Pre-Lithiation of High-Capacity Battery Electrodes

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Project ID
bat272

Overview

Timeline

- Start: Oct 1, 2017
- End: Sep 30, 2020
- Percent complete: 85%

Barriers

Barriers of prelithiation

- Low coulombic efficiency
- Low capacity
- High chemical reactivity

Targets: high-efficiency and high-energy batteries

Budget

- Total project funding
  $1050k from DOE
- Funding for FY19 $300k
- Funding for FY20 $450k

Partners

- Collaboration
  - BATT program PI's
  - SLAC: In-situ X-ray
  - Amprius Inc.
  - Stanford: Zhenan Bao

Project Objective and Relevance

Impact

Prelithiation can effectively compensate the 1st cycle lithium loss due to SEI formation and improve the initial coulombic efficiency. It is a general method can be applied to all kinds of anode materials and improve their battery performance.

Objectives

-Increase first-cycle Coulombic efficiency via anode prelithiation.

-Design and synthesize lithiated silicon to prelithiate various anode materials.

-Increase the stability of prelithiation reagents in both dry air and ambient air conditions.

-Design different prelithiation methods to optimize the reaction process.

-Design and fabricate fully lithiated anode materials to pair with high capacity lithium-free cathodes for next generation high energy density batteries.

Milestones for FY18 and 19

Month/year	Milestones
10/2018	Fabricate free-standing LixSn/graphene or LixAl/graphene foil as an alternative to lithium metal anodes (completed)
1/2019	Demonstrate anode prelithiation reagent with specific capacity >900 mAh/g with stability in ambient air (completed)
4/2019	Demonstrate heat-free and solution-free anode prelithiation method with optimized initial coulombic efficiency (completed)
7/2019	Demonstrate the morphology and structure evolution of silicon anode after the heat-free and solution-free prelithiation treatment (completed)
10/2019	Demonstrate prelithiated anodes with high initial Coulombic efficiency and excellent cycling stability for Li-LFP full cells (completed)
1/2020	Demonstrate a new one-step heat-free dry method for anode prelithiation (completed)
4/2020	Demonstrate the controllably increased initial Coulombic efficiency of Si anodes after one-step heat-free prelithiation (on track)

Approach/Strategy

Prelithiation reagents design and synthesis

1) Compensate 1st cycle anode capacity loss with anode prelithiation reagents (Li_xSi nanoparticles).
2) Achieve improved stability of anode prelithiation reagents in the dry and ambient air condition by exploring inorganic and organic coatings, such as Li_2O, LiF and artificial SEI-coating.

Prelithiation process design

1) Utilize pressure to achieve heat-free and solution-free new prelithiation method.
2) Achieve time-efficient prelithiation by designing the simultaneous prelithiation process and cell resting process, using lithium mask as prelithiation reagents to control prelithiation amount.

Structure and property characterization

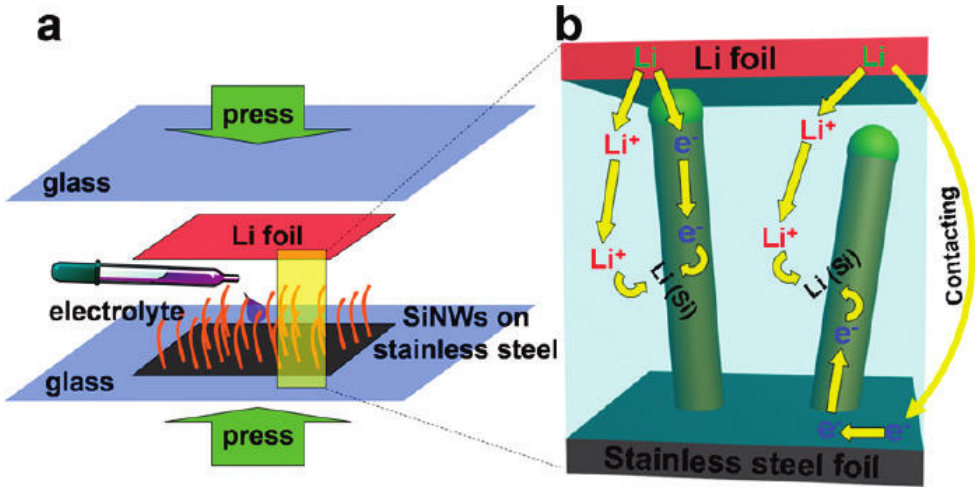
1) Ex-situ transmission electron microscopy
2) Ex-situ scanning electron microscopy
3) Ex-situ X-ray photoelectron spectroscopy
4) In operando X-ray diffraction and transmission X-ray microscopy

Electrochemical testing

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

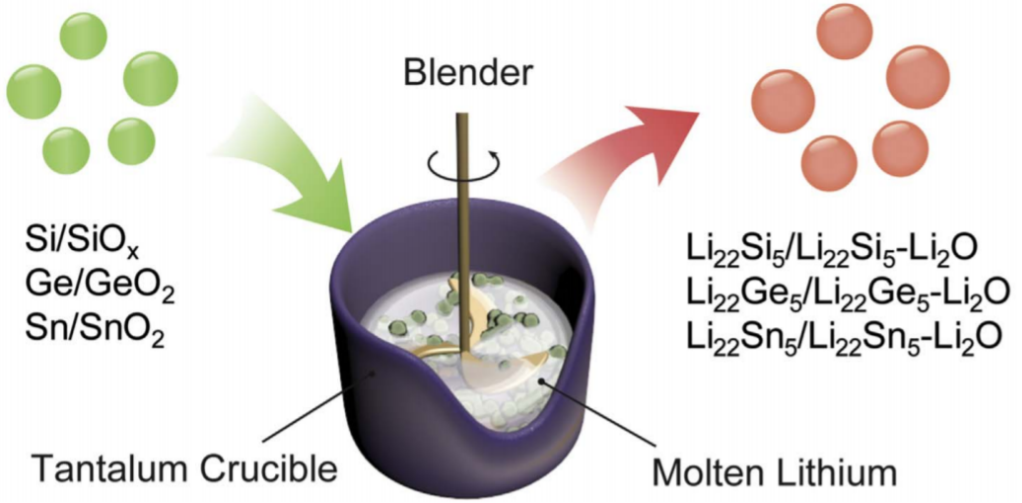
Previous Accomplishments on Prelithiation

