PennState

Multifunctional Lithium-Ion Conducting Interfacial Materials for Lithium-Metal Batteries

PI: Donghai Wang

The Pennsylvania State University

June 21-25, 2021

Project ID: bat513

Overview

Timeline

- Project start date: April 01, 2019
- Project end date: September 30, 2021
- Percent complete: 90%

Budget

- Total project funding
  - DOE share: $800K
  - Contractor share: $90K
- Funding received in FY 2020 and FY 2021
  - DOE share: $450,327
  - Contractor share: $45,000

Barriers

- Protective layers for Li metal anode
  - Thin, dense and uniform protective coating
  - Stable to over wide voltage range
  - Scalable and compatible with pouch cell

Partners

- Project lead
  - PSU
- Interactions/collaborations
  - Ashland

Relevance

Objectives

- To research, develop, and demonstrate multifunctional Li-ion conducting interfacial materials as a protective layer for Li metal anodes, enabling Li metal anodes to cycle with a high efficiency of ~99.9% at a high electrode capacity (4 mAh/cm^2) and a high current density (>2 mA/cm^2) for 400 cycles.
- Demonstrate Li-metal battery cells with an energy density of ~300 Wh/kg and a ≥80% capacity retention over 300 cycles using Li metal anodes with the developed protective layer.

Impacts

- Develop a new hybrid Li-ion conductor that enables safe and high-performance Li metal anodes.
- The use of the developed Li metal anodes enable Li-metal oxide batteries with high energy density and long cycling life.
- Promote increased adoption of electric and plug-in hybrid electric vehicles (EVs and PHEVs), and reduce petroleum consumption in the transportation sector by helping battery-powered vehicles become accepted by consumers as a reliable source of transportation.

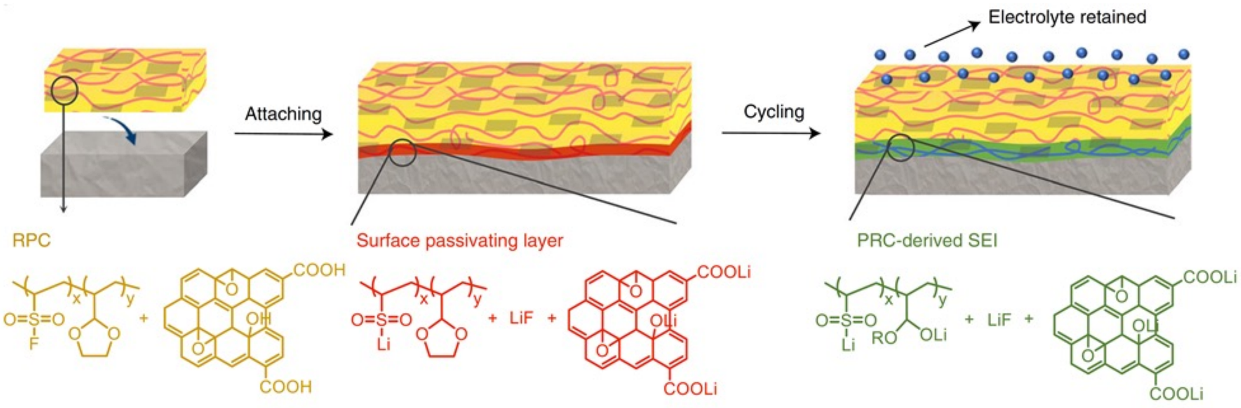
Milestones

Date	Milestones	Status
Sep. 2019	Identify the optimal composition of the Li-ion conducting materials and demonstrate Li metal batteries under high-capacity (4 mAh/cm^2) and lean-electrolyte (7 $\mu L/mAh$) conditions.	Complete
Mar. 2020	Optimize the Li-ion conducting materials based on the diagnostic results	Complete
Jul. 2020	Synthesis of the polymer (500 gram/batch) using a convenient and low-cost method	Complete
Jan. 2021	Develop protected Li anodes using optimal electrolyte, which have 99.9% CE of Li deposition at a capacity of 4 mAh/cm^2	Complete
Sep. 2021	Demonstrate pouch cells of Li metal batteries with a cycle life of 300 cycles under high-capacity (4 mAh/cm^2), lean-Li (2-fold excessive Li), and lean-electrolyte (4 $\mu L/mAh$) conditions.	In progress

Approach - Li Metal Protection Techniques

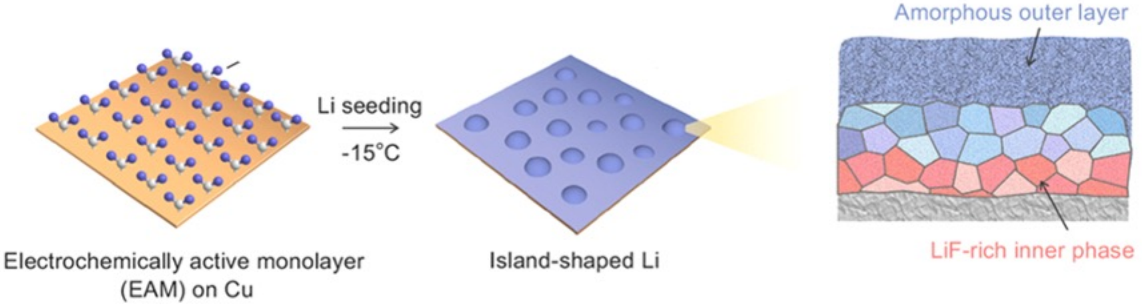
Li metal protection

I



Novel **reactive polymer coating** **onto Li metal anode to efficiently improve the Li metal battery performance under lean electrolyte, limited Li excess and high capacity conditions.**

