Ambient Temperature All-Solid-State Batteries Utilizing Sulfide Based Solid-Electrolytes

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2021 U.S. DOE Vehicle Technologies
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Overview

Timeline

- Project start date: Oct. 1, 2018
- Project end date: Sept. 30, 2021
- Percent complete: 86%

Budget

- FY19 : $400K
- FY20 : $450K
- FY21: $450K

Barriers

Performance: Demonstrating (i) SSBs with specific energy 500 Wh/kg over 1,000 cycles and (iii) solid electrolytes with ionic conductivity > 10^{-4} S/cm at room temperature
Interfacial Stability: Developing sulfide solid electrolytes which are stable against Li anodes and high voltage cathodes
Current Density: Achieving ≥2 mA/cm^2 at room temperature

Partners/Collaborators

- *Pacific Northwest National Laboratory*
  Electron microscopy, Dr. Chongmin Wang
- *Purdue University*
  SSB modeling, Prof. Partha Mukherjee
- *University of Maryland*
  Solid electrolyte optimization, Prof. Chunsheng Wang
- *Hunter's College, New York*
  Solid-state NMR, Prof. Steve Greenbaum

Relevance

Impact

Solid electrolytes (SEs) which have high Li^+ conductivity and form stable interfaces with electrodes are critical to enable Li metal solid-state batteries (SSBs) for EV applications.

Objectives

1. Synthesize sulfide-based superionic conductors and evaluate key properties (e.g., structure, Li^+ conductivity, and electrochemical stability window)
2. Develop coating strategies to improve interfacial stability between sulfide SEs and Li-ion cathodes
3. Study cathode interphase formation using EIS, vibrational spectroscopy, NMR, XRD, and electron microscopy.
4. Demonstrate Li metal SSBs cycled at room temperature and under low stack pressure (<1 MPa).

Relevance to VTO Mission

R&D efforts on SEs and interfaces are critical to meet the VTO's long term goal of 500 Wh/kg and 1,000 cycles for EV applications.

Milestones

Due Date	Description	Status
12/31/2020 (Q1)	Demonstrate and test hot-sintering method to fabricate composite thiophosphate SE-NMC cathodes.	Complete
03/31/2021 (Q2)	Optimize synthesis and processing conditions (for example, interfacial coatings and stack pressure) to minimize the ASR between argyrodite SEs and NMC cathodes.	Complete
06/30/2021 (Q3)	Perform Raman microscopy, NMR, and electron microscopy to characterize bulk argyrodite SE and cathode SE-interfaces to investigate capacity loss and degradation mechanisms.	In progress
09/30/2021 (Q4)	Select and optimize a few solid-state cathode compositions to demonstrate room-temperature cycling with LPS and/or argyrodite SEs. Stretch Goal: 50 cycles with < 20% capacity fade.	In progress

Solid-state batteries (SSBs) containing Li metal anodes have the potential to enable specific energies >400 Wh/kg. This project focuses on synthesis of Li^+ conducting sulfide-based solid electrolytes (SEs) and their integration with high energy cathodes.

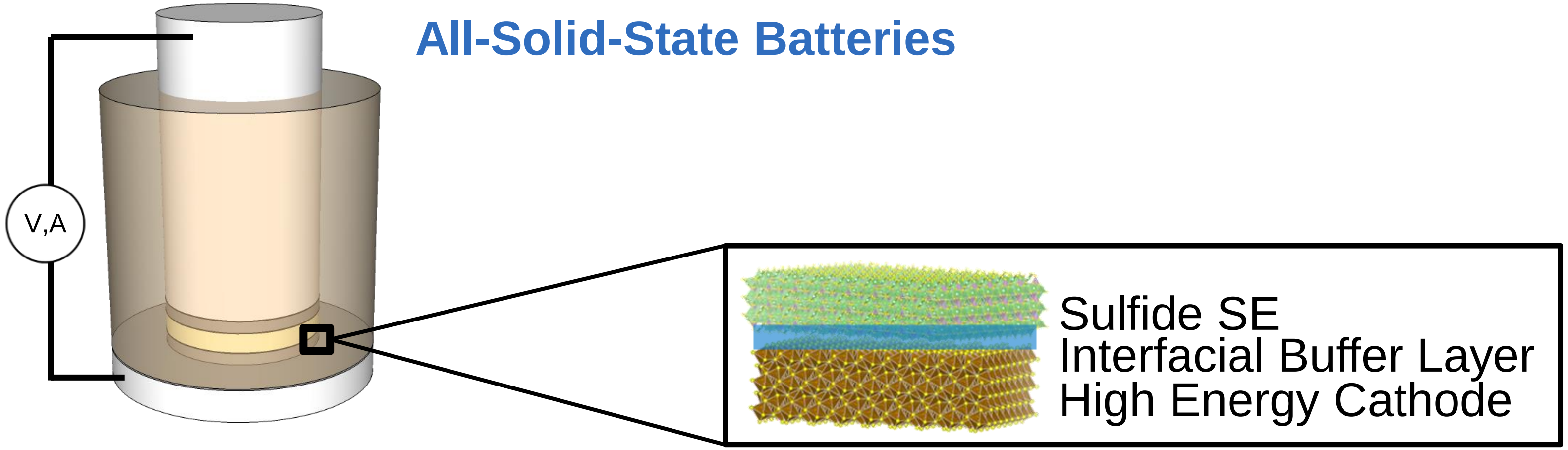
Sulfide SE Advantages

- Superionic conductivity (≥ 10^{-4} S/cm at 25°C)
- Scalable, low temperature synthesis: solvent-mediated routes enable control over composition, structure, and crystallinity
- Soft mechanical properties enable cold-pressing
- Earth abundant and potentially low cost

Challenges

- Chemically unstable in air
- Narrow electrochemical stability window
- Integration into solid-state batteries
  - Cathode/electrolyte interface
  - Li/electrolyte interface

All-Solid-State Batteries



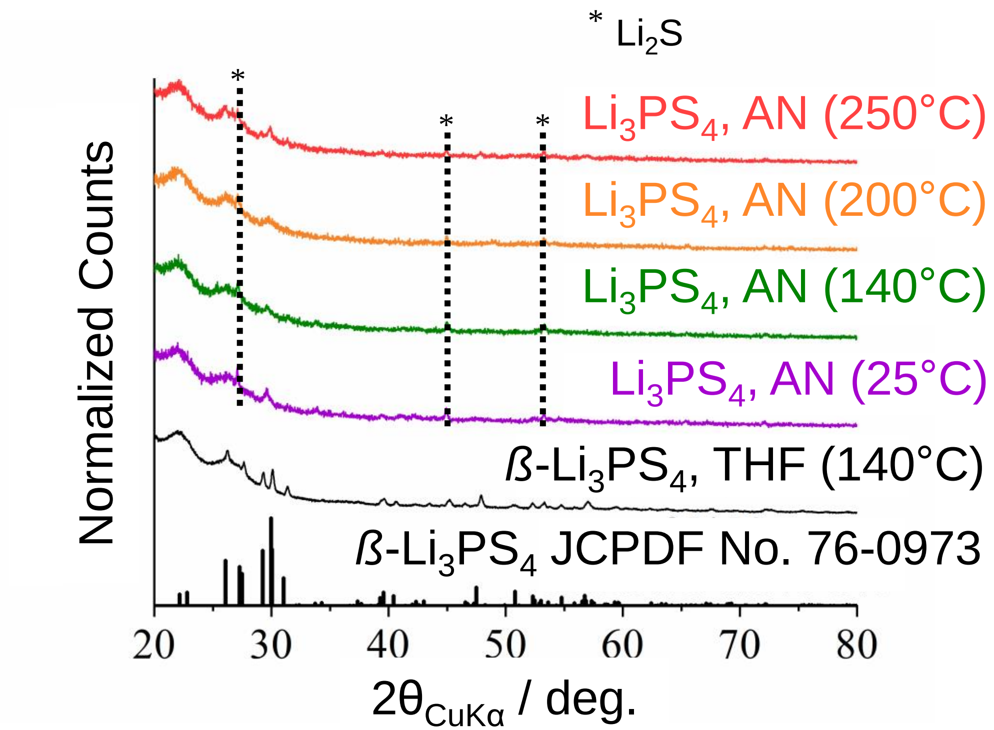
Key Project Goals:

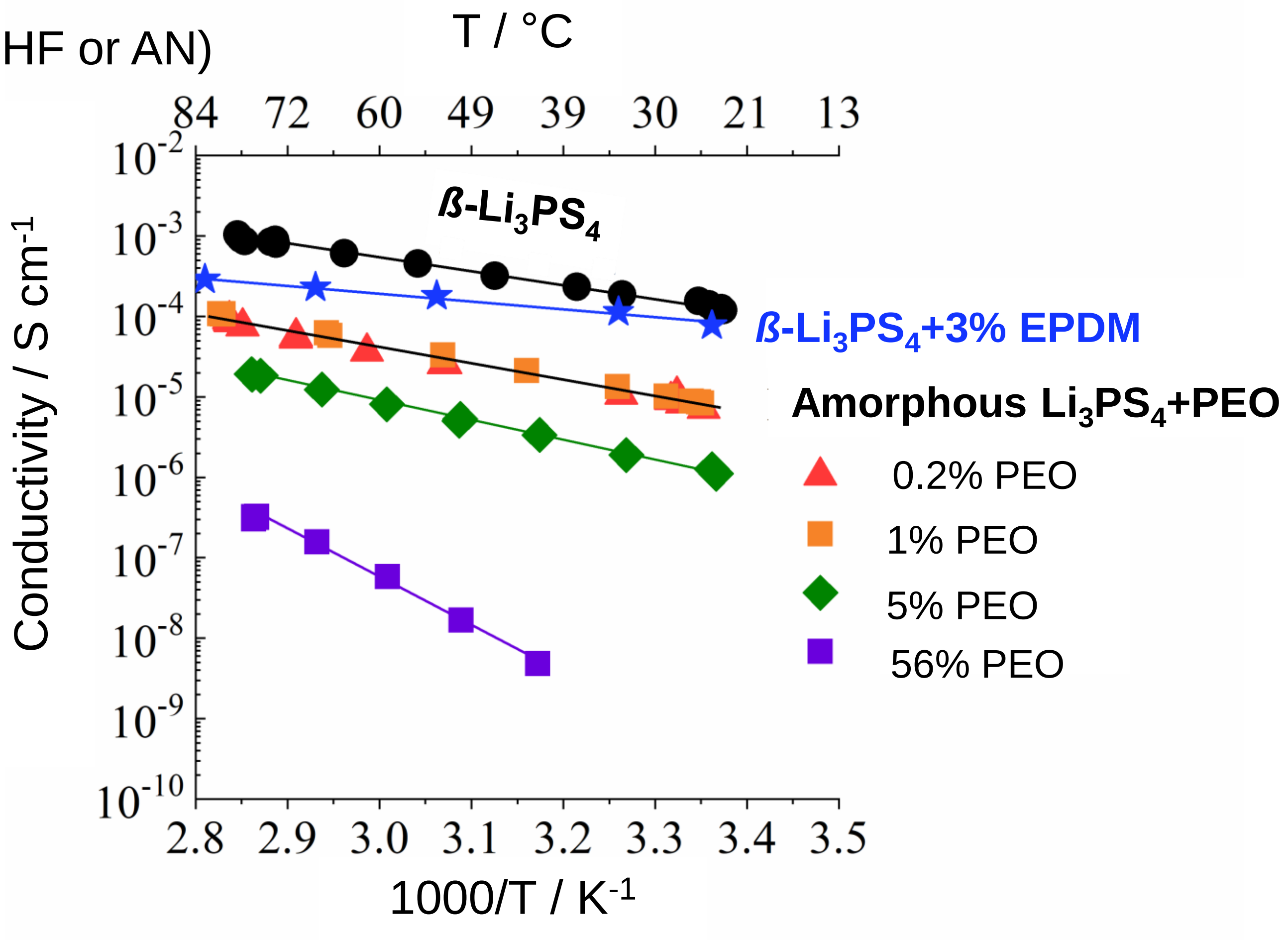
1. Synthesize superionic sulfide SEs using **scalable, solvent-mediated routes**
2. Develop structure/function correlations for sulfide SEs using **advanced characterization methods**
3. Improve cathode/SE and Li/SE compatibility by tuning composition and applying **interfacial buffer layers**.

FY20 Recap: ß-Li_3PS_4 and Li_3PS_4/PEO composites were produced through solvent-mediated routes. Structure and electrochemical properties are highly sensitive to synthesis conditions.

Solvent-Mediated Synthesis

- Blend Li_2S + P_2S_5 (3/1 molar ratio) in solvent (THF or AN)
- Dry at 25-45°C under vacuum
- Anneal at 140-250°C under Ar



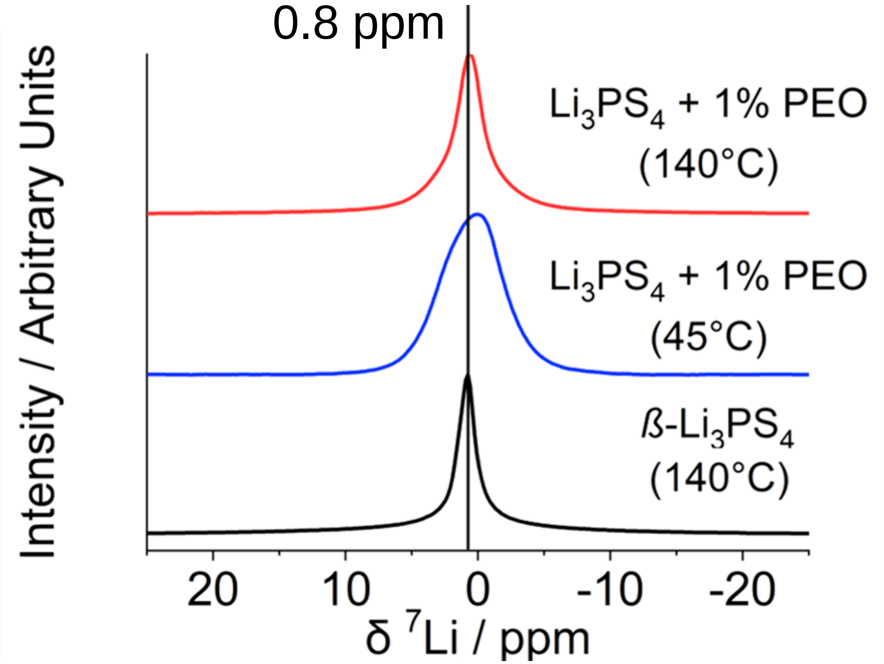


1. Lower conductivity of Li_3PS_4/PEO composites is due to the polymer binder and different P-S polyanionic network compared to ß-Li_3PS_4.
2. Amorphous Li_3PS_4-like product contains several polyanionic groups such as PS_4^{3-}, PS_3^{-} chains, and $P_2S_7^{4-}$.

