PennState

Laboratory of Energy Nanostructure

Electrochemically Responsive Self-Formed Li-ion Conductors for High Performance Li Metal Anodes

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Project ID: BAT330

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

Overview

Timeline

- Project start date: October 1, 2016
- Project end date: September 30, 2019
- Percent complete: 80%

Budget

- Total project funding
  - DOE share: $1,139,319
  - Contractor share: $126,733
- Funding received in FY 2019
  - $1,139,319

Barriers

- Li metal anode
  - Large volume change;
  - Instability of SEI layers;
  - Li continuous reaction with electrolyte
- Sulfur Cathode
  - Low utilization at high loading
  - Polysulfide dissolution and shuttling

Partners

- Project lead
  - PSU
- Interactions/collaborations
  - PNNL, PSU

Relevance/Objectives

Objectives

- Develop 1) a new Li metal host and 2) electrochemically responsive self-formed hybrid Li-ion conductors as a protective layer which allow high Coulombic efficiency (CE) (> 99.7%) and long dendrite-free cycling of Li metal for Li-S batteries.
- Development of functional sulfur cathode with high mass loading to pair with the protected Li metal anodes to achieve high-energy-density Li-S battery cells.

Impacts

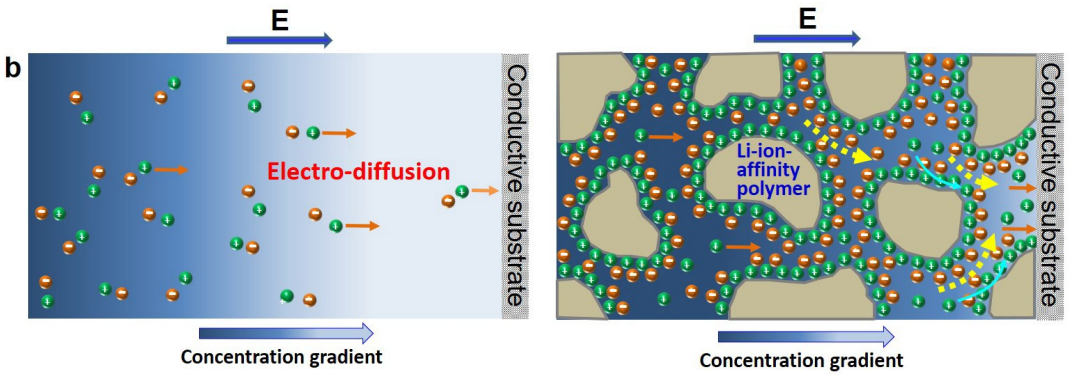
- Self-formed ion-conducting protective layers will stop lithium dendrite growth, prevent continuous SEI growth and enable lithium metal cycling with high CE and long cycle life.
- The new polymer hosted Li metal will enable Li metal cycling at high capacity with high CE for high-energy-density Li-S batteries.
- High-energy-density Li-S battery cells potentially lower the cost of batteries to promote increased adoption of electric and plug-in hybrid electric vehicles (EVs and PHEVs).

Milestones

Date	Milestones	Status
December 2018	Development of the organo-Li_xS_y/organo-$Li_xP_yS_z$ composite lithium protection layers with tuned functionality. Conduct characterization and performance tests on the materials.	Complete
May 2019	Demonstrate the uniform and dendrite-free Li deposition under the protection of the organo-Li_xS_y/organo-$Li_xP_yS_z$ composite lithium protective layers.	On track
July 2019	Optimize organo-Li_xS_y/organo-$Li_xP_yS_z$ composite lithium protective layer and demonstrate Li anodes cycling with ~99.4% CE for ~200 cycles.	On track
September 2019	Demonstrate Li anodes with optimized organo-Li_xS_y/organo-$Li_xP_yS_z$ composite lithium protective layer and ~99.7% CE for ~300 cycles.	On track

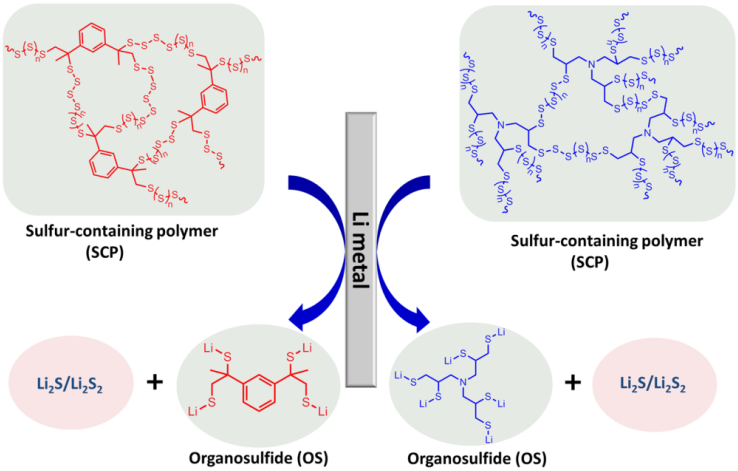
Approach/Strategy

Li-ion affinity sponge host



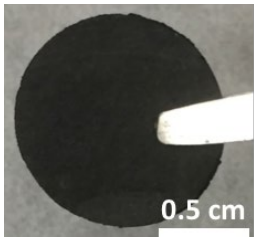
Electrokinetic effects enables dendrite-free plating/stripping of lithium in high zeta potential porous sponge.

Li metal protection



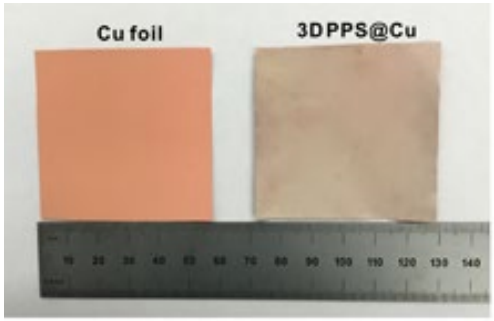
Develop novel **multiphase inorganic-organic hybrid ion conductors** to protect lithium metal cycling with high Coulombic efficiency.

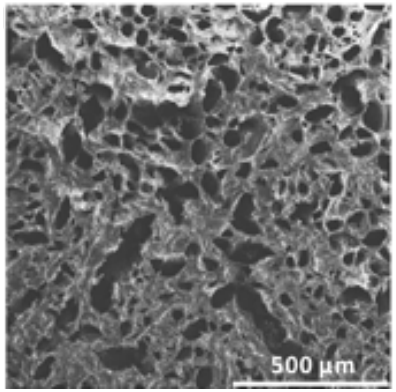
Functional sulfur cathode

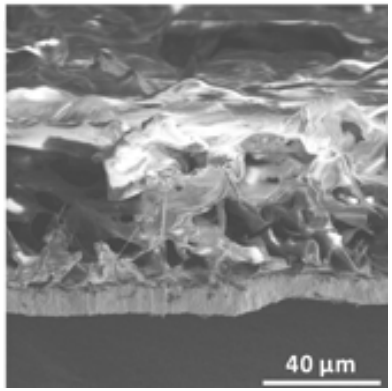


Functional carbon-S-polymer composite cathodes can suppress polysulfide dissolution and enable good cycling performance at low E/S ratio and high sulfur mass loading

Technical Accomplishment - 1. Stable Li metal by electrokinetic phenomena in Li-ion affinity sponge

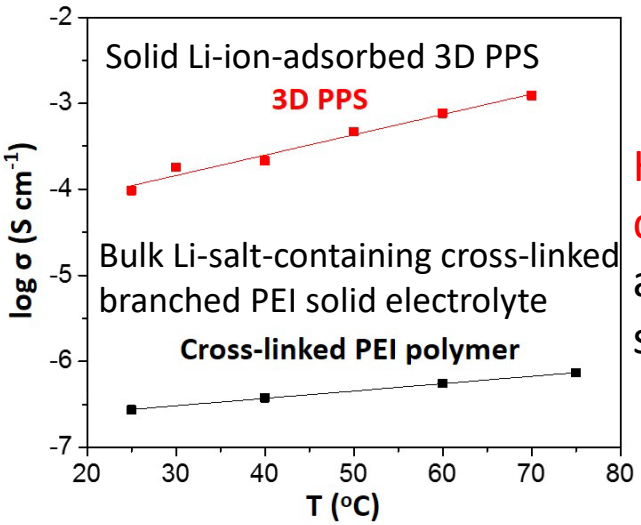




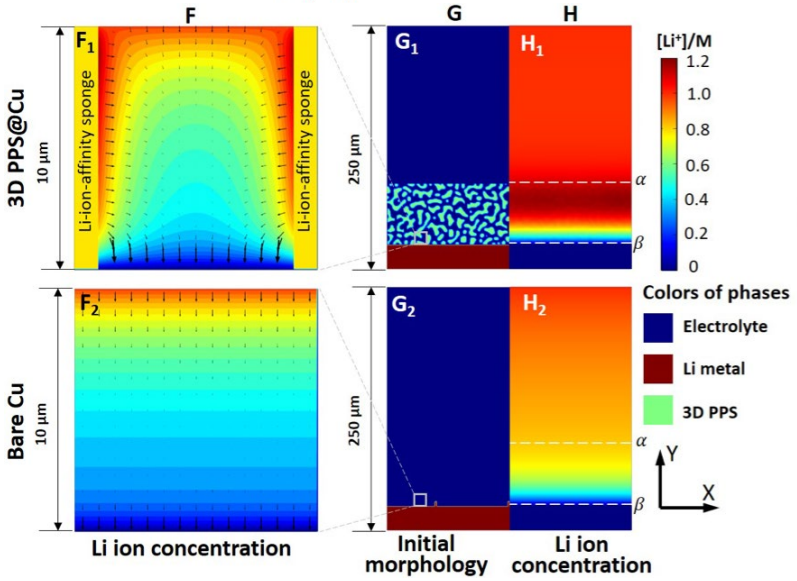


3D cross-linked porous polyethylenimine sponge (3D PPS)