II

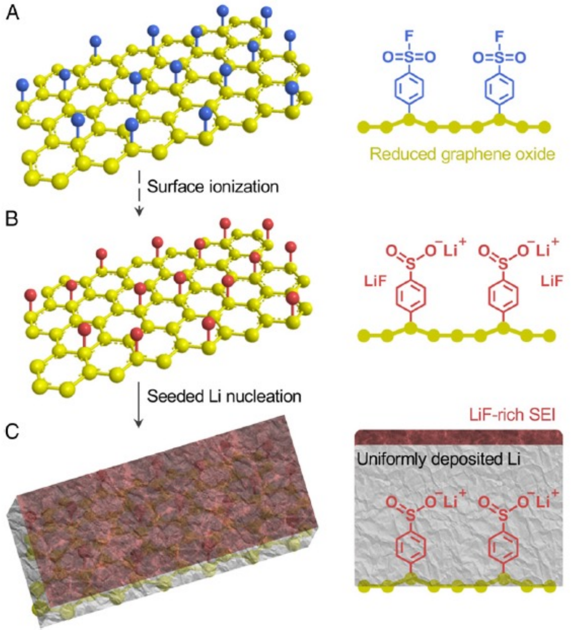


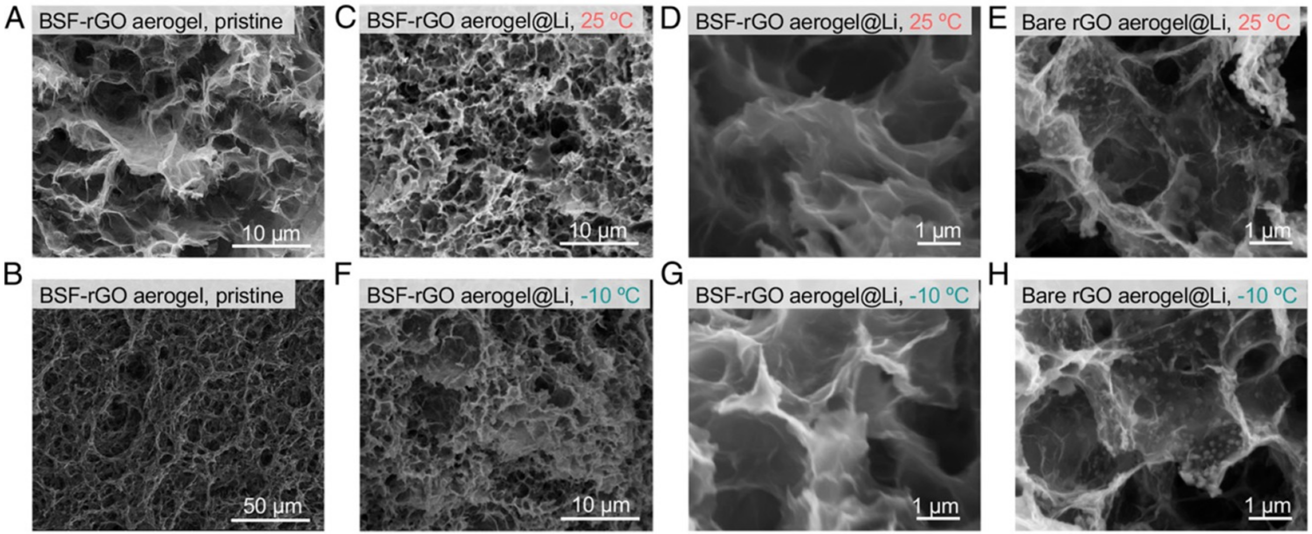
An **electrochemically active monolayer (EAM)** **strategy, can enable excellent cycling performance under high-current-density conditions.**

Nature Materials 2019, 18, 384-389 and *Nature Energy* 2020 5, 534–542.

Technical Accomplishment

1. Apply electrochemically active monolayer (EAM) to 3D porous rGO matrix

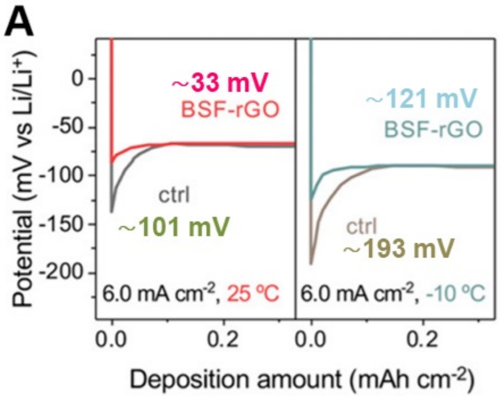




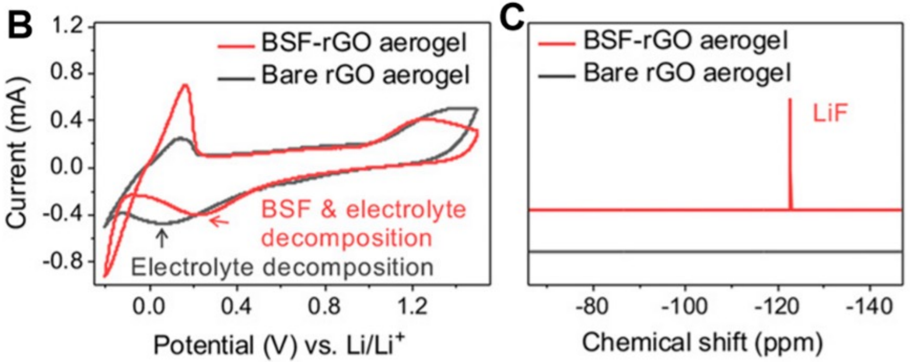
Uniform Li deposition regulated by BSF-rGO at 25 ^{o}C/-10 ^{o}C, under high-current-density conditions (Li deposition amount of 6.0 mAh cm^{-2} at a current density of 6.0 mA cm^{-2}, after 50 cycles)

Proc. Natl. Acad. Sci. U.S.A. **2020**, 117 (48), 30135–30141.

Electrochemical activity of the BSF on the rGO aerogel



Lower overpotentials at 25 °C and −10 °C, suggesting the BSF-rGO can effective regulate Li deposition.

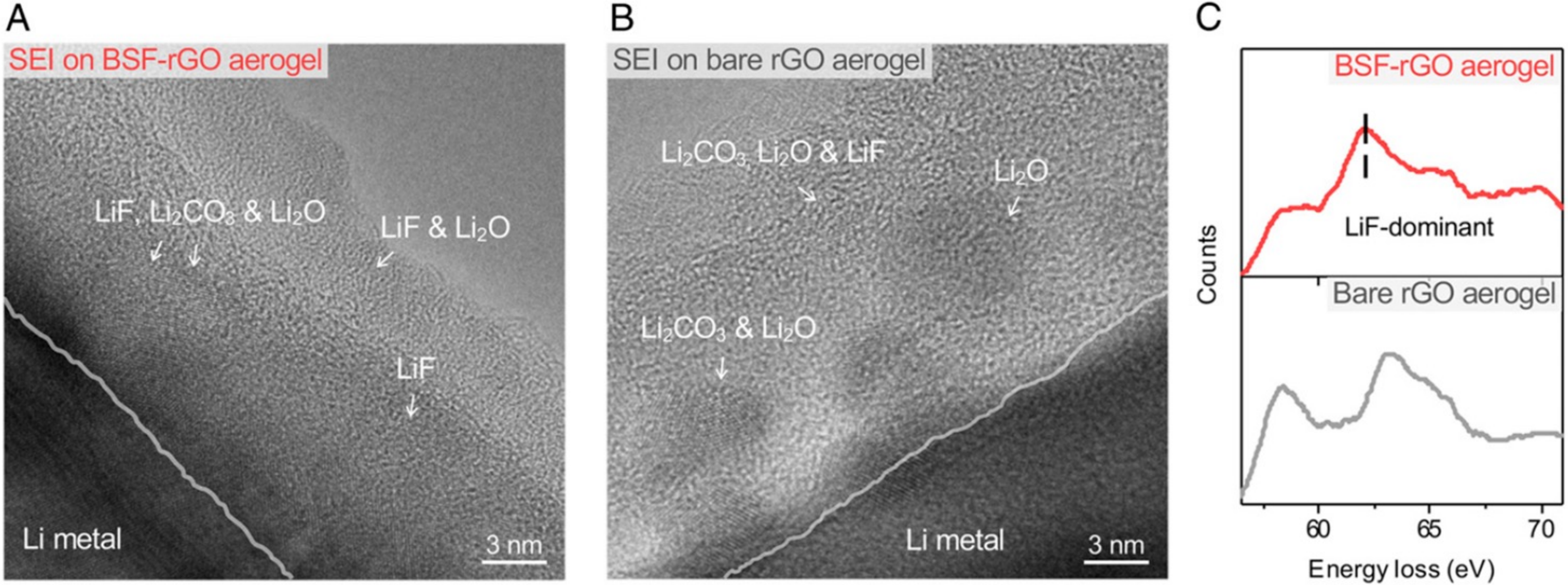


BSF is involved in SEI formation;
BSF decomposition occurs before the electrolyte.

