

Nanoscale Interfacial Engineering for Stable Lithium Metal Anodes

Yi Cui

Stanford University

June 9, 2016

Project ID
#ES274

Overview

Timeline

- Start: August 1, 2013
- End: July 31, 2017
- Percent complete: 75%

Budget

- Total project funding
\$1,350k
- Funding received in FY 2015
\$450k
- Funding for FY 2016
\$450k

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
 - BMR program PI' s
 - SLAC: In-situ X-ray
 - Amprius Inc.
 - Professor Steven Chu

Project Objective and Relevance

Objective

- Develop lithium metal anodes with high capacity and reliability for the next-generation high-energy-density rechargeable lithium-based batteries to power electric vehicles (HEV/PEV/EV).
- Design and fabricate novel chemically and mechanically stable 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 and additives on the performance and life time of lithium metal batteries.
- Develop scalable low-cost methods for the synthesis of nanostructured lithium metal anodes and interfacial protection materials.
- Project contents are directly aimed at the listed barriers: high cost, low energy density and short battery life.

Milestones for FY15 and 16

Month/ year	Milestones	Status
3/2015	Fabrication of interfacial protection materials, including interconnected carbon hollow spheres, layered h-BN and graphene with different thicknesses and defect levels.	Complete
6/2015	Determine the effect of LiNO_3 and lithium polysulfide on the cycling Coulombic efficiency of lithium metal anode.	Complete
9/2015	Demonstrate the guiding effect of polymer nanofibers for improved lithium metal cycling performance.	Complete
12/2015	Demonstrate the improved cycling performance of surface-engineered lithium metal anode under different current density and areal capacity.	Complete
3/2016	Achieve minimum relative volume change and effective dendrite suppression during electrochemical cycling via nanoporous host-lithium composite electrode design.	Complete
6/2016	Study the effects of substrate lithium affinity on the nucleation/growth behavior and Coulombic efficiency of lithium metal.	On track
9/2016	Demonstrate low-cost, scalable fabrication of porous host-lithium composite electrodes.	On track
12/2016	Demonstrate successful sealing of pinholes in h-BN thin film pinholes.	On track

Approach/Strategy

Advanced design and synthesis of interfacial protecting layers and nanostructured lithium metal electrodes

- 1) Engineer various interfacial protection materials with excellent chemical and mechanical stability (interconnected carbon hollow spheres, layered h-BN, graphene, etc.) 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.
- 3) Develop effective surface coating/modification techniques to achieve high lithium affinity on host materials.
- 4) Control the lithium deposition behavior through nanoparticle seeded growth and nanomaterials encapsulation

Structure and property characterization

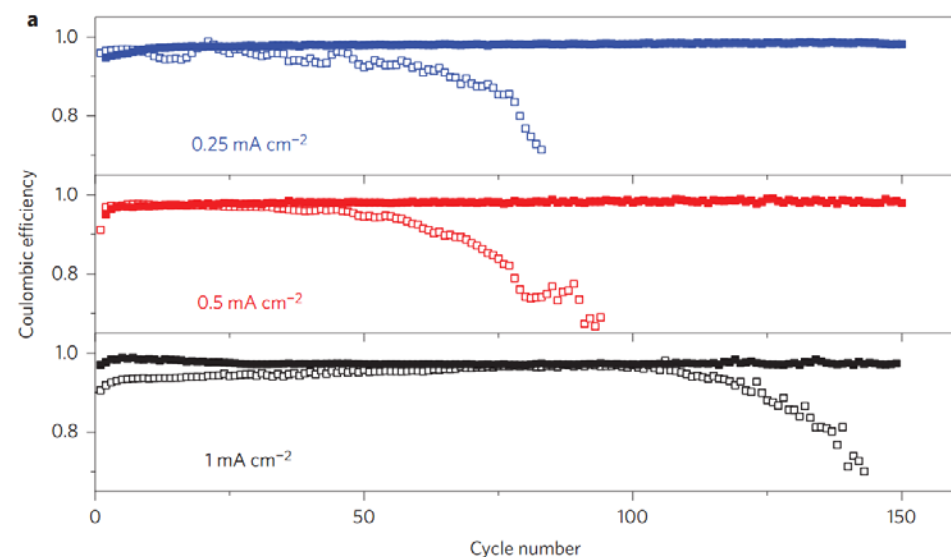
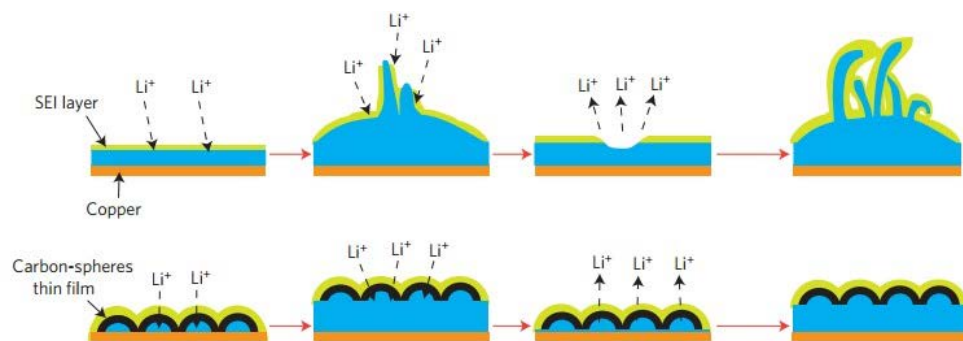
- 1) Ex-situ transmission electron microscopy & scanning electron microscopy
- 2) In-situ transmission electron microscopy
- 3) In-situ optical microscopy
- 4) X-ray diffraction
- 5) X-ray photoelectron spectroscopy
- 6) Fourier transform infrared spectroscopy

Electrochemical testing

- 1) Coin cells and pouch cells
- 2) A set of electrochemical techniques

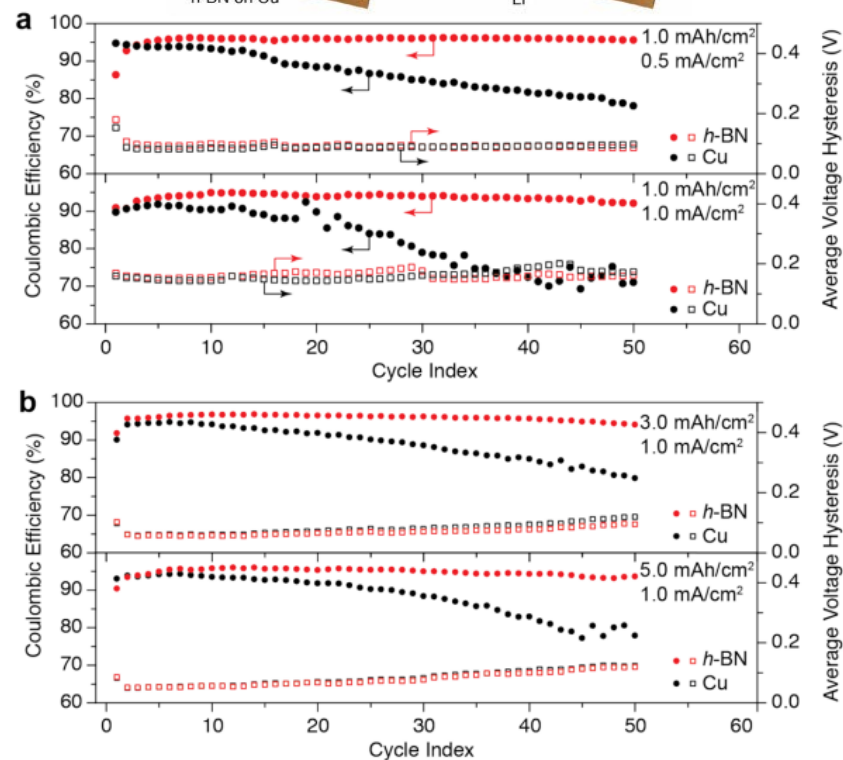
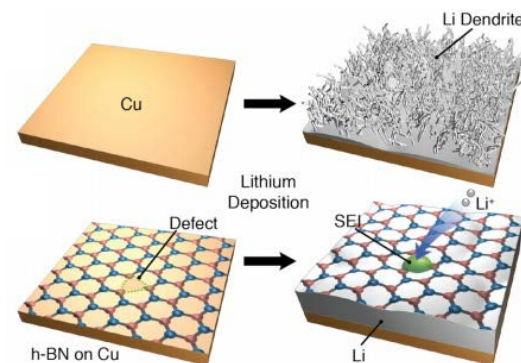
Previous Accomplishments on Lithium Metal Anodes

