Stabilizing Lithium-Metal Anode by Interfacial Layer

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Project ID #bat365

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start: Sept. 1, 2016
- End: Sept. 1, 2021
- Percent complete: 32%

Budget

- Total project funding
  $50m
- Funding received in FY 2017
  $10m
- Funding for FY 2018
  $10m

Barriers

- Barriers addressed

- Cost (A)
  Addressing the cost barrier requires developing lower-cost processing methods.
- Performance (C)
  Much higher energy densities are needed to meet both volume and weight targets.
- Life (E)
  Battery must provide significant energy over the life of the vehicle .

Partners

- Collaboration

- Battery500 program PIs
- Prof. Bruce Dunn (UCLA)
- Prof. Steven Chu (Stanford)

Project Objective and Relevance

Objectives

- Develop lithium metal anodes with high capacity and reliability for next-generation rechargeable batteries to power electric vehicles. (Battery500 goals)
- Design and fabricate novel interfacial layers between lithium metal and electrolytes to overcome the intrinsic material challenges that lead to short battery life, including lithium metal dendrite formation and severe side chemical reactions during electrochemical cycling.
- Understand the effects of interfacial protection materials on the performance and life time of lithium metal batteries.
- Develop scalable low-cost methods for the synthesis of interfacial protection materials.

-**Project contents are directly aimed at the listed barriers: high cost, low energy density and short battery life.**

Milestones for FY18

Month/ year	Milestones	Status
3/2018	Demonstrate successful sealing of pinholes in h-BN thin film, reduce defect density in Li metal protective coatings	Complete
6/2018	Generalizing the effects of polymer coatings on Li metal deposition (polymer mechanics)	Complete
9/2018	Generalizing the electrochemical effects of polymer coatings on Li metal deposition (polymer chemistry)	On track
12/2018	Explore multilayer, multifunction coatings on Li metal	On track

Approach/Strategy

Advanced design and synthesis of interfacial protecting layers

1)Engineer various interfacial protection materials with excellent chemical and mechanical stability, both inorganic and polymeric, to suppress lithium dendrite formation during electrochemical cycling and to improve Coulombic efficiency.

2)Develop/discover stable, light-weight host materials with high lithium affinity for the fabrication of nanoporous lithium-host composite electrodes with minimum relative volume change during cycling and improved electrochemical performance.

Structure and property characterization

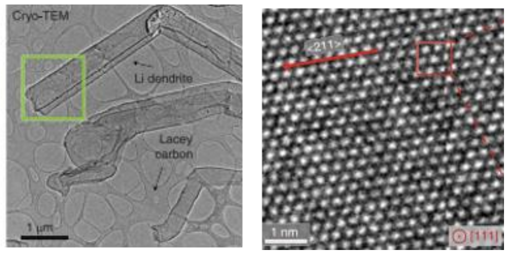
1) Ex-situ transmission electron microscopy & scanning electron microscopy
2) In-situ transmission electron microscopy
3) Cryo electron microscopy
4) In-situ optical microscopy
5) X-ray diffraction
6) X-ray photoelectron spectroscopy
7) Fourier transform infrared spectroscopy

Electrochemical testing

1) Coin cells and pouch cells
2) A set of electrochemical techniques (ultramicroelectrode, etc.)

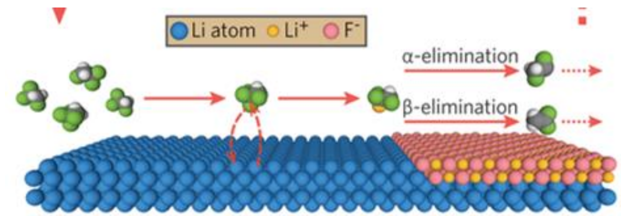
Selected Accomplishments on Lithium Metal Anode Through Battery500 (FY17)

Cryo-TEM of Li metal



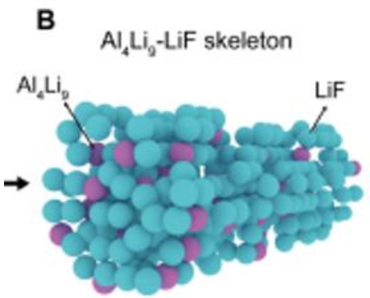
Science, **358**, 506 (2017)

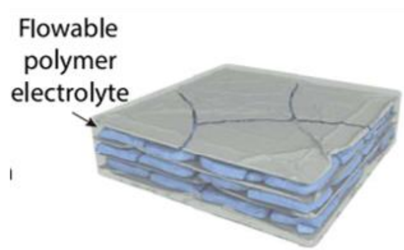
Interfacial Engineering



J. Am. Chem. Soc., **139**, 11550 (2017)
Nano Lett. **17**, 3731 (2017)
Nano Lett. **17**, 5171 (2017)
ACS Nano **11**, 7019 (2017)

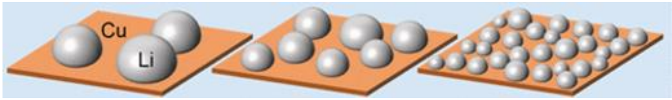
Lithium hosts





Proc. Natl. Acad. Sci., **114**, 4613 (2017)
Sci. Adv. **3,** e1701301 (2017)
Sci. Adv. **3**, eaao0713 (2017)

Li electrochemistry

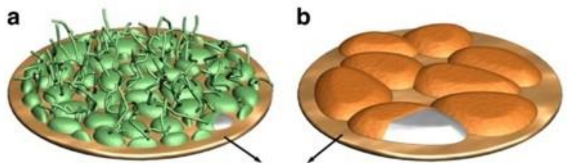


Nat. Energy **1**, 16010 (2016)
Proc. Natl. Acad. Sci., **114,** 12138 (2017)
Nano Lett. **17**, 1132 (2017)

BATTERY 500 CONSORTIUM

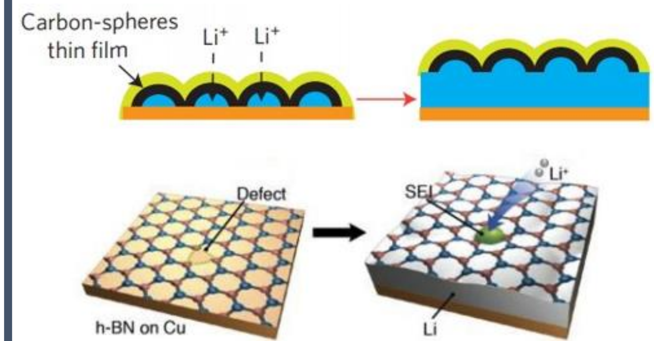
Approaches/Strategies for Lithium Metal Anodes

