Lithium Dendrite Prevention for Lithium Batteries

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Overview

Timeline

- Start date: Oct. 2021
- End date: Sept. 2024
- Percent complete: 50%

Barriers

- Growth of lithium (Li) dendrites
- Low Coulombic efficiency (CE)
- Lack of mechanistic understanding
- Safety and thermal stability

Budget

- Project funding: $1,200k
  - DOE share 100%
- Funding received in FY22: $400k
- Funding received in FY23: $400k

Partners

- Argonne National Laboratory
- University of Arkansas
- University of Houston
- Organizations under US-Germany Energy Storage Collaboration Program

Relevance

- Enable Li metal to be an effective anode in rechargeable Li metal batteries with good thermal stability and safety.
- Develop three-dimensional (3D) porous substrates as current collectors for Li metal anode to improve utilization of Li metal anode and enhance cycle life of Li metal batteries.
- Develop a double-protection layer (DL) for Li metal anode to enhance cycle life of Li metal batteries.
- Obtain mechanistic insight on Li metal deposition/stripping behavior.

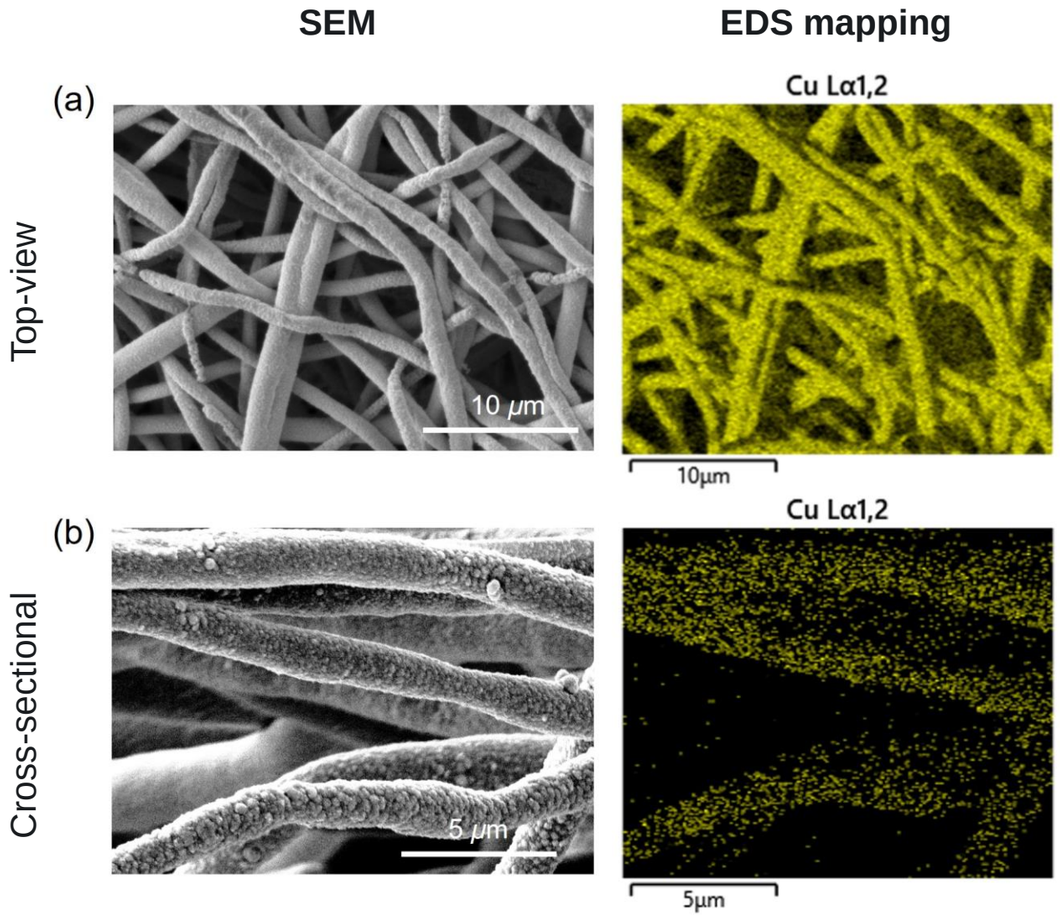
Milestones

Date	Milestones	Status
Sept. 2022	Evaluate effect of new separator and 3D-structured current collector on cycling performance of Li||$LiNi_xMn_yCo_{1-x-y}O_2$ (NMC) cells.	Completed
Dec. 2022	Optimize preparation conditions to make flexible 3D-structured current collectors with full coverage of thin Cu film.	Completed
March 2023	Evaluate Li deposition morphology and cell performance of 3D-strucutred current collectors in Li||NMC cells.	Completed
June 2023	Fabricate DL-protected Li metal anode and investigate its effect on deposited Li morphology.	On track
Sept. 2023	Evaluate cell performance of DL-protected Li in Li||NMC cells.	On track

Approaches

- Continue the development of current collectors with 3D structure for Li metal anode to suppress Li dendrite growth, increase Li utilization, and extend cycle life of Li metal batteries.
- Develop artificial protection layers on Li metal anode to improve the cycling stability of Li metal batteries (Li||NMC).
- Conduct mechanistic studies on Li deposition behavior to lay groundwork for future improvement of Li metal batteries.

