Li Dendrite-Free Li_7N_2I-LiOH Solid Electrolytes for High Energy Lithium Batteries

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2021 DOE Vehicle Technologies Office Annual Merit Review

Project ID: bat481

Overview

Timeline

- Starting date: Oct. 2020
- Ending date: Sept. 2022
- 50% complete

Budget

- Total project funding:
  - DOE $1,000k
  - Contractor share: $250,000
- Funding for FY 2020: $321k
- Funding for FY 2021 $334k

Barriers and Technical Targets

- Unstable SE/Li interface: Develop a solid-state electrolyte (SSE) or SEI layer that is stable against Li and lithiophobic.
- Dendrite mechanism: Propose dendrite suppression criteria and validate
- Low energy density: Use 3D supporter for SSE and cathodes to enable 350 wh/kg

Partners

- US Army Research Lab
- Brookhaven National Lab
- Saft America Inc

Relevance

Impact

Development of high-energy rechargeable Li metal all-solid-state batteries for future vehicle electrification

Objective

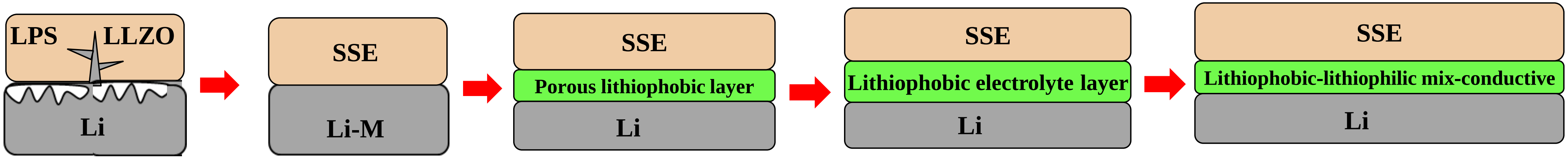
- Develop SSE stable against Li metal anode
- Develop Li dendrite suppression criterion in SSE
- Develop lithium dendrite-free bi-layered SSE for high energy density cells.

Milestones

Month/Year	Description of Milestone or Go/No-Go Decision	Status
December 2020	The critical overpotential and set-up standard area specific resistance are determined	Complete
March 2021	Develop a Li dendrite suppression criterion based on the Li dendrite formation mechanism	Complete
June 2021	Combining the Li dendrite formation mechanism and kinetics, a comprehensive Li dendrite criterion will be established	On Target
September 2021	Doped Li/Li_7N_2I-LiOH/Li cells are charged/discharged at a current of 3.0 mA/cm^2 and capacity of 3.0 mAh/cm^2 for 300 cycles. Critical current of Li_7N_2I-LiOH electrolytes should be >4 mA/cm2 at 3 mA/cm2 of current.	On Target
September 2021	Li/Li_7N_2I-LiOH/Li cells are charged/discharged at a current of 3.0 mA/cm^2 and capacity of 3.0 mAh/cm^2 for 300 cycles without Li dendrite. Analysis indicates technical approach capable of achieving performance targets	On Target

Approach

Li dendrite suppression in solid electrolyte batteries



Li dendrite growth

Enhancing Li self-diffusivity by adding trace metal

Introducing a stable porous lithiophobic LiF-Li_3N layer

Introducing a stable lithiophobic Li_7N_2I-LiOH electrolyte layer

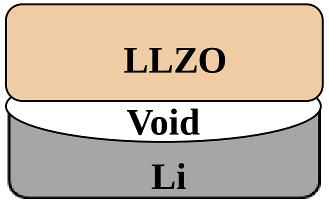
Introducing a mixed electronic/ionic conductive and lithiophobic-lithiophilic gradient layer

- **Use high-rate Li-alloy anode to prevent formation of void and achieve a high critical current density (CCD)**
- **Insert a highly lithiophobic, ionic conducting and electronic insulating LiF-Li_3N layer between Li and solid-state electrolyte to suppress Li dendrite growth**
- **Insert a lithiophobic, ionic conducting and electronic insulating Li_7N_2I-LiOH electrolyte layer between Li and solid-state electrolyte to suppress Li dendrite growth**
- ***In-situ* form a mixed electronic/ionic conductive and lithiophobic-lithiophilic gradent layer between Li and solid-state electrolyte to suppress Li dendrite growth**

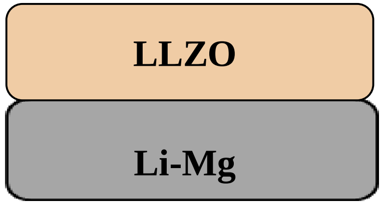
Accomplishments

Enhancing the Li diffusivity to increase the critical current density

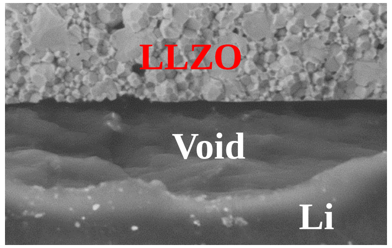
Void formation at Li/LLZO interface during the cycling promote Li dendrite growth