Electrolyte Tuning



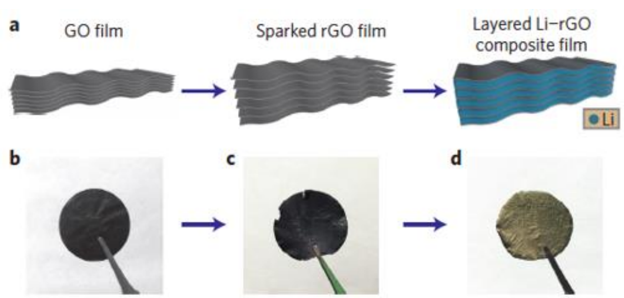
Nature Commun. **6**, 7436 (2015)
Proc. Natl. Acad. Sci., **114,** 12138 (2017)

Artificial SEI Engineering



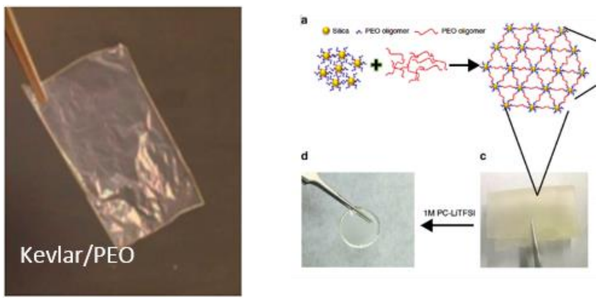
Nat. Nanotechnol. **9**, 618 (2014)
Nano Lett. **14**, 6016 (2014)
Nat. Energy **1**, 16010 (2016)

Li Hosts & Scaffolding



Nat. Commun. **7**, 10992 (2016)
Nat. Nanotechnol. **11**, 626 (2016)
Sci. Adv. **3,** e1701301 (2017)

Tough Polymer/Gel Electrolyte



Kotov, N. A., *et al. Nature Commun.* **2015**, *6*, 6152
Archer, L. A., *et al. Nat. Commun.* **2015**, *6*
Lin, D., *et al. Adv. Mat.* **2016.**

BATTERY 500 CONSORTIUM

Tough vs. Soft Polymers for Li metal

Tough, high modulus polymers suffer from poor contact with Li metal during deposition and stripping.

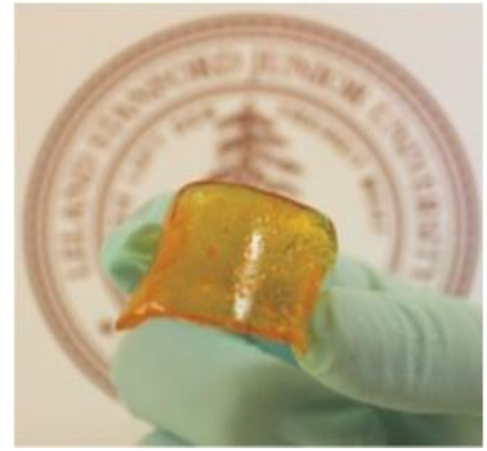
Soft, flowable viscoelastic polymers can accommodate volume change and preserve the polymer-Li interface.

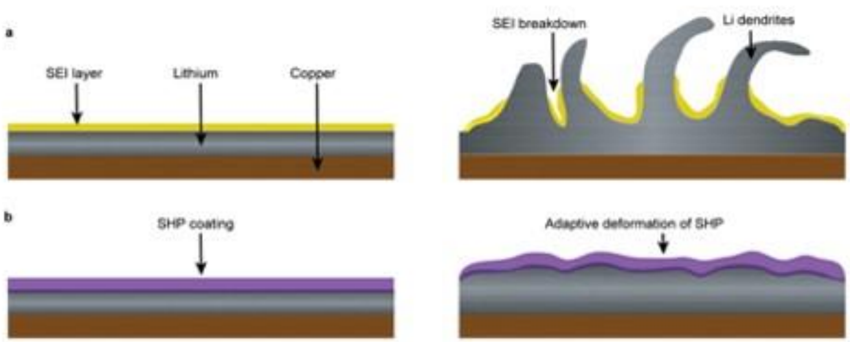
Accomplishment

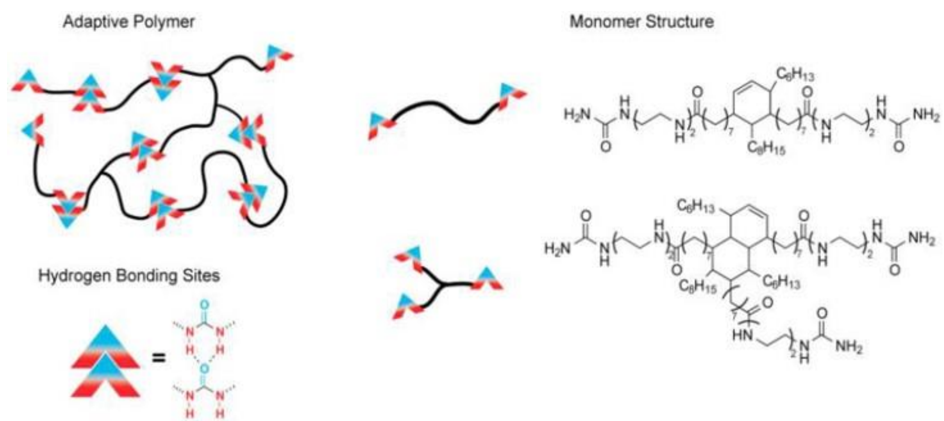
Soft, dynamic polymer coating for Lithium – Self-healing polymer

Self-healing polymer (SHP)

- Viscoelastic supramolecular polymer
- Low glass transition temperature
- Promotes uniform Li deposition





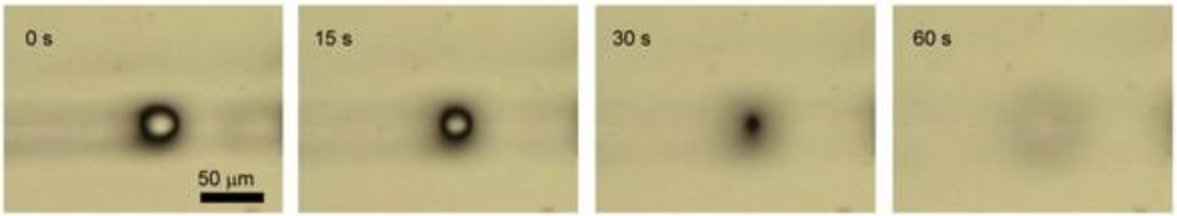


ACS Energy Lett. 1247–1255 (2016)