High pore volume: ~5.5 $cm^3\ g^{-1}$; high porosity: 87%



Higher Li-ion conductivity in Li-ion adsorbed polymer sponge



Increased local Li-ion concentration and reduced concentration polarization

Electrokinetic phenomena to promote enhanced Li-ion transport in 3D PPS host

High zeta potential: +42 mV in the electrolyte (1.0 M LiTFSI/DOL+DME)

Electroosmosis:

PEI modified plastic tube bridge

Control, un-modified plastic tube bridge

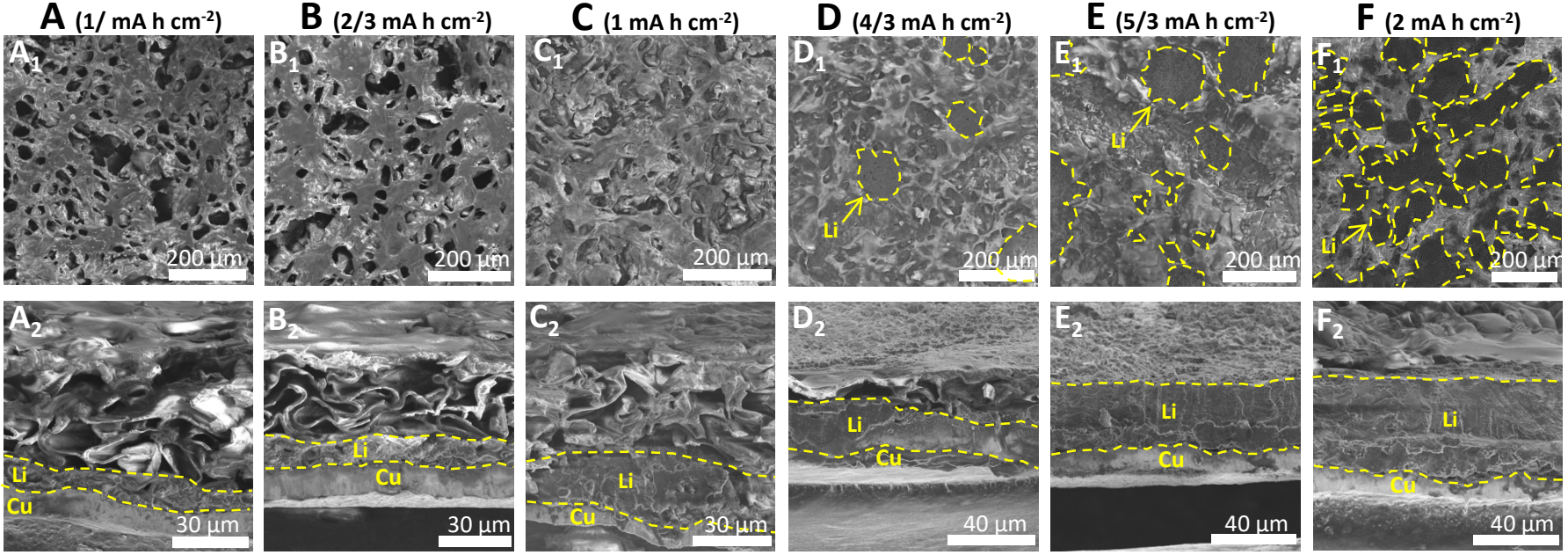
-

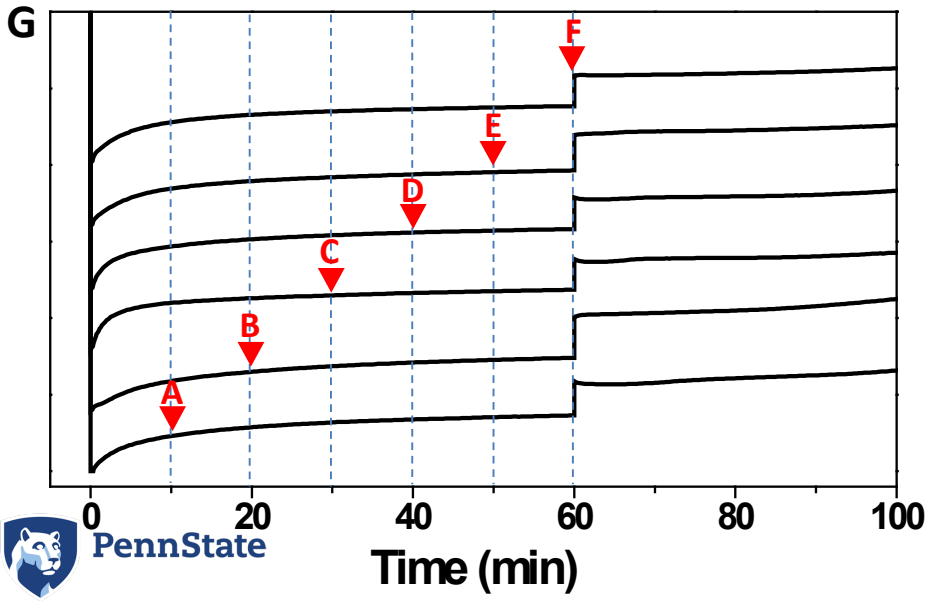
+

Applied electric field

5 V cm^{-1}

Morphology evolution of the Li deposited within theLi-ion affinity polymer sponge

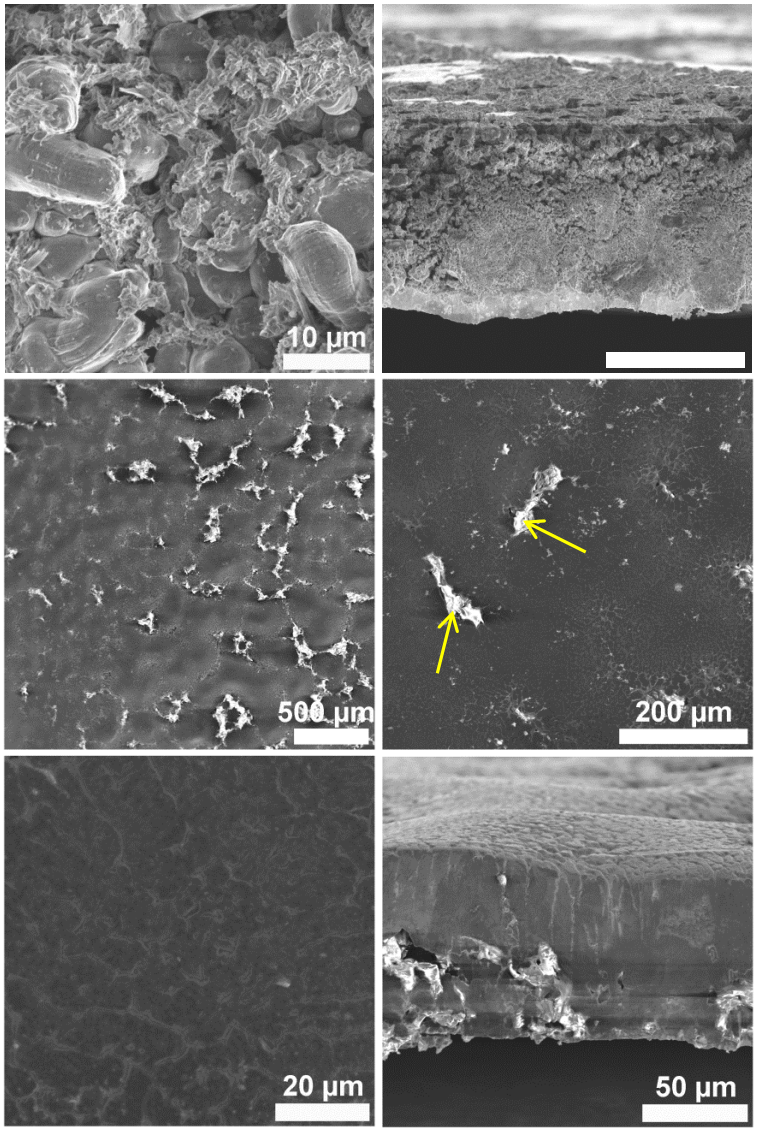




Bottom up and conformal growth of Li metal within the Li-ion affinity polymer sponge