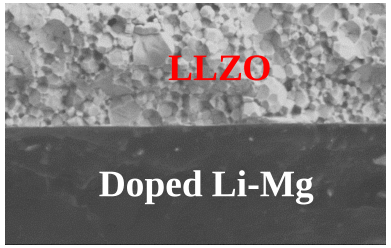
Void formation and Li dendrite growth



Enhancing Li self-diffusivity by adding trace metal

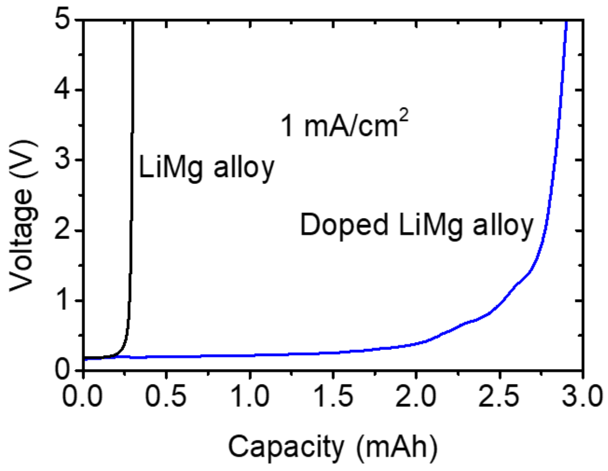


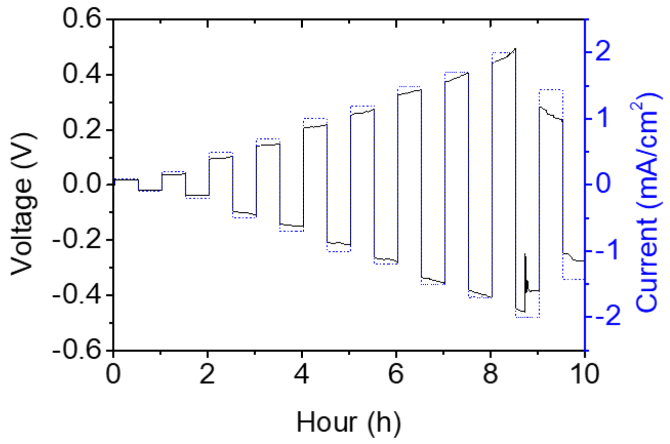
Void formation due to low Li diffusivity



Void-free of Li-Mg alloy due to a high Li diffusivity

Adding Mg into Li increases the Li diffusivity and enhances the areal capacity and critical current density

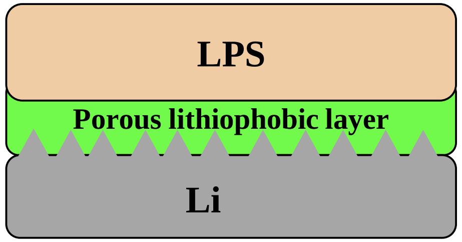




- **At a current of 1.0 mAcm^{-2} , Doped Li-Mg alloy can enhance the areal capacity from 0.25 mAh/cm^2 to 2.7 mAh/cm^2**
- **Doped Li-Mg alloy enables a high CCD of 2.0 mA/cm^2 for the garnet (LLZTO) SSE.**

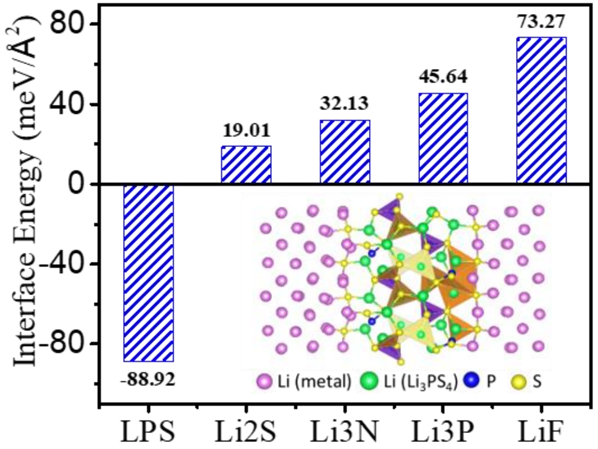
Accomplishments

Lithiophobic porous LiF-Li_3N electrolyte interlayer for Li dendrite suppression

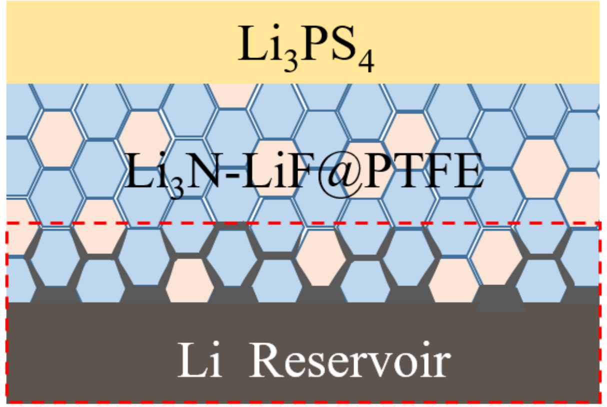


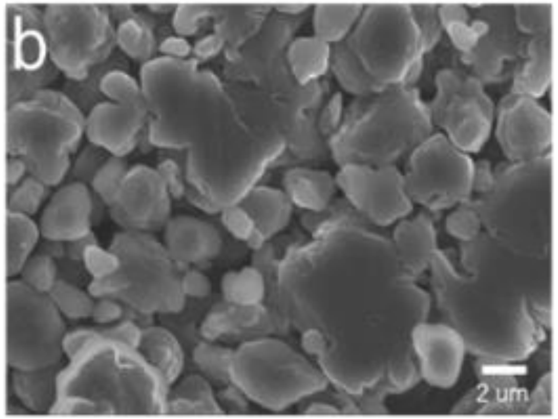
Introducing a stable porous lithiophobic LiF-Li_3N layer

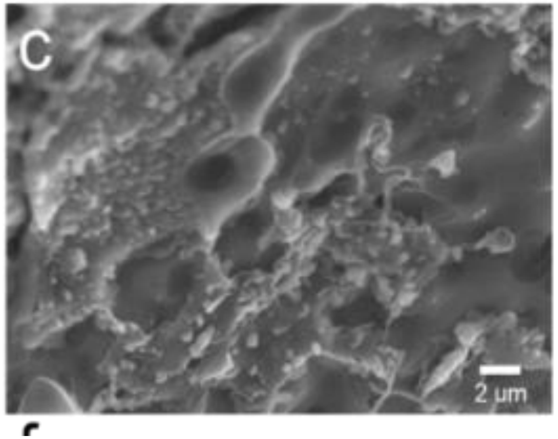
Selection of LiF-Li_3N interlayer

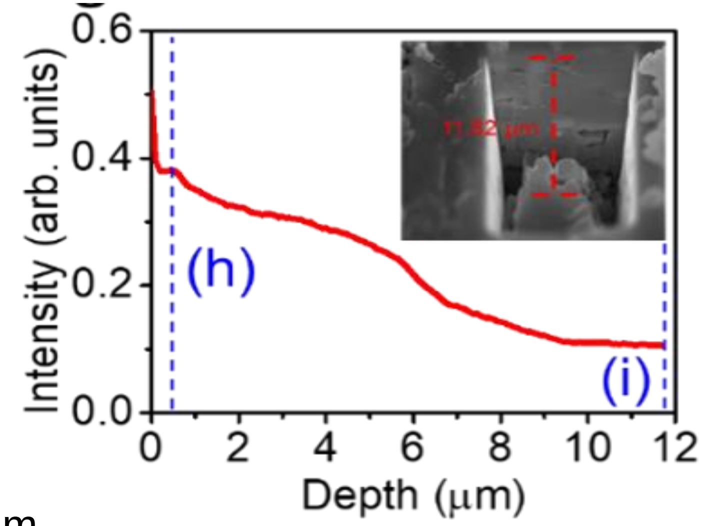


- **Energy analysis and first-principles calculation predict that LiF and Li_3N with a high interface energy and high Li-ion conductivity promise interphase for dendrite suppression.**
- **A porous Li_3N-LiF interphase layer functions as Li reservoir during cycling.**