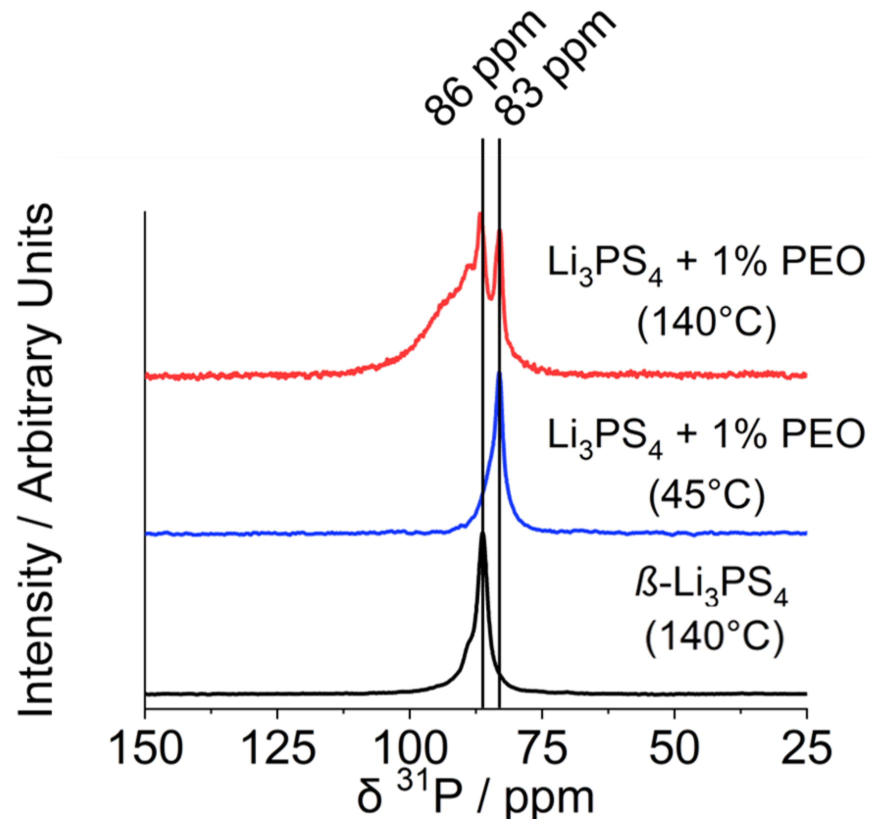
Solid-state NMR was used to further characterize ß-Li_3PS_4 and composite Li_3PS_4+1% PEO SEs. Li^+ mobility (based on FWHM of ^7Li peak) correlates well with measured conductivity.

Sample	Annealing T (°C)	σ_{Li+} at RT (S/cm)	^7Li FWHM (Hz)
Li_3PS_4 + 1% PEO	45	4.5×10^{-9}	618
Li_3PS_4 + 1% PEO	140	8.7×10^{-6}	239
ß-Li_3PS_4	140	1.2×10^{-4}	165

^7Li NMR



^{31}P NMR

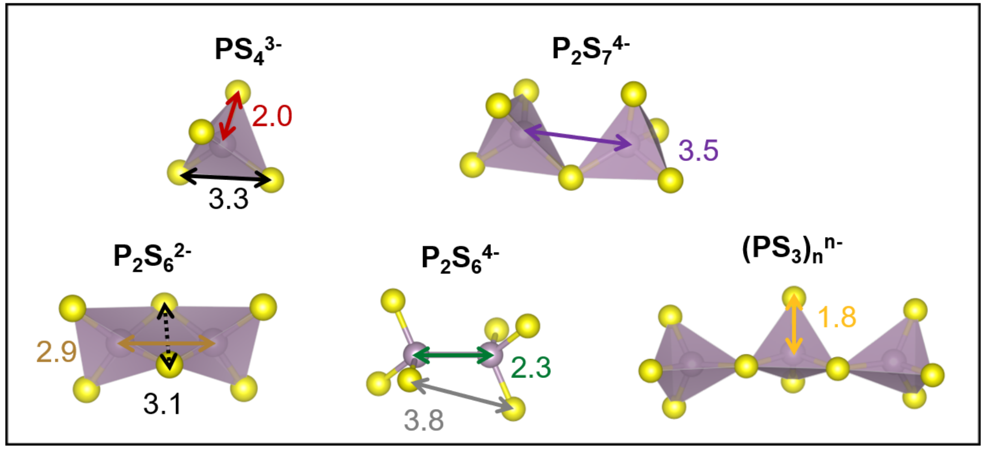


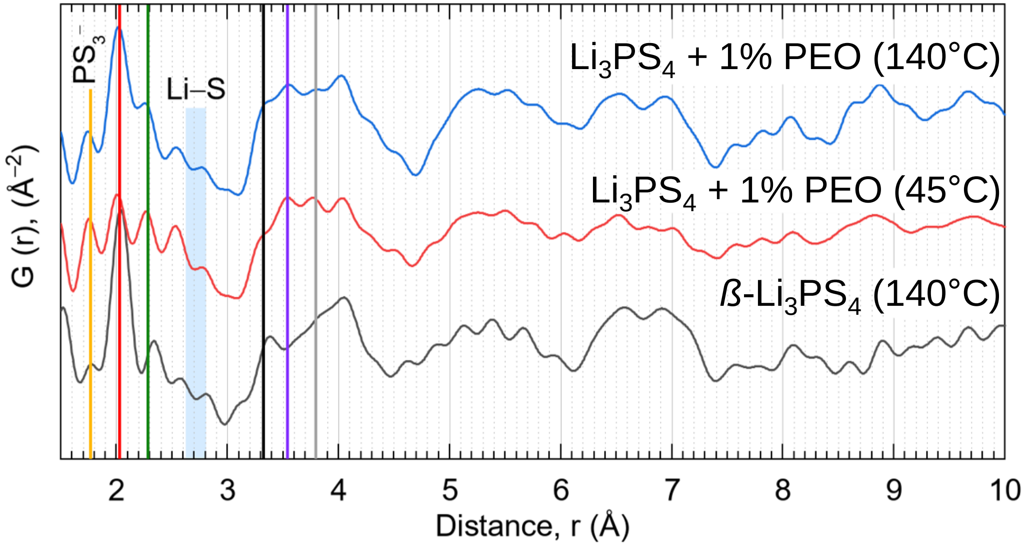
1. Increased ^7Li linewidth of the composites confirms the presence of less mobile Li^+ ions in lower symmetry environments.
2. Multiple ^{31}P bands indicate diverse P coordination in Li_3PS_4/PEO.

Collaboration with S. Greenbaum, Hunter College

Neutron scattering provides key insights on the microstructure of sulfide SEs prepared using solvent-mediated routes.

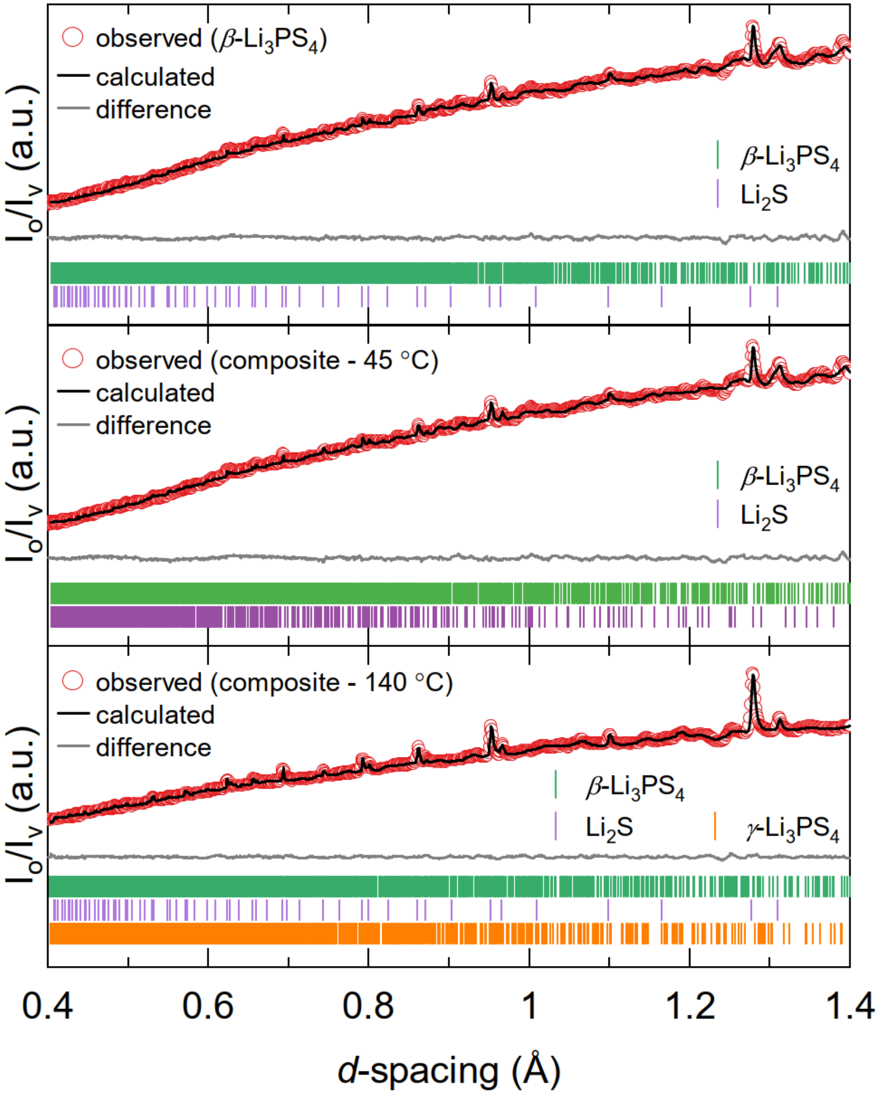
Distinct P-S polyanions identified with nPDF