Accomplishment

Soft, dynamic polymer coating for Lithium – Self-healing polymer

Rapid healing of pinhole in polymer film
(Ensures uniform coating of Li)



Conformal coating of high aspect ratio structure
(Dendrite or filamentary Li analogue)

Air stable coating of Li metal

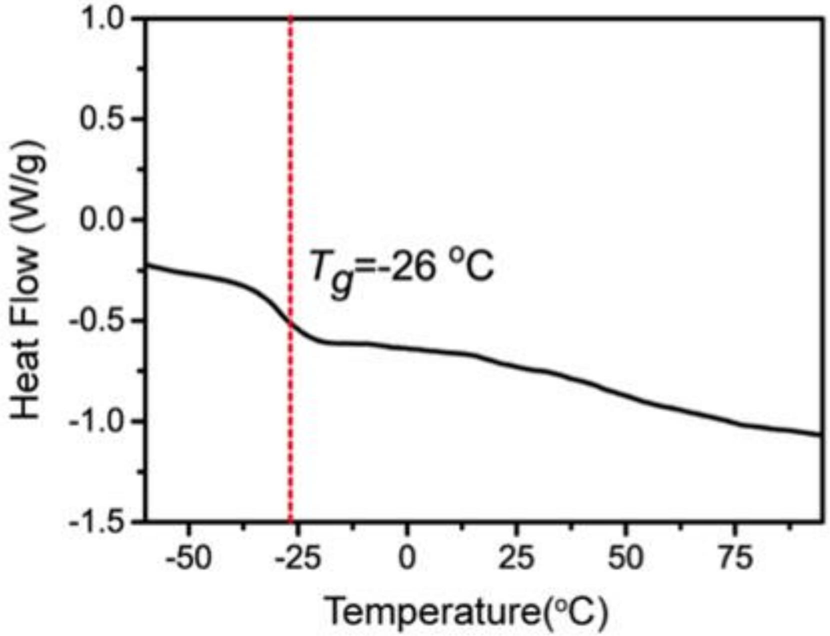
ACS Energy Lett. 1247–1255 (2016)

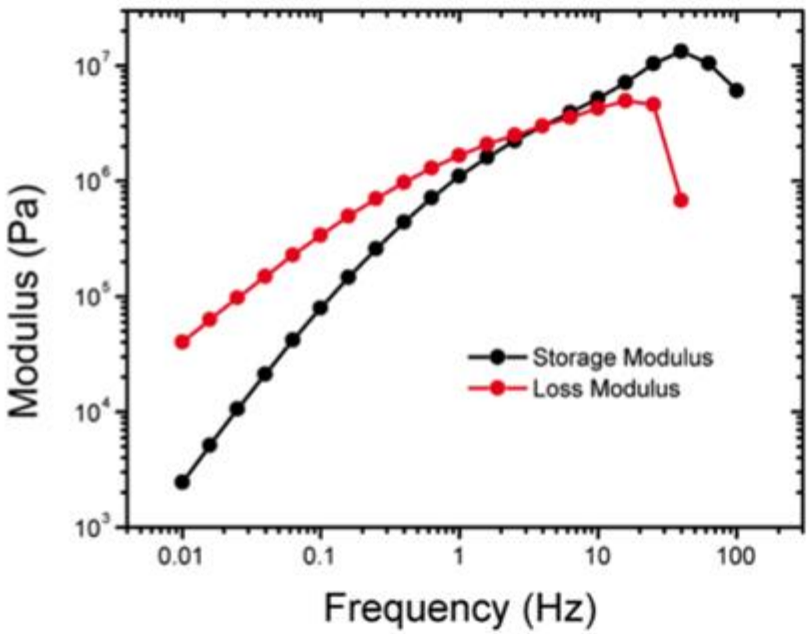
Accomplishment

Soft, dynamic polymer coating for Lithium – Self-healing polymer

Soft, viscoelastic coating is flowable at room temperature.

It can conformally coat uneven Li growths and cracks in SEI.



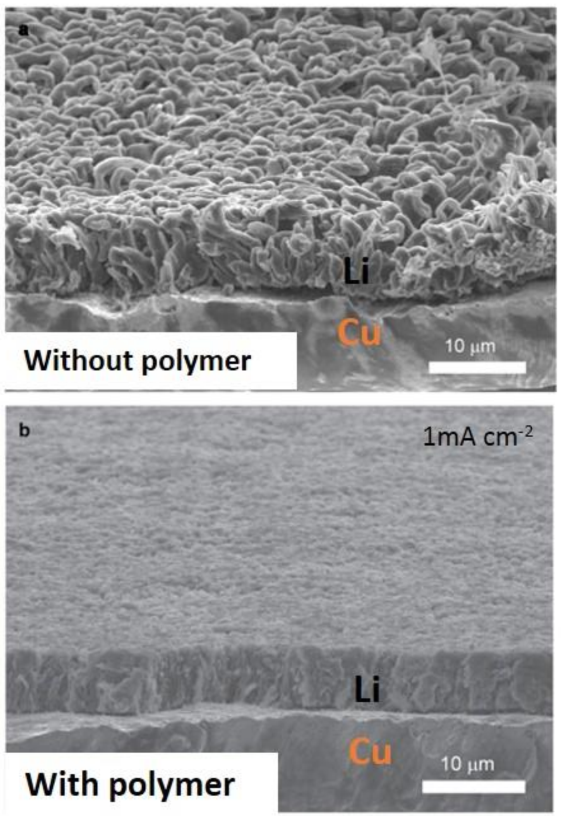


ACS Energy Lett. 1247–1255 (2016)

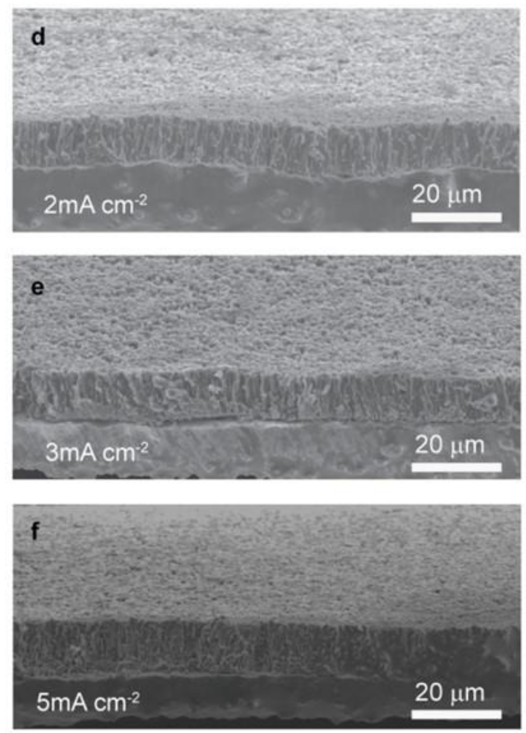
Accomplishment

Soft, dynamic polymer coating for Lithium – Self-healing polymer

- Li deposited on Cu without the polymer coating is high-aspect ratio, promoting side reactions through high surface area.
- Li deposited with the polymer coating is **dense, compact, and uniform.**