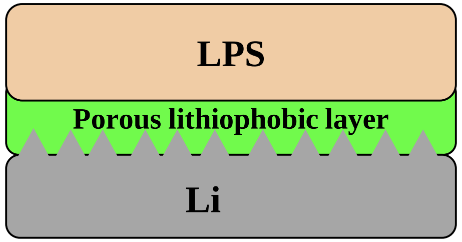


Depth profiling of Li at the interface indicates the Li penetration can be blocked within 10 μm

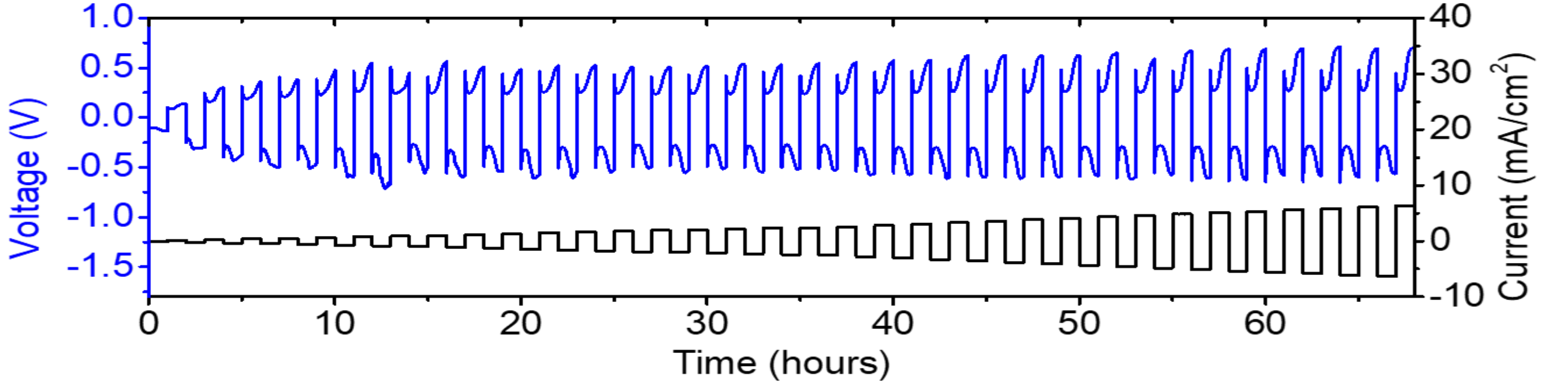
Advanced Materials, 2020, 2002741

Accomplishments

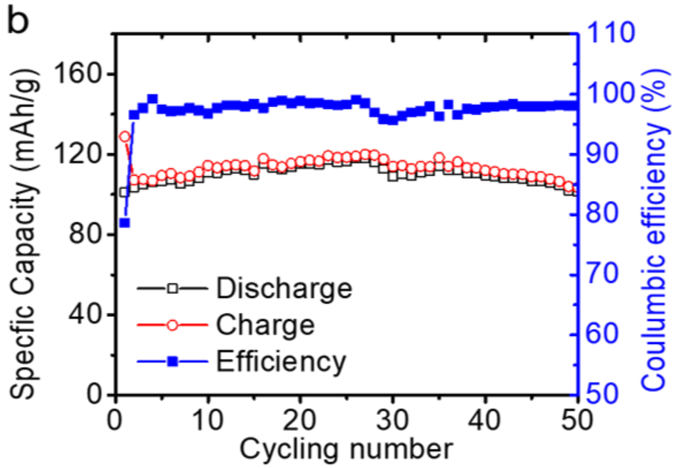
Lithiophobic porous LiF-Li$_3$N electrolyte interlayer for Li dendrite suppression



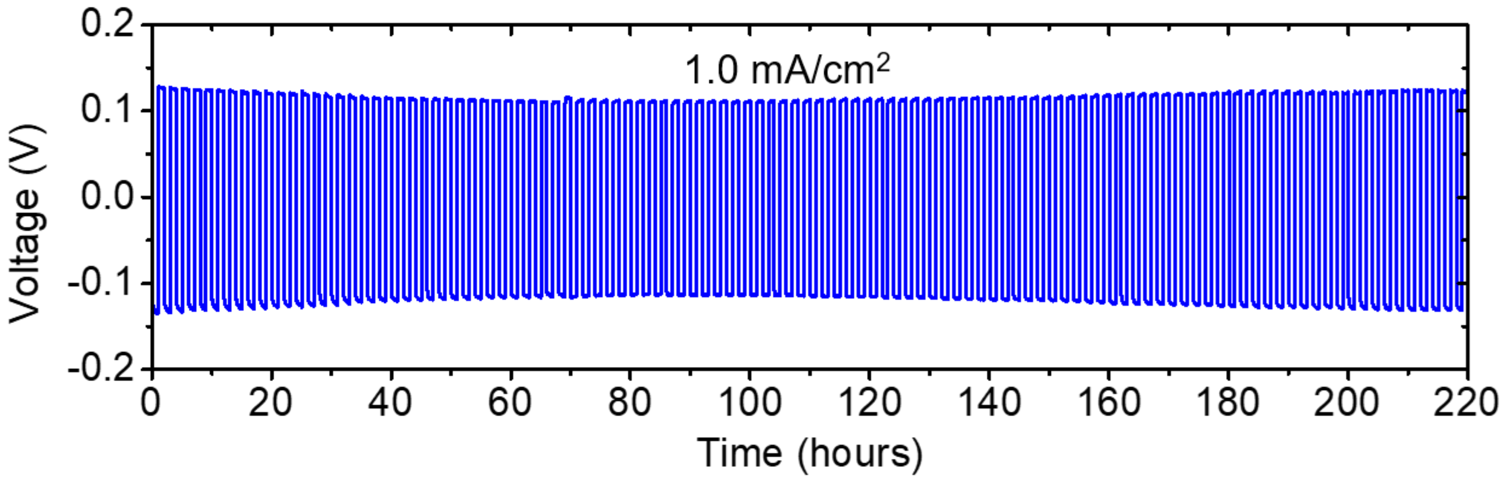
Introducing a stable porous lithiophobic LiF-Li$_3$N layer