Interconnected hollow carbon spheres



Cui group, *Nature Nanotech.* **9**, 618 (2014)
(Collaborated with Prof. Steven Chu)

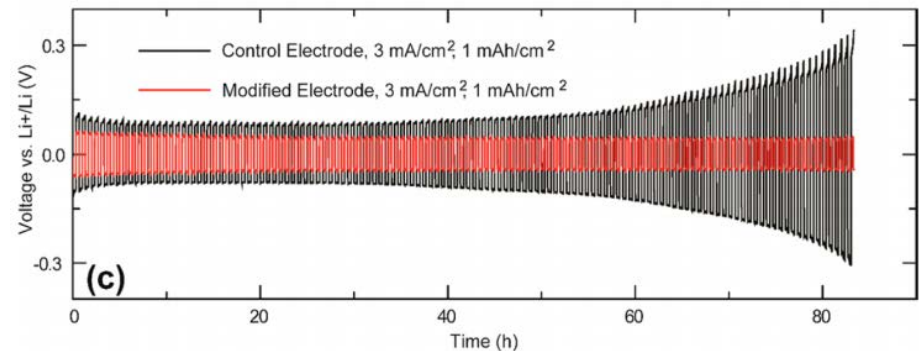
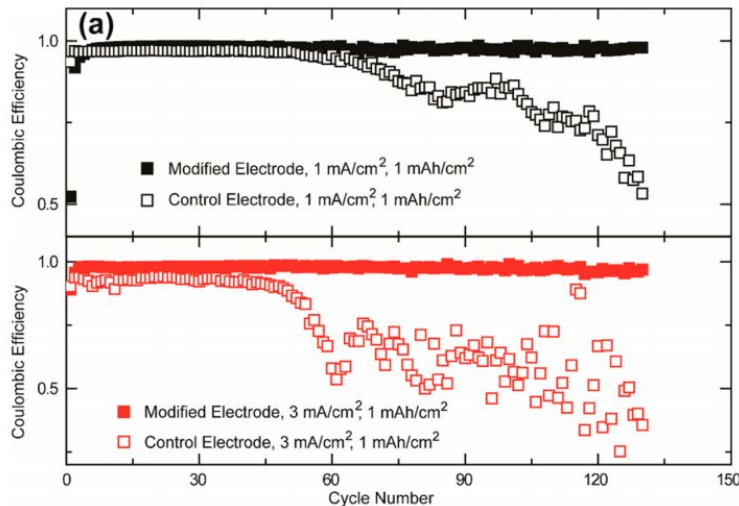
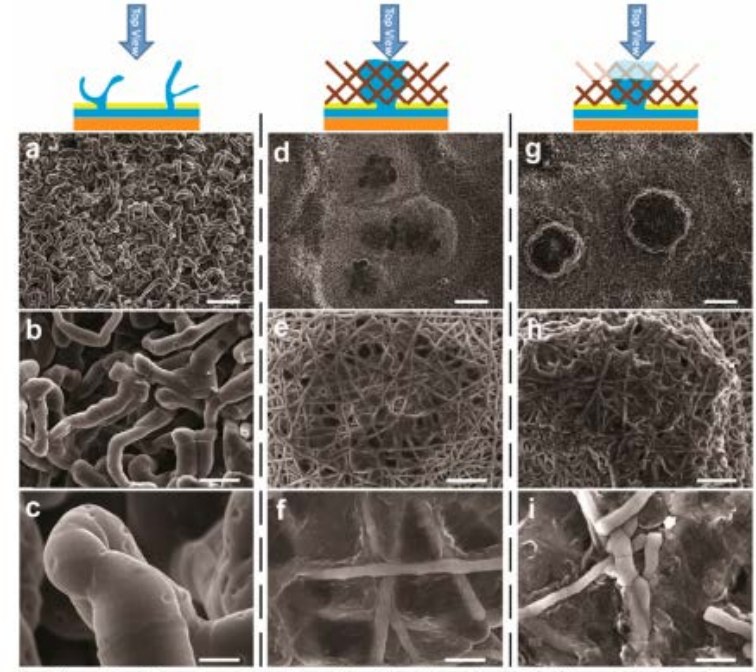
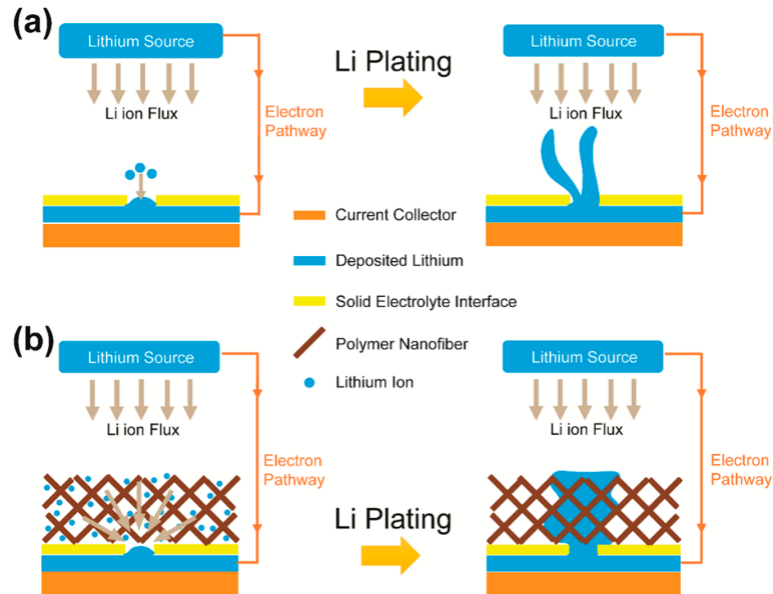
2D h-BN, graphene



Cui group, *Nano Lett.* **14**, 6016 (2014)
(Collaborated with Prof. Steven Chu)