With polymer, higher charging rates

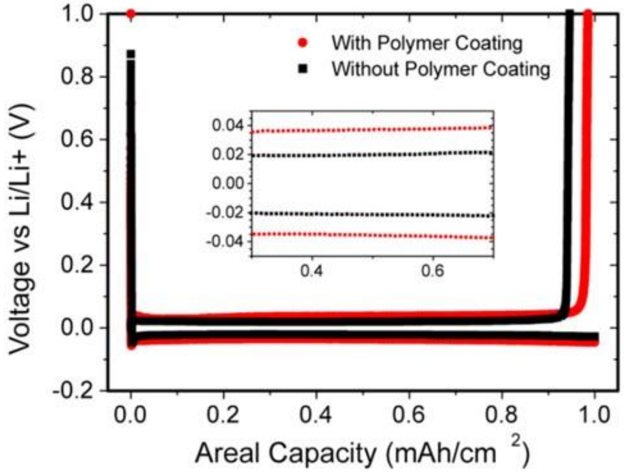


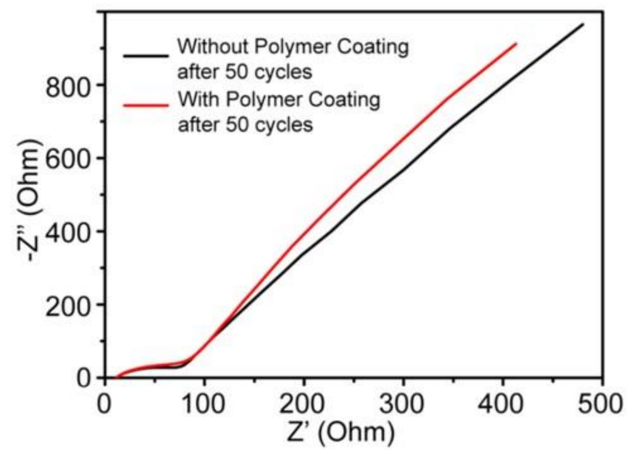
ACS Energy Lett. 1247–1255 (2016)

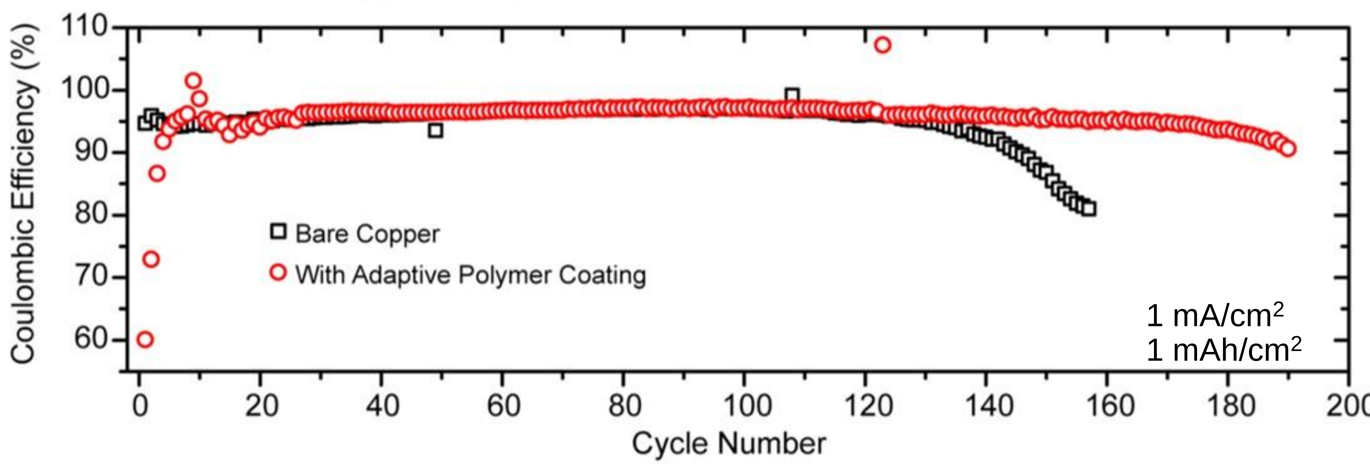
Accomplishment

Soft, dynamic polymer coating for Lithium – Self-healing polymer

Polymer coating has good Li-ion conductivity and improves cycle life of Li metal anode.







1M LiTFSI
1 wt% $LiNO_3$
DOL/DME
75 uL

Li|Cu, strip to 1 V

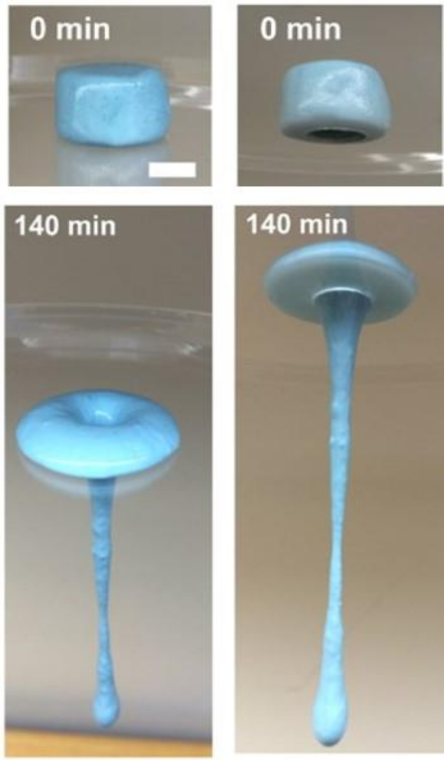
ACS Energy Lett. 1247–1255 (2016)