Li plating/stripping profiles of Li/Li$_3$N-LiF/LPS/Li3N-LiF/Li at a step-wise current. Li$_3$N-LiF interphase layer enable Li$_3$PS$_4$ to achieve CCD of 6 mA/cm^2 for at 6.0 mAh/cm^2



Coulombic efficiency and capacity stability Li|Li$_3$N-LiF|LPS|LCO cells

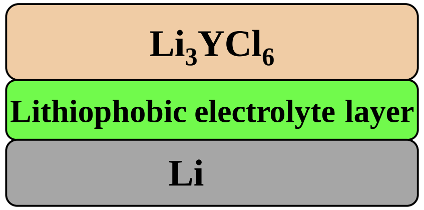


Li$_3$N-LiF interphase layer enable a long-term cycling at current density of 1.0 mA/cm^2 with the capacity of 1.0 mAh/cm^2

Advanced Materials, 2020, 2002741

Accomplishments

Lithiophobic Li_7N_2I-LiOH interlayer and Li_3YCl_6 electrolytes

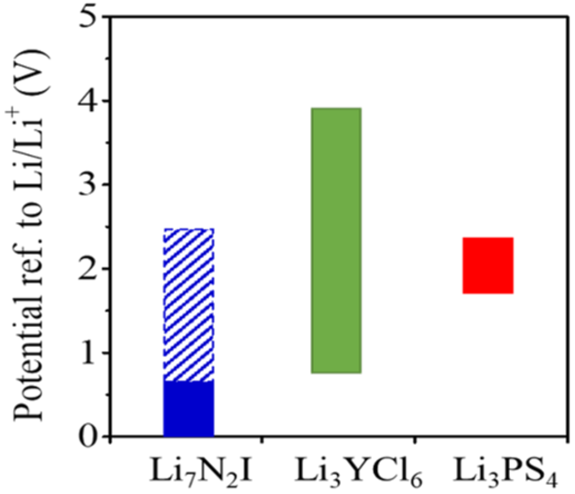


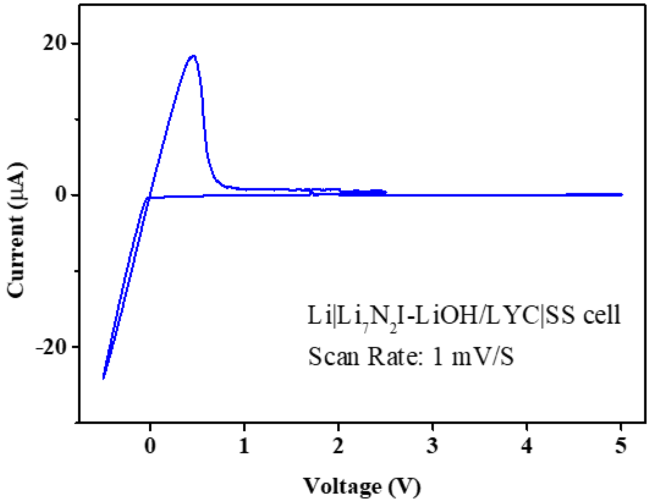
Li_3YCl_6

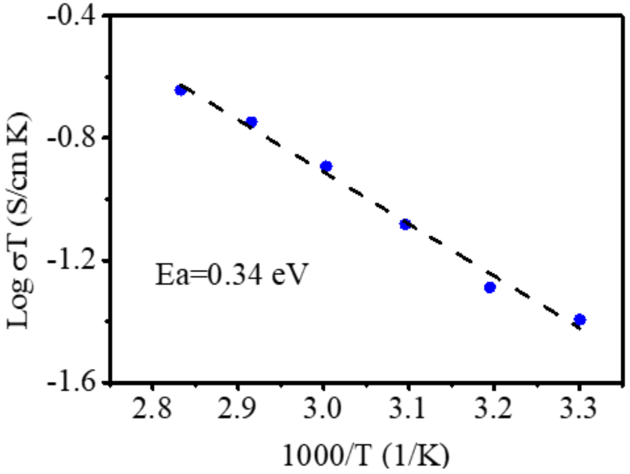
Lithiophobic electrolyte layer

Li

Introducing a stable lithiophobic Li_7N_2I-LiOH electrolyte layer



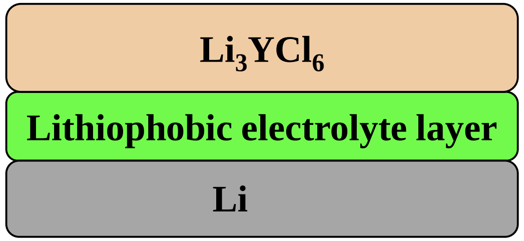




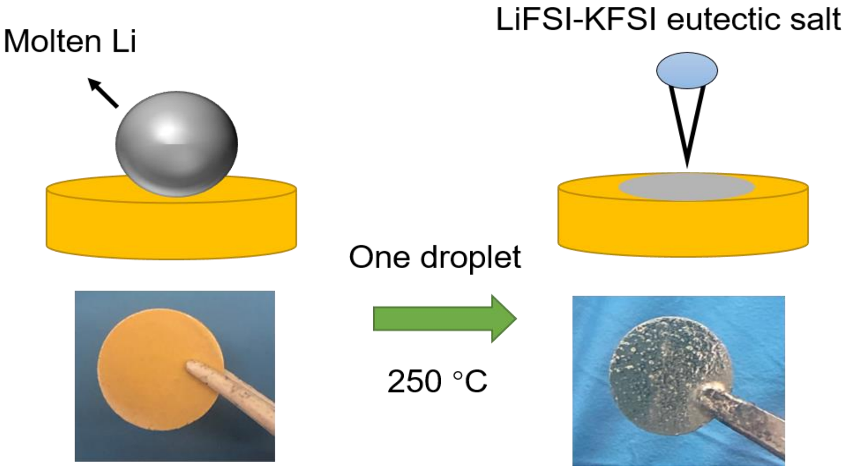
- **First-principles calculation indicates Li_7N_2I-LiOH is stable against Li metal.**
- **Li_7N_2I-LiOH|Li_3YCl_6 bi-layer SSE has a large electrochemical window from 0 to 5 V.**
- **Activation energy is fitted to be 0.34 eV by electrochemical impedance spectra at temperature from 30 to 80 ℃.**
- **Ionic conductivity of Li_7N_2I-LiOH and Li_3YCl_6 are $5×10^{-4}$ S/cm**