Accomplishment

Polymeric nanofiber cap layer-Characterizations and performance



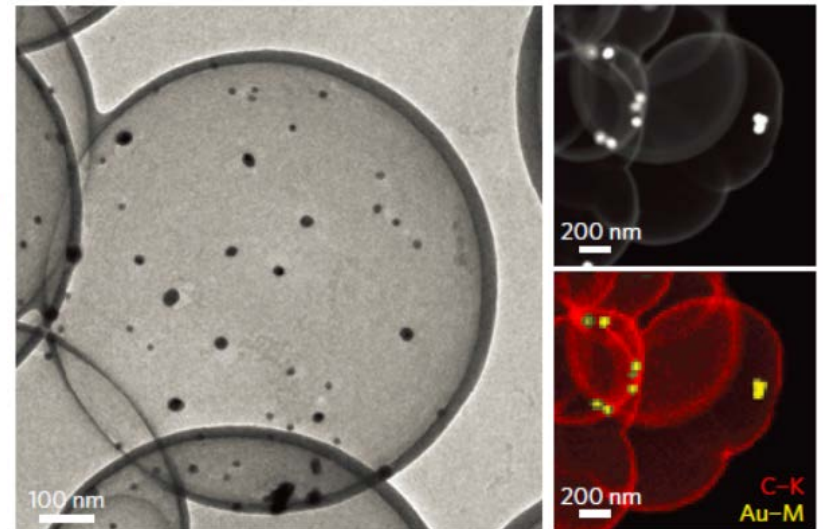
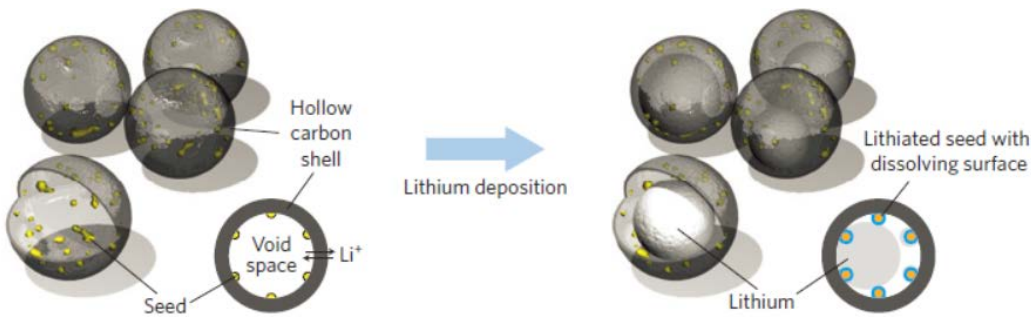
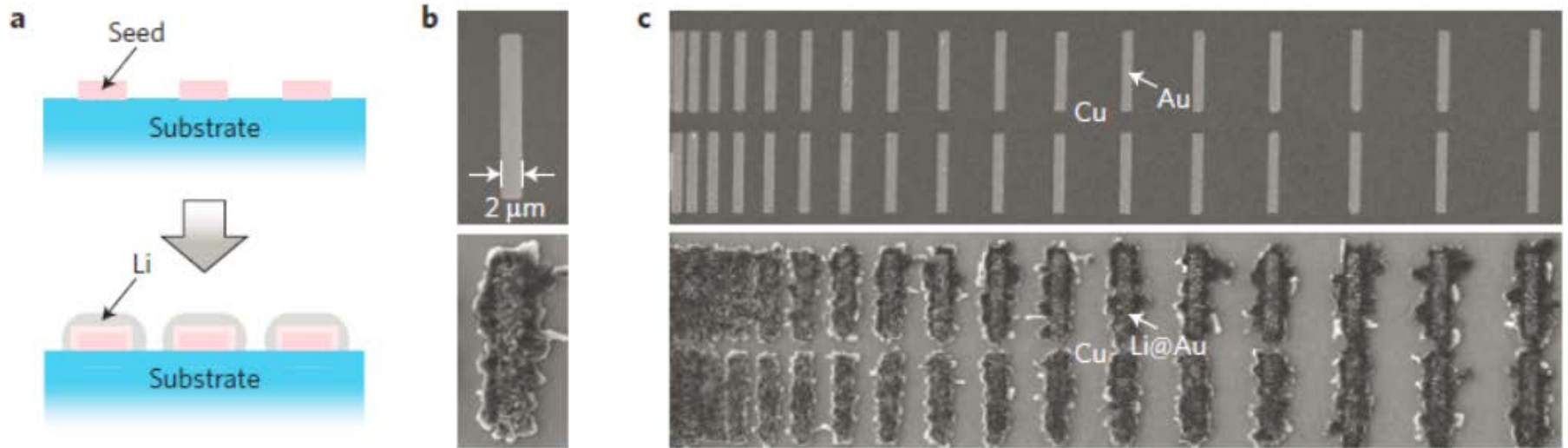
Cui group, *Nano Lett.* **15**, 2910 (2015)
(Collaborated with Prof. Steven Chu)

Selective lithium deposition with nano-sized seeds-Mechanism



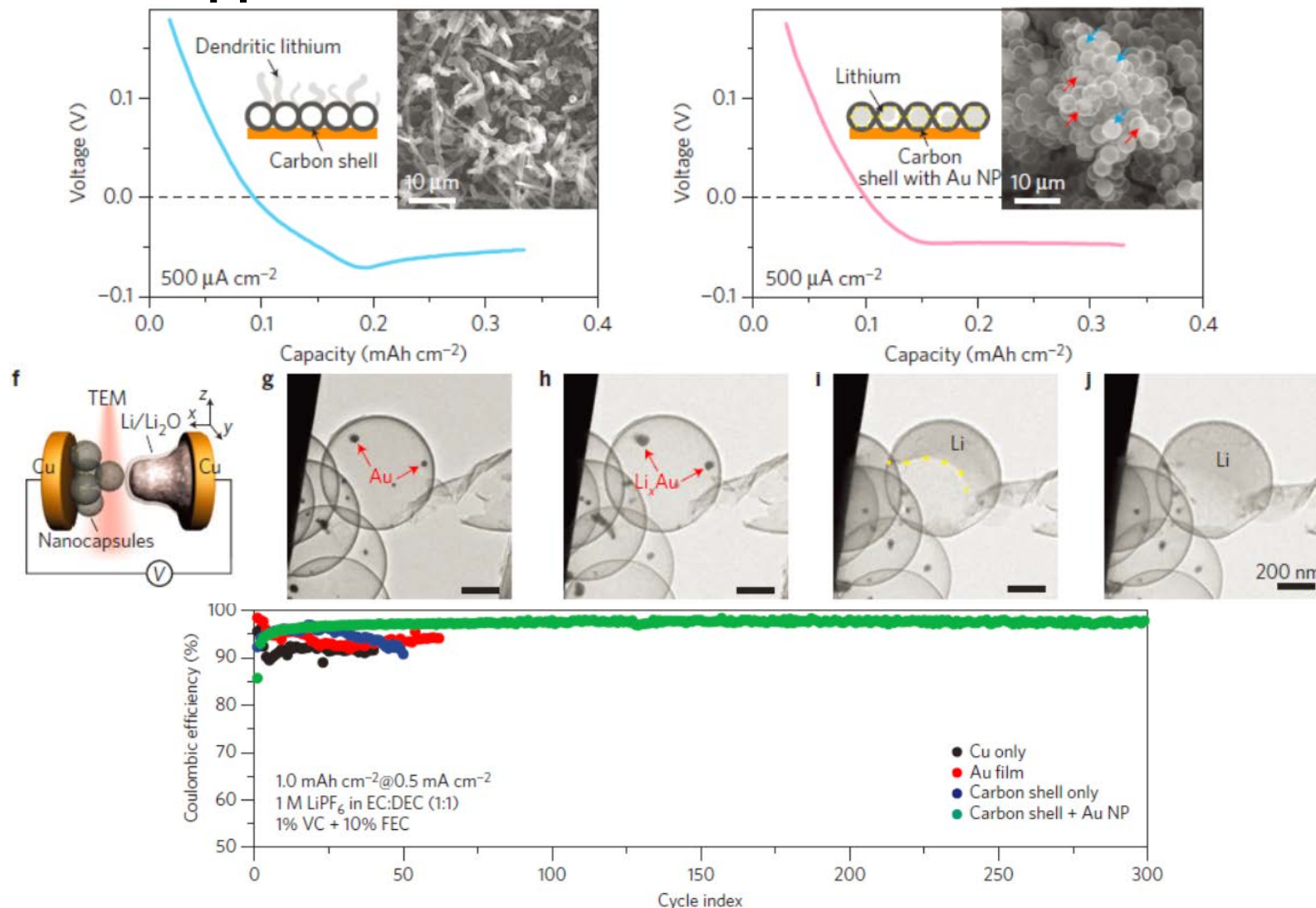
Accomplishment

Selective lithium deposition with nano-sized seeds -Characterizations and structure design