Prelithiation of Si nanowires via electrochemical shorting mechanism



Cui group, *ACS Nano 5*, 6487 (2011)

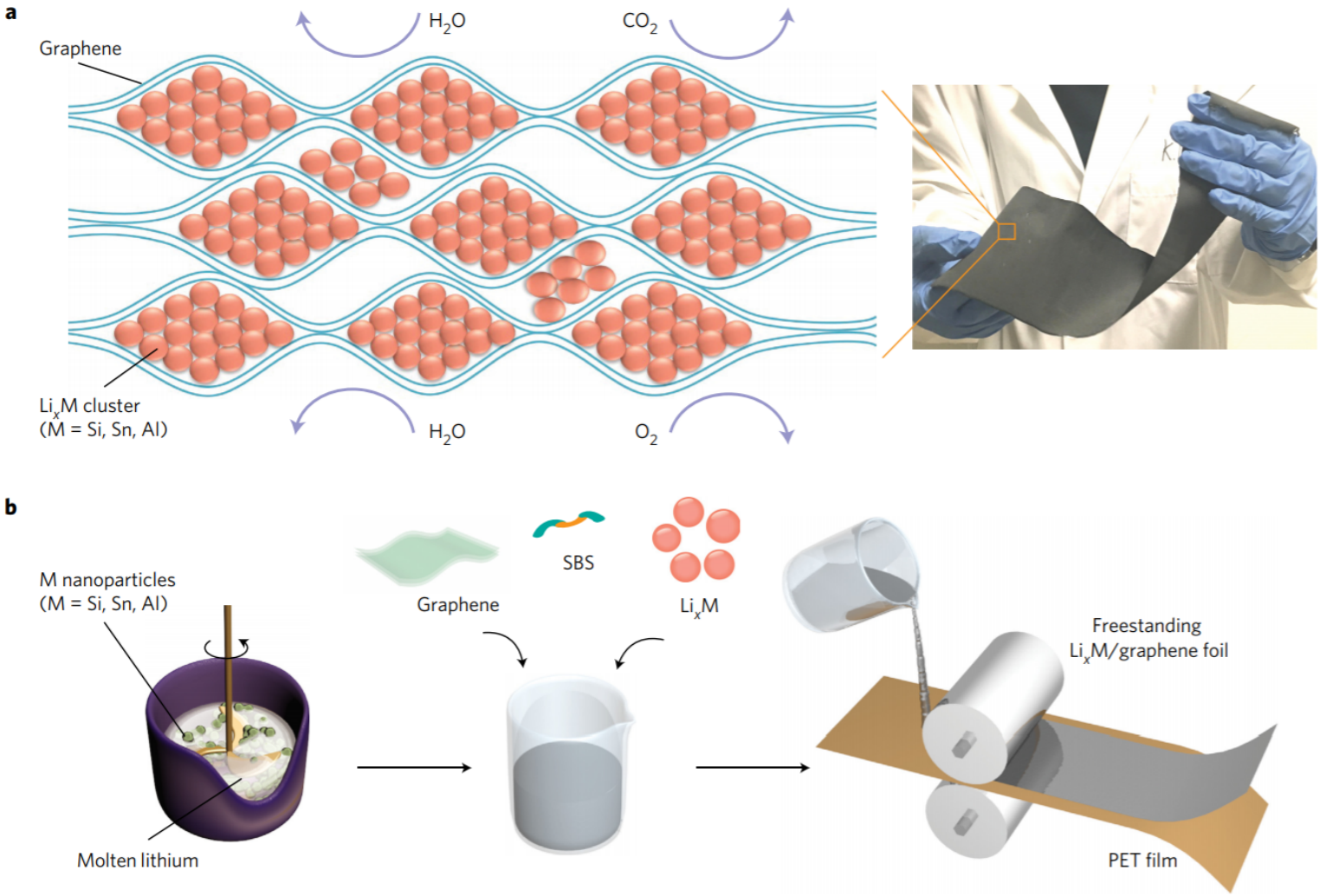
Prelithiation using Li_xM (M = Si, Ge, Sn) nanoparticles



Cui group, *Energy Storage Materials*, 10, 275 (2018)

Accomplishment

Air-stable and freestanding lithium alloy/graphene as an alternative to lithium metal anodes
-Synthesis and characterizations