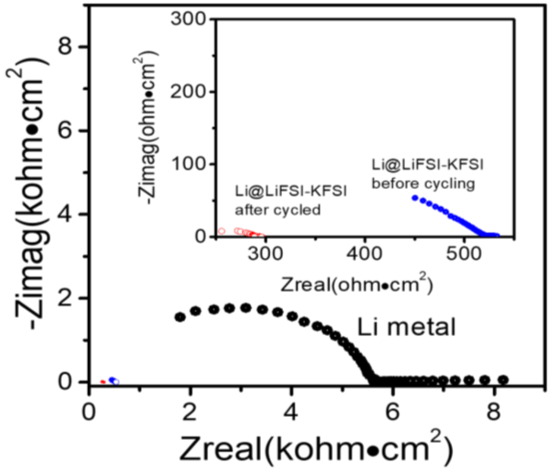
Accomplishments

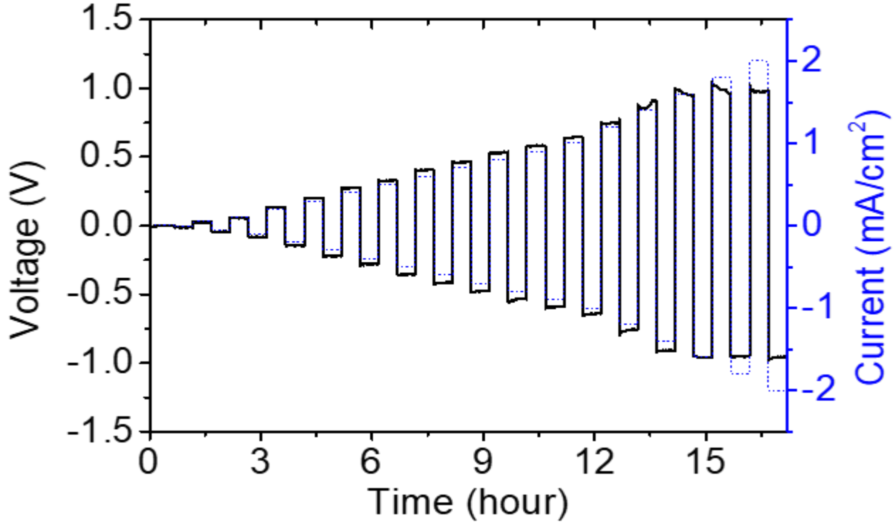
Lithiophobic Li_7N_2I-LiOH inter-layer



Introducing a stable lithiophobic Li_7N_2I-LiOH electrolyte layer



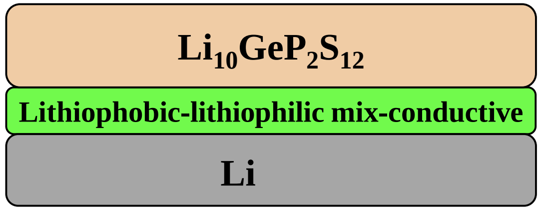




- Lithiophobic Li_7N_2I-LiOH can be wetted with Li by reacting with molten **LiFSI-KFSI** eutectic molten salt at 250 ℃ and reduce the interface resistance.
- Li_7N_2I-LiOH electrolyte can achieve a critical current density of >2 mA/cm^2 with the capacity of >1 mAh/cm^2.

Accomplishments

Lithiophobic-lithiophilic gradient & ionic conductive LiF-Li_xMg interlayer



$Li_{10}GeP_2S_{12}$

Lithiophobic-lithiophilic mix-conductive

Li

Introducing a mixed electronic/ioni conductive and lithiophobic-lithiophilic gradient layer

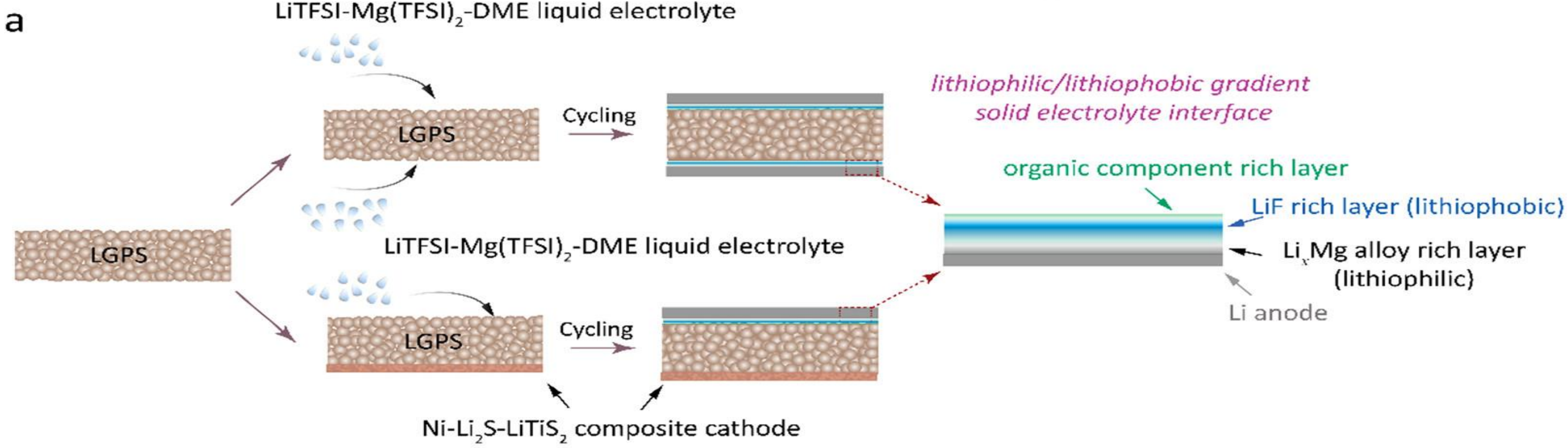
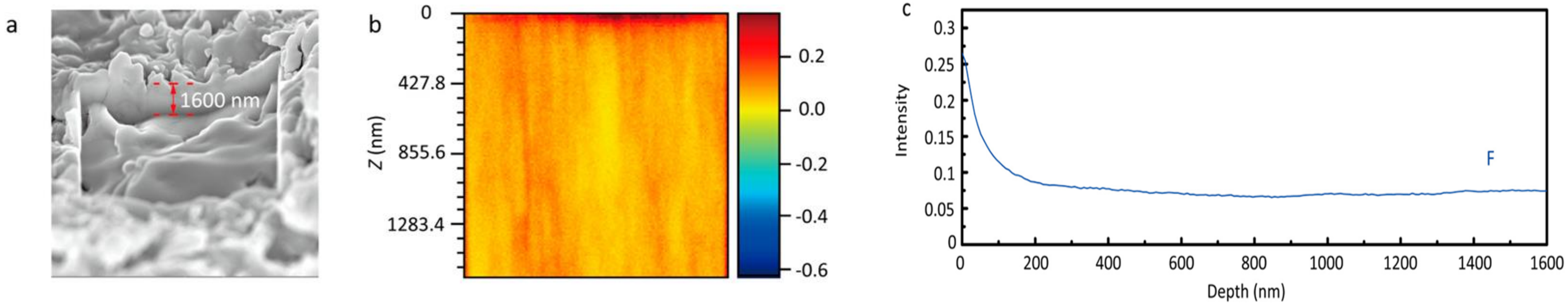