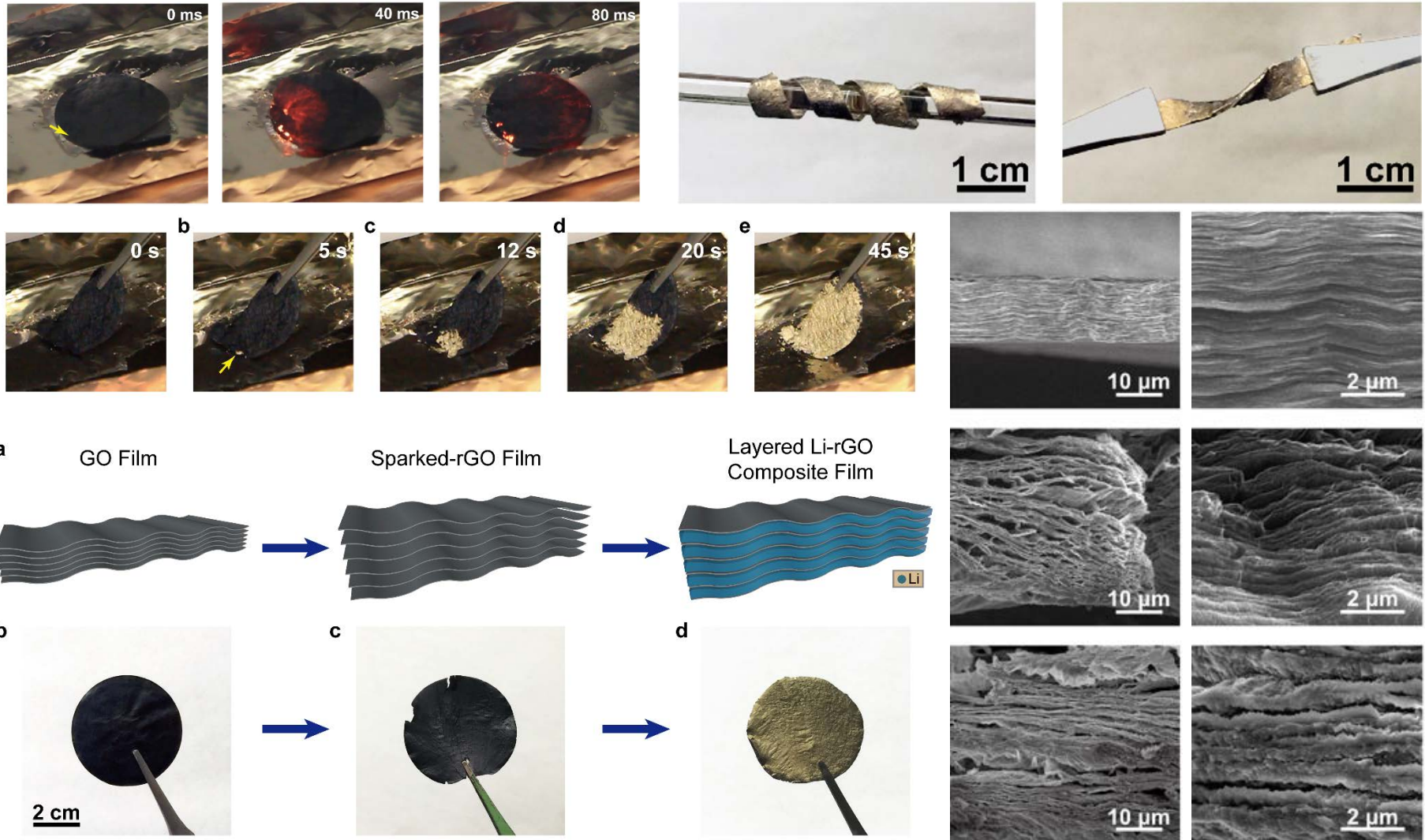
Accomplishment

Selective lithium deposition with nano-sized seeds -Dendrite suppression and electrochemical performance



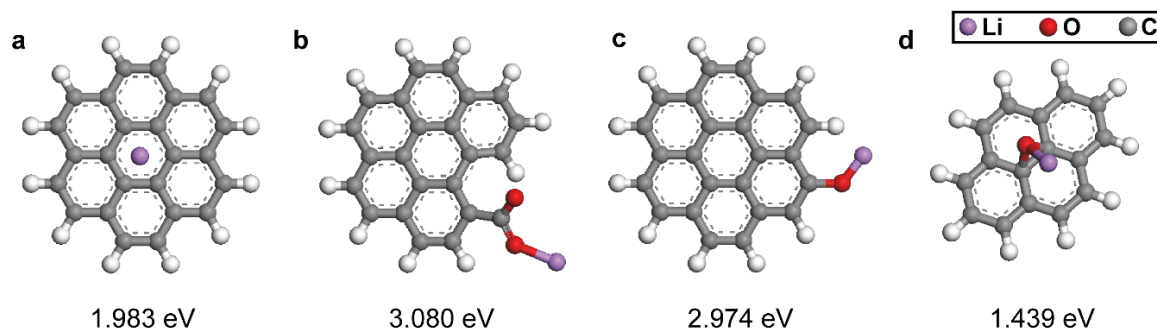
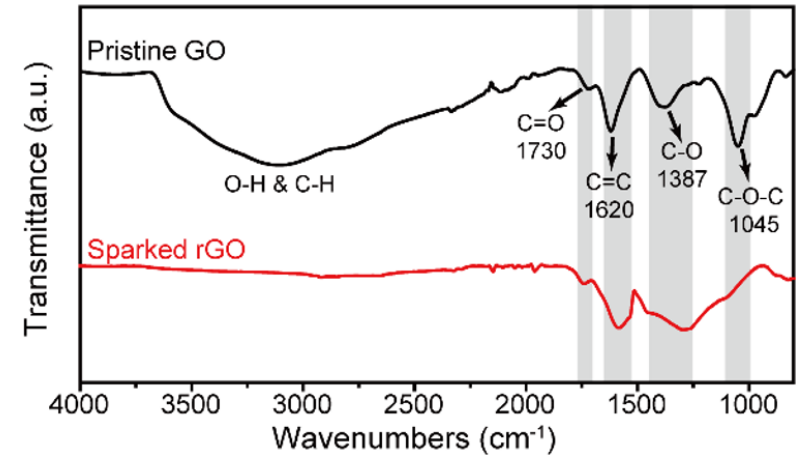
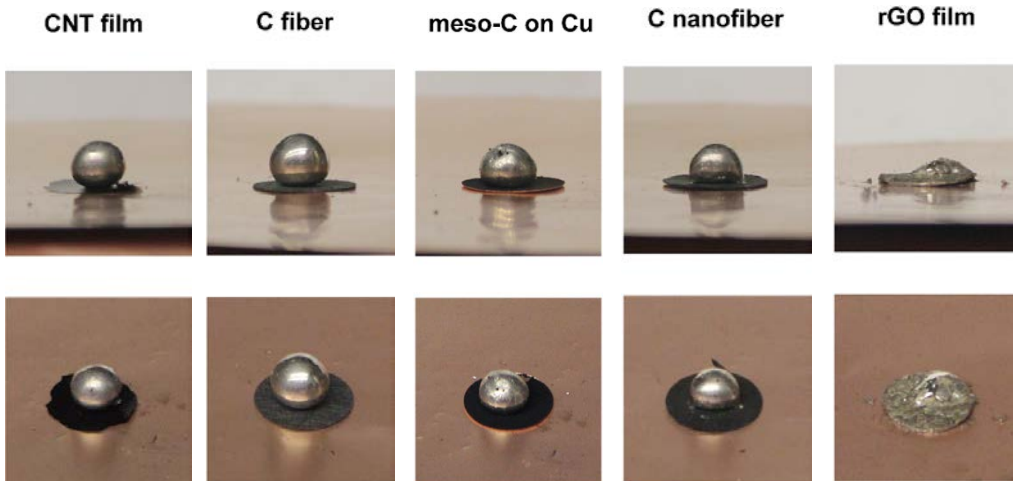
Accomplishment

Layered reduced graphene oxide as a stable host for lithium metal -Fabrication and properties