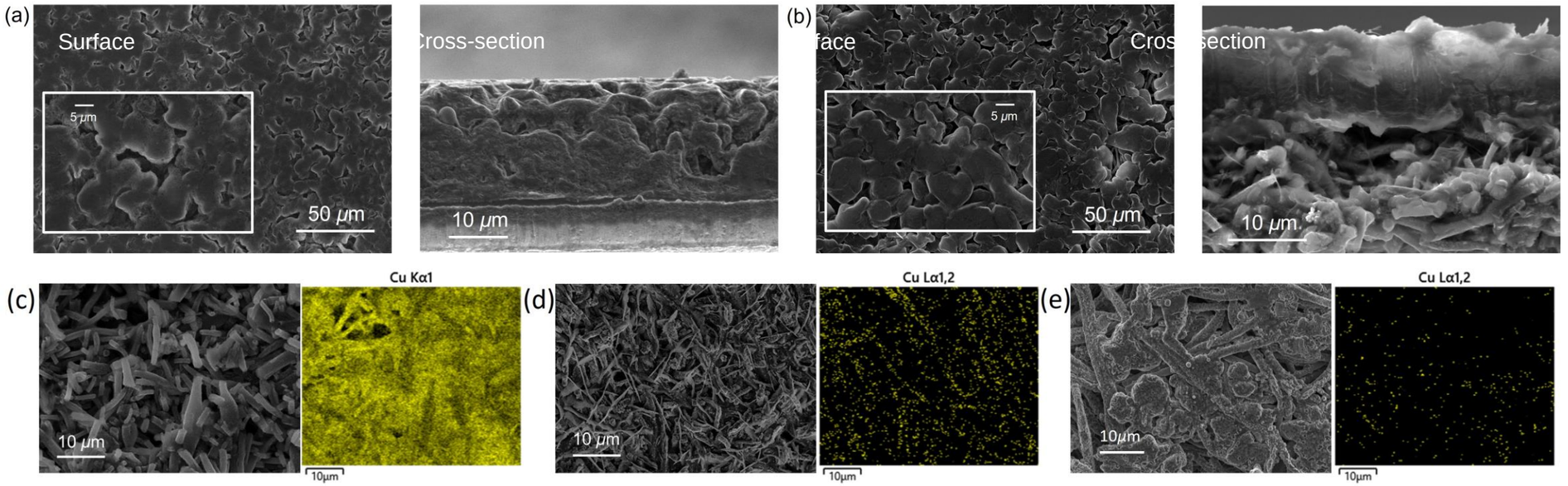
Technical Accomplishments and Progress
— Fabrication of 3D current collector



- Electronspun polyimide (PI) was selected as the precursor because of its high thermal stability.
- Copper (Cu) coated PI (Cu@PI) current collector was fabricated via electroless plating of porous PI membrane in an appropriate electroless plating solution containing Cu ions.
- Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) images demonstrate that Cu is uniformly coated on all PI fibers not only on the surface but also the inside of the PI membrane after the synthesis optimization.

❖ **Cu@PI is successfully fabricated as a 3D current collector.**

Technical Accomplishments and Progress
— Li deposition morphology on 3D current collector