Illustration of *in-situ* formation of the Li_xMg/LiF/polymer (lithiophilic–lithiophobic) solid electrolyte interphase between Li and LGPS after dropping 1.0 M LiTFSI-Mg(TFSI)$_2$-DME liquid electrolyte onto the LGPS membrane surface.

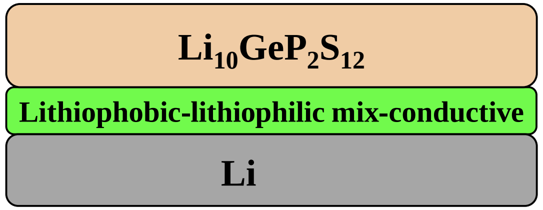


ACS Energy Lett. 2021, 6, 3, 862–868

(a) Crater sputtered by a Ga^+ ion beam for the cycled LGPS in Li/Mg(TFSI)$_2$-LiTFSI-DME@LGPS/Li cell. (b) ToF-SIMS analysis for F element in the cycled Li of Li/Mg(TFSI)$_2$-LiTFSI-DME@LGPS/Li cell. (c) F element distribution of cycled Li in Li/Mg(TFSI)$_2$-LiTFSI-DME@LGPS/Li cell.

Accomplishments

Lithiophobic-lithiophilic gradient & ionic conductive LiF-Li_xMg interlayer

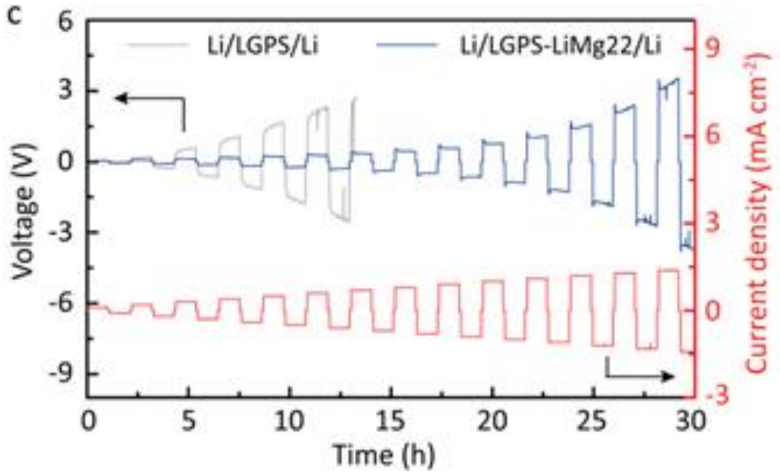


$Li_{10}GeP_2S_{12}$

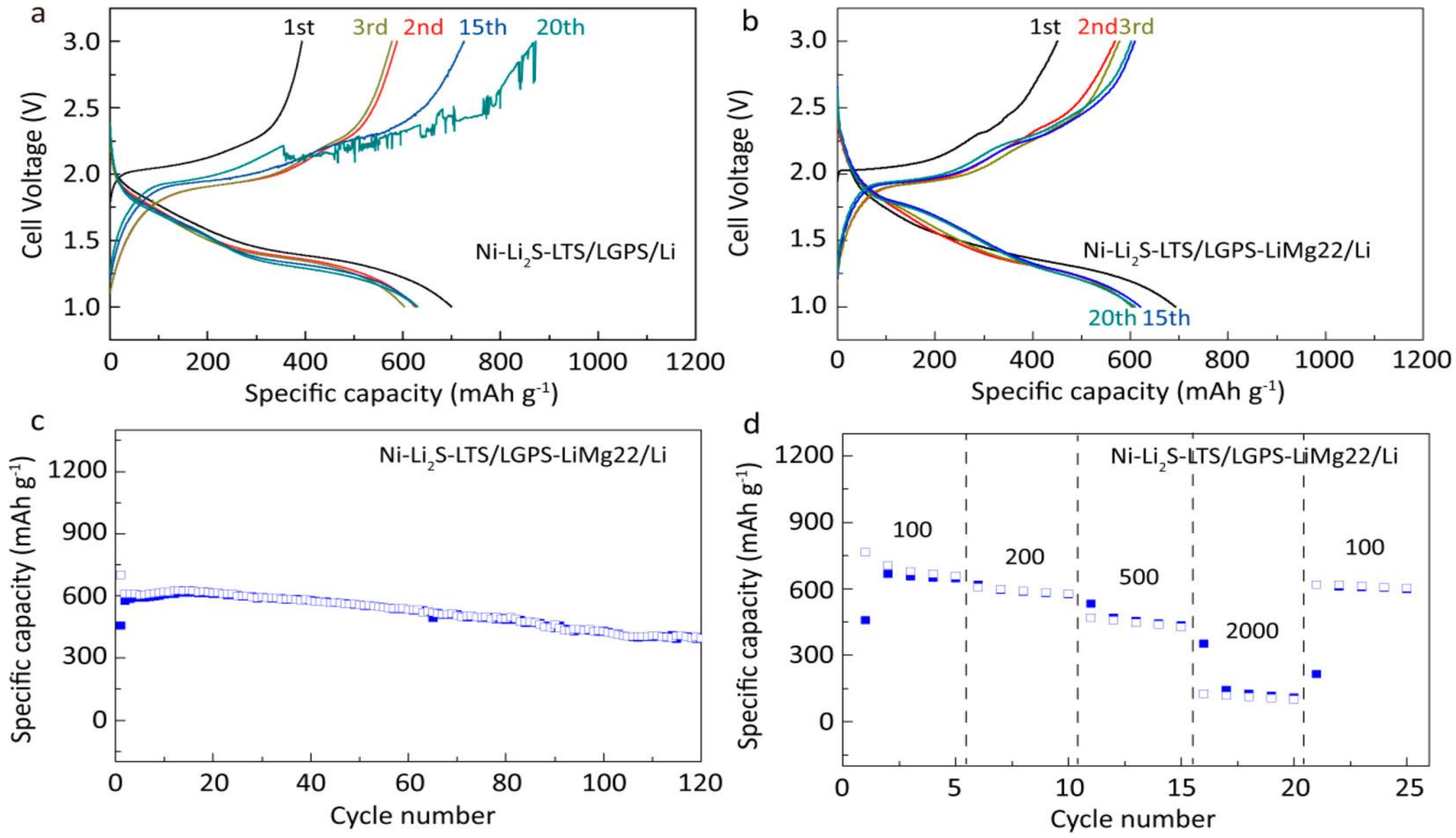
Lithiophobic-lithiophilic mix-conductive

Li

Introducing a mixed electronic/ionic conductive and lithiophobic-lithiophilic gradient layer