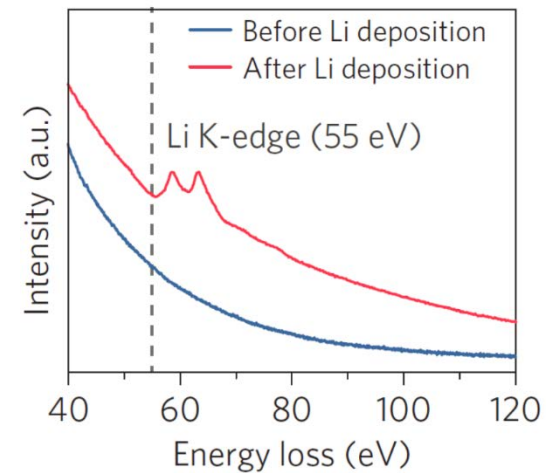
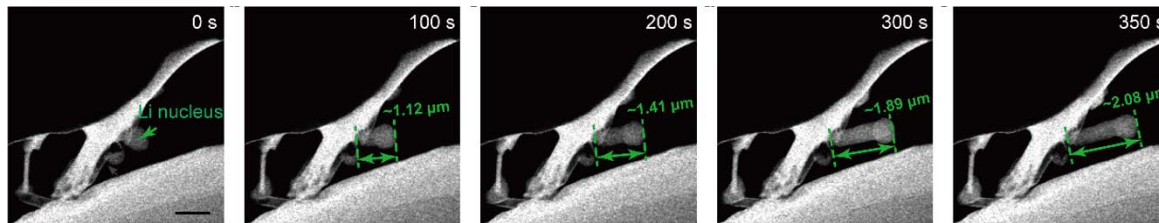
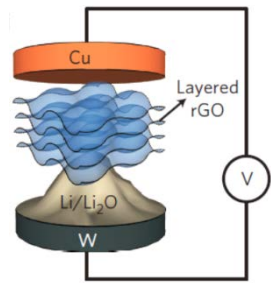
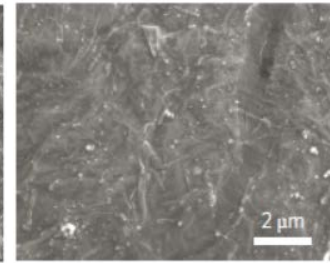
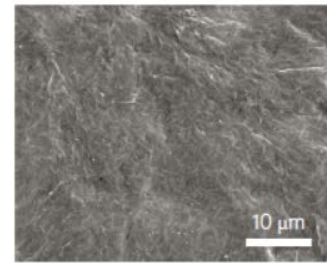
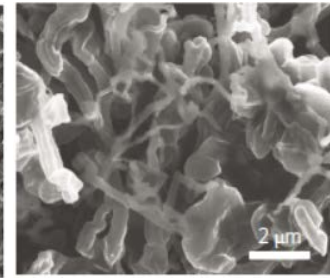
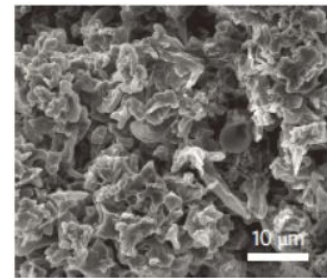
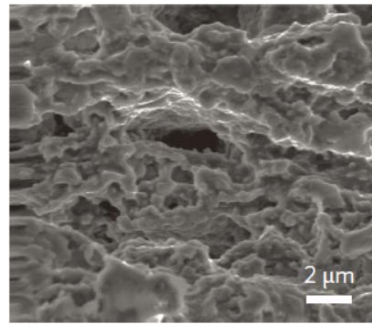
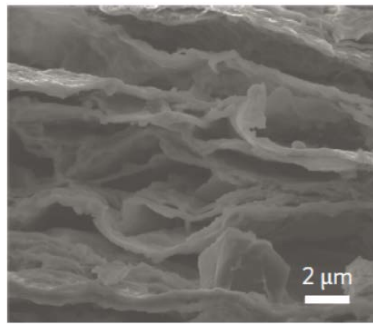
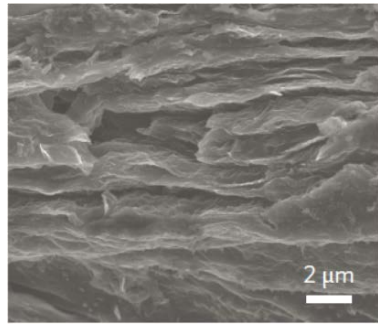
Accomplishment

Layered reduced graphene oxide as a stable host for lithium metal -Unique 'lithiophilic' surface



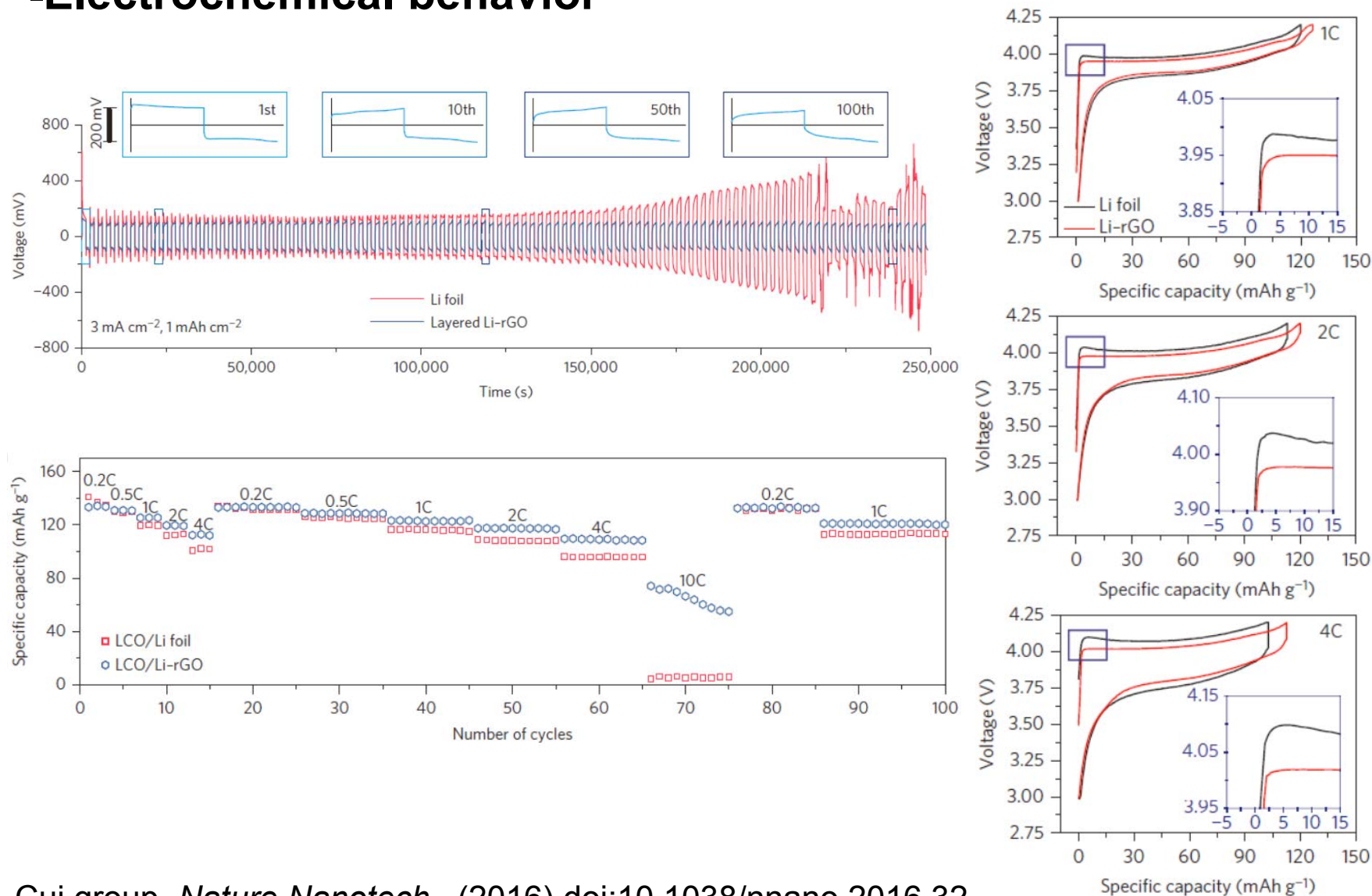
Accomplishment

Layered reduced graphene oxide as a stable host for lithium metal -Lithium deposition behavior