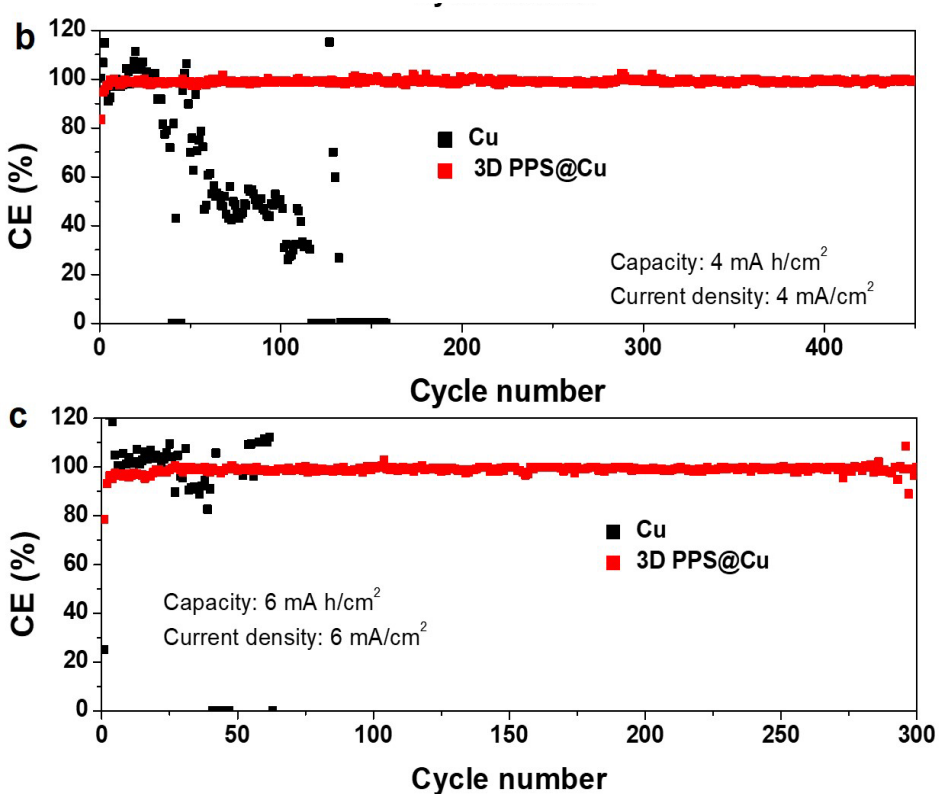
Nature Energy ***3***, 1076-1083 (2018)

SEM images of the deposited Li



Current: 6 mA/cm^2 and Capacity: 6 mA h/cm^2

Cu foil

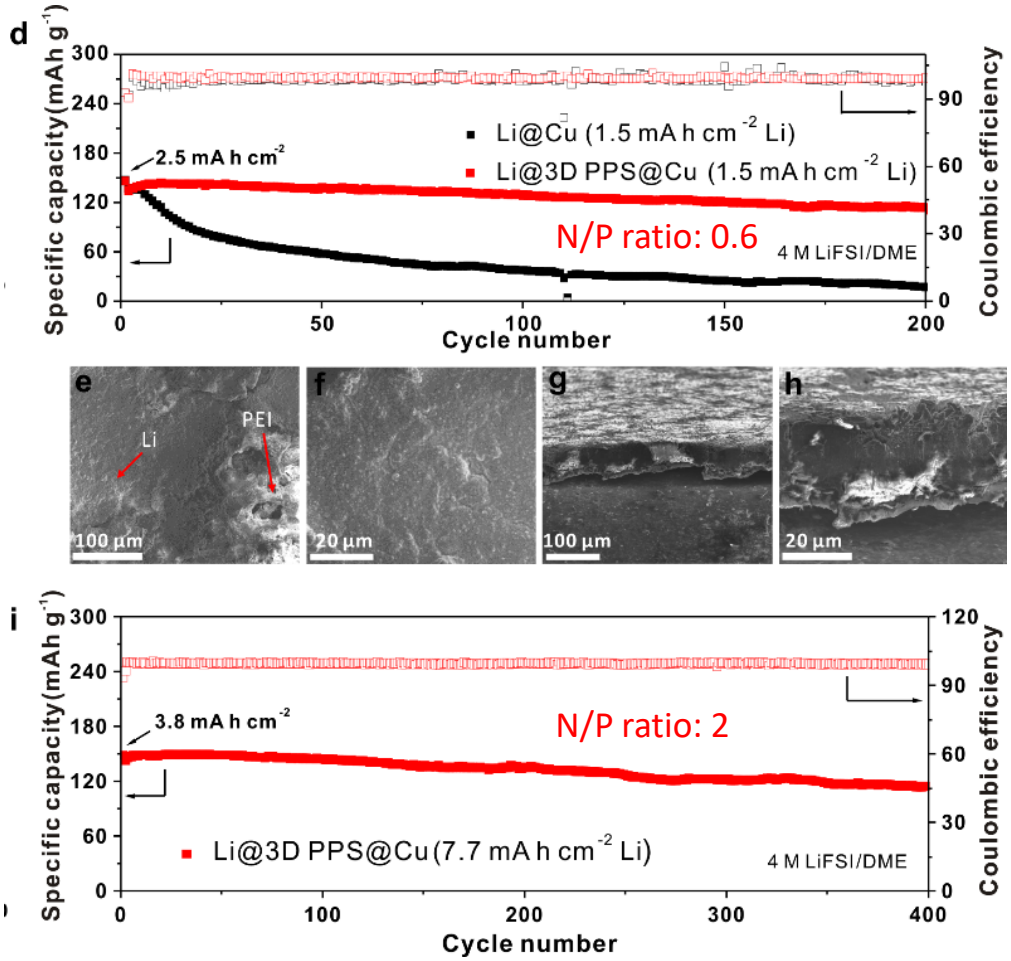


3D PPS@Cu

Exhibited a long cycle life over 450 cycles with an average CE as high as 99% against Cu foil at the conditions of 4 mAh/cm^2 and 4 mA/cm^2

Electrochemical performance of Li||$LiFePO_4$ cells at different N/P ratios

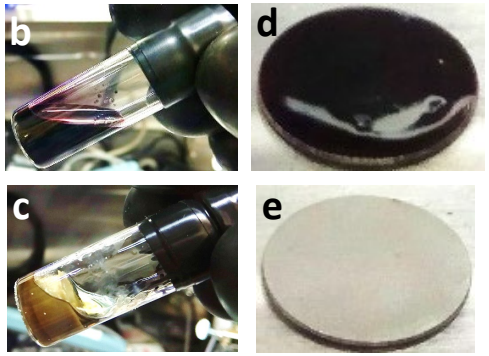
N/P ratio: the areal lithium ratio of negative to positive electrodes

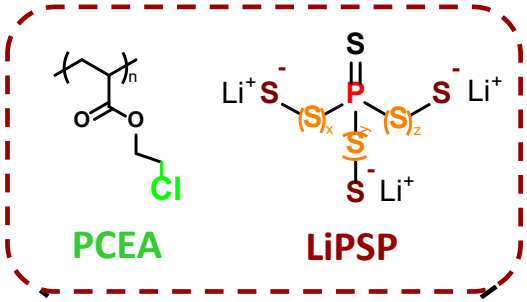


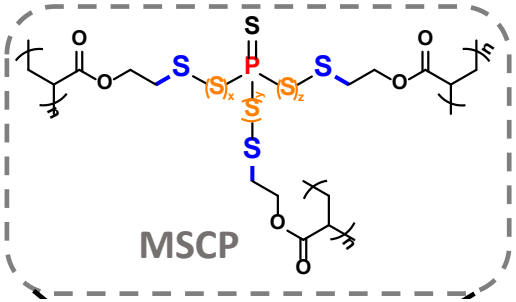
At a N/P ratio of 0.6, stable cycling performance over 200 cycles with an average CE of ~99.7% in the Li||$LiFePO_4$ cell with areal capacity of 2.5 mAh cm^{-2}

At a N/P ratio of 2, stable cycling performance over 400 cycles with an average CE of ~99.78% in the Li||$LiFePO_4$ cell with areal capacity of 3.8 mAh cm^{-2}

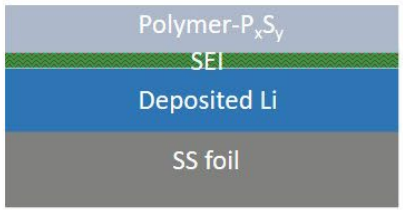
Technical Accomplishment - 2. Organo-Li_xS_y/organo-$Li_xP_yS_z$ composite lithium protection layers