Structures with high P coordination numbers (e.g., PS_4^{3-} and $P_2S_7^{4-}$) correlate with higher Li^+ mobility compared to other polyanions (e.g., $(PS_3)_n^{n-}$ chains and $P_2S_6^{4-}$).

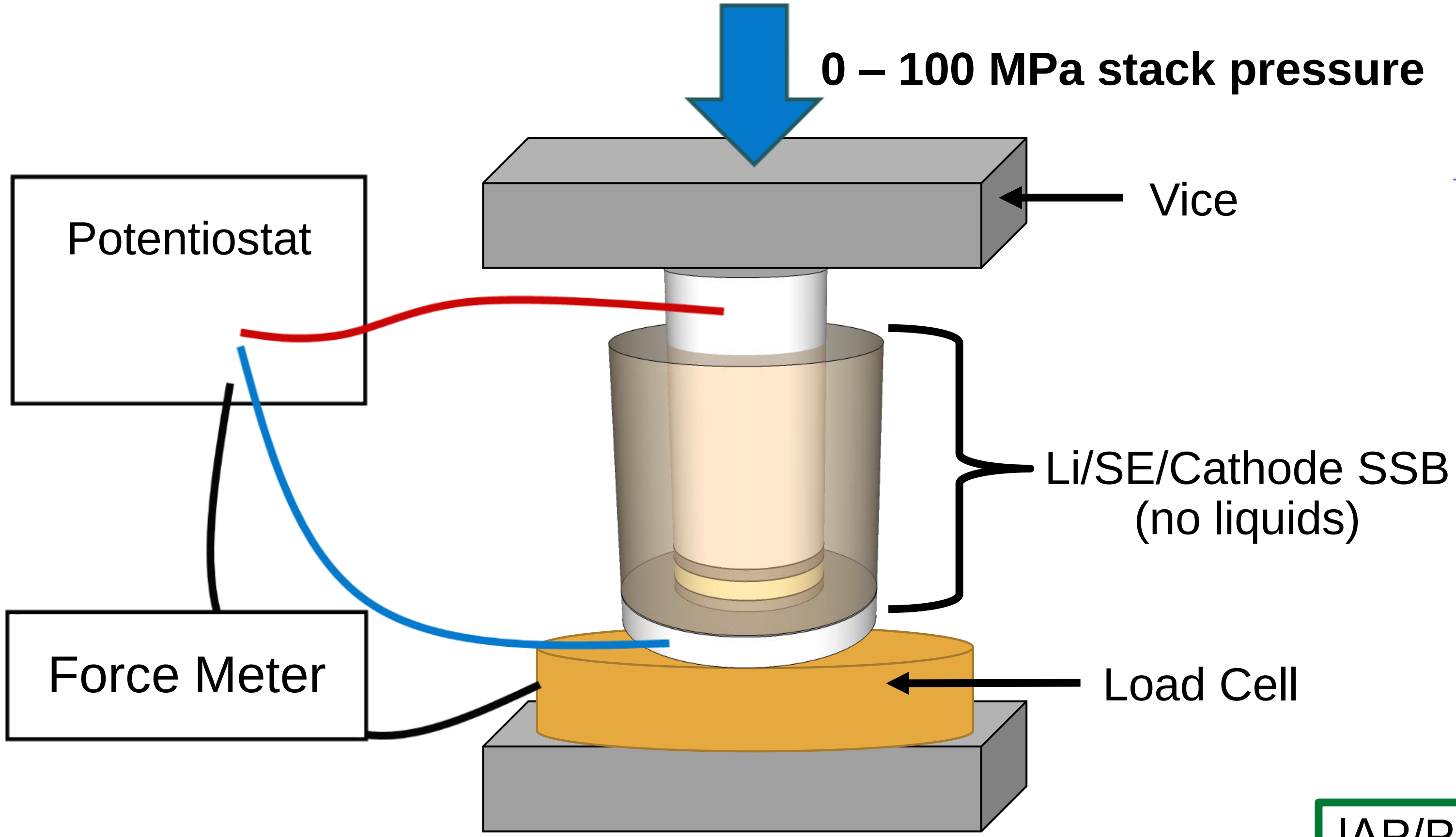
Neutron Diffraction + Refinement



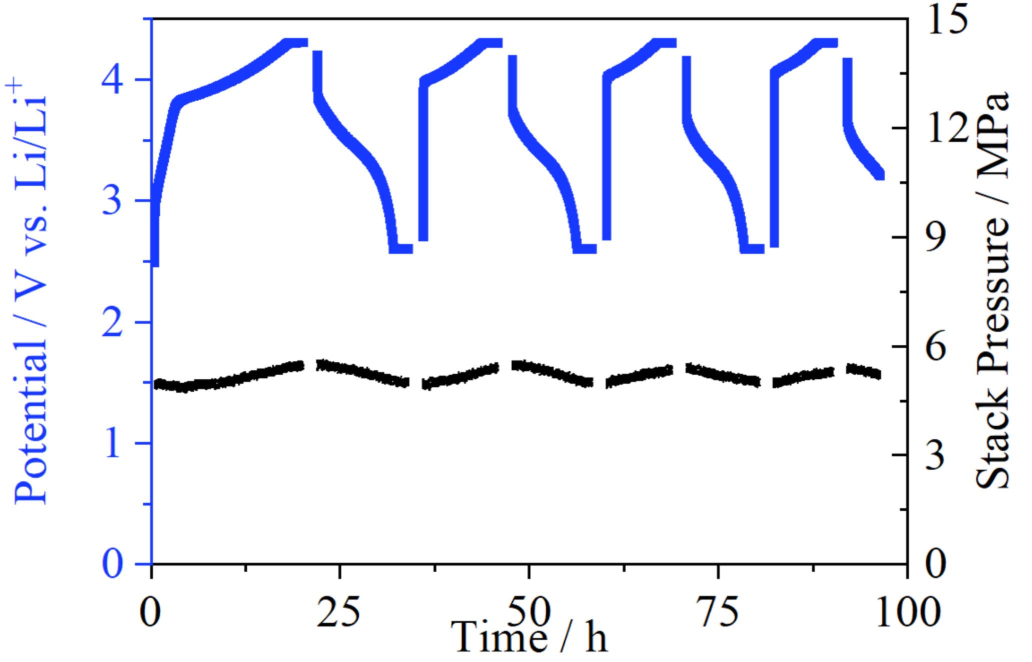
All samples contained trace residual solvent (H absorption background) and amorphous domains (diffuse scattering features)

Collaboration with J. Liu, P.-H. Chien, ORNL

Setup was developed for *in-operando* stack pressure measurements on Li metal SSBs cycled at room temperature. Target stack pressure is <1 MPa for practical cells.