LiF was detected in the decomposition products by NMR.

Proc. Natl. Acad. Sci. U.S.A. **2020**, 117 (48), 30135–30141.

Nanostructure of SEI enabled by the BSF-rGO aerogel

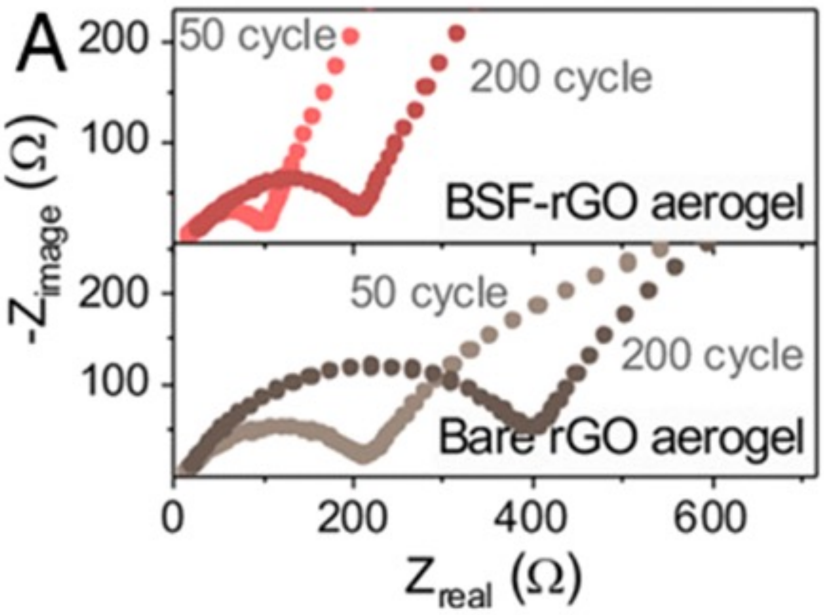


The SEI in presence of BSF-rGO aerogel:

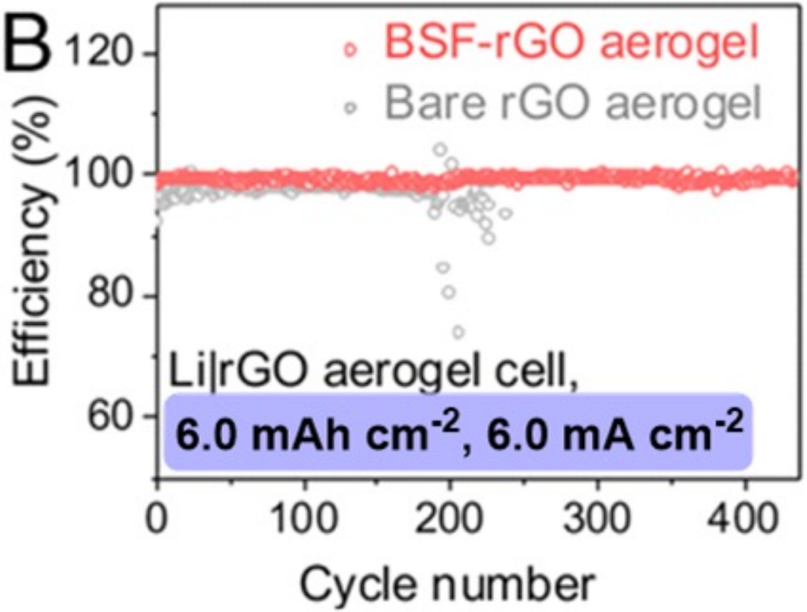
Homogeneous; an amorphous layer with rich LiF nanocrystals and small amount of Li_2CO_3 and Li_2O nanocrystals.

Proc. Natl. Acad. Sci. U.S.A. **2020**, 117 (48), 30135–30141.

Stable cycling of BSF-rGO aerogel@Li anodes



Time dependent Nyquist plots, Li|Li cells at −10 °C



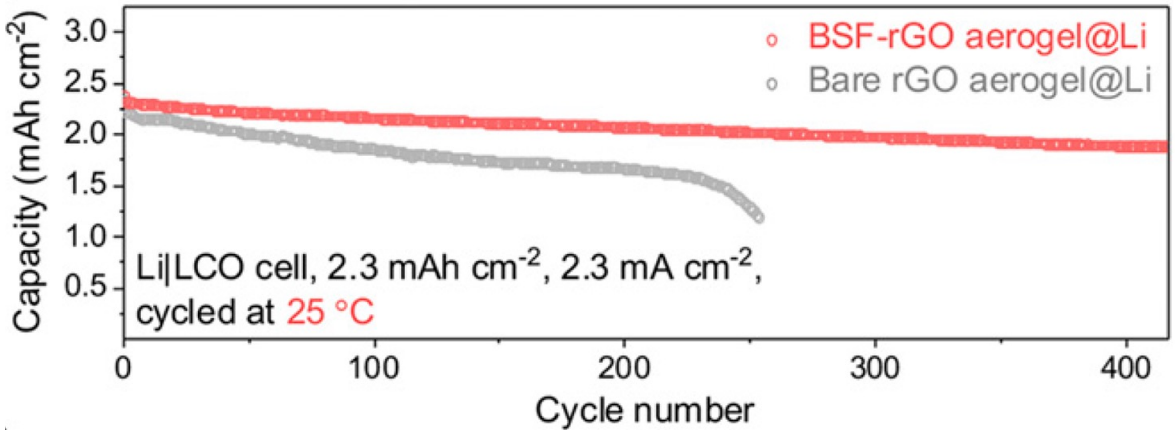
Coulombic efficiency testing, Li|rGO aerogel cells

The limited impedance increasing indicated the BSF-rGO can suppress SEI reformation.

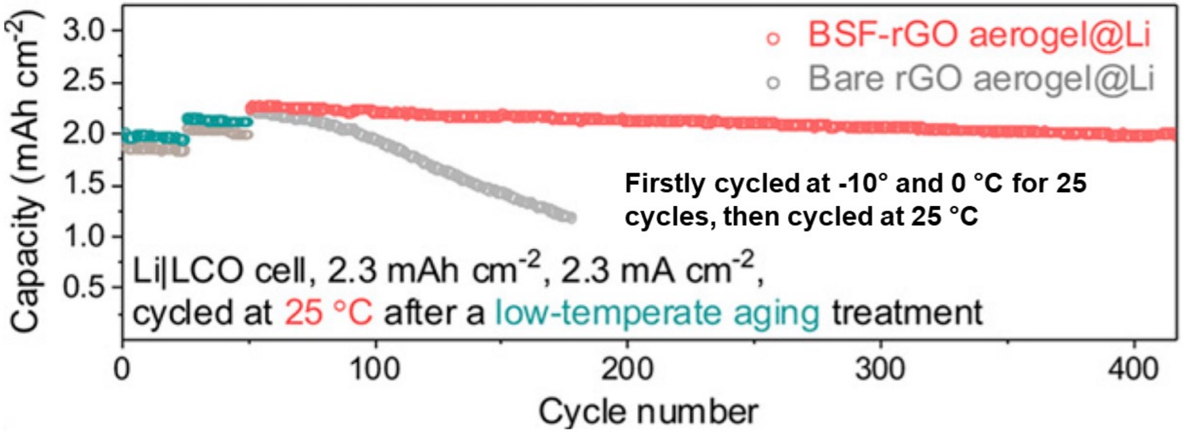
Average Coulombic efficiency of 99.2% over 400 cycles at high current density of 6.0 mA cm^{-2}.