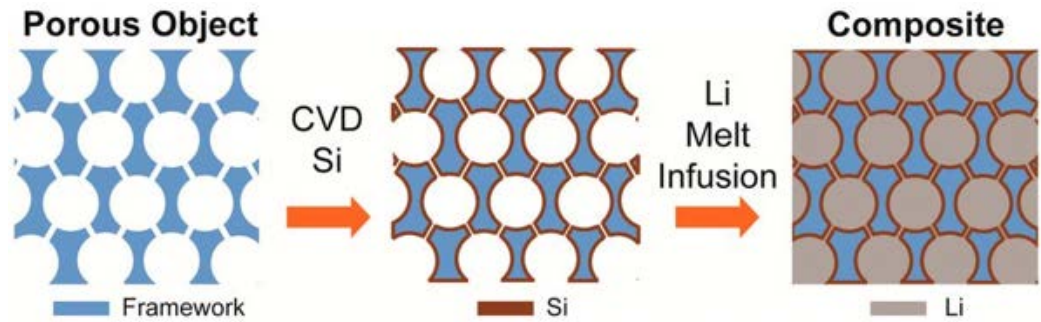
Accomplishment

Layered reduced graphene oxide as a stable host for lithium metal -Electrochemical behavior



Accomplishment

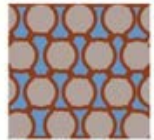
Universal silicon coating for lithiophilic surface-Method



Uncoated Porous Object



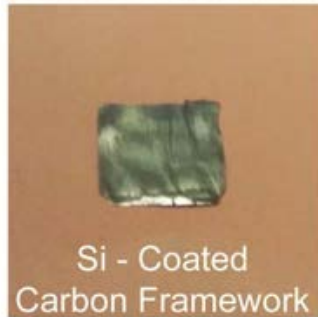
Si - Coated Porous Object



Carbon Framework



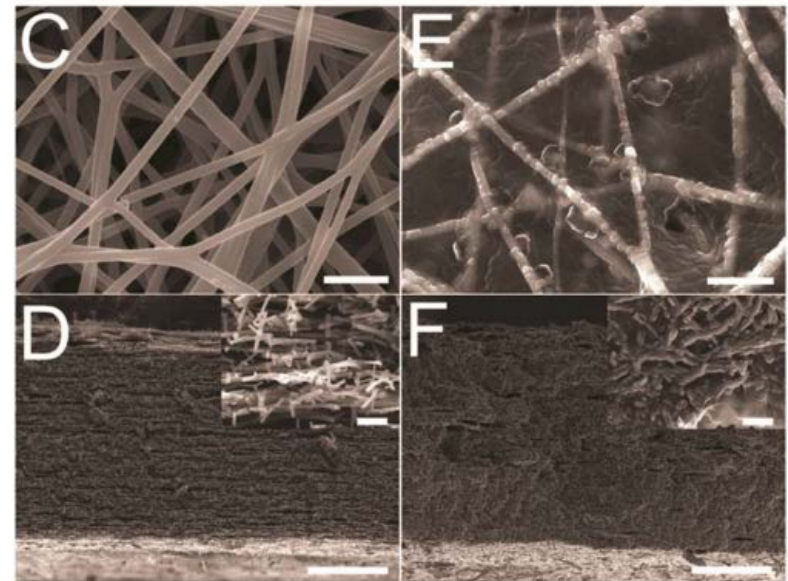
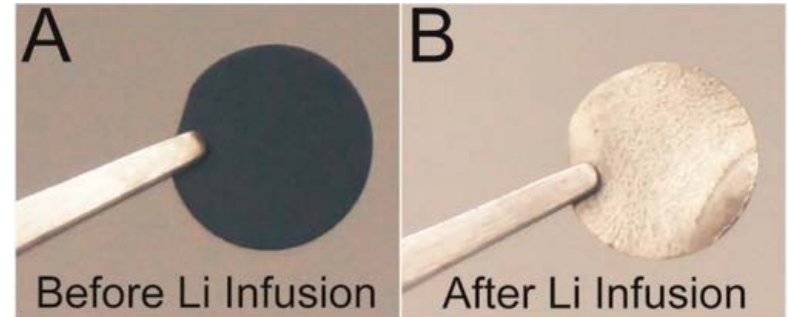
Metal Foam



Si - Coated Carbon Framework

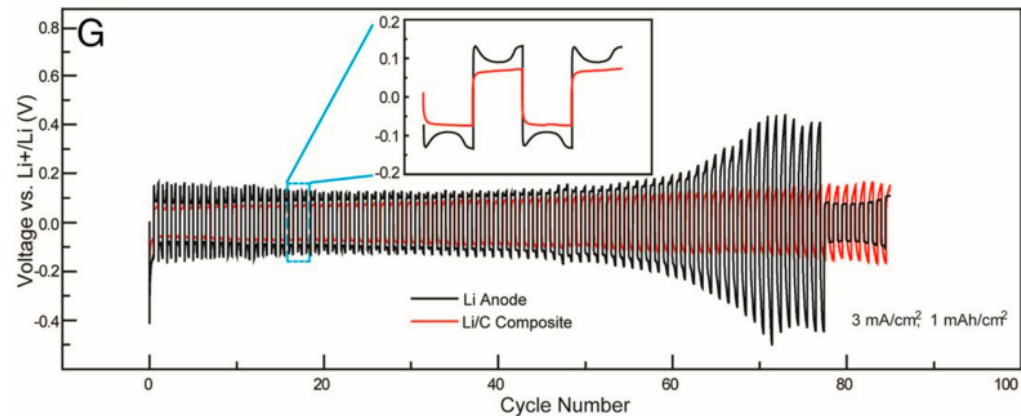
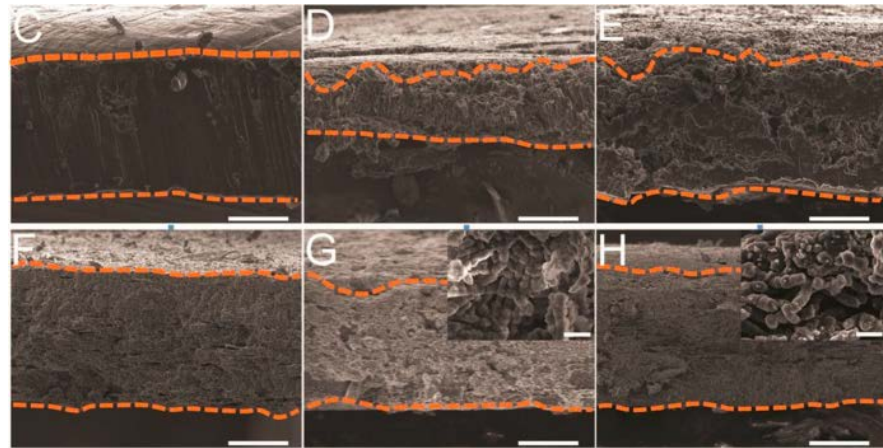
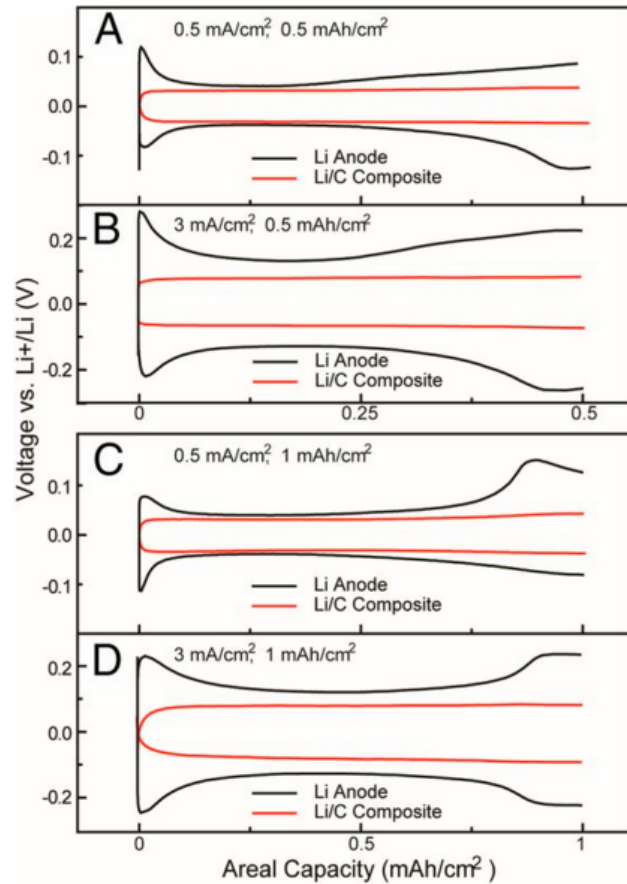