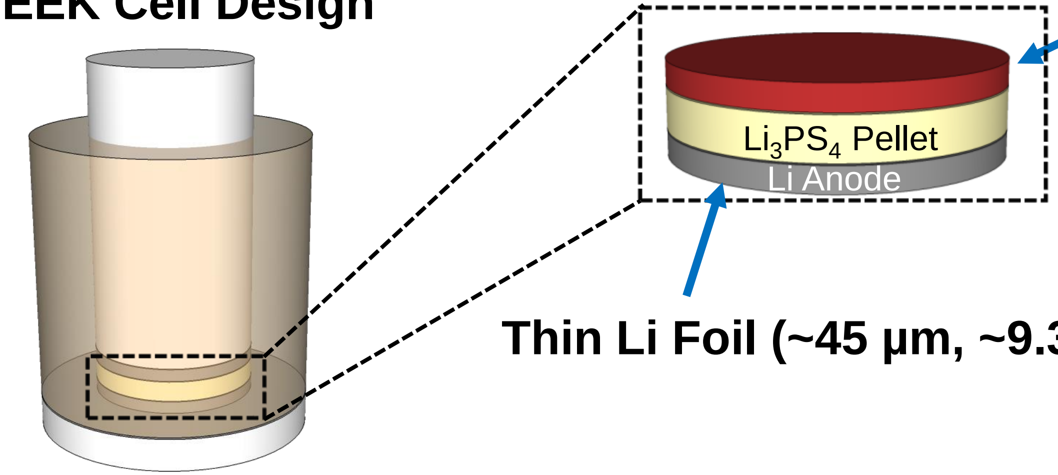
NMC|LPS|Li SSB Cycling



|ΔP/P| ~0.15 during cycling due to electrode volume changes. Effects of different cathode formulations and the corresponding stress evolution can be readily evaluated.

Performance of composite NMC cathodes was benchmarked in Li metal SSBs cycled at room temperature using a moderate stack pressure of 5 MPa.

PEEK Cell Design



Composite Cathode

- 60 wt% NMC811
- 30 wt% β-Li_3PS_4 (LPS)
- 10 wt% Carbon
- 6.6 mg_{NMC}/cm^2 (1.3 mAh/cm^2 for 200 mAh/g)

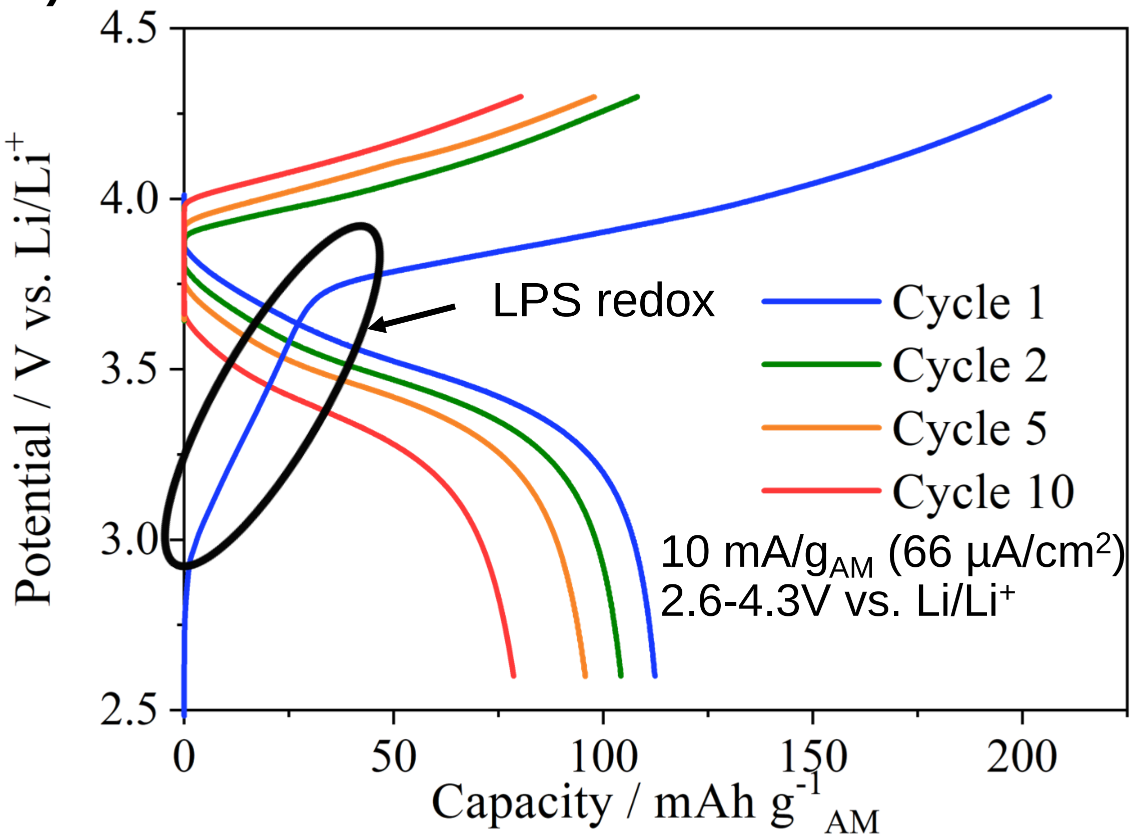
Thin Li Foil (~45 µm, ~9.3mAh/cm²)

Experimental Details

1. Press Li/SE/Cathode pellet at ~500 MPa
2. Apply 5 MPa during cycling

Summary of Results

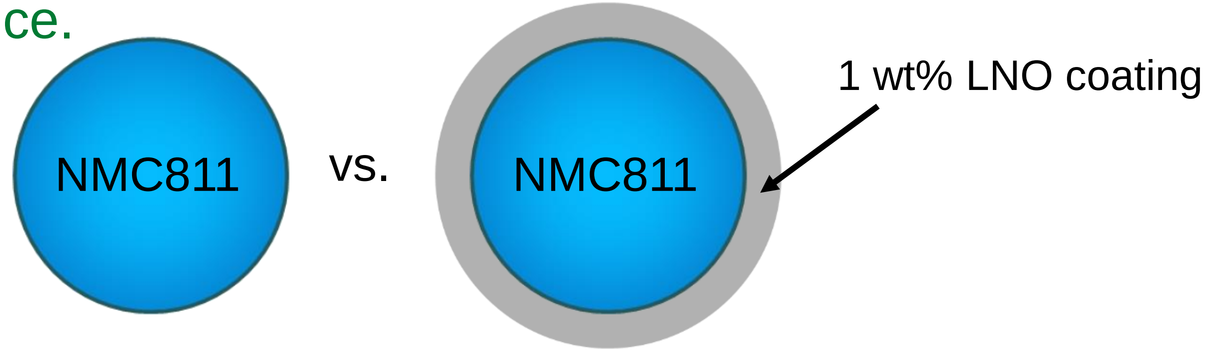
1. Cell exhibits high initial charge capacity ~200 mAh/g but suffers from low initial CE (~50%) due to SE oxidation
2. Extended cycling results in gradual capacity fade and increasing voltage hysteresis, likely due to unstable cathode/electrolyte interface.