Proc. Natl. Acad. Sci. U.S.A. **2020**, 117 (48), 30135–30141.

Electrochemical performance enhanced by BSF-rGO aerogel@Li anodes



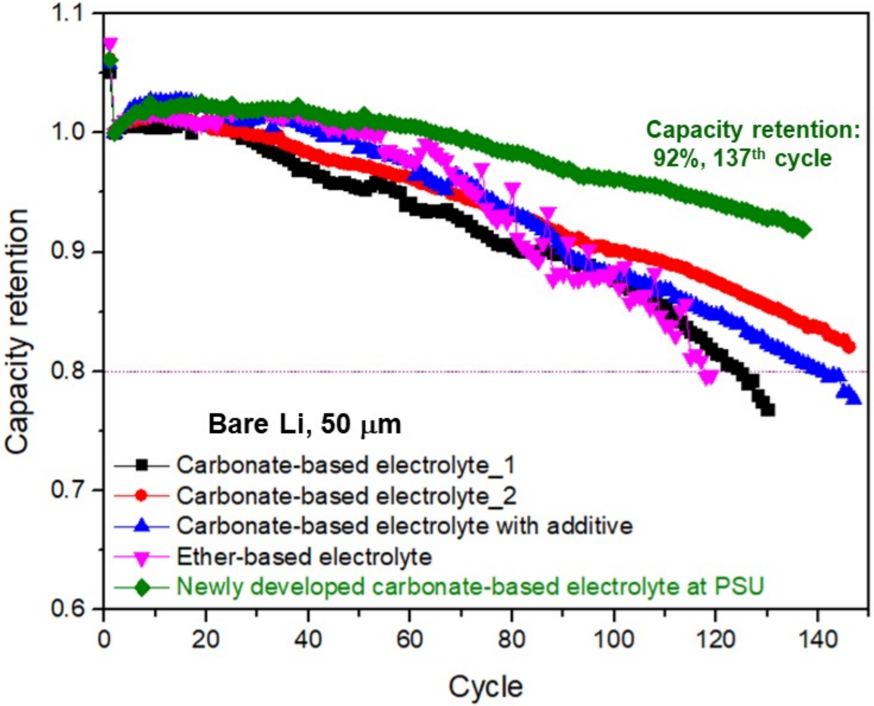
The cell with the BSF-rGO aerogel@Li anode can deliver a capacity retention of **83.6% after 400 cycles** at 1C rate and 25 °C.

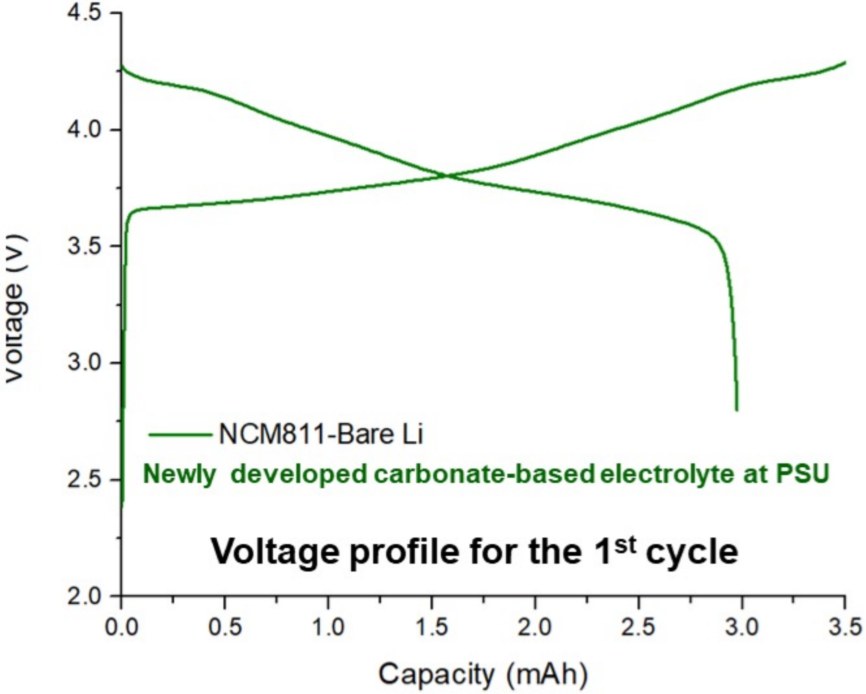


The cell with the BSF-rGO aerogel@Li anode, firstly cycled at −10 and 0 °C for 25 cycles, can deliver a capacity retention of **85.3% after 400 cycles** at 1C rate.

Proc. Natl. Acad. Sci. U.S.A. **2020**, 117 (48), 30135–30141.

2. New carbonate-based electrolyte for Li metal battery



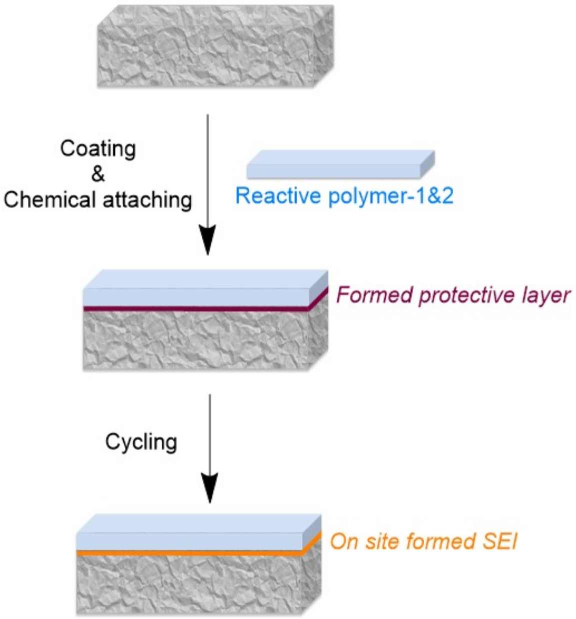


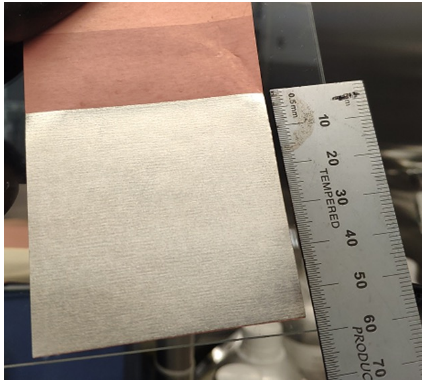
Electrolyte: 30 μL (10 μL/mAh) for all cases; Charge to 4.3 V, discharge to 2.8 V; 0.2C charge/0.5C discharge

A new carbonate-based electrolyte was developed, can efficiently improve the cycling stability of Li metal batteries under limited Li excess (50 μm) and high capacity (NCM811, areal capacity: 3.5 mAh/cm^2) conditions.