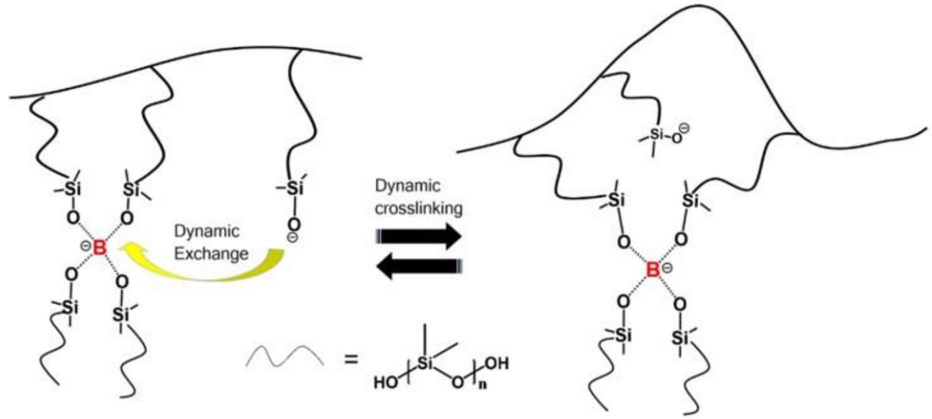
Accomplishment

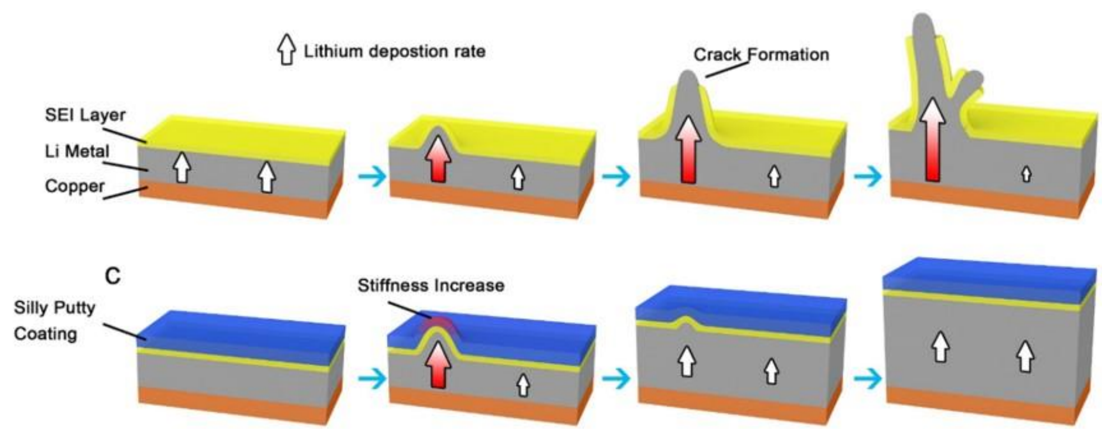
Soft, dynamic polymer coating for Lithium – "Solid-liquid" hybrid

Silly Putty (SP)
- Liquid-like at rest
- Solid-like upon stress

Dynamic crosslinks enable flowability while providing mechanical stiffness upon dendrite growth.







J. Am. Chem. Soc. 139, 4815 (2017)

Accomplishment

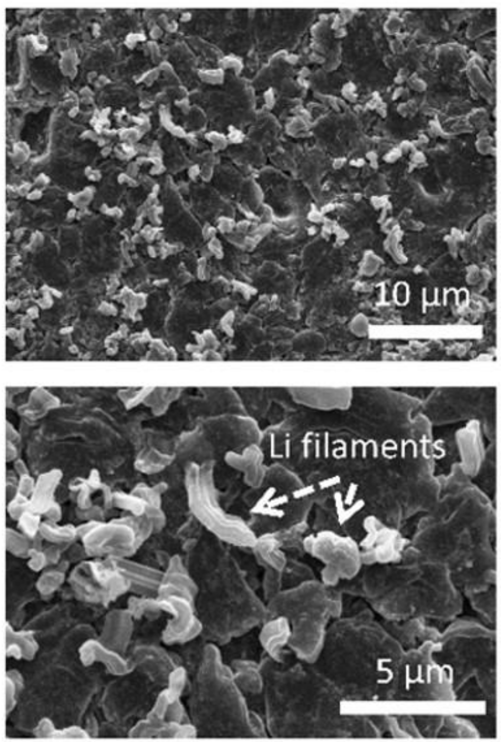
Soft, dynamic polymer coating for Lithium – “Solid-liquid” hybrid

- Without the SP coating, Li filaments are visible seen growing out of cracks between Li grains after 75 cycles of deposition and stripping.

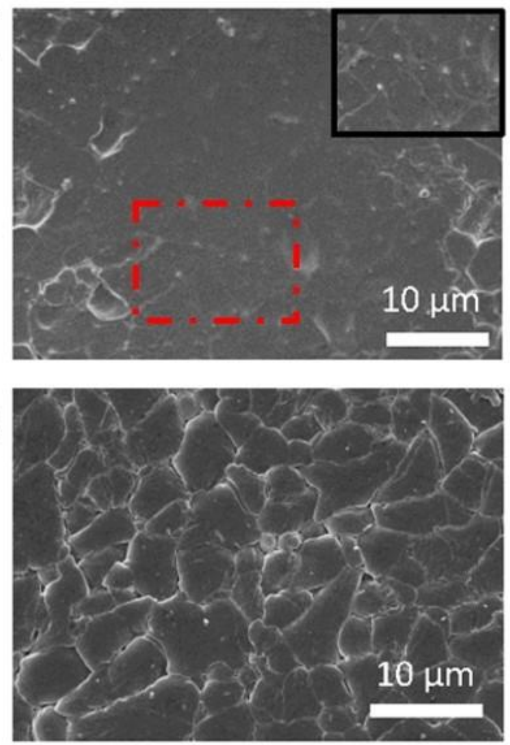
- With the SP coating, Li grains are tightly compacted with no apparent Li filament growth visible, resulting from the responsive mechanical properties of the SP.

Li electrodes after 75 cycles

Without SP coating



With SP coating



(Coating present)

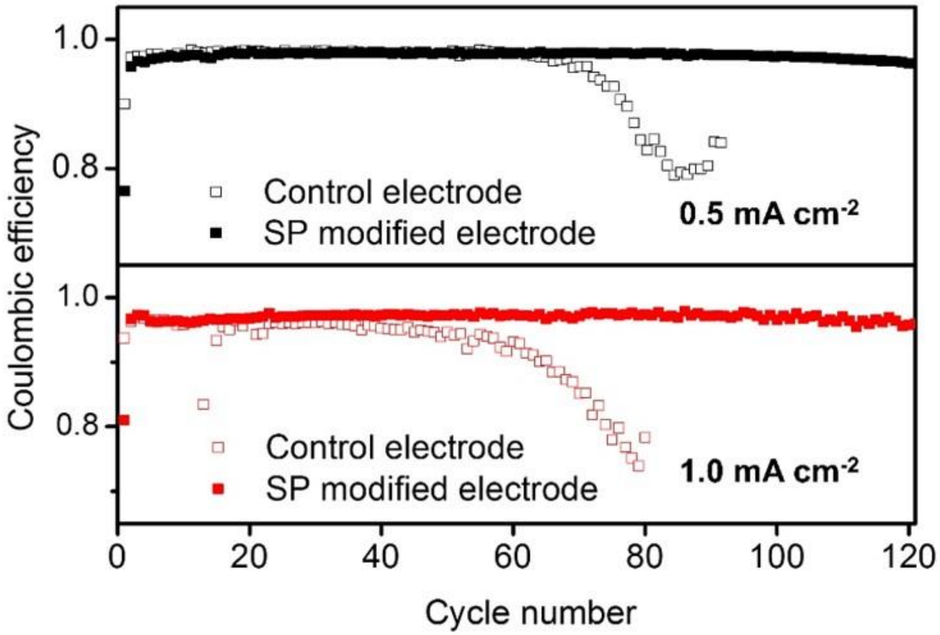
(Coating removed)