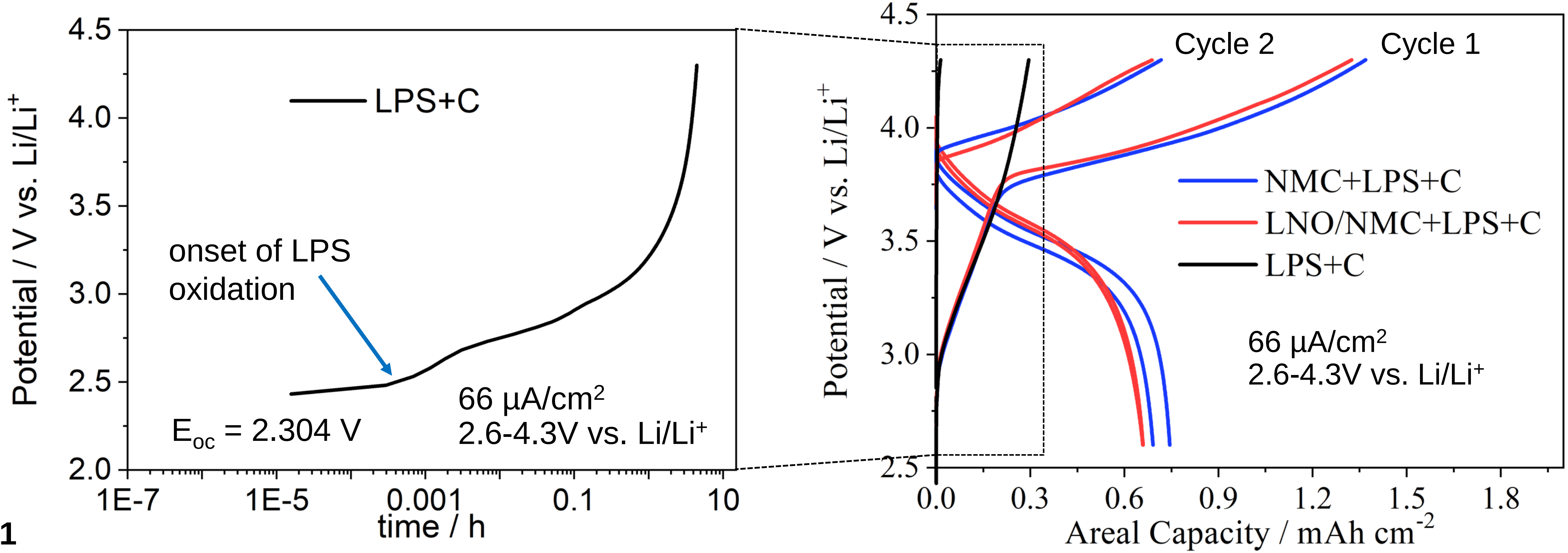


Low initial coulombic efficiency of solid-state NMC cathodes is due to oxidative decomposition of ß-Li_3PS_4 at potentials >2.6 V vs. Li/Li^+. Adding buffer layer (e.g., $LiNbO_3$) on active material particles had only minimal impact on the performance.

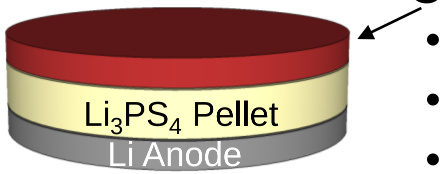
Composite Solid-State Cathodes

- 60 wt% NMC811 with/without $LiNbO_3$ (LNO) coating
- 30 wt% ß-Li_3PS_4 (LPS)
- 10 wt% Carbon
- 6.6 mg_{NMC}/cm^2 (4.4 mg_{LPS+C}/cm^2)





Removing high surface area carbon from composite cathode improves first cycle efficiency at the cost of capacity utilization. Notably, NMC111 could be cycled using low stack pressure (0.3 MPa).



Composite Cathode

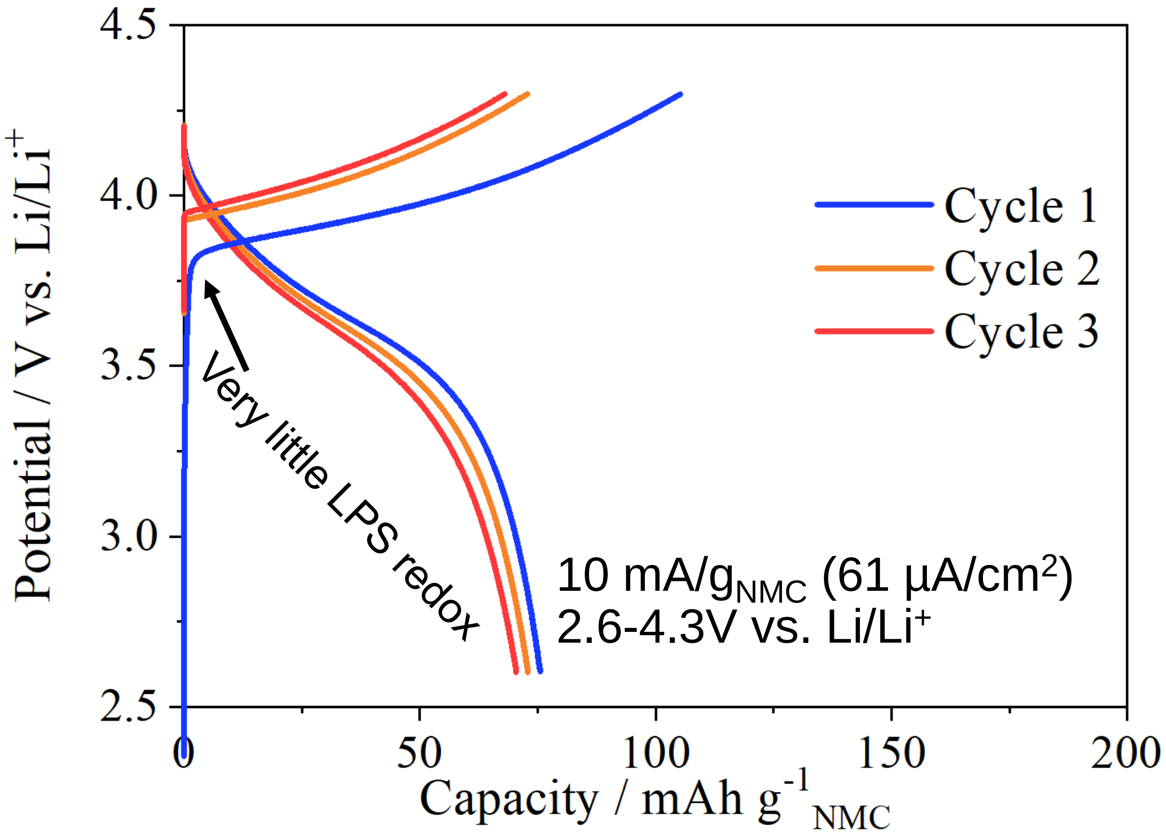
- 70 wt% NMC111
- 30 wt% ß-Li$_3$PS$_4$
- 6.1 mg$_{NMC}$/cm^2

No carbon!

1st cycle performance of NMC with/without carbon additive

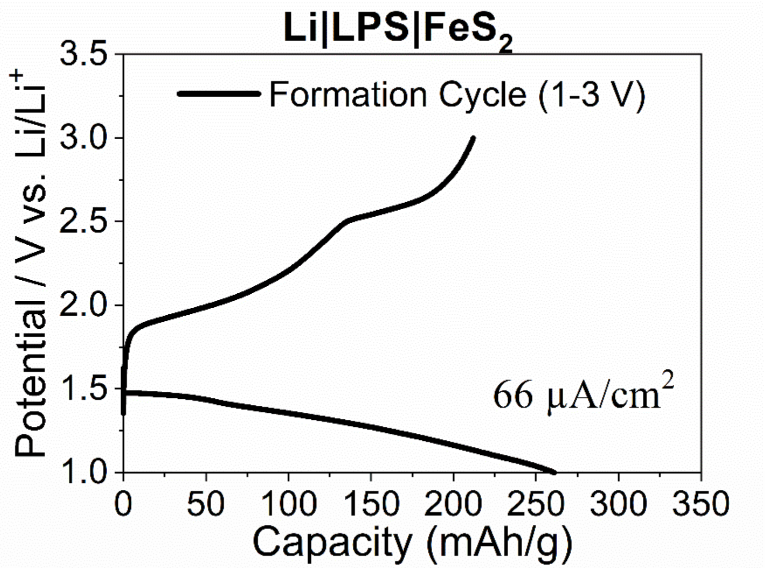
Active Material	Carbon (wt%)	Catholyte	Q_{charge} (mAh/g)	$Q_{discharge}$ (mAh/g)	CE (%)
NMC811	10	ß-Li$_3$PS$_4$	206	112	54
NMC111	0	ß-Li$_3$PS$_4$	105	76	72

Stack Pressure ~0.3 MPa

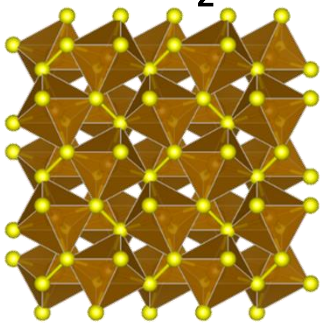


1. High surface area carbon exacerbates ß-Li$_3$PS$_4$ decomposition during charging.
2. Carbon-free composite cathodes must utilize active materials with high electronic conductivity.