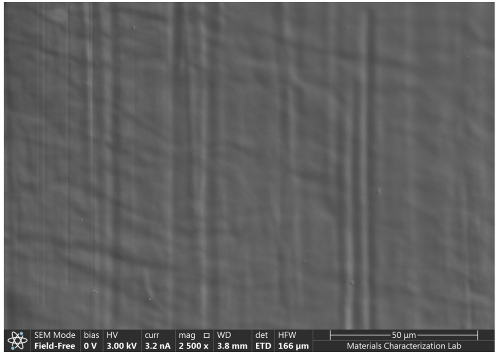
Technical Accomplishment

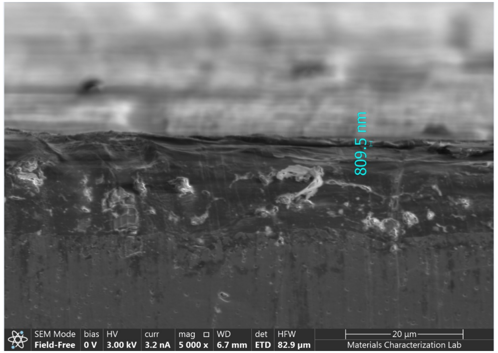
3. Novel polymers coating for Li metal anode protection





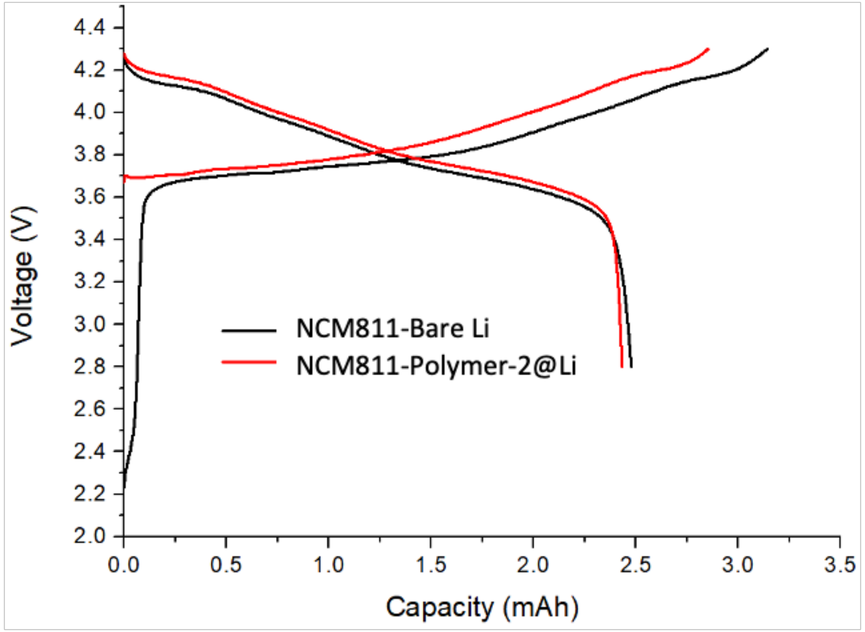
Polymer-2@Li

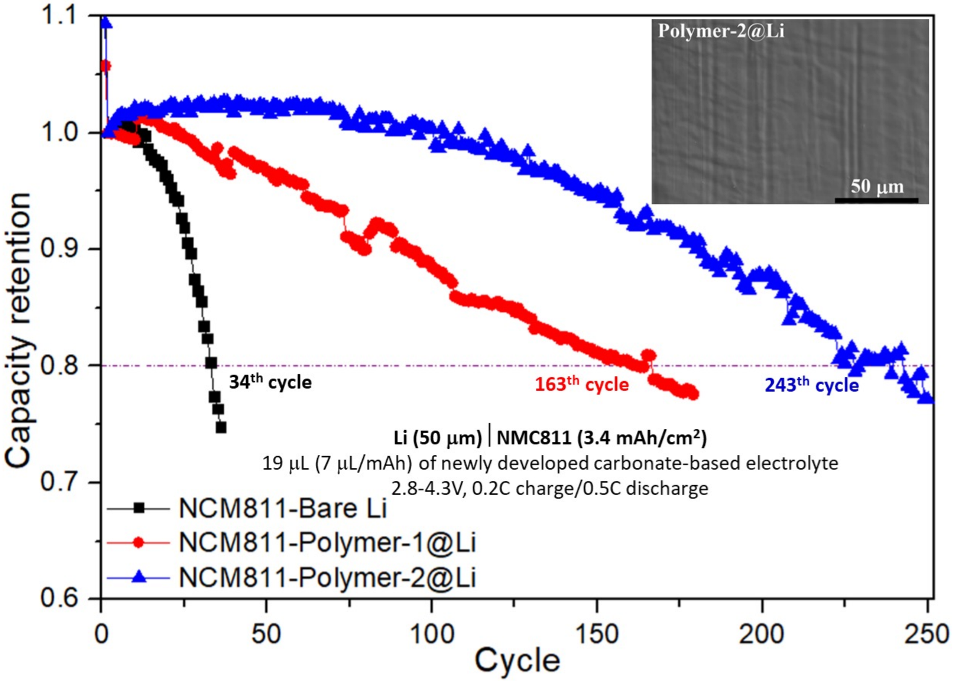




Both of the novel polymer-1 and polymer-2 can efficiently improve the Li metal battery performance.
Polymer-2@Li anode delivered a capacity retention of 80% after 243 cycles at high areal capacity and lean electrolyte conditions.