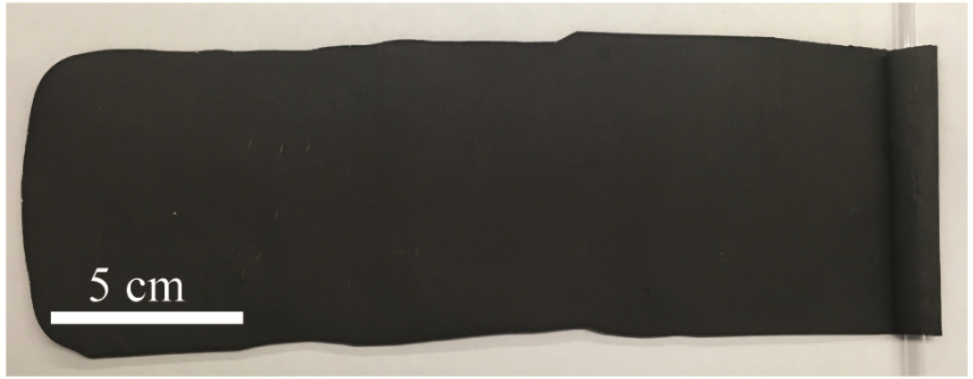


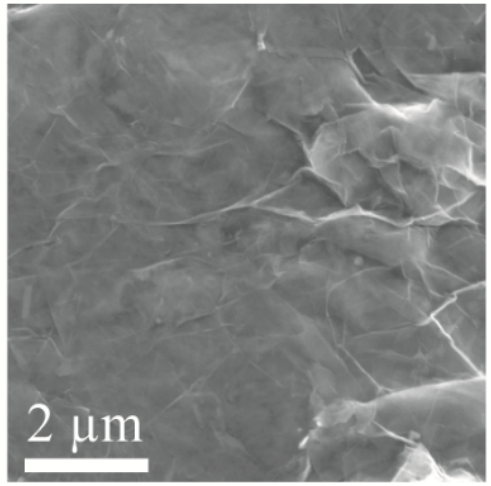
Cui group, *Nature Nanotechnology* 12, 993 (2017)

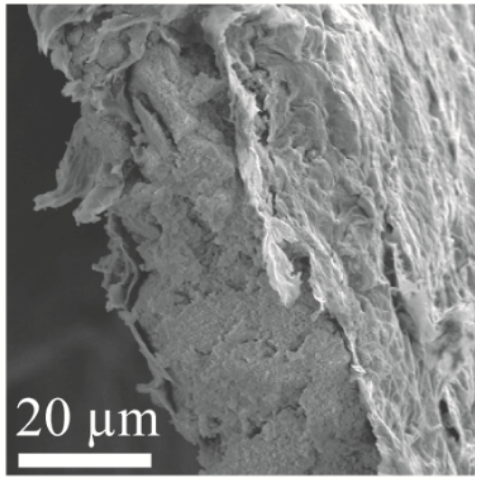
Accomplishment

Air-stable and freestanding lithium alloy/graphene as an alternative to lithium metal anodes
-Synthesis and characterizations