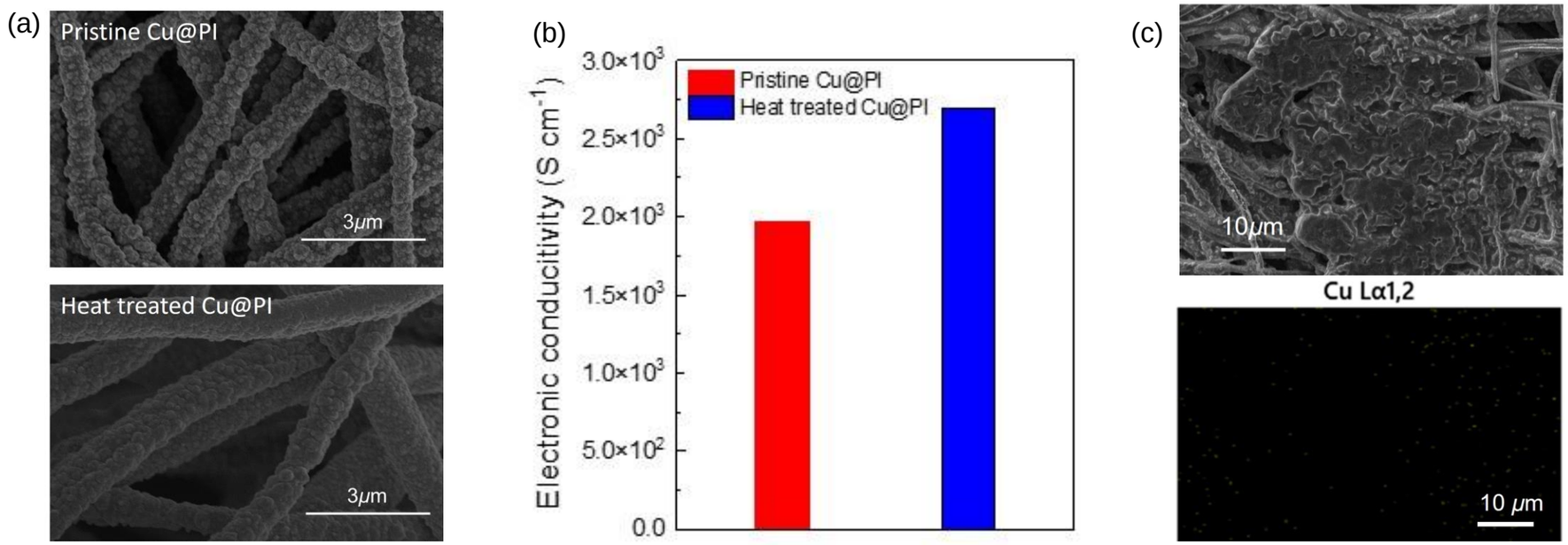


- (a,b) SEM images of deposited Li (4 mAh cm^{-2}) morphologies on (a) bare Cu foil and (b) Cu@PI mat at a current density of 0.4 mA cm^{-2}.
- (c-e) SEM and EDS mapping images for backside of Li (4 mAh cm^{-2}) deposited Cu@PI mat at a current density of (c) 0.4 mA cm^{-2}, (d) 0.2 mA cm^{-2}, and (e) 0.13 mA cm^{-2}.

- On top surface, Li deposits on bare Cu and Cu@PI show very similar morphologies and particle size.
- Despite of uniform coating of Cu on PI fibers, Li didn't deposit through all thickness direction at a high current density of 0.4 mA cm^{-2}. When Li deposition current density was reduced to 0.13 mA cm^{-2}, the back of Cu@PI substrate was almost fully covered by Li and Cu is only barely detected by EDS mapping indicating Li was deposited through the thickness direction.

❖ **The electronic conductivity of Cu@PI mat needs to be further improved to enhance Li deposition.**

Technical Accomplishments and Progress
— Optimization of 3D current collector



- (a) SEM images and (b) electronic conductivities of pristine Cu@PI and heat treated Cu@PI. (c) SEM and EDS mapping images for backside of Li deposited for 4 mAh cm^{-2} on heat treated Cu@PI at a current density of 0.4 mA cm^{-2}

➢ After heat treatment, Cu@PI presents smoother surface morphology and increased electronic conductivity (2.69×10^3 S cm^{-1}) compared to pristine Cu@PI (1.97×10^3 S cm^{-1}).

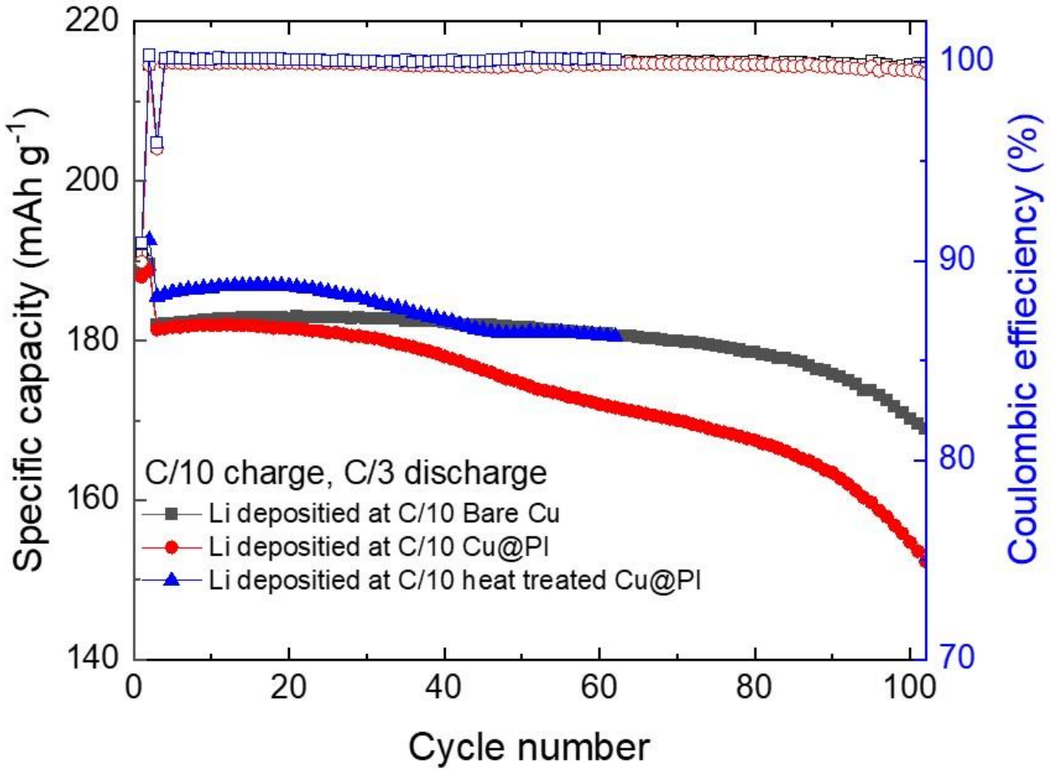
➢ Heat treated Cu@PI shows improved Li deposition up to the back side of Cu@PI, even better than Li deposited on the back of pristine Cu@PI at a lower current density.