3. Novel polymers coating for Li metal anode protection

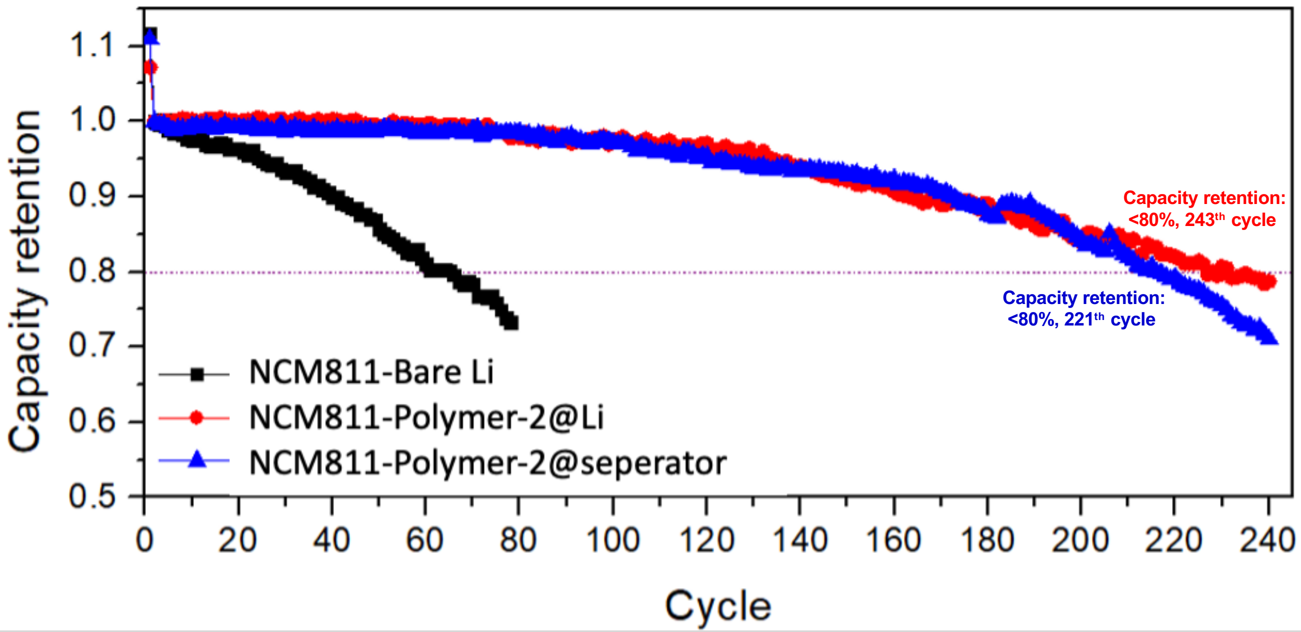




Both of the novel polymer-1 and polymer-2 can efficiently improve the Li metal battery performance.
Polymer-2@Li anode delivered a capacity retention of 80% after 243 cycles at high areal capacity and lean electrolyte conditions.

4. Novel polymers coating on separators for Li metal anode protection

- **Cycling stability comparison**



NCM811 (areal capacity: 3.4 mAh/cm²).
Lean electrolyte: E/C 7–10 μL/mAh, carbonate-based electrolyte for all cases.
Charge to 4.3 V, discharge to 2.8 V.
0.2C charge/0.5C discharge

Responses to Previous Year Comments

Comment 1: "Bottom-up design approaches were adopted to tackling the stability issue of a metallic Li anode. In the project, both an RPC and EAM were utilized to suppress the growth of Li dendrite. The advantage of these approaches is that the formation of the protective layer was driven by thermodynamics. However, the components used were electrochemically active or electronically conductive. The reviewer stated that the potential impact of residual electronic-conductive components is unknown."

Response 1: We thank the reviewer for the comments. The components used are electronically insulating. The residual components are ionically conductive and electronically insulating that can promote uniform Li flux and work as a polymeric SEI protection layer for Li metal anode.

Comment 2: "The reviewer remarked that the presentation needs to address two issues: the function of the GO materials and the interaction of the polymer with GO materials; and the mechanism of Li-ion transport in this composite layer."

Response 2: We thank the reviewer for the suggestions. The GO composite was employed to offer mechanical strength and help prevent Li dendrite growth upon cycling. The understanding of the Li-ion transport mechanism within the GO composite still needs further study.

Partners/Collaborators

- Collaboration with Dr. Alan Goliaszewski at Ashland Specialty Ingredients G.P. on the scale-up preparation of the Li-ion conducting materials.

- Collaboration with Dr. Adri van Duin on computational modeling from Penn State University.

Remaining Challenges and Barriers

- Further prevent the side reaction between electrolyte and protected Li metal anode.
- Completely suppress the Li dendrite formation.
- Application of the protected Li metal anodes under practical conditions.

Proposed Future Work

Ongoing (FY21)	Demonstrate pouch cells of Li metal batteries with a cycle life of 300 cycles under high-capacity (4 mAh/cm^2), lean-Li (2-fold excessive Li), and lean-electrolyte (4 $\mu L/mAh$) conditions.

Summary

- Develop a novel BSF-rGO aerogel as the Li metal anode host though chemically covalent bonding approach, to stabilize the interface of Li metal anodes under high-current-density conditions (6 mA cm^{-2}).

- Develop novel polymer-A-1 and polymer-P-1 for Li metal anode protection to enable long-cycling Li metal cell with a capacity retention of 80% after 242 cycles under lean electrolyte (7 μL/mAh), limited Li excess (50 μm) and high capacity conditions (3.4 mAh/cm^2).

Acknowledgement

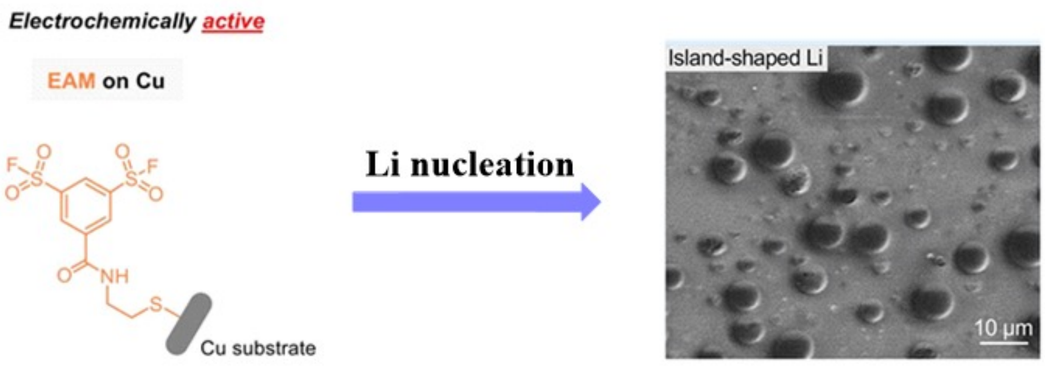
Support from David Howell and Tien Duong

at the US Department of Energy’s Office of Vehicle Technologies

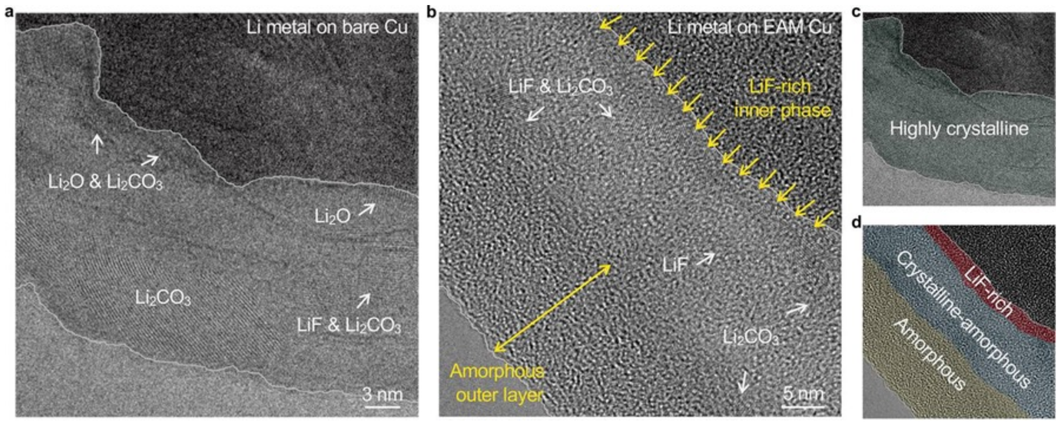
is greatly appreciated.