Galvanostatic cycling of Li/LGPS (300 μm) /Li cells using LGPS with and without $Mg(TFSI)_2$-LiTFSI-DME treatment at step-increased current densities. The time for each charge and discharge process is 1 h.



Galvanostatic charge/discharge profiles of (a) Ni-Li_2S-$LiTiS_2$/LGPS/Li and (b) Ni-Li_2S-$LiTiS_2$/LGPS-LiMg/Li all-solid-state batteries. (c) Galvanostatic cycling profiles of Ni-Li_2S-$LiTiS_2$/LGPS-LiMg/Li all-solid-state battery at a current density of 100 mA g^{-1}. (d) Rate capability of a Ni-Li_2S-$LiTiS_2$/LGPS-LiMg/Li all-solid-state battery.

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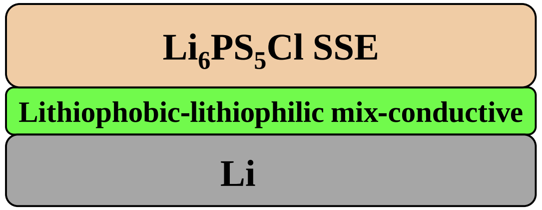
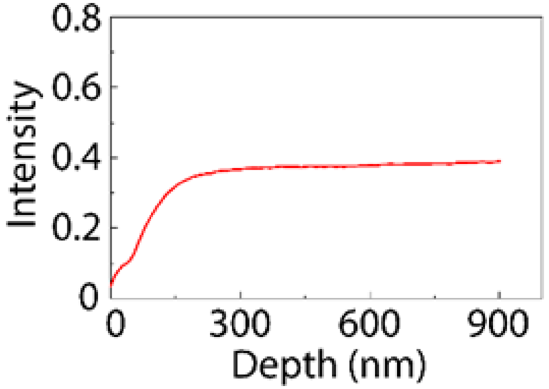
2021, 6, 3, 862–868

Accomplishments

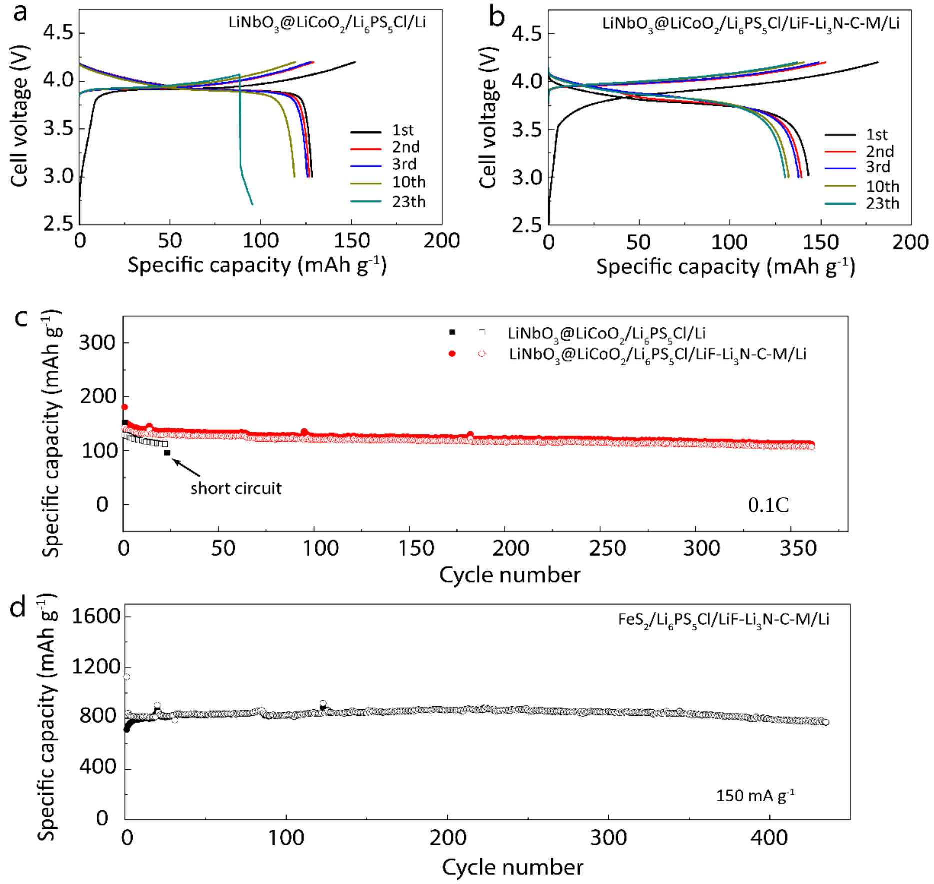
Lithiophobic-lithiophilic gradient &mixed ionic/electronic conductive LiF-C-Li$_x$M interlayer