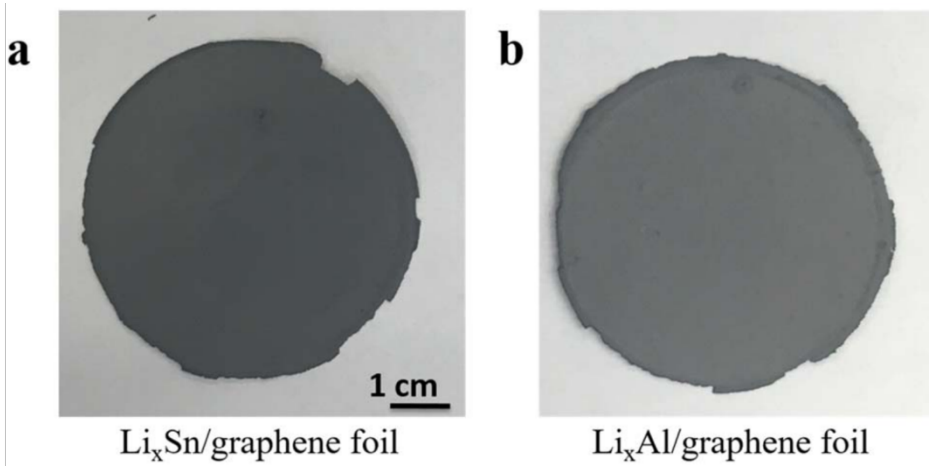
LixSi/graphene foil







LixM (M = Sn and Al) /graphene foil



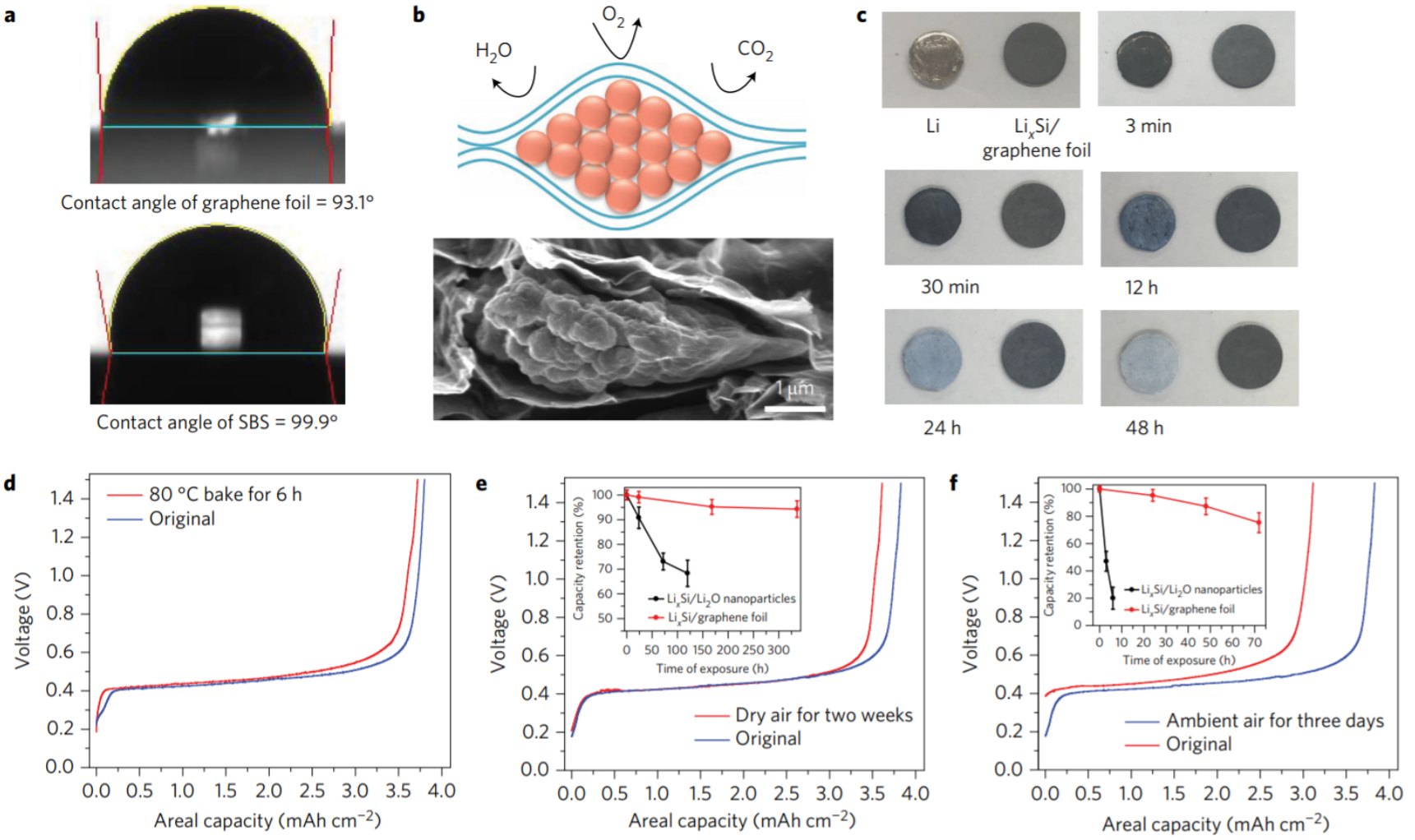
Li_xSn/graphene foil

Li_xAl/graphene foil

Cui group, *Nature Nanotechnology* 12, 993 (2017)

Accomplishment

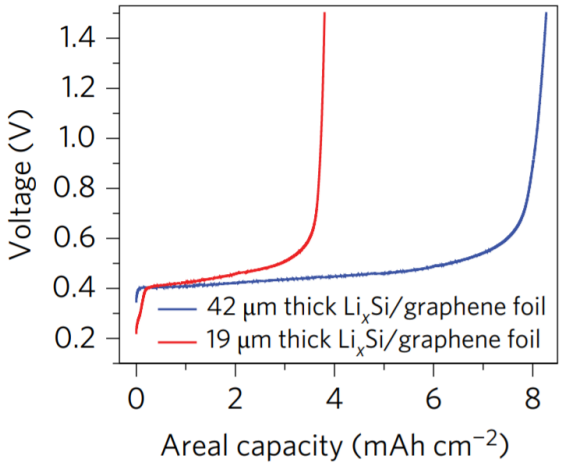
Air-stable and freestanding lithium alloy/graphene as an alternative to lithium metal anodes
-Stability in dry air and ambient air

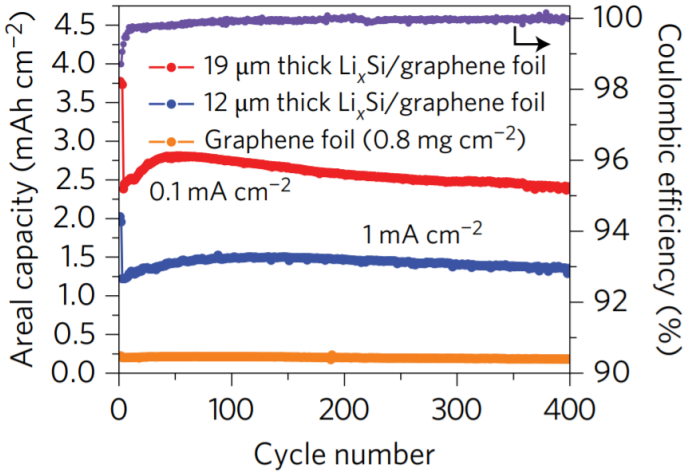


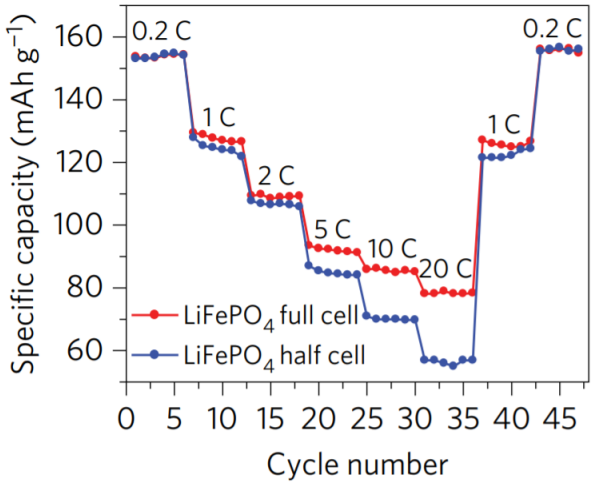
Cui group, *Nature Nanotechnology* 12, 993 (2017)