Si - Coated Metal Foam



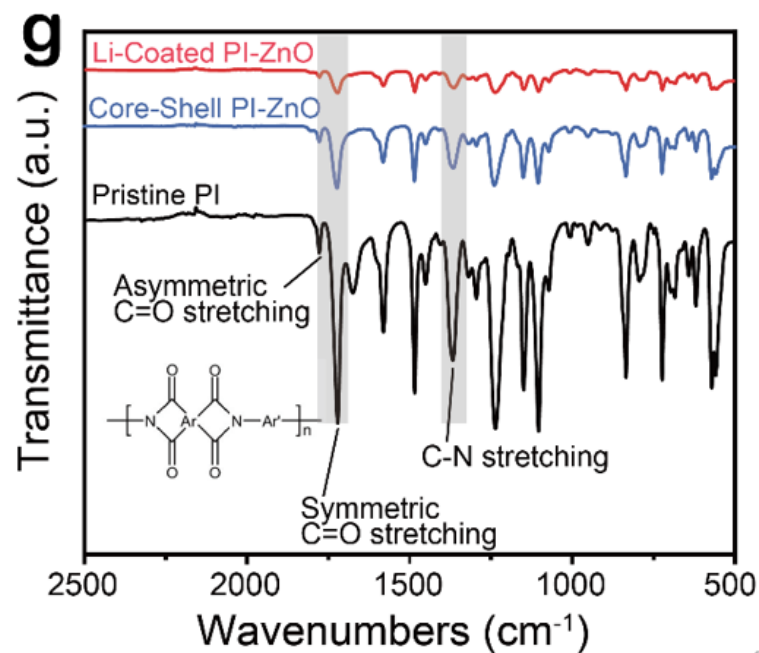
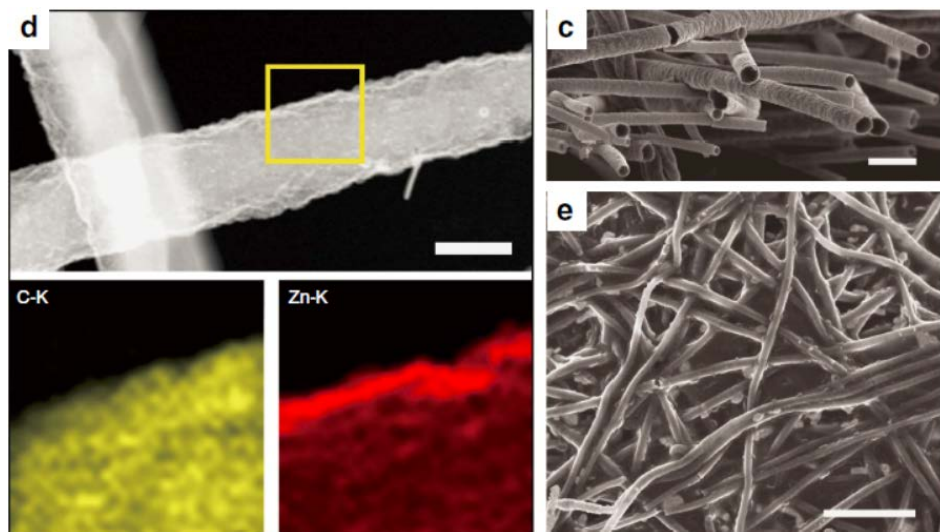
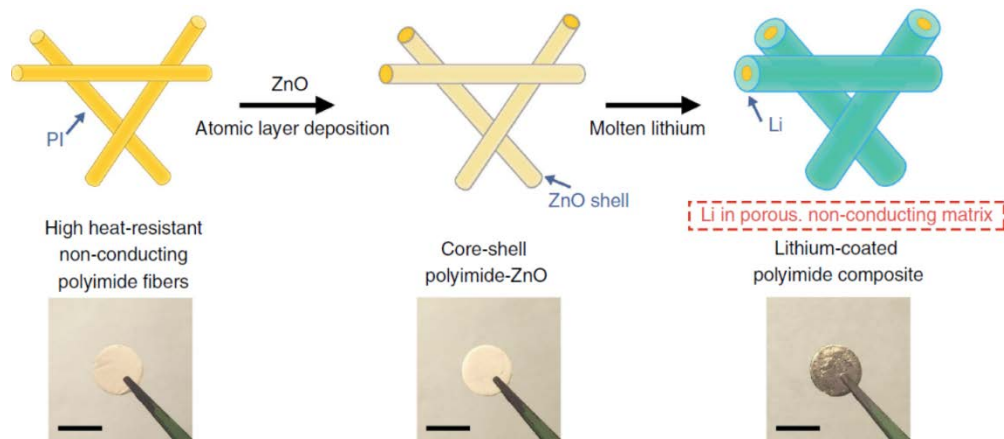
Accomplishment

Universal silicon coating for lithiophilic surface -Characterizations and performance