❖ **Heat treatment enhanced electronic conductivity of Cu@PI and enabled more uniform deposition of Li on 3D current collector.**

Technical Accomplishments and Progress
— Electrochemical performance of Li||NMC622 cells with 3D current collector

Li||NMC622 cells:

- Anode: 5 mAh cm^{-2} of Li deposited on bare Cu or Cu@PI at 0.1C
- Electrolyte: LiFSI-1.2DME-3TTE by mol., 75 µL
- Charge/discharge voltage range: 2.8-4.4 V (vs Li/Li^+)
- 2 formation cycles at C/10
- 1C = 4.5 mA cm^{-2}



- Heat treated Cu@PI leads to higher capacity at initial cycles compared to pristine Cu@PI and Bare Cu. The test is still under evaluation.
- The increased electronic conductivity and improved Li deposited morphology of Cu@PI lead to better cycle performance.

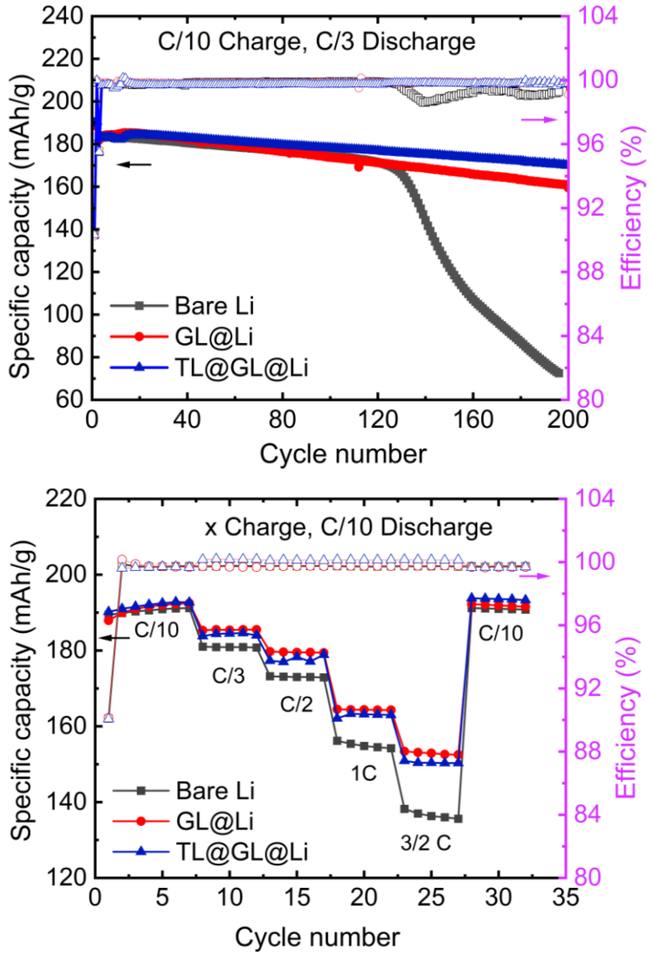
❖ **The physicochemical property of Cu@PI affects the cycling performance of Li||NMC622 cells.**

❖ Further optimization is currently under way.

Technical Accomplishments and Progress
— Effect of single and double layer artificial SEIs on Li metal battery

Li||NMC622 cells:
- 50 µm thick Li
- 75 µL electrolyte of LiFSI-1.2DME-3TTE by mol.

- Voltage range: 2.8-4.4 V (vs Li/Li^+)
- 2 formation cycles at C/10
- 1C = 4.2 mA cm^{-2}



- In collaboration with Prof. Xiangbo Meng at University of Arkansas.
- Single or double artificial protection layers have been investigated to prevent side reactions between Li metal anode and the electrolytes.
- A single layer of Li glycerol (GL) coated Li metal (GL@Li) was realized by using molecular layer deposition (MLD) on a 50 µm of Li metal surface, and a top layer coated Li metal (TL@GL@Li) was prepared by coating a crosslinked polymer layer on the GL@Li.
- During long-term cycling, TL@GL@Li delivers a higher capacity retention of 92.9% after 200 cycles compared to GL@Li (87.7%) and bare Li (36.2%).
- Both GL@Li and TL@GL@Li show improved charge rate capability compared with bare Li.