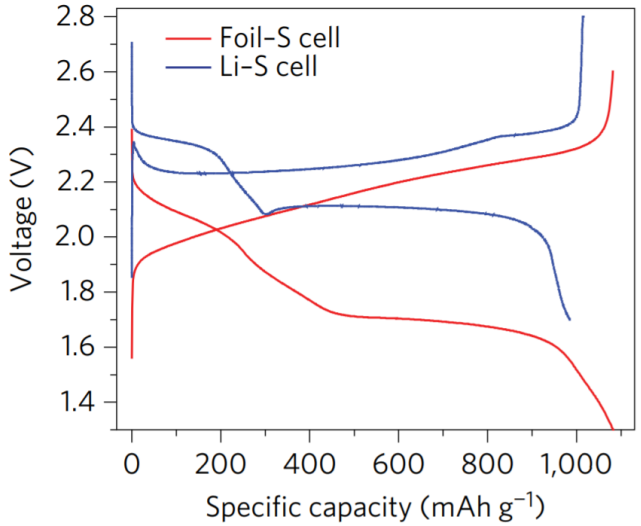
Accomplishment

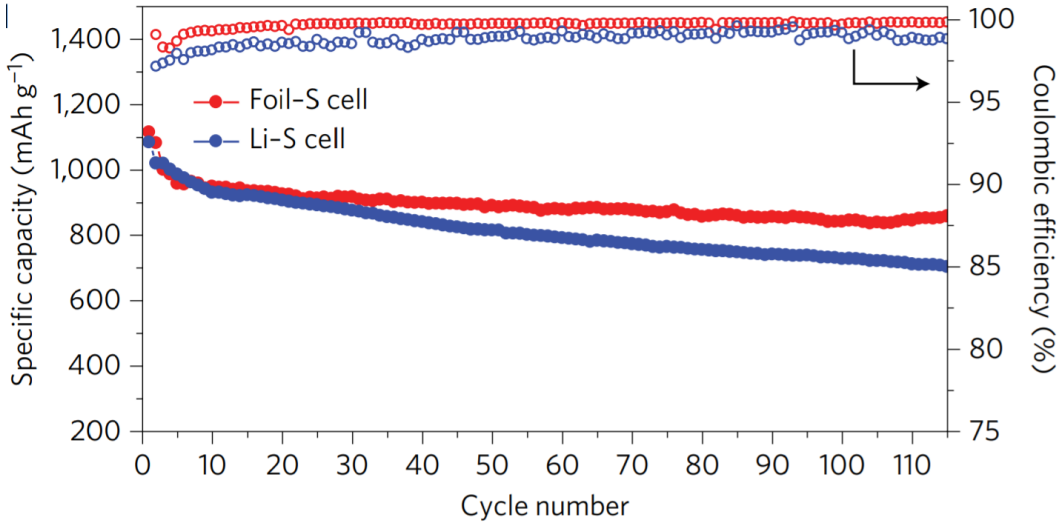
Air-stable and freestanding lithium alloy/graphene as an alternative to lithium metal anodes
-Battery performance