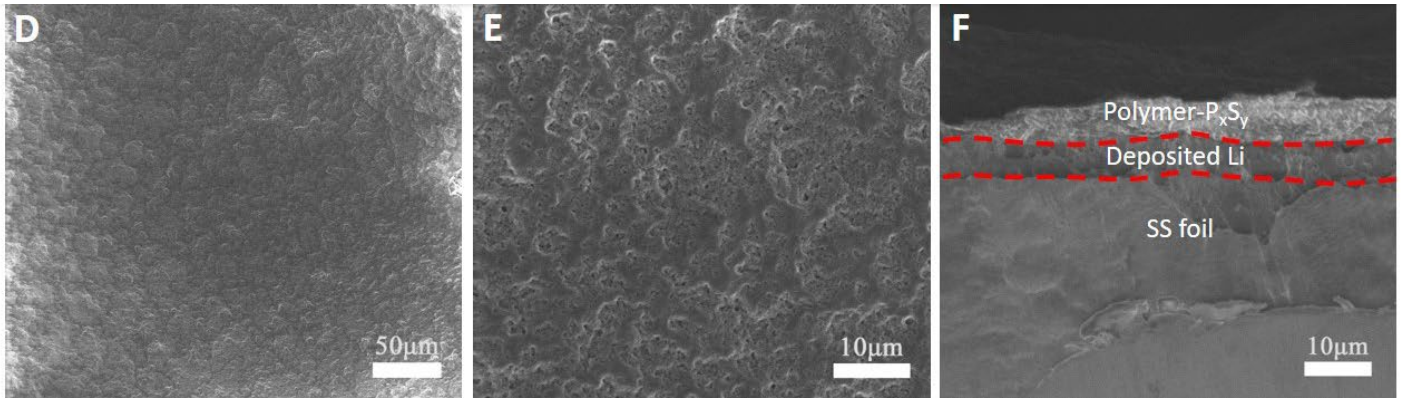




Organo-Li_xS_y/organo-$Li_xP_yS_z$ composite lithium protection layers

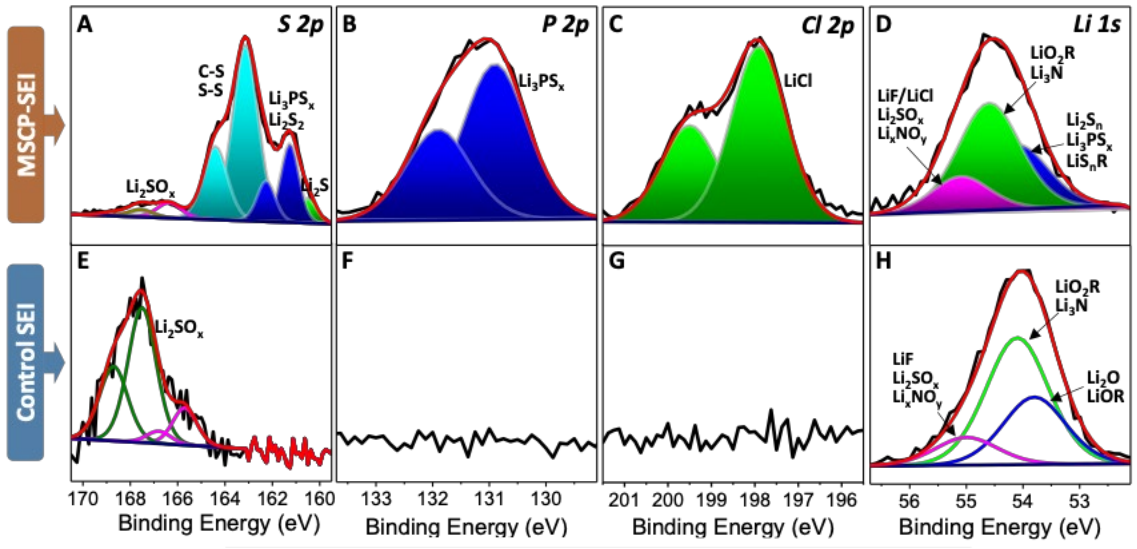


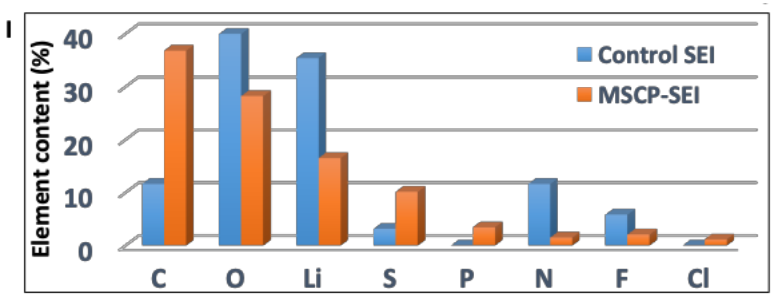
Li deposition on Polymer-P_xS_y protected SS foil



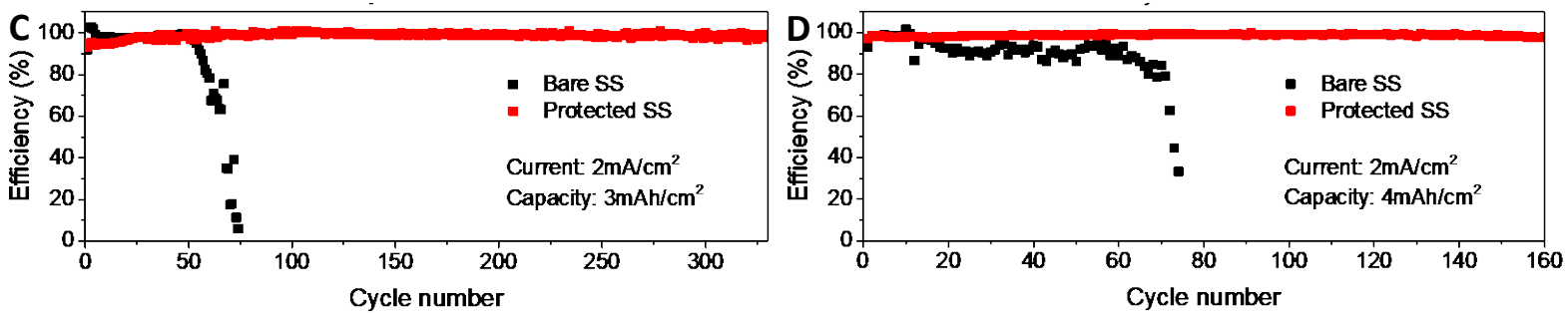
Dendrite-free Li deposition at 2 mA cm^{-2} and 2 mAh cm^{-2}

Hybrid lithium protection layers enable stable Li metal anodes





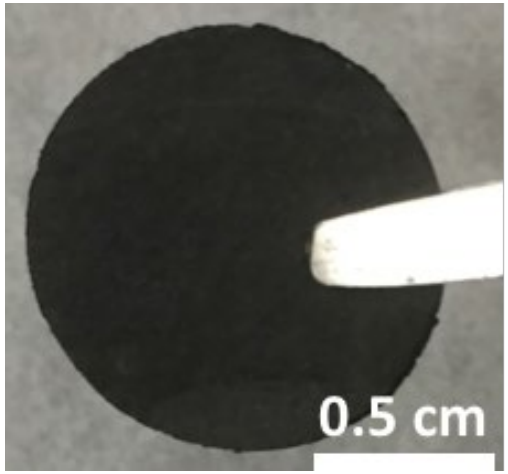
The existence of Li_3PS_x and polymer-tethered organo(poly)sulfide can be confirmed from XPS spectra. The hybrid SEI shows a higher content of C, S, and P, but a lower content of O, Li, N and F, compared with that of control SEI.

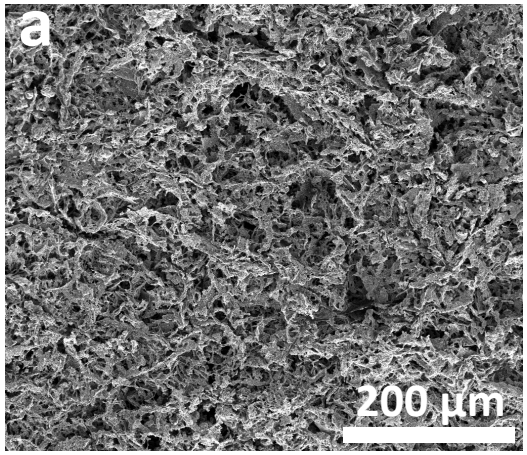


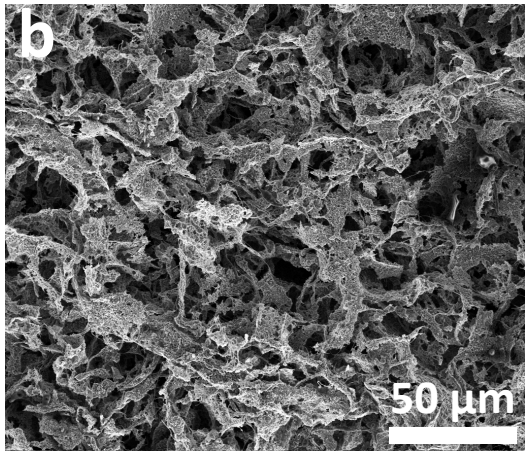
The cells using hybrid SEI protected stainless steel foil show stable cycling with improved average CE (i.e., 98.5%) than that using a bare stainless steel foil.