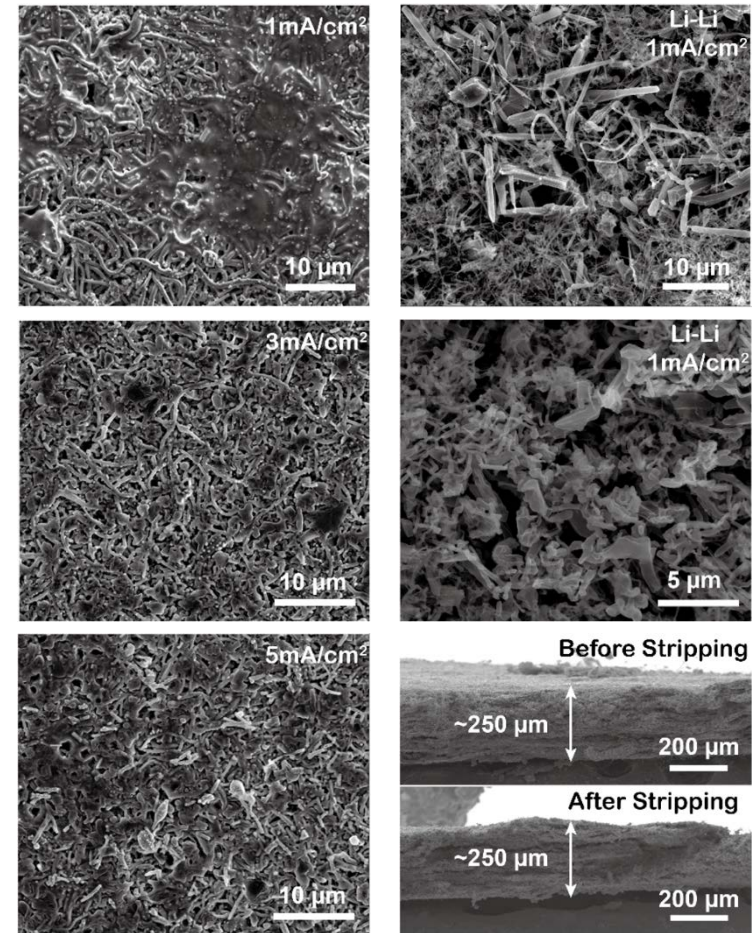
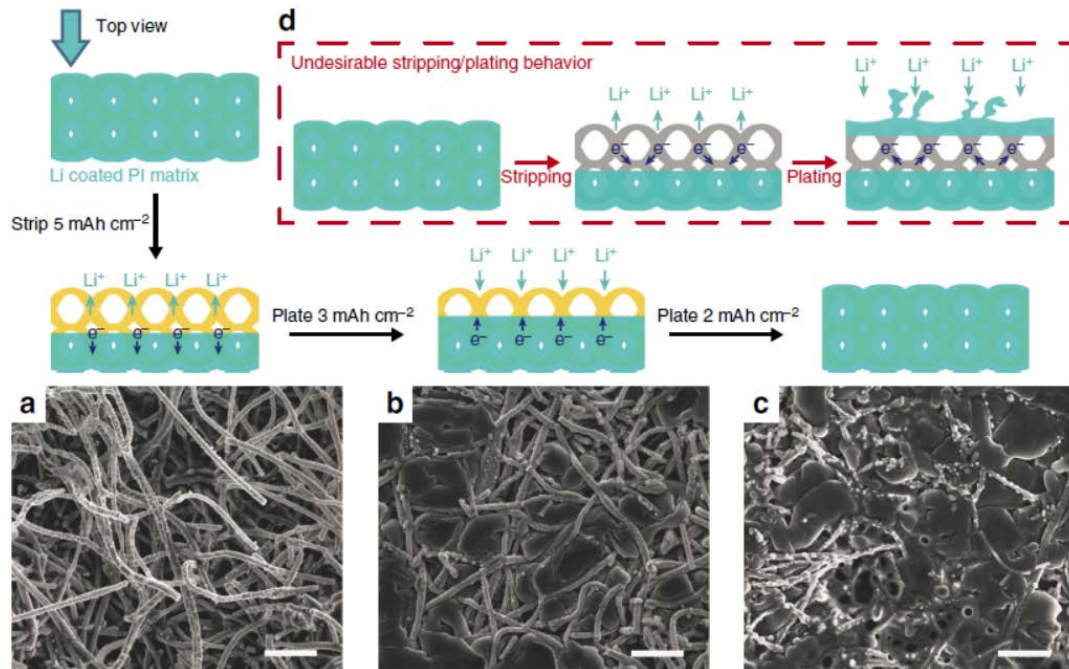
Accomplishment

Non-conductive polymeric matrix as the host for lithium metal -Synthesis and characterizations



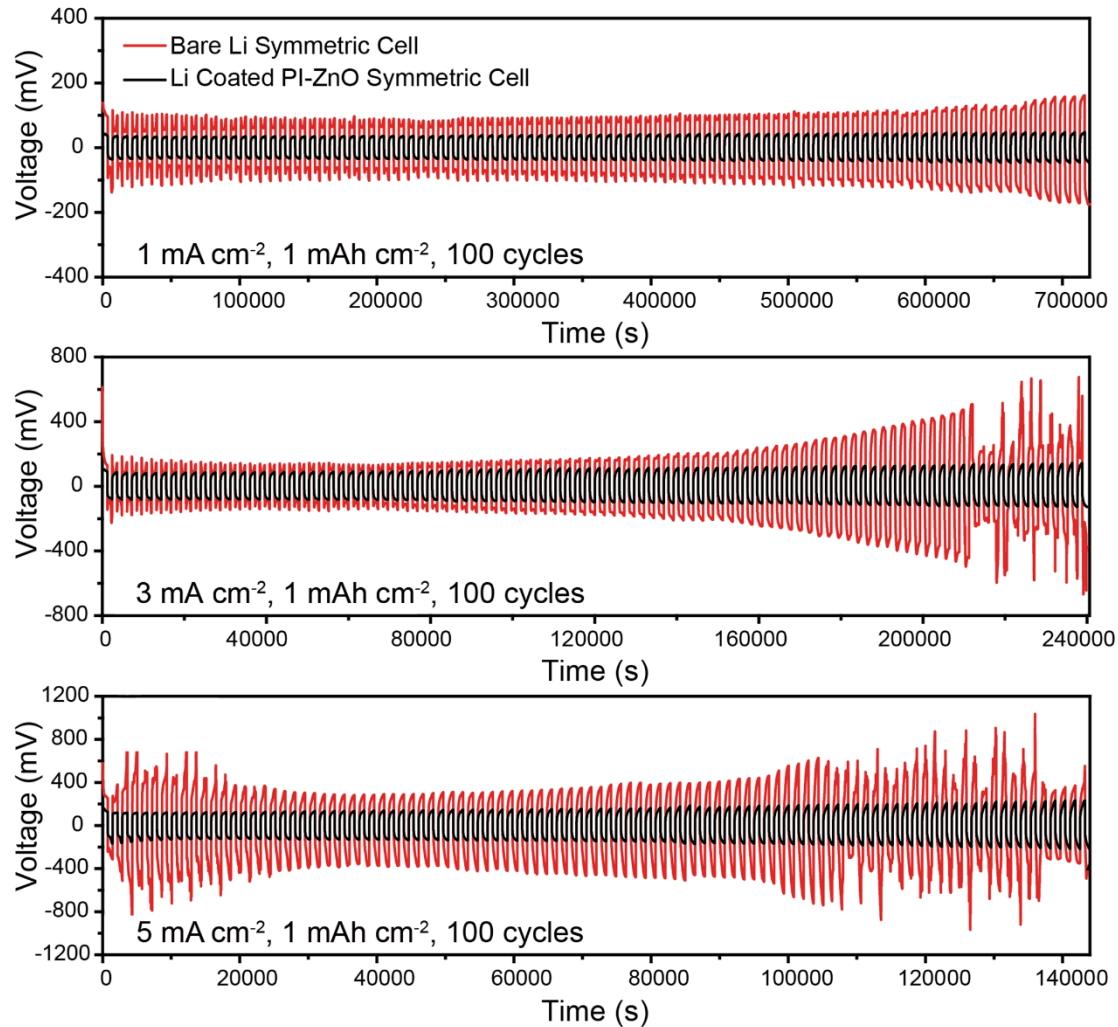
Accomplishment

Non-conductive polymeric matrix as the host for lithium metal -Lithium deposition behavior



Accomplishment

Non-conductive polymeric matrix as the host for lithium metal -Electrochemical performance



Responses to Previous Year Reviewers' Comments

Not Applicable

Collaboration and Coordination



SLAC: In-situ X-ray, Prof. Mike Toney



Companies: Amprius Inc.

- BMR program PI' s
- Professor Steven Chu

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.
- Stable interface engineering needs to be further applied on nanoporous lithium metal electrodes.

Proposed Future Work

FY 2016

- To further understand the nucleation behavior of lithium metal in different electrolytes and on different substrates.
- To integrate stable artificial interface into the stable host for lithium metal.

FY 2017

- To further improve the Coulombic efficiency of lithium metal cycling in both ether and carbonate based electrolyte.
- To achieve more stable cycling of lithium metal at high current density ($5\text{-}10\text{ mA cm}^{-2}$).
- To achieve more stable cycling of lithium metal at high areal capacity. ($3\text{-}5\text{ mAh cm}^{-2}$).

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.