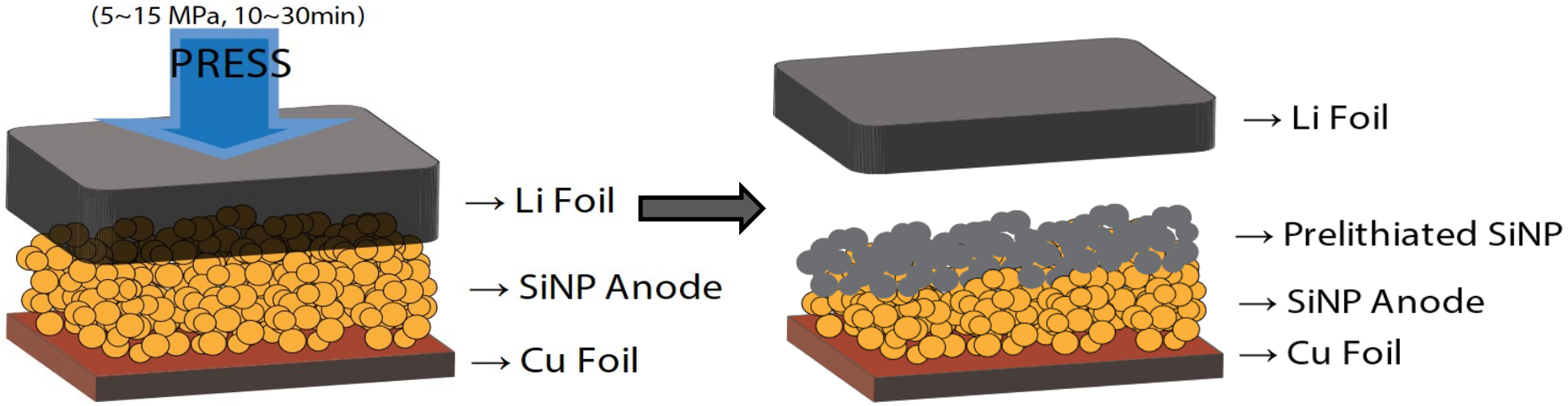


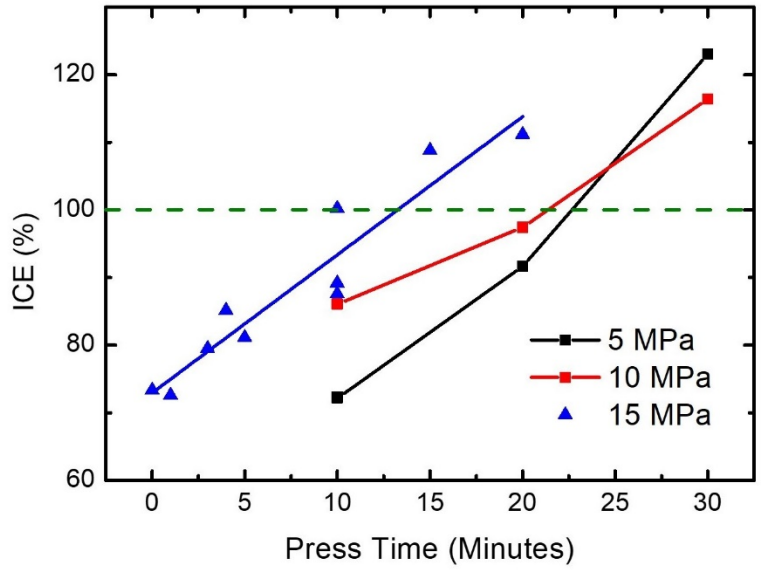


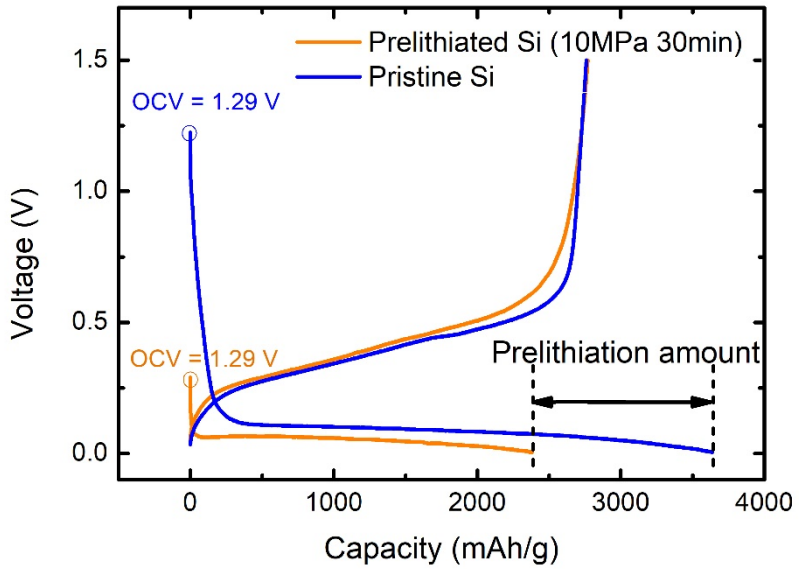
Cui group, *Nature Nanotechnology* 12, 993 (2017)

Accomplishment

A new heat-free and solution-free anode prelithiation method via pressing -schematic and initial Coulombic efficiency improvement