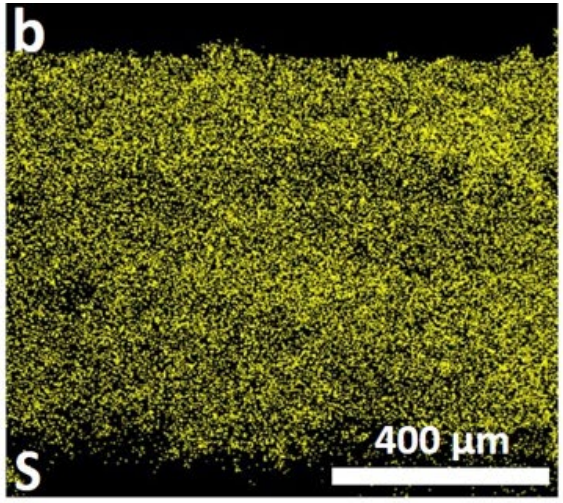
Technical Accomplishment - 3. Sulfur cathode and additives

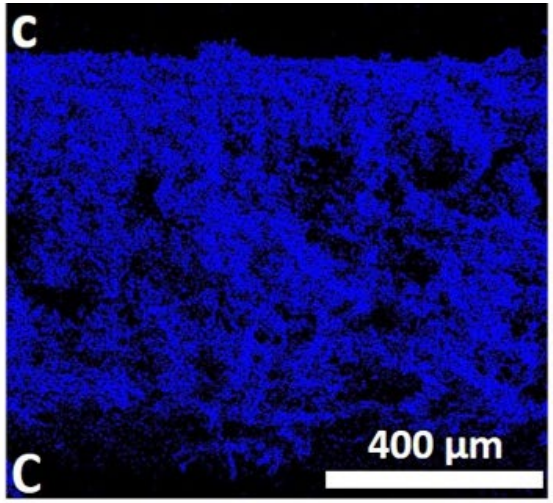
Functional carbon-S-polymer composite cathodes were fabricated with high sulfur mass loading ranging between 7-12 mg S/cm^2 and a capability of polysulfide adsorption.

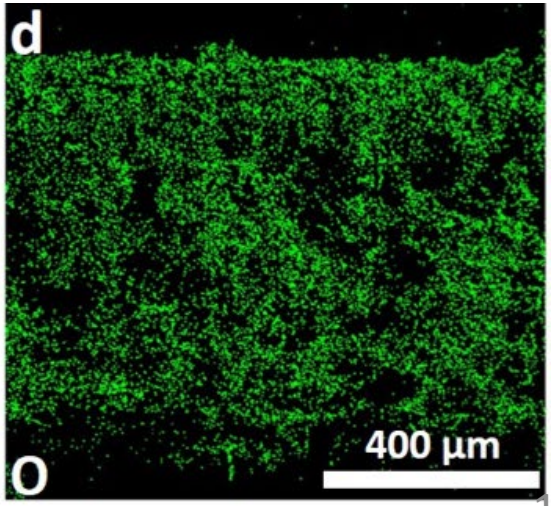






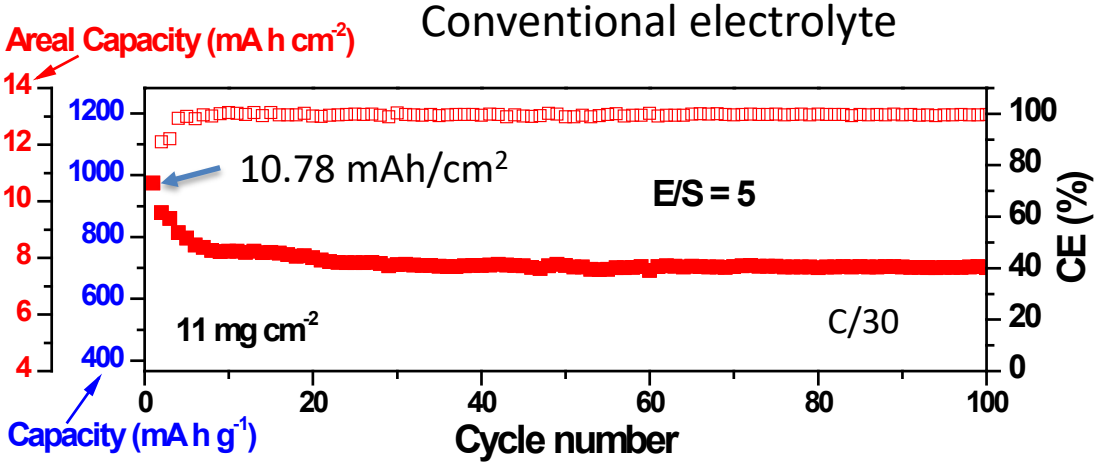


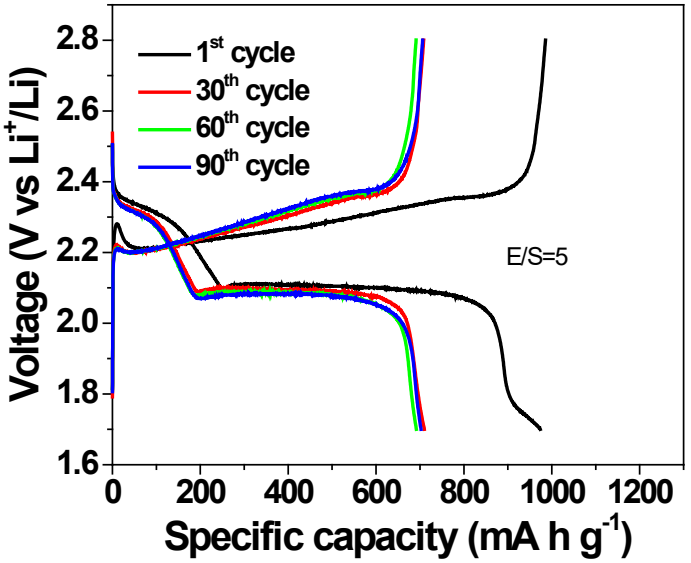


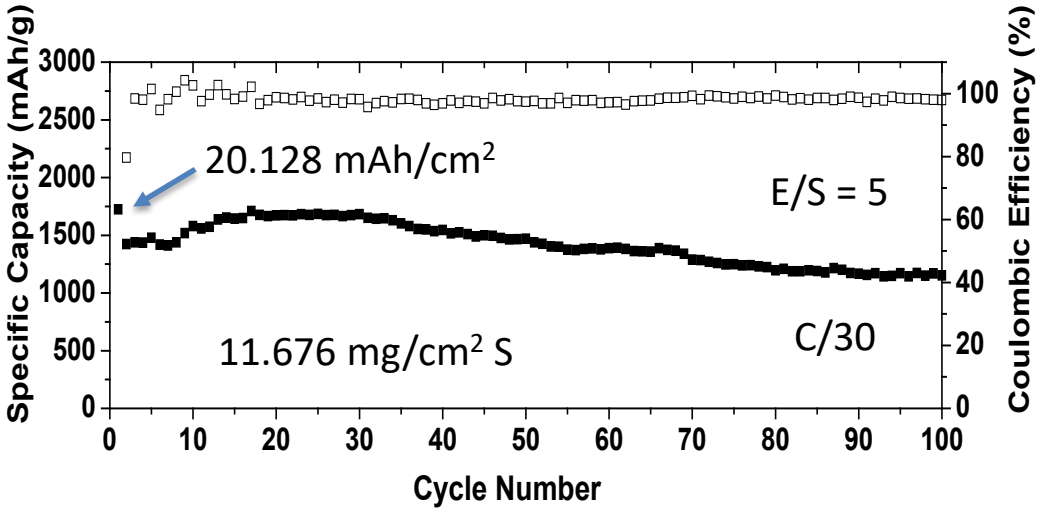


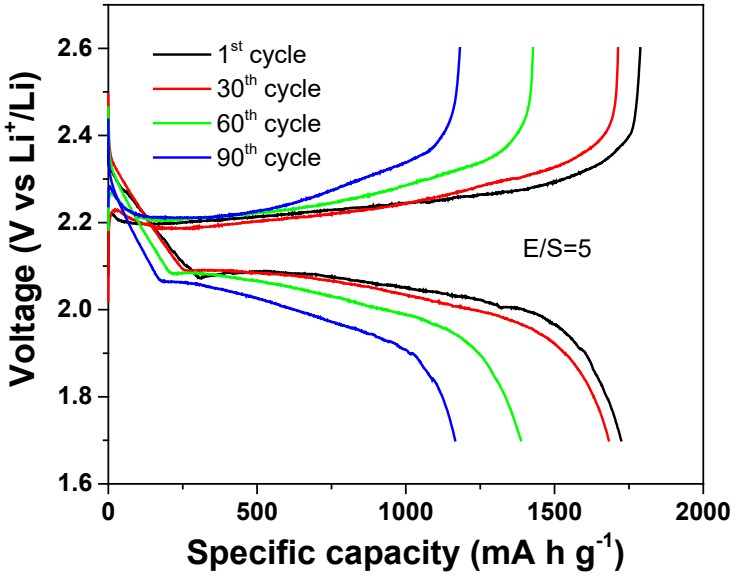
Electrochemical performance of functional sulfur cathode at low E/S ratio

Conventional electrolyte









Conventional electrolyte with additives

Improve sulfur utilization while achieving high energy density

Conventional electrolyte:

E/S ratio (µl/mg)	5	3
Energy density (Wh/kg)	237	308
Sulfur utilization (the 1st cycle)	58.2%	52%