FeS_2 solid-state cathode showed excellent reversibility and cyclability when using a ß-Li_3PS_4 catholyte/separator due to the cathode's moderate operating voltage (< 3 V vs. Li/Li^+).



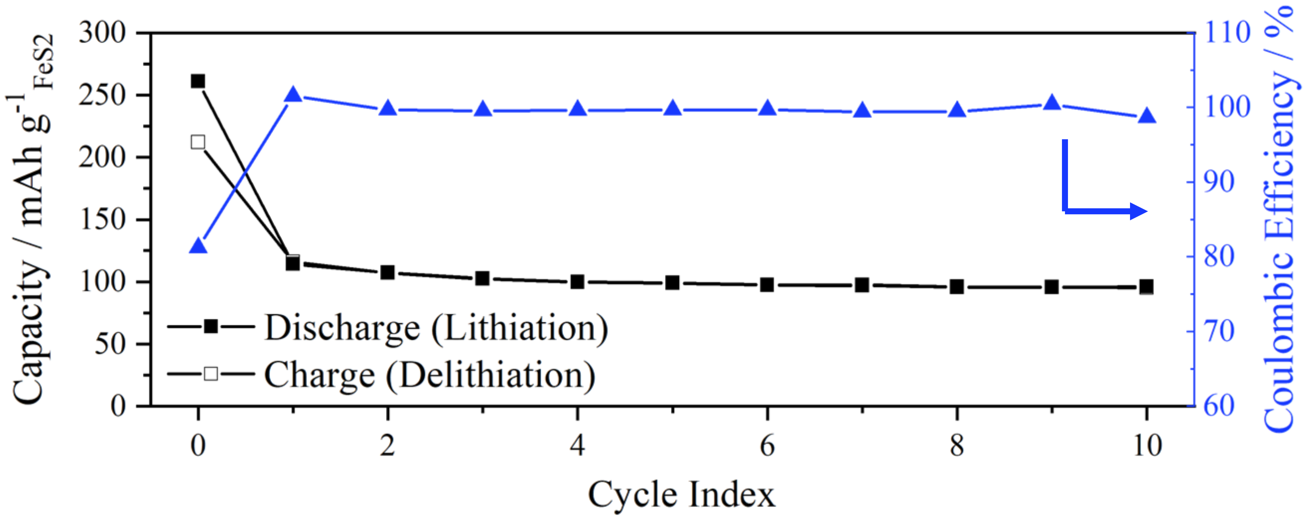
FeS_2

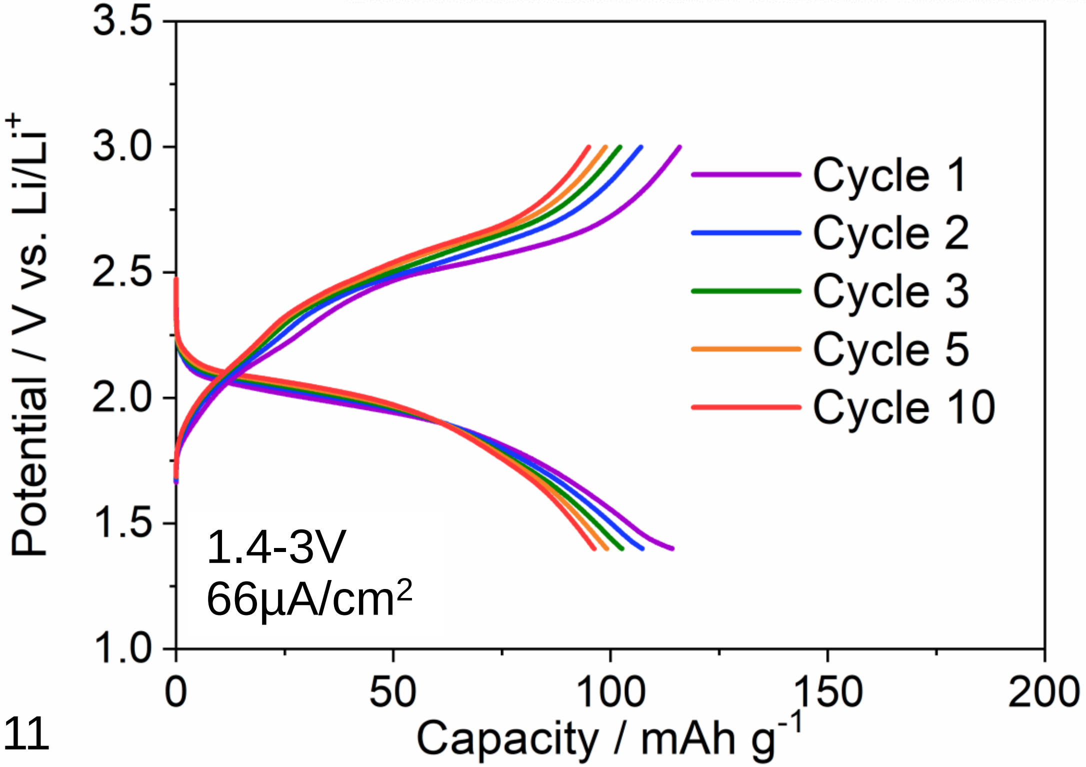


Composite FeS_2 Solid-State Cathode

- 60 wt% FeS_2
- 30 wt% ß-Li_3PS_4
- 10 wt% carbon
- Loading: 6.6 mg FeS_2/cm^2
  - 5.9 mAh/cm^2 for 4 electron transfer

$FeS_2 + 4\,Li^+ + 4\,e^- \leftrightarrow$ **$Fe^0 + 2Li_2S$** ($Q_{theor.}$ = 223*n mAh/g)





Initial CE = 81% for FeS_2 vs. 54% for NMC811

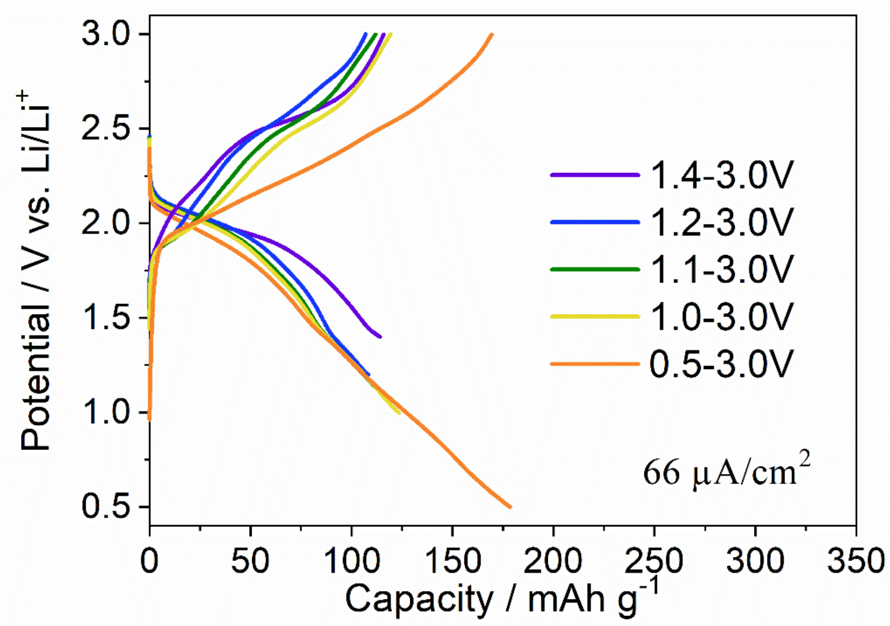
Avg. CE (cycles 2-10) = 99.8% for FeS_2 vs. 98.2% for NMC811