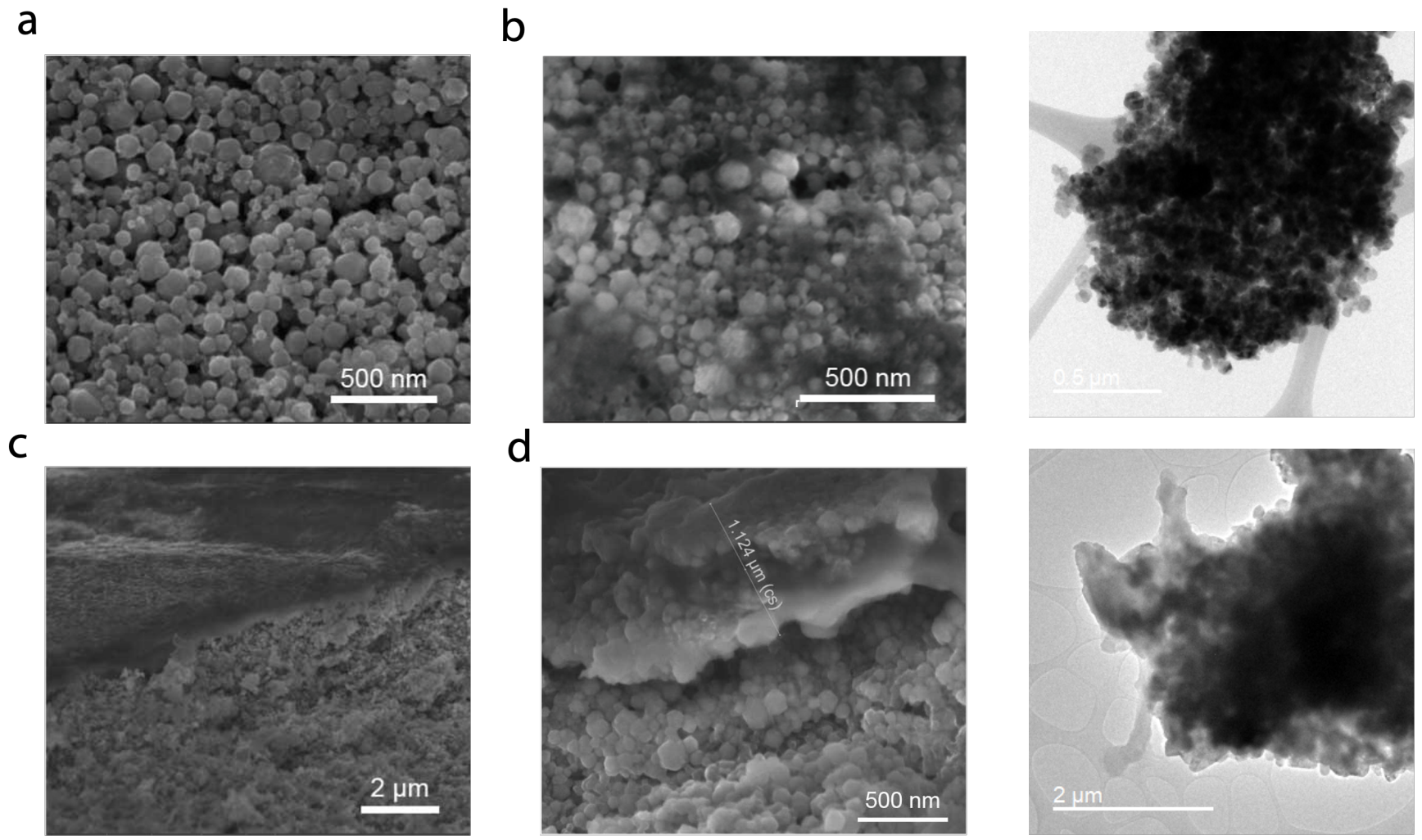




paper is under preparation

Accomplishment

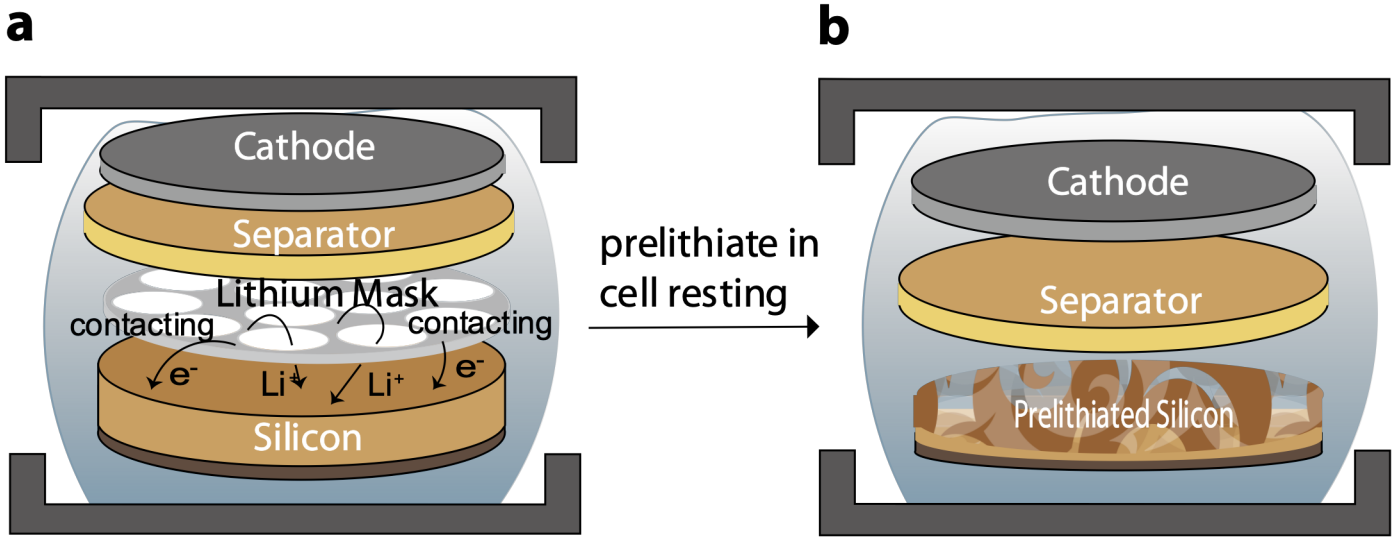
A new heat-free and solution-free anode prelithiation method via pressing
-morphology and structure evolution



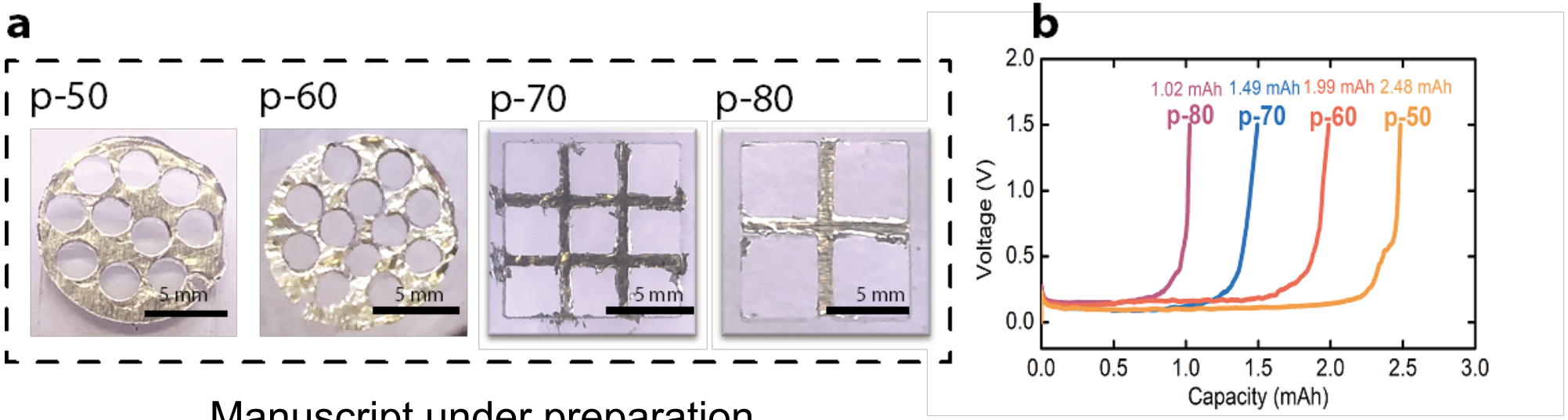
paper is under preparation

Accomplishment

Thin lithium mask for controllable one-step heat-free prelithiation -schematic and lithium mask reagent