J. Am. Chem. Soc. 139, 4815 (2017)

Accomplishment

Soft, dynamic polymer coating for Lithium – "Solid-liquid" hybrid

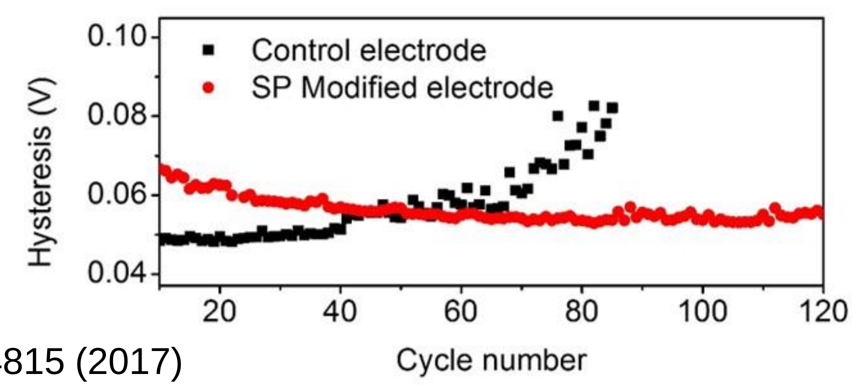
Improved cycling stability & decreased overpotential during extended cycling.



1 mAh/cm²

1M LiTFSI
1 wt% $LiNO_3$
DOL/DME
60 uL

Li|Cu, strip to 2 V



J. Am. Chem. Soc. 139, 4815 (2017)

Accomplishment

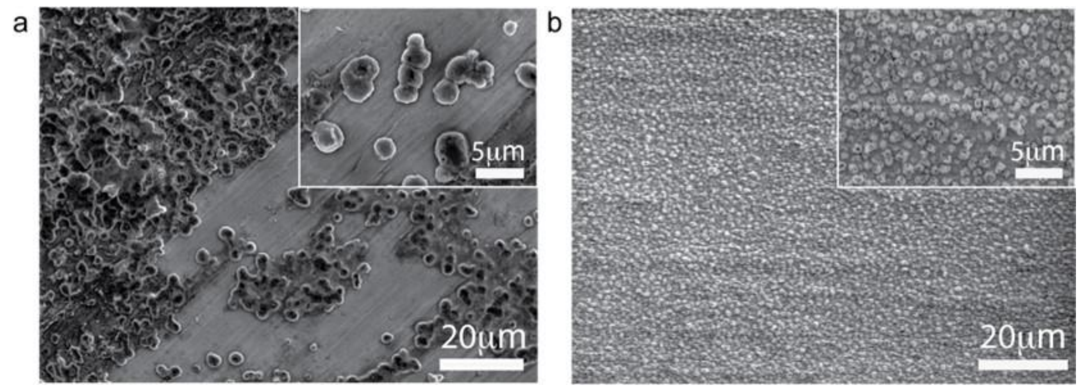
Soft, dynamic polymer coatings for Lithium – Li Nucleation

Both polymers (SHP & SP) affect Li nucleation to positively boost Li electrode performance.

Without SHP coating

With SHP coating

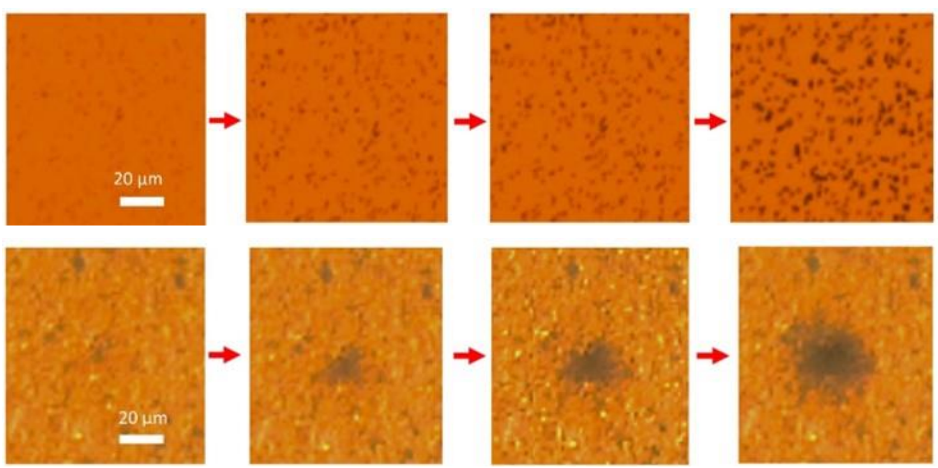
Increased ↑ nuclei density, leading to denser, more uniform deposits.