Conventional electrolyte with additive

E/S ratio (µl/mg)	5	3.5
Energy density (the 1st cycle) (Wh/kg)	412	432
Energy density (the 40th cycle) (Wh/kg)	368	386
Sulfur utilization (the 1st cycle)	~64.7%	~61%

11 mg S/cm²

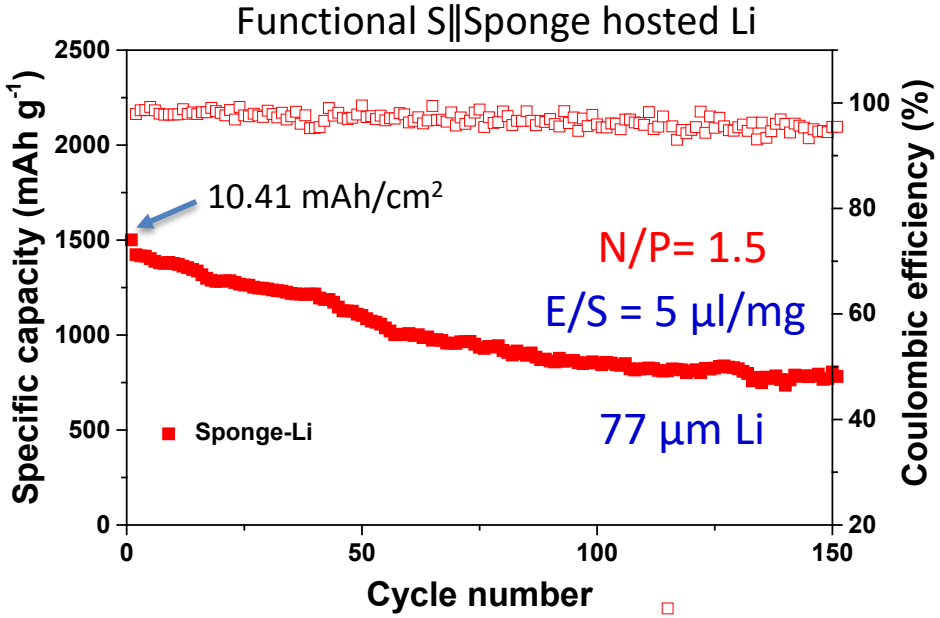
Energy density = (Areal capacity*voltage)/mass of (200 µm Li foil+electrolyte+cathode)

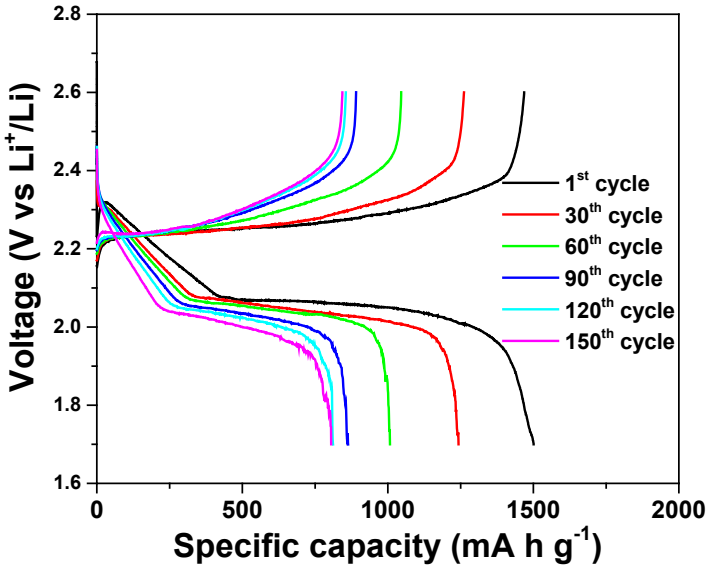
Technical Accomplishment – 4. Li-S battery cells at low N/P ratio

Functional sulfur cathode paired with the sponge hosted thin Li anode

Cells	N/P Ratio	E/S	Sulfur Loading	Initial Areal Capacity	Calculated Energy density (1st cycle) (Wh/kg)
Functional-S‖Sponge-Li (77 µm)	1.5	5	7 mg/cm^2	10.4 mAh/cm^2	374

Energy density = (Areal capacity*voltage)/mass of (Li foil+electrolyte+cathode)





The polymer sponge hosted Li anode enable Li-S battery cell cycling at condition of a low N/P ratio of 1.5, an E/S ratio of 5, and a high sulfur mass loading (7 mg S/cm^2).

Responses to Previous Year Comments

Comment 1: CEs for all three electrolyte are around 99% is too low for a practical cell.
Response 1: We have demonstrated improved average CE reaching 99.1% at a deposition capacity (2 mAh/cm^2) and high current density (2 mA/cm^2). We also demonstrated the Li||$LiFePO_4$ full cell (areal capacity of 2.5 mAh/cm^2) can maintain a stable cycling performance over 200 cycles with an average CE of ~99.7% at a N/P ratio of 0.6.

Comment 2: The project team does not indicate how much excess Li is used in the cell for full cycling.
Response 2: Li||$LiFePO_4$ full cell (areal capacity of 2.5 mAh/cm^2) can maintain a stable cycling performance over 200 cycles with an average CE of ~99.7% at a N/P ratio of 0.6. The Li-S battery cells can cycle over 150 cycles with a N/P ratio of 1.5 and a high sulfur loading cathode (area capacity of 10 mAh/cm^2).

Comment 3: Does Li_2S and Li_2S_2 form in the course of the reduction of the sulfur-and-Li-containing developed organic additives, and how the formed SEI interacts with the polysulfides dissolved in the electrolyte.
Response 3: The Li_2S and Li_2S_2 and Li_3PS_x will form and participate the formation of the hybrid cross-linked polymeric-inorganic SEI layers. The as-formed hybrid SEI layer is stable and inhibit further reaction between Li and polysulfides.

Partners/Collaborators

- Collaboration with Dr. Long-Qing Chen and Dr. Seong Kim at PSU on modeling and characterization of Li dendrite growth under the SEI layer.
- Collaboration with Dr. Jun Liu at PNNL on fabrication of Li-S batteries.

Remaining Challenges and Barriers

- Achieving higher Coulombic efficiency for lithium deposition/dissolution at high deposition capacities and current densities.
- Completely suppressing the shuttle effects of Li-S batteries.
- Higher rate cycling of Li-S batteries at high sulfur loading, low E/S ratio condition, and low N/P ratio.

Proposed Future Work

Ongoing (FY19)	Demonstrate uniform and dendrite-free lithium deposition under protection of the organo-Li_xS_y/organo-$Li_xP_yS_z$ composite lithium protection layers. (In progress)
	Optimize the organo-Li_xS_y/organo-$Li_xP_yS_z$ composite lithium protection layers and demonstrate lithium anodes cycling with ~ 99.4% CE for ~ 200 cycles. (Q3)
	Demonstrate lithium anodes with optimized organo-Li_xS_y/organo-$Li_xP_yS_z$ composite lithium protection layers and ~ 99.7% CE for ~ 300 cycles. (Q4)

Summary

- Stable Li metal enabled by electrokinetic phenomena in a Li-ion affinity sponge can achieve high Li plating/stripping CEs at both high deposition capacity and high current density, even at low temperature.

- The organo-Li_xS_y/organo-$Li_xP_yS_z$ composite lithium protection layers effectively suppress growth of dendrite Li and improve the Li plating/stripping CE and cycling life.

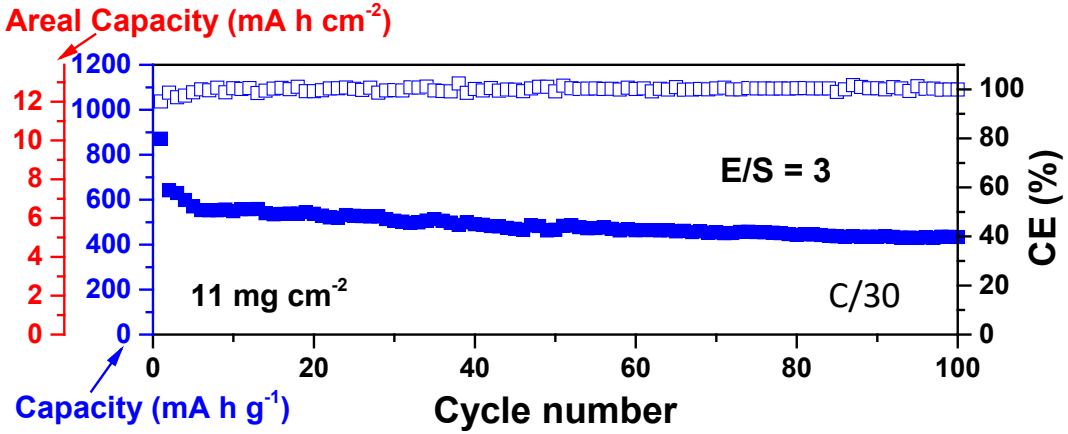
- Novel cathodes with high sulfur mass loading (11 mg cm^{-2}) delivers good cycling performance at a low E/S ratio of 5 and a low N/P ratio of 1.5.