Technical Back-Up Slides

EAM-Regulated Li nucleation and SEI



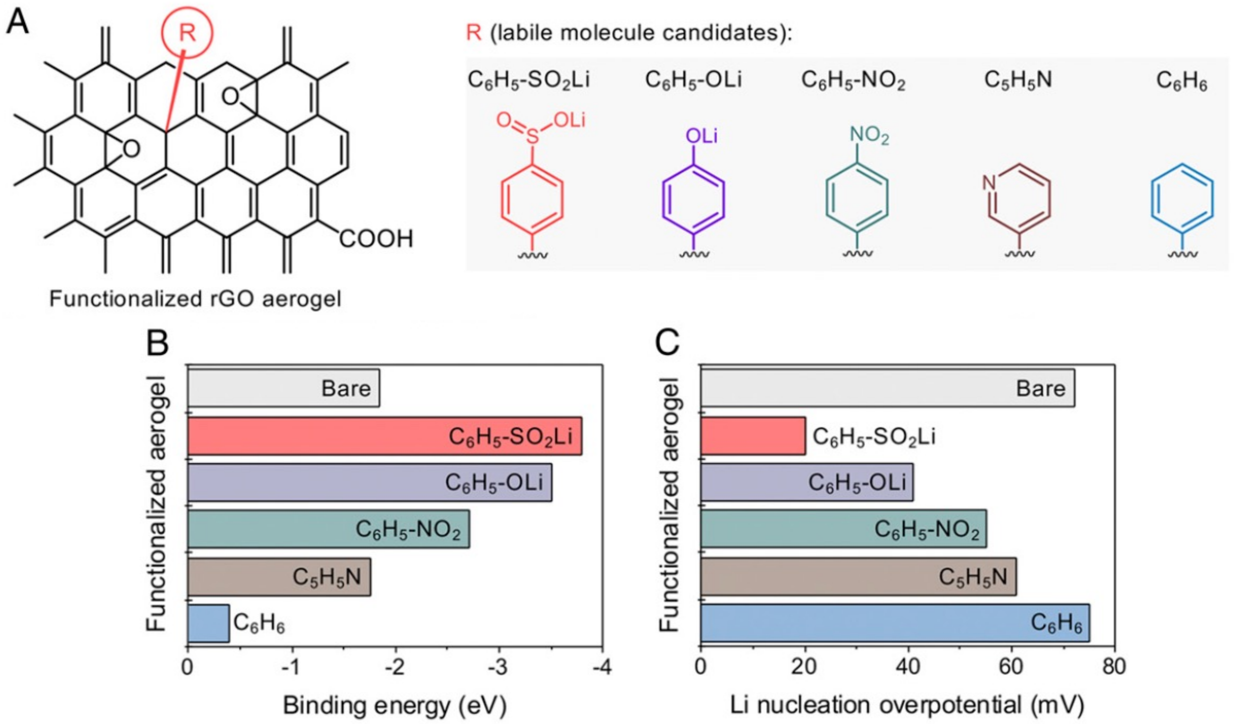
The electrochemical active monolayer (EAM) carrying benzenesulfonyl fluoride enables the island-shaped Li nucleation.



The EAM modification on Cu providing the LiF-rich inner phase and amorphous outer layer, can efficiently improve the cycling performance of Li metal batteries at -15 ^{o}C.

Nature Energy ***2020****, 5, 534–542.*

Functionalization of the rGO aerogel surface by conjugated molecules



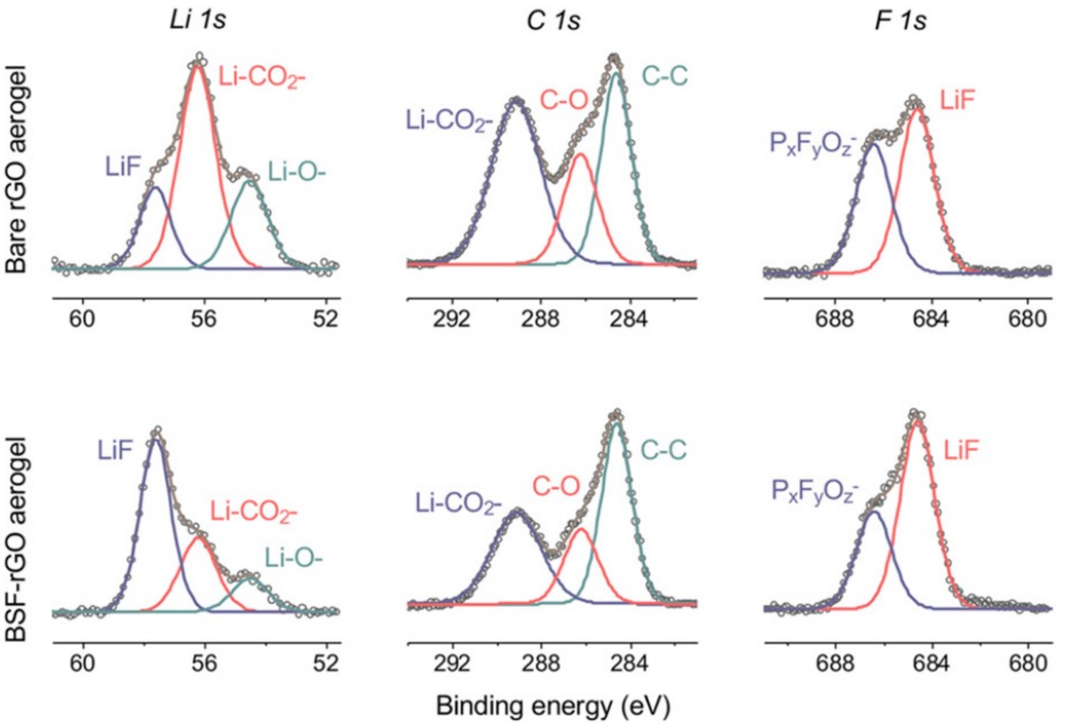
Comparison of the binding energy for Li atoms

Comparison of Li nucleation overpotential

BSF-Derived anion, benzenesulfonate, offered the highest Li binding energy (−3.79 eV) and the lowest Li nucleation overpotential (~20 mV) among the candidates.

Proc. Natl. Acad. Sci. U.S.A. **2020**, 117 (48), 30135–30141.