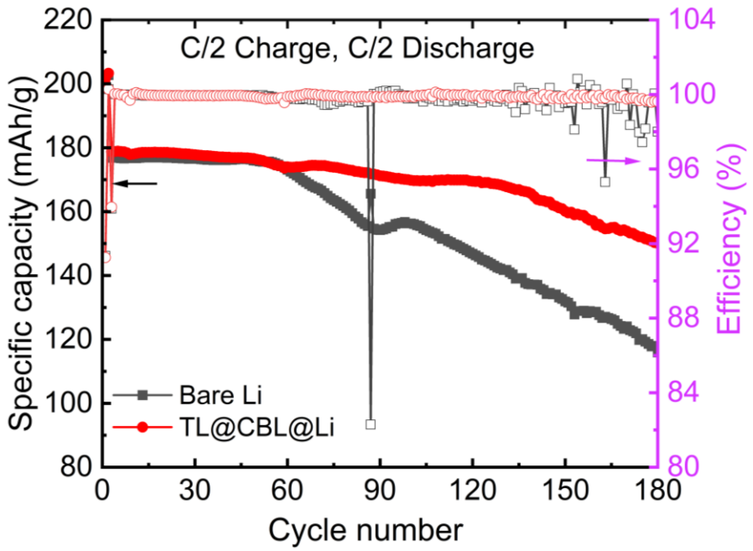
- **The improved high rate electrochemical performance of GL@Li and TL@GL@Li could be attributed to GL layer and the crosslinked polymer-based TL forming a robust and stable artificial SEI on Li metal anode.**

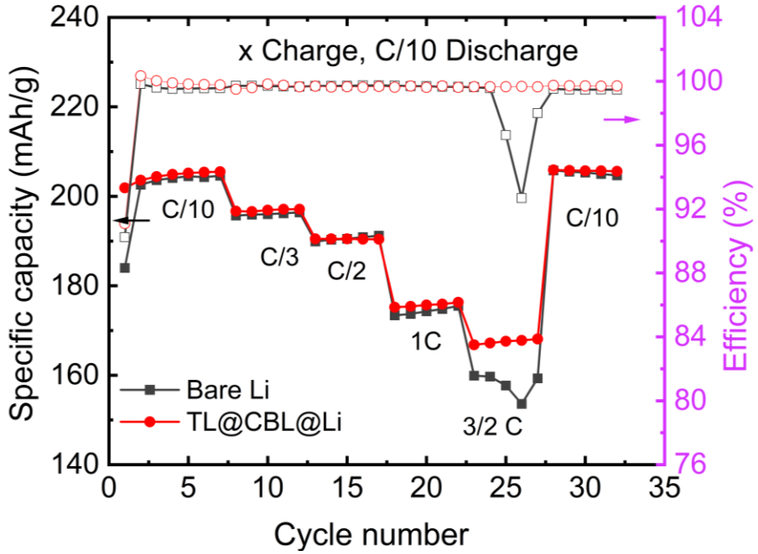
Technical Accomplishments and Progress

— Effect of composite double layer artificial SEI on Li metal battery

Li||NMC622 cells:
- 50 µm thick Li
- 75 µL electrolyte of LiFSI-1.2DME-3TTE by mol.

- Voltage range: 2.8-4.4 V (vs Li/Li^+)
- 2 formation cycles at C/10
- 1C = 4.8 mA cm^{-2}