Acknowledgement

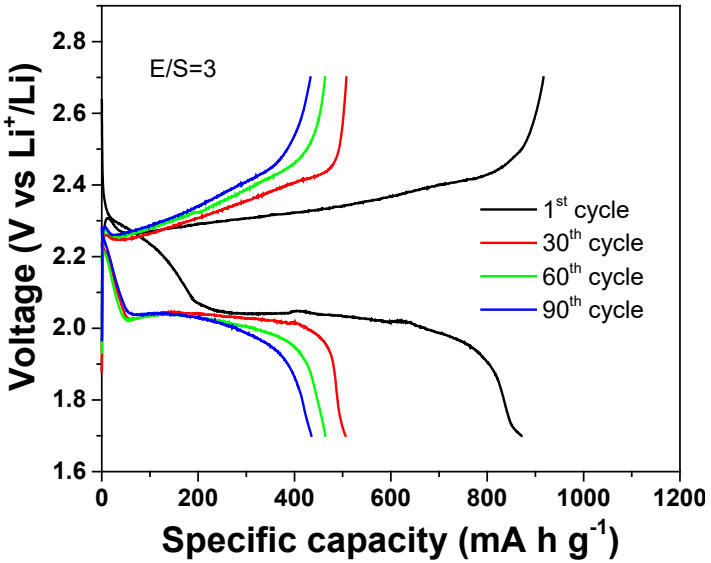
Support from Tien Duong and David Howell of the US Department of Energy's Office of Vehicle Technologies is greatly appreciated.

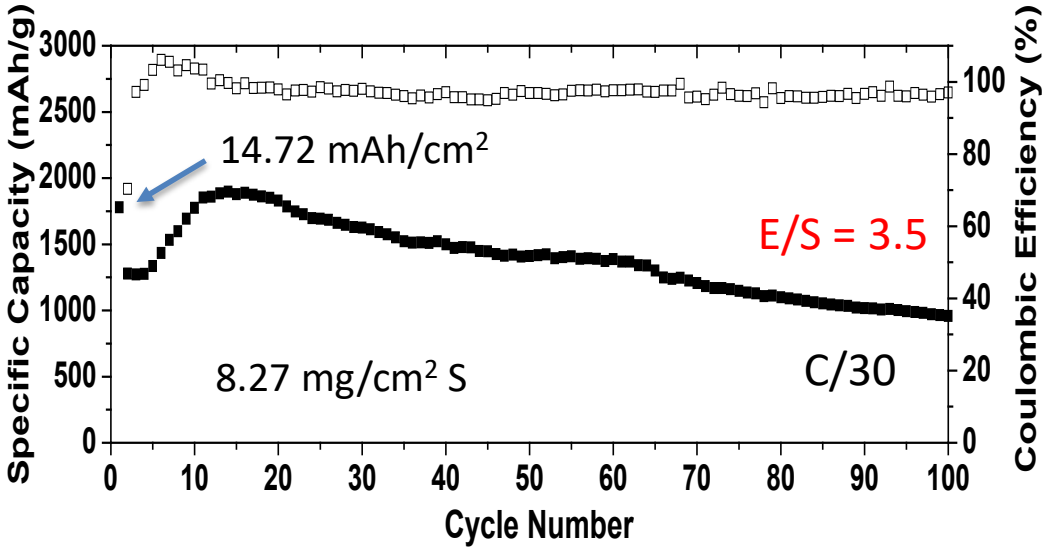
Technical Back-Up Slides

Electrochemical performance of functional sulfur cathode at low E/S ratio with new electrolyte additives