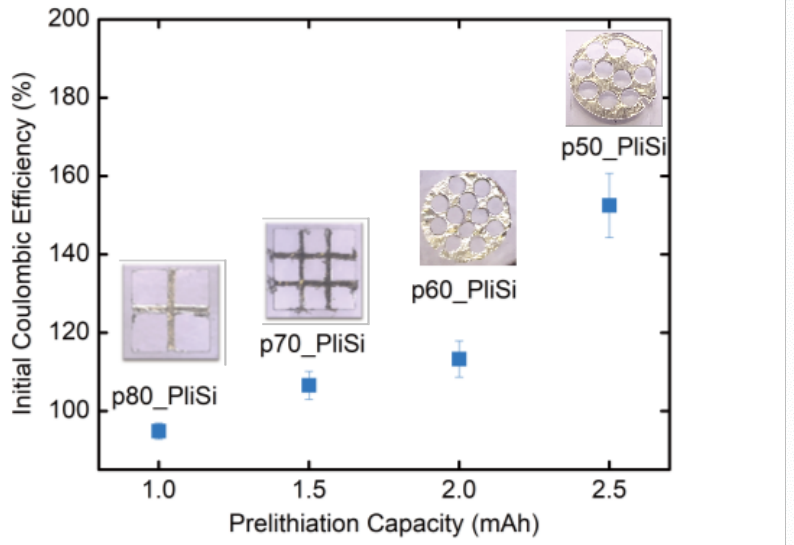
Solution-Free
Heat-Free
Time efficient
Controllable

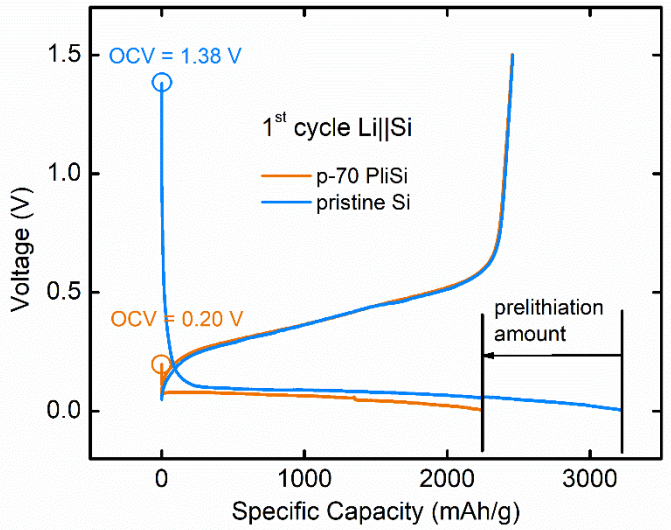


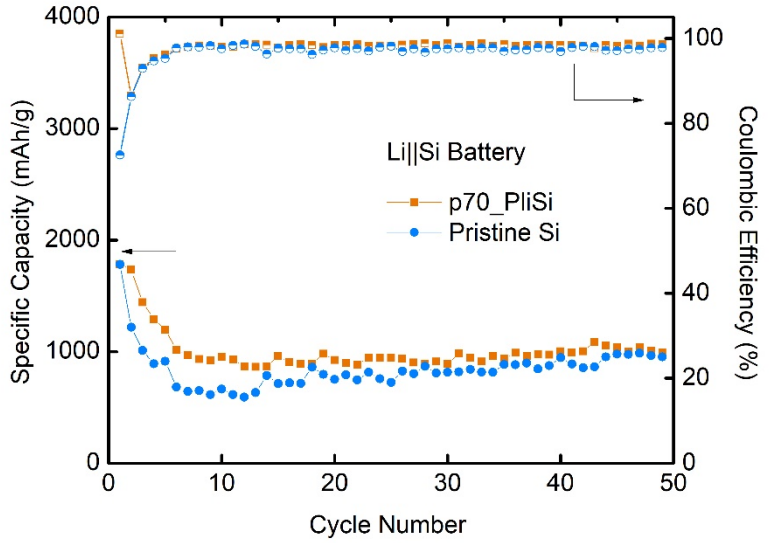
Manuscript under preparation

Accomplishment

Thin lithium mask for controllable one-step heat-free prelithiation -battery performance







Cycle	Pristine Si CE%	p70_ PliSi CE%
1	72.5	101.2
2	86.3	86.4
3	92.9	93.1

Manuscript under preparation

Responses to Previous Year Reviewers' Comments

Not applicable

Collaboration and Coordination

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

Companies: Amprius Inc.

Stanford: Professor Zhenan Bao

Remaining Challenges and Barriers

- It is difficult to further decrease the capacity in lithium mask to pair it with relatively high initial CE anodes like graphite.

- The interaction between prelithiation reagent and the electrolyte and its impact in battery performance remain unclear.

- It is difficult to fabricate Li-rich anode materials with fine structures and stable cycling.

Proposed Future Work

- To develop ultra-thin Li as new type of prelithiation reagent with low capacity for broadening the prelithiation application in different anodes.
- To explore other materials with high prelithiation capacity and stability.
- To explore other prelithiation mechanism with high efficiency and controllable prelithiation amount.
- To understand the interaction between prelithiation reagents and the electrolyte by cyro-EM and other advanced characterization techniques.
- To synthesize fully-lithiated anode materials with fine structures and stable cycling and then pair them with high capacity Li-free cathode materials.
- To synthesize over-lithiated anode materials as new type of lithium metal for broader applications.

Summary

- **An air-stable and freestanding lithium alloy/graphene foil is developed as an alternative to lithium metal anodes.**

- A large-scale free-standing lithium alloy/graphene foil (8 cm * 24 cm) can be fabricated.
- The lithium alloy/graphene foil shows high stability in both dry air and ambient air.
- The lithium alloy/graphene foil can be paired with lithium-free cathode and shows good cyclability.

- **A new heat-free and solution free prelithiation method is developed via pressing.**

- The method is applied to partially prelithiate silicon anodes, whose initial coulombic efficiency can be improved in a controllable manner.
- The morphology characterization reveals the surface (~1 μm) of the silicon anode is prelithiated after pressing.

- **A new one-step heat-free prelithiation method is developed using lithium mask as prelithiation reagent.**

- The method can achieve simultaneous prelithiation and cell resting, which optimizes the efficiency of prelithiation reaction.
- The degree of prelithiation can be controlled by the porosity of lithium mask.