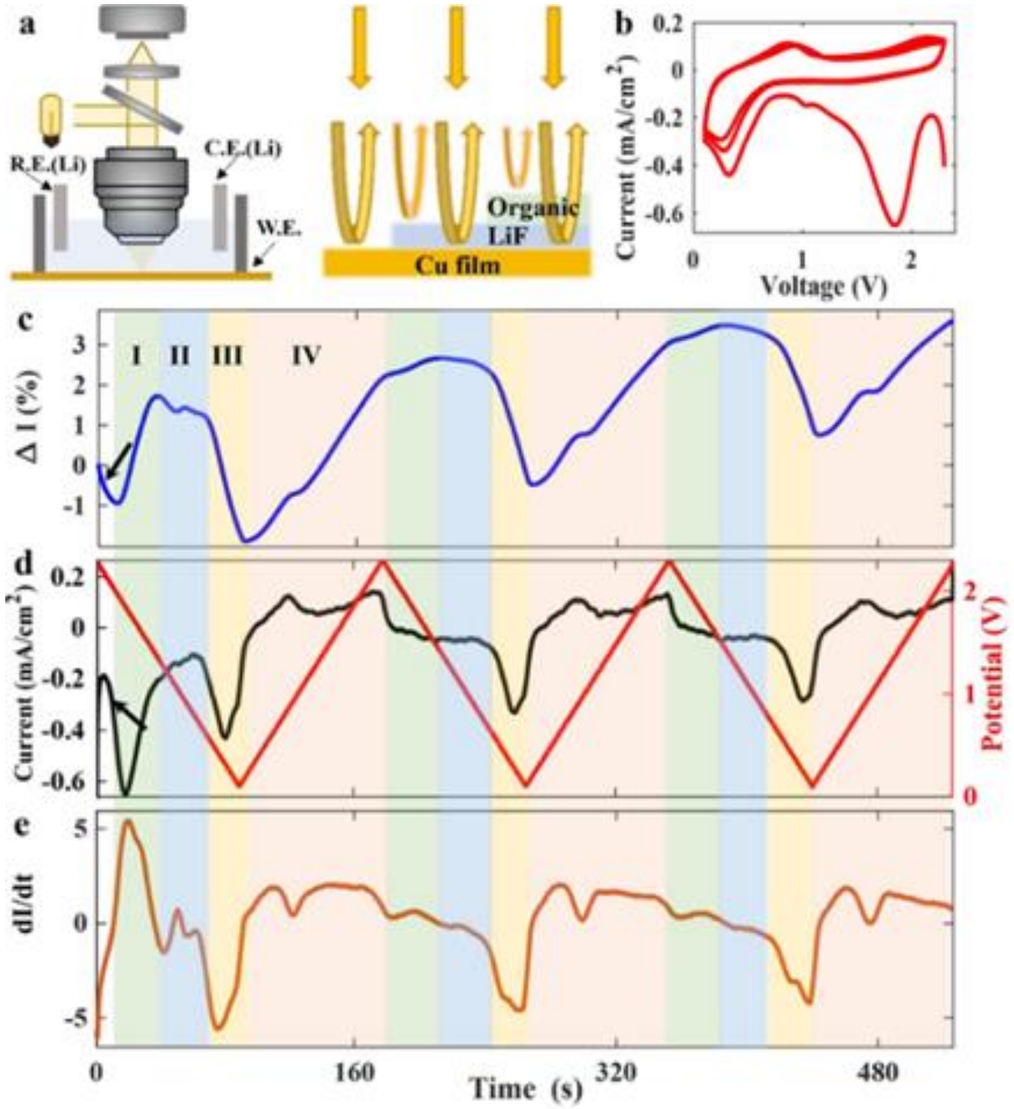




- As another bottom layer candidate, the composite bottom layer (CBL) was applied to get an improved cycle performance of Li||NMC811.
- TL@CBL@Li exhibits higher capacity retention of 84.0% after 180 cycles compared to bare Li (65.6%) at a high current density of C/2.
- TL@CBL@Li delivers higher performance compared with Bare Li at 3/2 C in the C-rate charging capability test.

❖ **The improved high rate electrochemical performance of TL@CBL@Li is associated the double layer coating having a combination of good mechanical and electrochemical properties.**

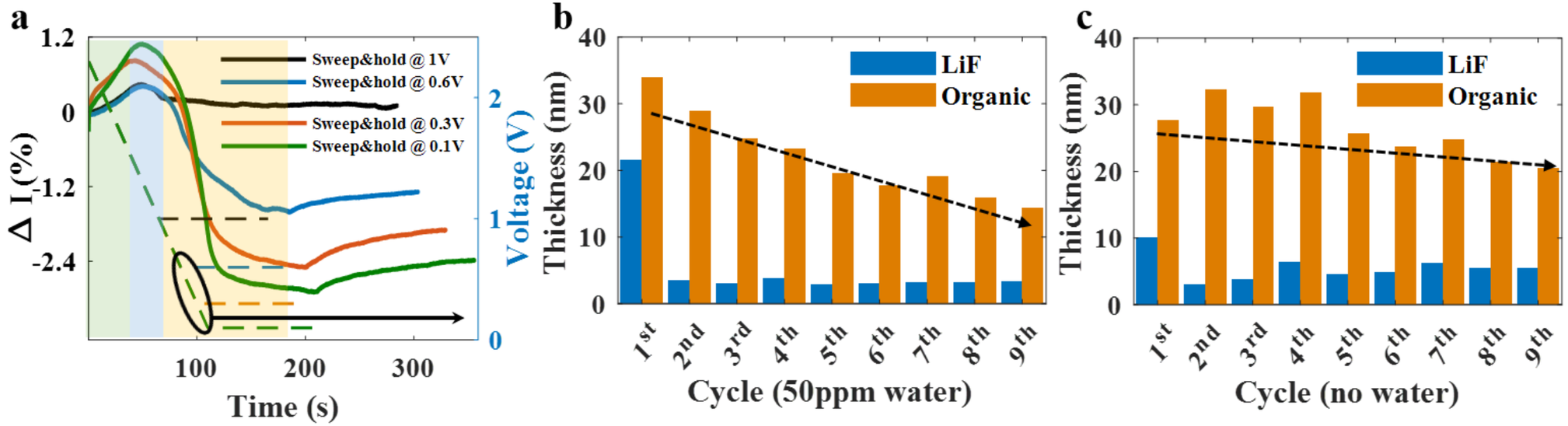
Technical Accomplishments and Progress
— In-situ characterization of SEI formation dynamics using reflection interference microscope (RIM)