Bigger ↑ nuclei sizes (Li grains), decreased surface area of Li

Without SP coating

With SP coating

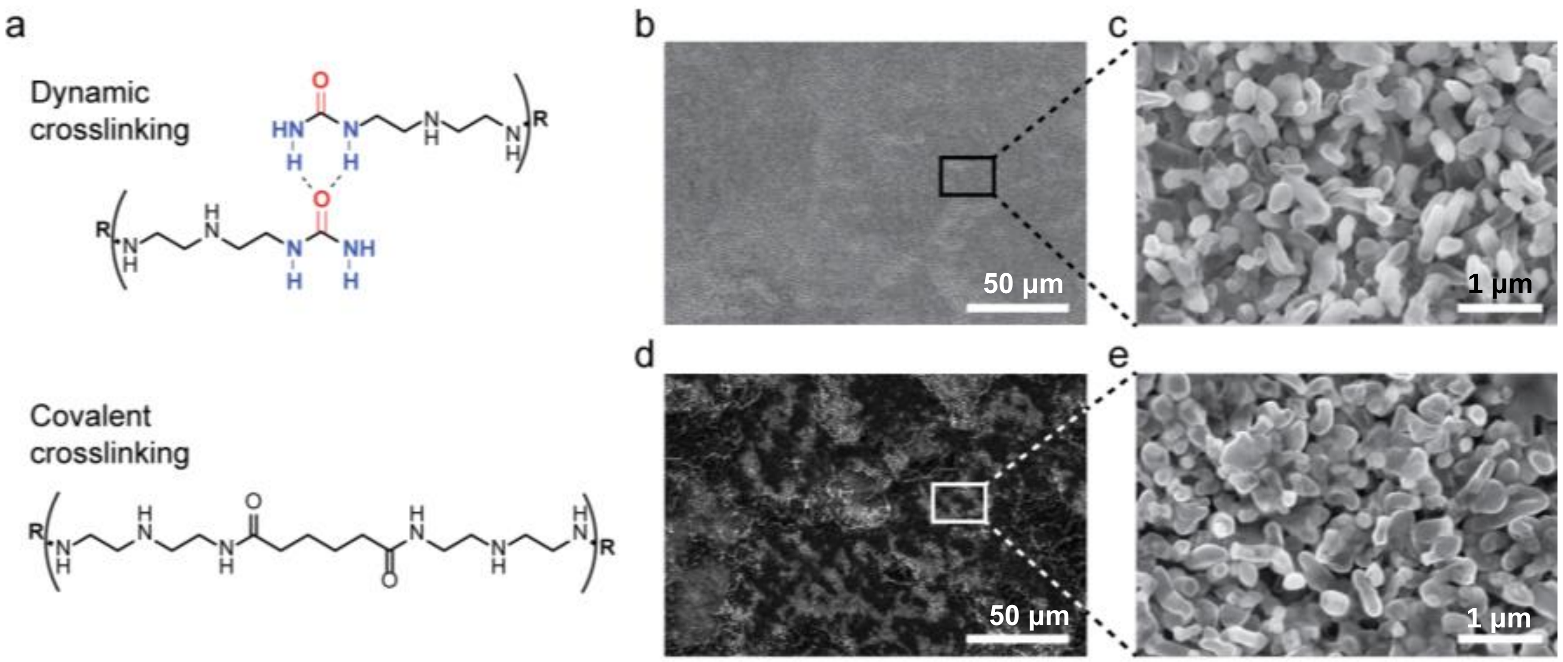


J. Am. Chem. Soc. 139, 4815 (2017), *ACS Energy Lett.* 1247–1255 (2016)

Accomplishment

Polymer Coating: Mechanics vs. Chemistry

- We found that polymer mechanics / film quality influences deposition uniformity on the electrode scale.
- We discovered that polymer chemistry (backbone, functional groups) influences Li deposit morphology.
- Li/Li^+ electrochemical kinetics can be tuned by properties such as surface energy and dielectric constant.

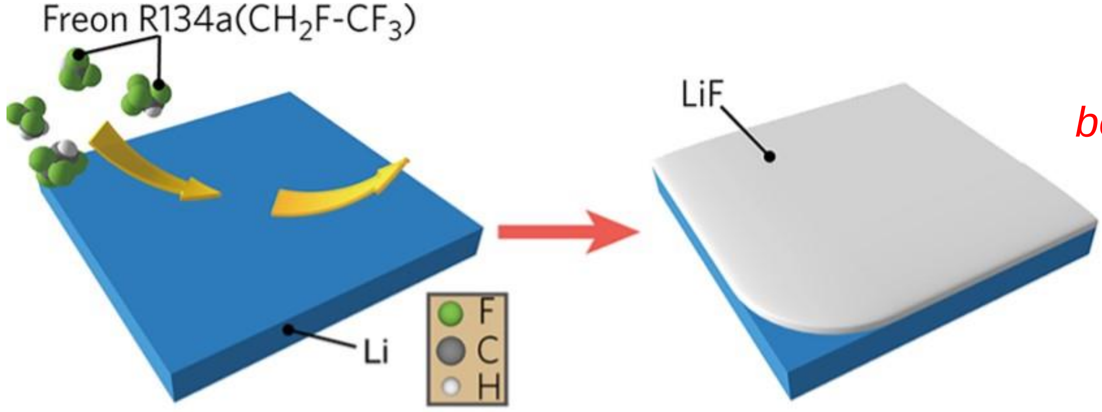


In preparation (2018)

Accomplishment

Conformal inorganic coatings via gas-phase reaction

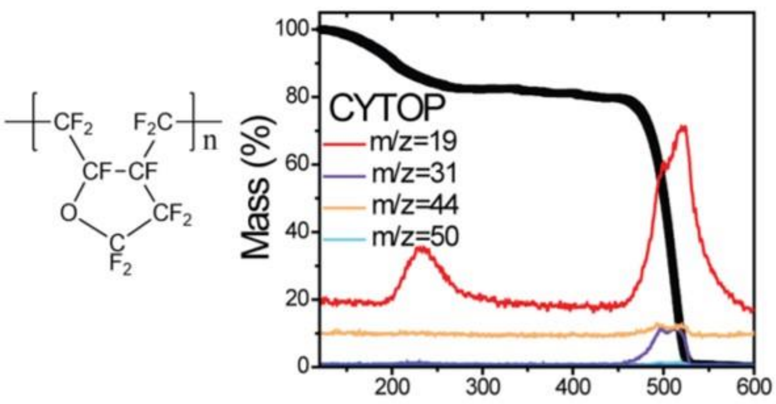
LiF: extremely low solubility in electrolyte, wide electrochemical window

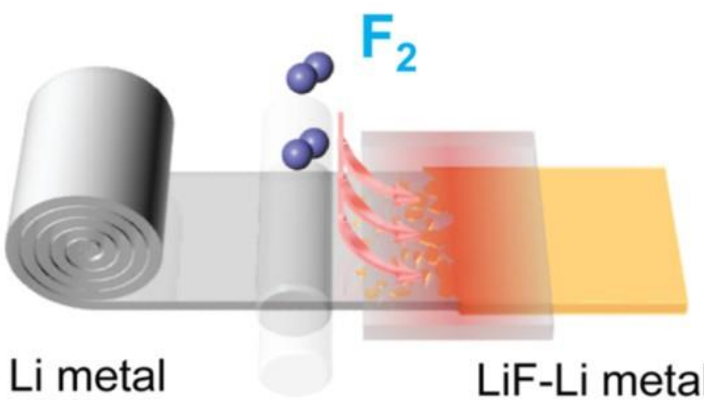


LiF coating by reaction between Freon and metallic Li

Nano Lett. **17**, 3731 (2017) (Collaborated with Prof. Bruce Dunn)