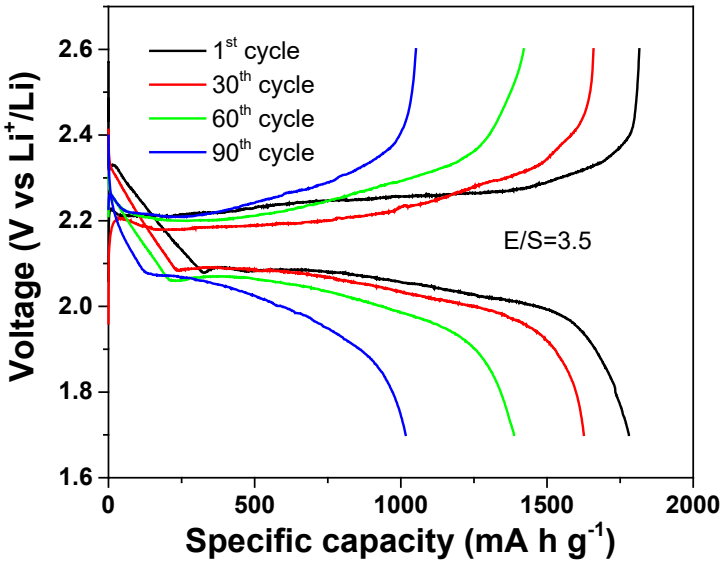


Conventional electrolyte



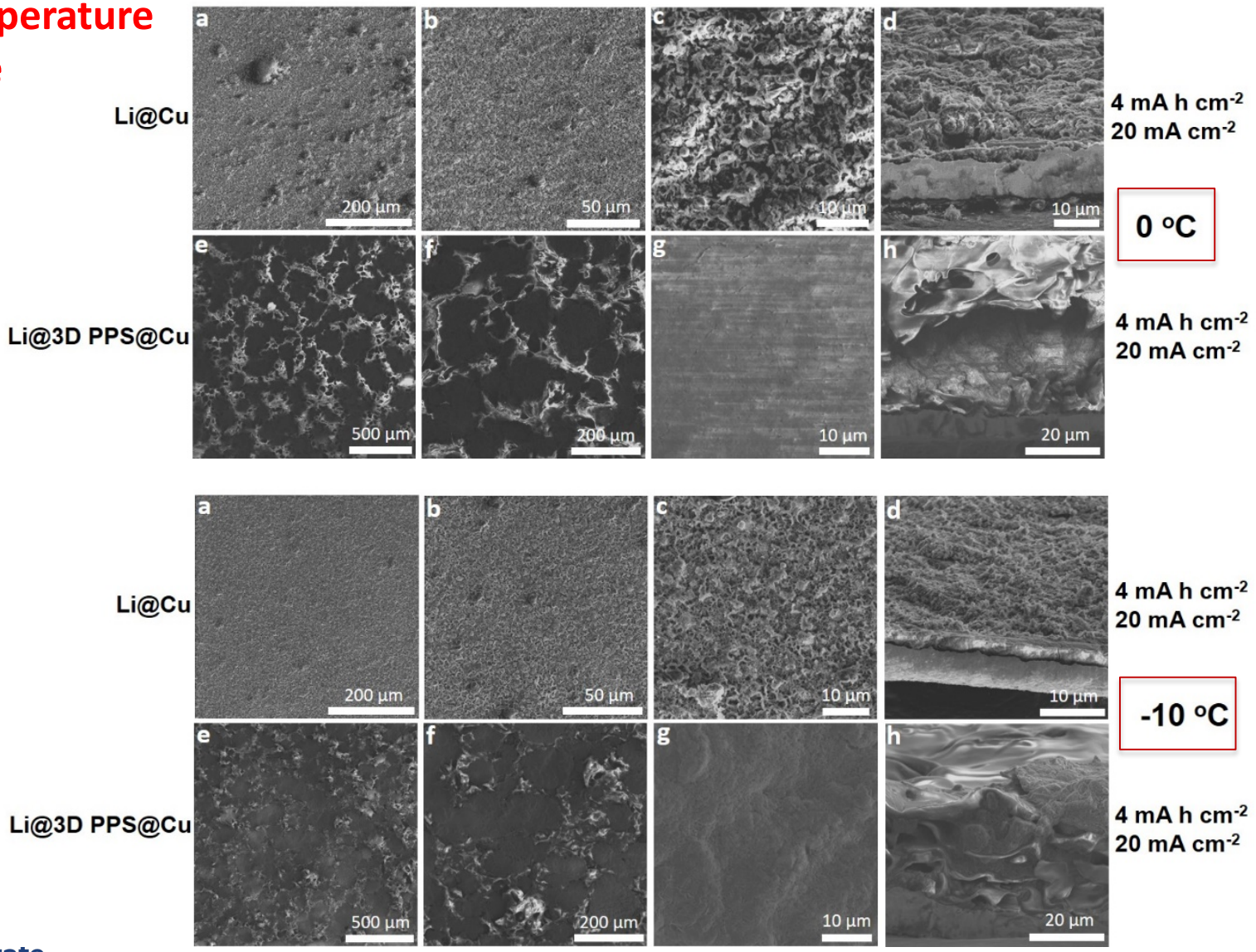


Conventional electrolyte with additives



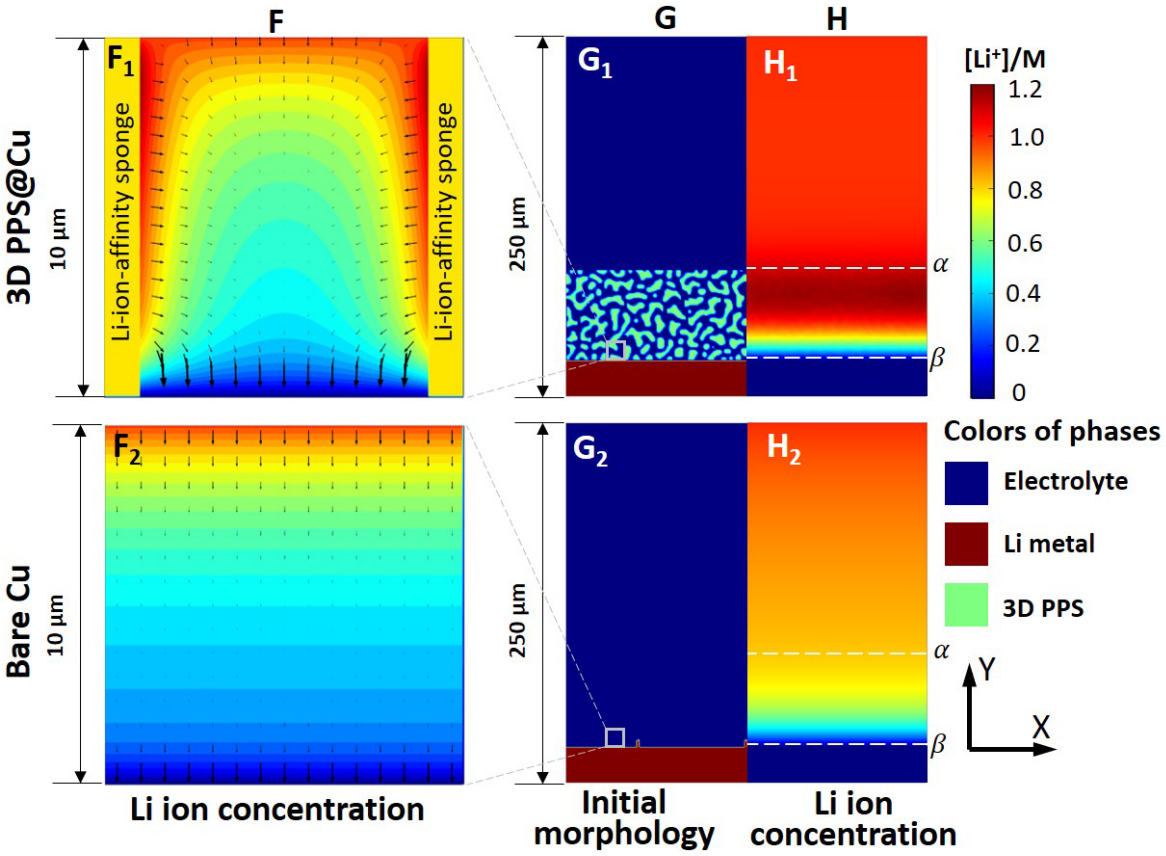
Dendrite-free Li plating/stripping at low temperature

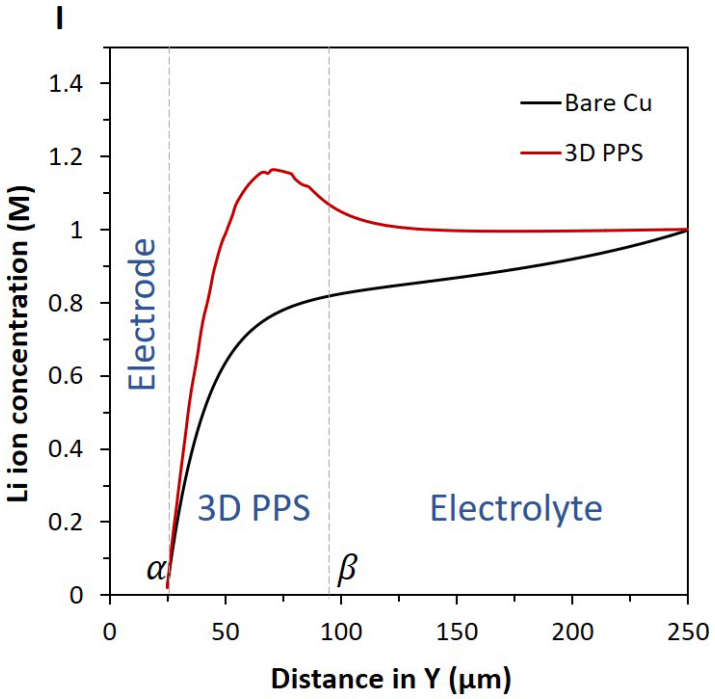
Low temperature
High rate



1.0 M LiTFSI in DOL and DME (V/V = 1) with 1 wt% $LiNO_3$

Li-ion electrokinetic self-concentrating/ pumping mechanism from 2D simulations

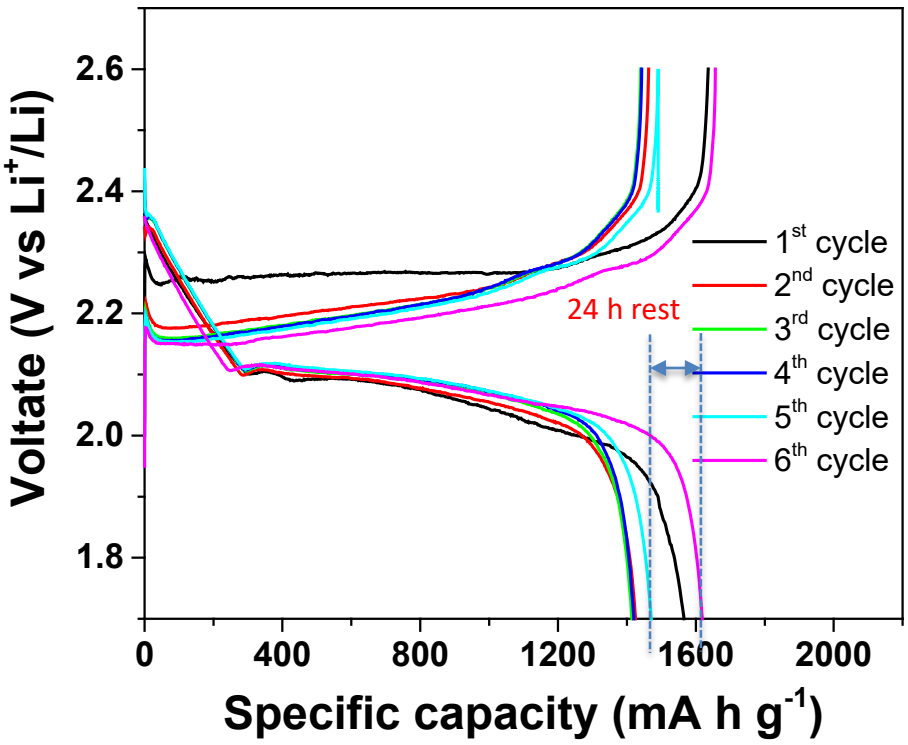




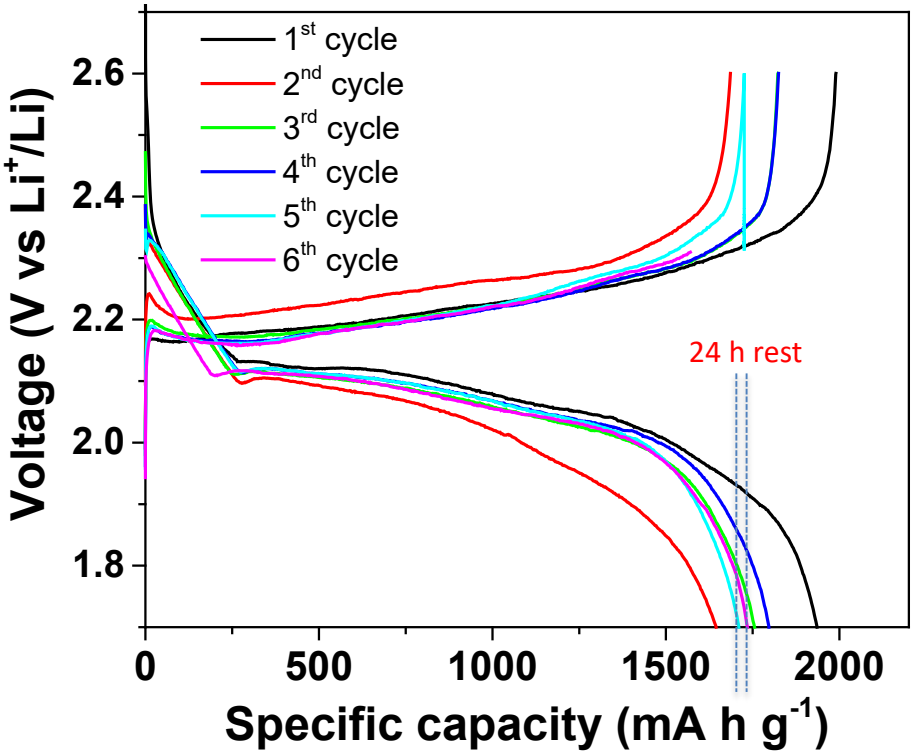
Low self-discharge for the Li-S battery cells

Self-discharge

E/S=8 C/30



Sample 1



Sample 2

5th cycle-6th cycle: 24 h rest

Conventional electrolyte with additives