- In collaboration with Prof. Xiaonan Shan and Dr. Guangxia Feng at University of Houston.
- **a**, Schematic diagram of using RIM to image the SEI formation dynamics.
- **b**, CV curves of the first three cycles in 1 M $LiPF_6$/PC with 50 ppm H_2O as additive.
- **c**, Optical reflection signal (RIM signal) during the first three CV cycles on Cu electrode in 1 M $LiPF_6$/PC with 50 ppm H_2O additive. I, II, III, and IV are four sections that correspond to LiF-rich layer formation (Section I), EDL formation (Section II), organic-rich SEI deposition (Section III), and re-oxidization (Section IV).
- **d,** Corresponding current density (black curve and left axis) and voltage (red curve and right axis) in the first three cycles of CV scans.
- **e,** Derivative of optical signals (the curve in **c)**.

➢ **RIM exhibits extremely high sensitivity towards SEI formation process.**

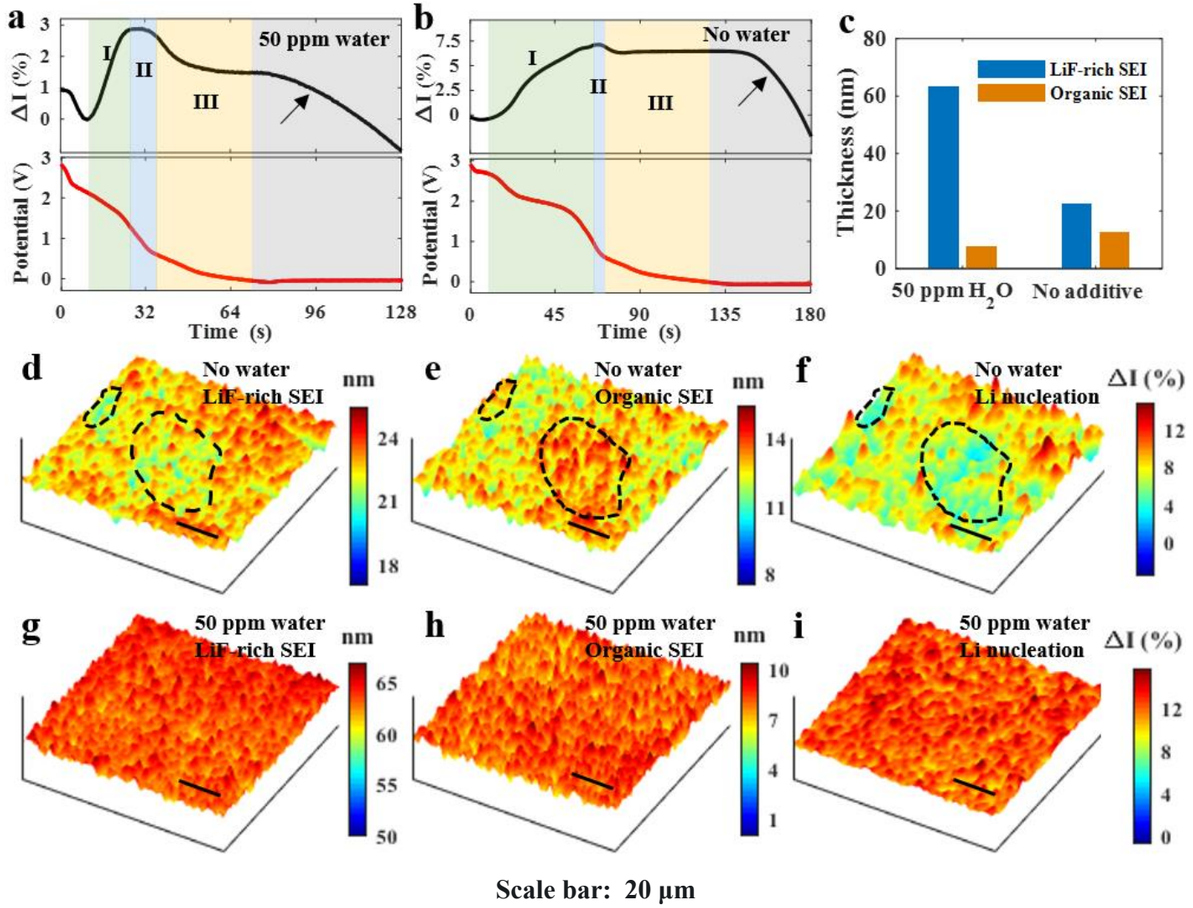
Technical Accomplishments and Progress
— Investigation on SEI growth using RIM



- **a**, Scan-hold-release experiments at different conditions. The solid lines are RIM signals, whereas the dashed lines represent the corresponding potential (to the right axis). **b**, The thickness accumulation of the LiF-rich layer (blue bar) and the organic-rich layer (orange bar) in each CV cycle in 1 M $LiPF_6$/PC with 50 ppm H_2O additive. **c**, The thickness accumulation of the LiF-rich layer (blue bar) and the organic-rich layer (Orange bar) in each CV cycle in 1 M $LiPF_6$/PC without H_2O additive.