LiF coating using fluorine gas generated by CYTOP decomposition



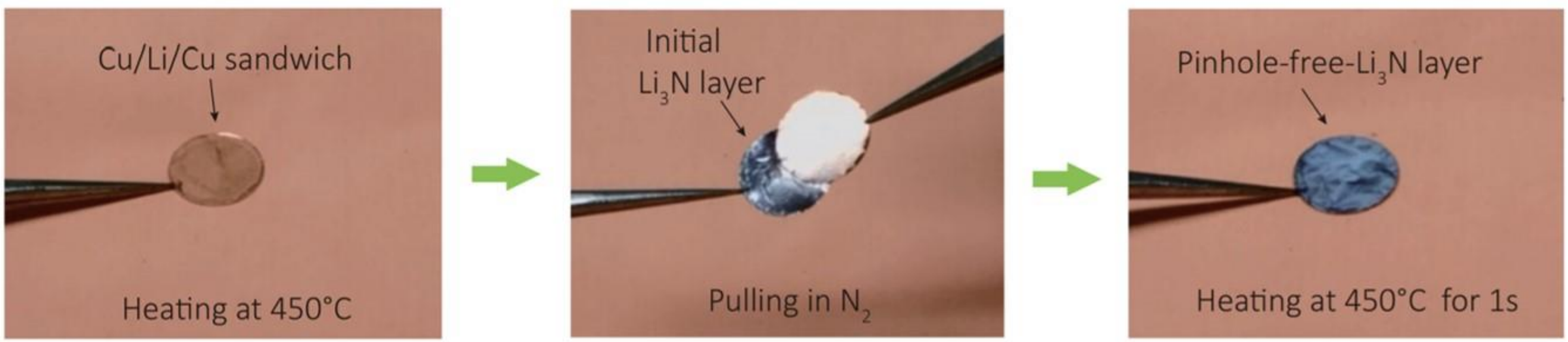


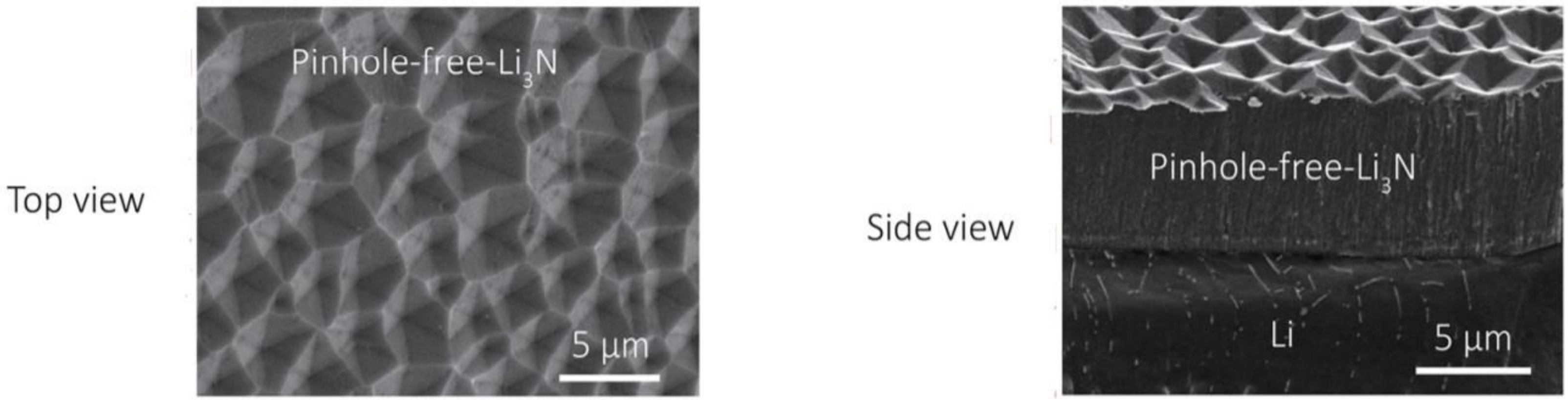
J. Am. Chem. Soc. **139**, 11550 (2017)

Accomplishment

Conformal inorganic coatings via gas-phase reaction

Pinhole-free Li_3N: reacting clean molten lithium foil directly with pure nitrogen





ACS Cent. Sci. **4**, 97 (2018)

Responses to Previous Year Reviewers' Comments

Not applicable

Collaboration and Coordination

SLAC NATIONAL ACCELERATOR LABORATORY — Dr. Mike Toney

Stanford University — Prof. Jian Qin
Prof. Reinhold Dauskardt
Dr. Steven Chu

Pacific Northwest NATIONAL LABORATORY — Dr. Jun Liu

UCLA — Prof. Bruce Dunn

Remaining Challenges and Barriers

- Coulombic efficiency is still not high enough to minimize lithium loss during extended cycles.

- It remains challenging to maintain even Li deposition and good cycling stability of lithium metal under high current density.

- Further studies are necessary to maintain a stable SEI when cycling lithium metal at high areal capacity.

- Coating polymers directly on Li metal can be challenging; solvent-free or direct methods may be required.

Proposed Future Work

FY 2018

- To elucidate the critical parameters (chemical, mechanical, etc.) for polymers which enable functional Li metal coatings.
- Provide polymer coatings and Li metal protection methods in coin cells for stage 2 coin cell testing.
- New polymer membranes and Li metal anode incorporated in pouch cells required to reach 350 Wh/kg cells based on Battery 500 cell design.

FY 2019

- To understand the effect of interfacial SEI components and structure on Li/Li^+ kinetics and cycling performance (*e.g.* using cryo-EM).
- To further improve the Coulombic efficiency of lithium metal cycling in both ether and carbonate based electrolyte (additives, multifunction/multilayer coatings)

Summary

- **Objective and Relevance:** The goal of this project is to develop stable and high capacity lithium anodes from the perspective of nanomaterials design to enable the next-generation lithium metal-based batteries to power electric vehicles, which is highly relevant to the VT Program goal.
- **Approach/Strategy:** This project combines advanced nanomaterials synthesis, characterization, battery assembly and testing, which has been demonstrated to be highly effective.
- **Technical Accomplishments and Progress:** This project has produced many significant results, meeting milestones. They include identifying the key challenges in lithium metal anodes, using rational materials design, synthesizing and testing, and developing scalable and low-cost methods. The results have been published in top peer-reviewed scientific journals. The PI has received numerous invitations to speak in national and international conferences.
- **Collaborations and Coordination:** The PI has established a number of highly effective collaborations.
- **Proposed Future Work:** Rational and exciting future has been planned.