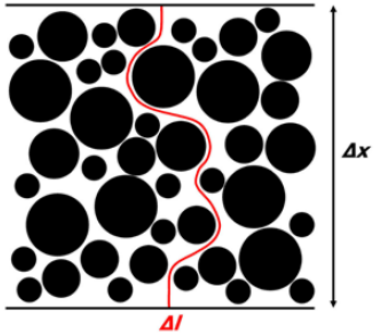
Technical Back-up Slides: Quantification of physical property of the porous copper

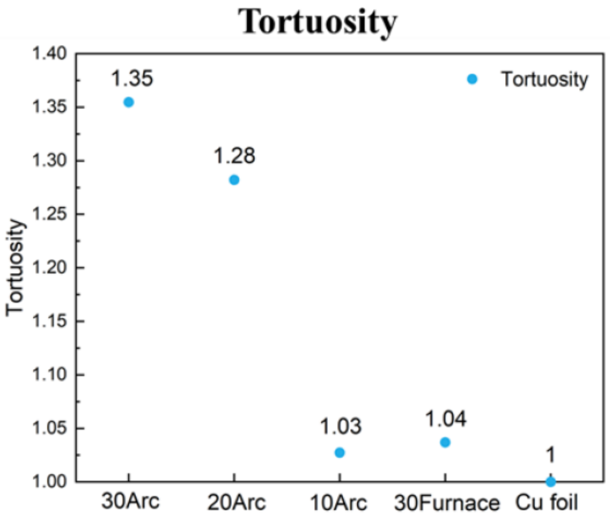
Micro CT for 3D Cu tortuosity/surface area quantification

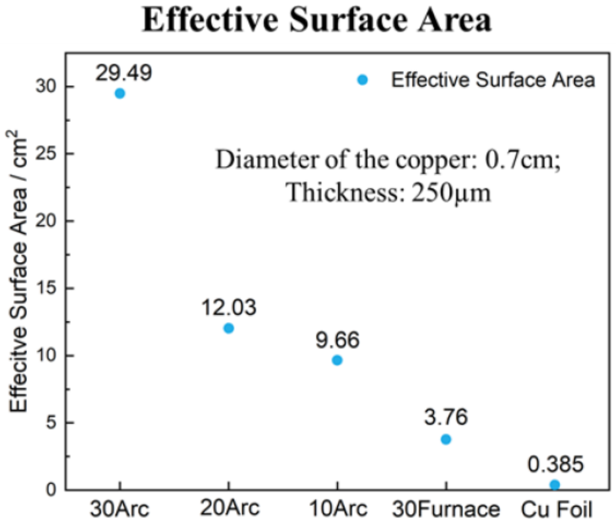




$$\tau = \frac{\Delta l}{\Delta x}$$

Tjaden et al., *International Materials Reviews,* (2018)





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