- The thicknesses of LiF-rich inner layer and organic-rich outer layer can be correlated to the intensities of the RIM signals.
- The presence of trace amount of water (50 ppm) in electrolyte induces a thicker and higher quality LiF-rich layer at the inner SEI and a much thinner organic-rich layer in the outer SEI.

Technical Accomplishments and Progress
— Investigation of SEI on Li nucleation using RIM



- **a-b**, Constant current measurement in 1 M $LiPF_6$/PC with 50 ppm H_2O (**a**), and without water additive (**b**), at 0.1 mA cm^{-2}. Top: optical reflection responses; Bottom: corresponding potentials.
- **c**, Thicknesses of LiF-rich and organic-rich layers are extracted from the experiments in **a** and **b**.
- **d-f**, Morphology maps of LiF-rich SEI layer (**d**) and organic-rich SEI layer (**e**) in electrolyte without water, and (**f**) the optical response of Li nucleation in electrolyte without water.
- **g-i**, Morphology maps of LiF-rich SEI layer (**g**) and organic-rich SEI layer (**h**) in electrolyte with 50 ppm water, and (**i**) the optical response of Li nucleation in electrolyte with 50 ppm water.
- Note that ΔI in **f** and **i** are the intensity change caused by Li nucleation and bigger ΔI means more Li nucleation.

➢ **The presence of trace amount of water (50 ppm) in electrolyte induces a thicker and higher quality LiF-rich layer at the inner SEI and a much thinner organic-rich layer in the outer SEI, which leads to less electrolyte consumption, and more uniform Li nucleation on electrode surface.**

Responses to Previous Year Reviewers' Comments

- This project was not reviewed last year.

Collaboration and Coordination with Other Institutions

- Argonne National Laboratory
  - Dr. Yuepeng Zhang, Ashley Simmons, and Dr. Jungkuk Lee for providing electrospun PI membranes.
- University of Arkansas
  - Dr. Xiangbo Meng and Xin Wang for performing GL@Li coating with MLD.
- University of Houston
  - Dr. Xiaonan Shan and Dr. Guangxia Feng for conducting operando reflection interference microscopy measurements.
- US-Germany Energy Storage Collaboration Program
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  - Massachusetts Institute of Technology: Prof. Yang Shao-Horn
  - Helmholtz Institute Münster: Prof. Martin Winter, Dr. Isidora Cekic-Laskovic
  - Helmholtz Institute Ulm / Karlsruhe Institute of Technology: Prof. Stefano Passerini, Prof. Dominic Bresser
  - Helmholtz Institute Ulm / German Aerospace Center: Prof. Arnulf Latz, Dr. Birger Horstmann
  - Karlsruhe Institute of Technology: Prof. Ulrike Krewer

Remaining Challenges and Barriers

- Cu@PI 3D-structured current collector still cannot operate at high current density.
- Li deposition/stripping behavior on Cu@PI is still not very unclear.
- Factors controlling SEI formation, Li nucleation and growth, and battery performance are not completely understood.
- Safety concern of Li metal batteries is still not solved.

Proposed Future Work

- Develop the optimized 3D-structured current collectors for Li metal anode.
- Understanding the Li deposition/stripping behavior on Cu@PI 3D-structured current collectors including side reaction.
- Investigate effects of the double layers on SEI formation and Li nucleation rate and growth rate at different conditions.
- Post-mortem analyses for Li metal batteries.

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

Summary

- Developed 3D-structured current collectors for Li metal anode
  - Electronspun PI was selected as the precursor and Cu nano particles are uniformly coated on the PI fibers via the electroless plating.
  - After heat treatment, Cu@PI shows a smother surface morphology and an increased electronic conductivity.
  - Li deposited on heat treated Cu@PI exhibits a smoother morphology and lead to higher capacity in Li||NMC622 battery.
- Investigated effects of artificial SEI layers on performances of Li metal batteries
  - Li glycerol-contained double layer coated Li (TL@GL@Li) showed improved capacity retention of 92.9% after 200 cycles at C/10 charging and C/3 discharging compared to bare Li (36.2%) in 4.2 mAh cm^{-2} Li||NMC622 cells.
  - TL@CBL@Li brought higher capacity retention of 84.0% after 180 cycles compared to bare Li (65.6%) at high cycling current rate of C/2 with the improved C-rate charging capability in 4.8 mAh cm^{-2} Li||NMC811 cells.
- Investigated SEI formation using operando RIM
  - The correlation between the quality of the LiF-rich inner layer in the SEI and the thickness of the organic-rich outer layer has been clearly observed.
  - The quality of the SEI also affects Li nucleation on the electrode surface.

Acknowledgements

- Financial support from the DOE VTO BMR Program is greatly appreciated.
- DOE / BER / EMSL for microscopic and spectroscopic characterizations and computational calculations.
- Team Members:

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