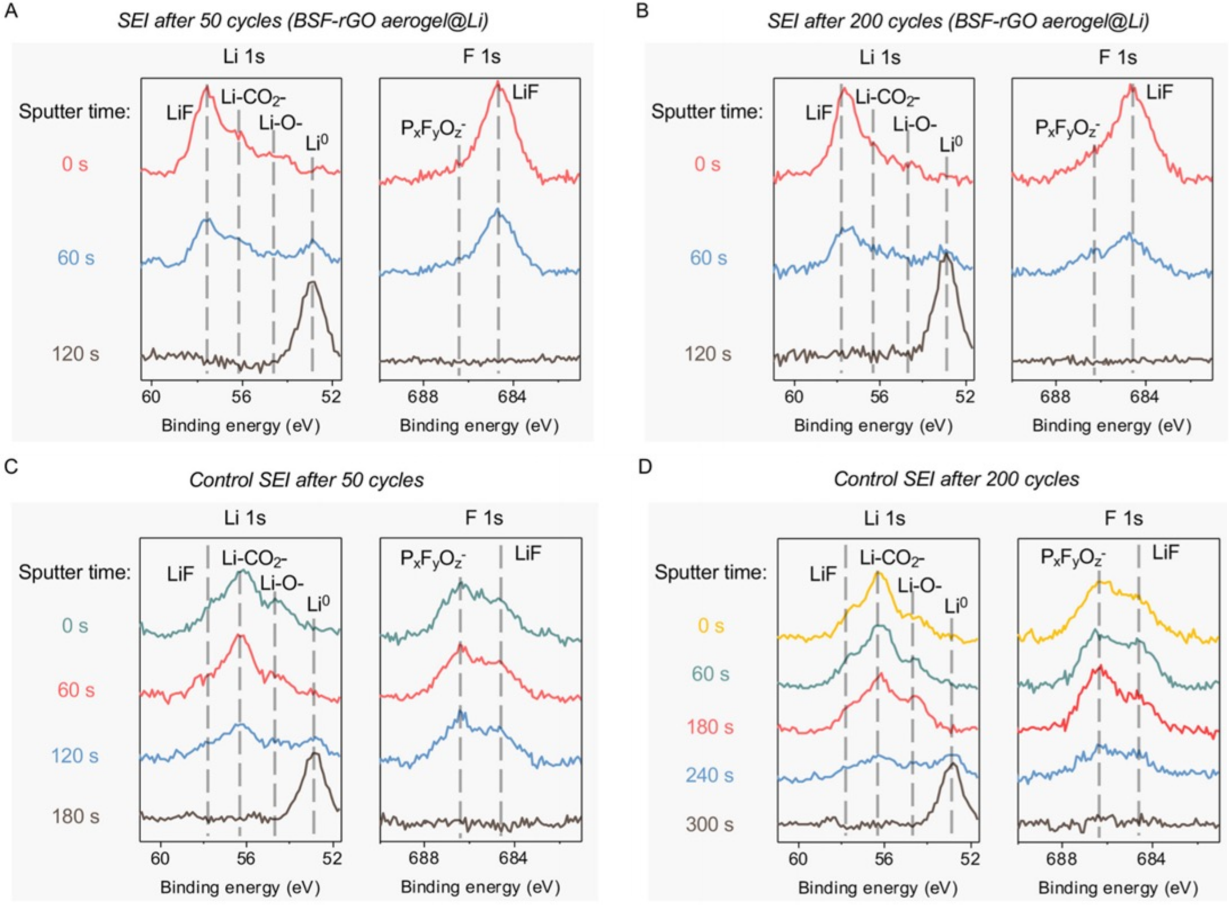
Composition of the SEI layers enabled by the BSF-rGO aerogel



The XPS data further confirmed the LiF-rich SEI, while small amount of Li_2CO_3 and Li_2O in the presence of BSF-rGO aerogel

Proc. Natl. Acad. Sci. U.S.A. **2020**, 117 (48), 30135–30141.

SEI thickness changes upon cycling by XPS depth profiling



BSF-rGO aerogel@Li electrodes:
SEI layers after 50 and 200 cycles have a similar thickness of 10-20 nm.

Bare rGO aerogel@Li electrodes:
SEI thickness increases from 20-30 to 40-50 nm from 50 to 200 cycles.

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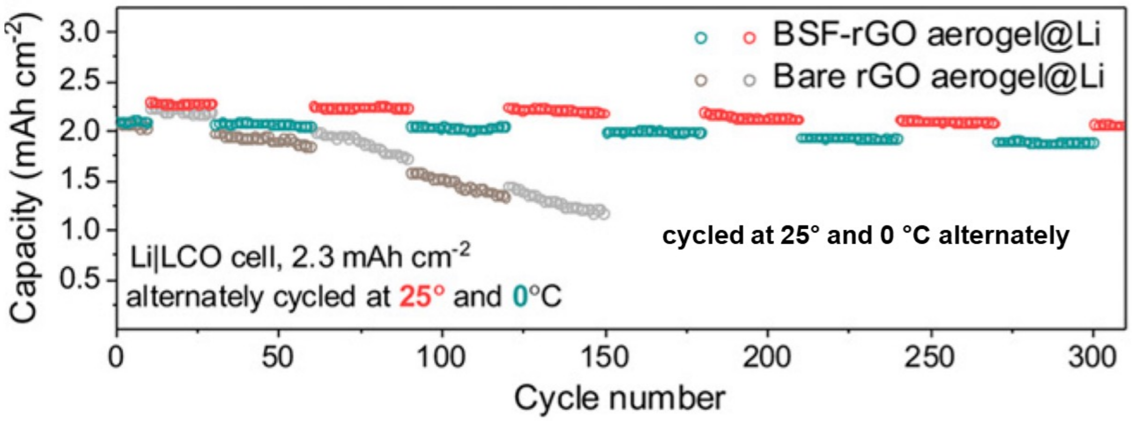
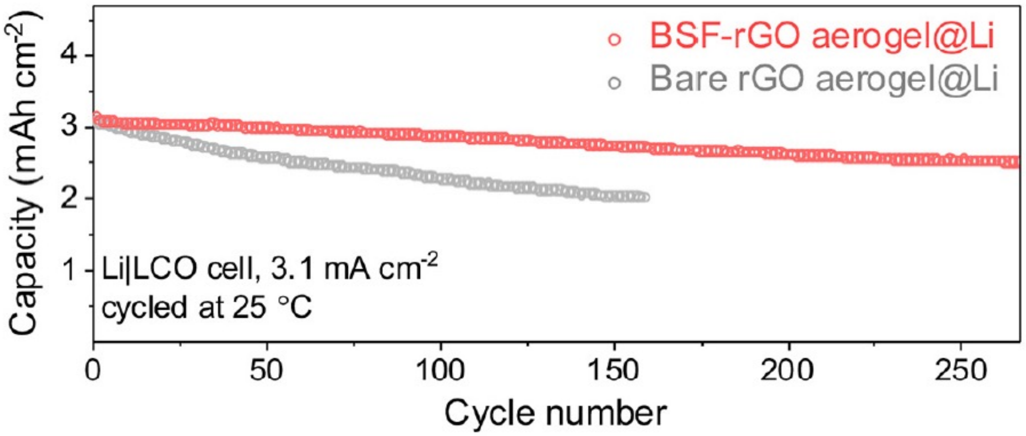
Electrochemical performance enhanced by BSF-rGO aerogel@Li anodes



The cell with the BSF-rGO aerogel@Li anode, cycled alternately at 25 and 0 °C, can deliver a comparable cycling stability to that cycled at 25 °C.



A Li|LCO cell with an high areal capacity of 3.1 mAh cm^{-2} demonstrated a capacity retention of 81.6% after 250 cycles, while the control cell incorporating a bare rGO aerogel@Li anode faded very fast (63.6% capacity retention within 160 cycles).

Proc. Natl. Acad. Sci. U.S.A. **2020**, 117 (48), 30135–30141.