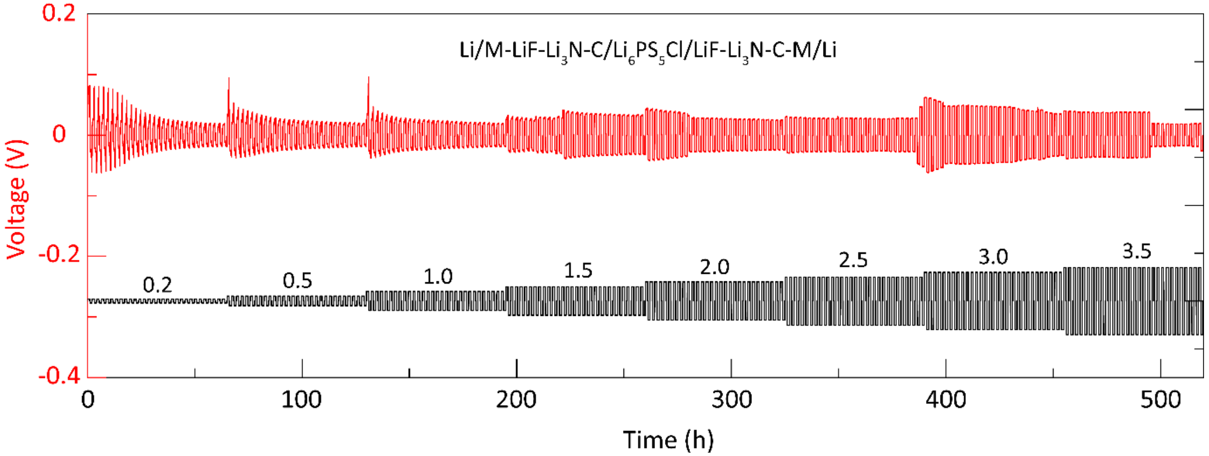


Introducing a mixed electronic/ionic conductive and lithiophobic-lithiophilic gradient layer



F distribution at M-LiF-Li$_3$N-C/SS interlayer





Voltage profiles of Li/M-LiF-Li$_3$N-C/Li$_6$PS$_5$Cl/LiF-Li$_3$N-C-M/Li cell at different current densities, the time for each charge and discharge is 1 hour

Charge/discharge curves and cycle stability of (a,c) LiNbO$_3$@LiCoO$_2$/Li$_6$PS$_5$Cl/Li and (b,c) LiNbO$_3$@LiCoO$_2$/Li$_6$PS$_5$Cl/LiF-Li$_3$N-C-M/Li cell (loading: 0.5mAh cm^{-2}). (d) Cyclic performance of FeS$_2$/Li$_6$PS$_5$Cl/LiF-Li$_3$N-C-M/Li cell (loading: 1.38mAh cm^{-2}).

Responses to Previous Year Reviewers’ Comments

This project was not reviewed last year.

Collaborations

National Institute of Standards and Technology

- Neutron characterization for Li dendrite propagation inside the SSEs.

Brookhaven National Lab

- Synchrotron techniques/capabilities for characterization the stability of SSEs.

Saft America

- Synthesis and characterization of high-capacity cathodes

NIST National Institute of Standards and Technology U.S. Department of Commerce

BROOKHAVEN NATIONAL LABORATORY

saft a company of TOTAL

Remaining Challenges and Barriers

Main barriers: Development of high energy all-solid state Li batteries with long cycles.

Challenges

- Understanding the correlation among critical current, critical overpotential, areal capacity and the intrinsic properties of solid state electrolytes (such as lithiophobicity, thermodynamic stability to Li, solid electrolyte interphase, porosity, thickness, ionic and electronic conductivity etc)
- Fabrication of thin electrolytes and thick cathodes with robust cycling stability.
- A dendrite-free cell still requires a decent mechanical properties of the SSEs, which calls an improvement of manufacturing process of the SSEs.

Proposed Future Research

Develop and validate the Li dendrite suppression criterion based on the thermodynamic of Li dendrite formation

- ➢ Understanding the correlation of critical overpotential and intrinsic property of the solid state electrolytes through thermodynamic analysis.

Develop a comprehensive Li dendrite criterion by combining the Li dendrite formation thermodynamics and kinetics.

- ➢ Understanding the Li dendrite growth kinetics in solid electrolytes

Improve the mechanical properties by advancing manufacturing process

- ➢ Kevlar fiber as supporter the enhance the strength
- ➢ Hot-press the pellet to mitigate the pores and cracks.

Apply the established approaches to synthetic assembling high energy batteries

- ➢ High-voltage battery with NMC 811 cathode
- ➢ High-capacity battery with Li_2S cathode

Any proposed future work is subject to change based on funding levels

Summary

Accomplishments:

- Li_7N_2I-LiOH SSE that is thermodynamically stable and has a high lithiophobisity against Li was synthesized and characterized.
- Ionic conductive LiF-Li_3N layer with a high interfacial energy enable Li_3PS_4 to achieve a high CCD of 6 mA/cm^2 and a long-term cycling stability at 1mA/cm$^{2.}$
- Mixed ionic/electronic conductive and lithiophobic-lithiophilic gradient LiF-Li_3N-C-M layer enable to achieve a Li plating/stripping Coulombic efficiency of 99.6% at a current of 0.2 mA cm^{-2} and capacity of 0.2 mAh cm^{-2} and a critical current of 3.5 mA cm^{-2} at 3.5 mAh cm$^{-2.}$

Impact toward VTO objectives

- This project systematically studied the pathway for all-solid-state Li metal batteries for future vehicle electrification, including theoretical analysis of failure mechanism, design of functional materials, and manufacturing process. A roadmap for high energy all-solid-state battery has been proposed.