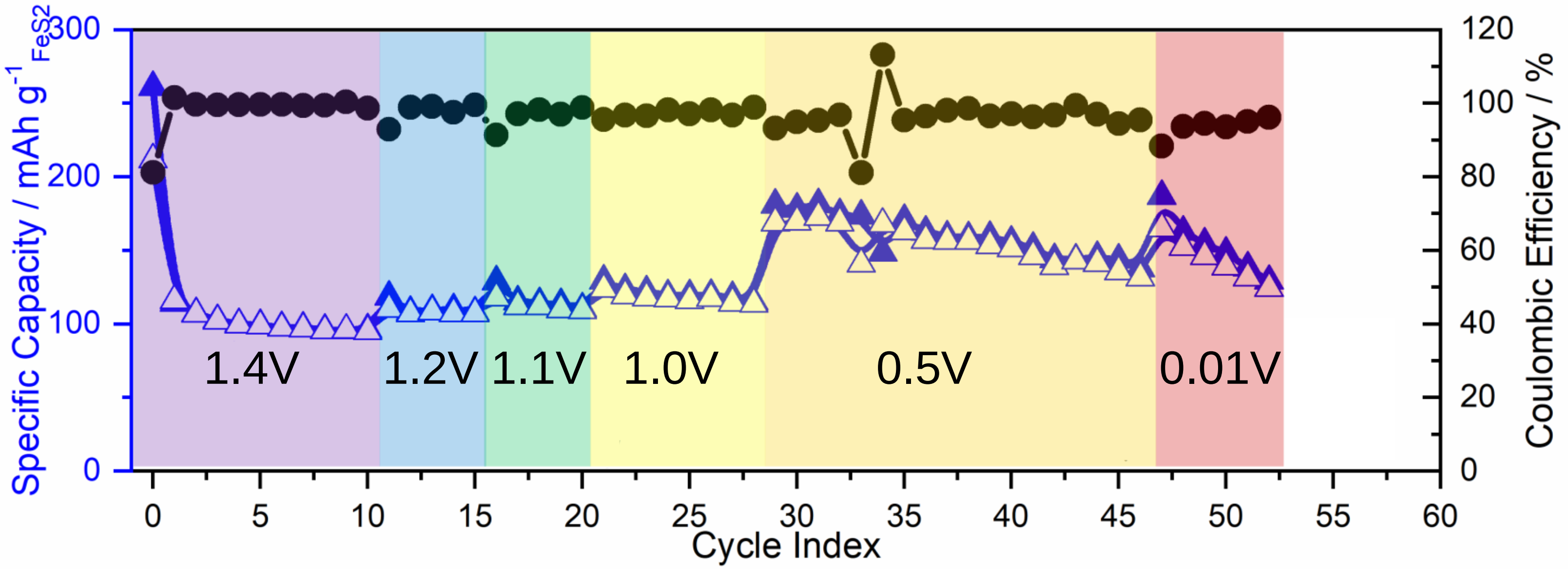
Decreasing lower cutoff voltage increased FeS_2 capacity at the expense of lower CE and stability due to poor reversibility of conversion reaction.

$FeS_2 + 4\,Li^+ + 4\,e^- \leftrightarrow$ **$Fe^0 + 2Li_2S$** ($Q_{theor.} = 223*n$ mAh/g)

Experimental Details

Cell Configuration: Li|LPS|FeS_2+C+LPS
Current Density: 66 µA/cm^2
Upper Cutoff Voltage: 3.0 V vs. Li/Li$^+$
Lower Cutoff Voltage: Varied (0.01-1.4V)





1. Using Li metal anode, cell exhibited capacity ~0.5-1 mAh/cm^2 over 50 cycles at room temperature.
2. Detailed studies on carbon distribution and particle size are needed to optimize FeS_2 performance.

Responses to Previous Year Reviewers’ Comments

This project was not reviewed in FY20.

Collaboration and Coordination with Other Institutions

Pacific Northwest NATIONAL LABORATORY

Electron Microscopy
Dr. Chongmin Wang

HUNTER The City University of New York

Nuclear Magnetic Resonance (NMR) Studies
Prof. Steve Greenbaum

PURDUE UNIVERSITY

SSB Cathode Microstructure and Interfaces Modelling
Prof. Partha Mukherjee

UNIVERSITY OF MARYLAND

Solid Electrolyte Optimization
Prof. Chunsheng Wang

Remaining Challenges and Barriers

1. SSBs with sulfide SE separators typically require high stack pressures to enable cycling at room temperature. Strategies (e.g., improving Li wettability) need to be developed to reduce stack pressure to <1 MPa for practical devices.

2. This project has focused primarily on sulfide SEs produced through solvent-mediated routes. Even after annealing, these materials still contain trace amounts of solvent which may affect SSB performance. Alternate synthesis methods which eliminate solvent processing (e.g., mechanochemical routes) are planned as the next step.

3. Studying buried interfaces in SSBs is difficult, especially when using pellet-type cells which may fracture when harvesting components for *ex-situ* analysis. Advanced *in-situ* methods are needed to gain insights on interphase evolution in SSBs.

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

Proposed Future Research

1. Improve chemical and redox stability of sulfide-based SEs by partial substitution with halides and/or polyanions.

2. Optimize composition and architecture of solid-state conversion cathodes containing earth abundant active materials (e.g., S and FeS_2) which operate at moderate voltages (<3 V vs. Li/Li^+). These materials mitigate sulfide SE oxidation but require careful optimization of carbon distribution, particle size, and loading.

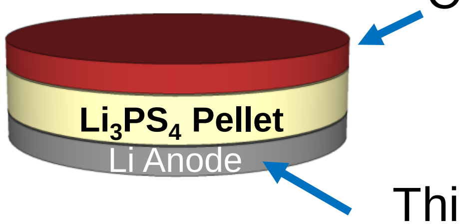
3. Optimize slurry casting procedures to produce sulfide SE layers ≤ 50 µm thick. Thin separators are critical to attain high cell-level energy densities.

4. Evaluate how excess Li inventory affects SSB performance. Practical cells should contain minimal/no excess Li in the anode.

5. Compare the structure and performance of sulfide SEs prepared through alternate synthesis routes (e.g., mechanochemical methods). Equipment for such studies has been acquired, and preliminary investigations are underway.

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

Summary



Composite Cathode
(~1 mAh/cm^2)

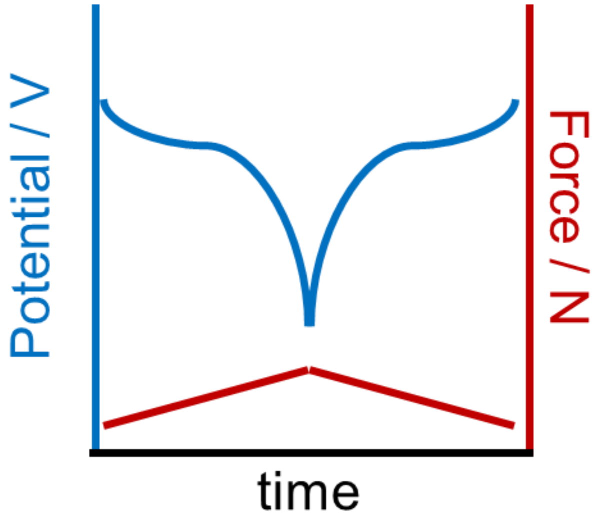
Thin Li Foil
(~45 µm)

Technical Approach:

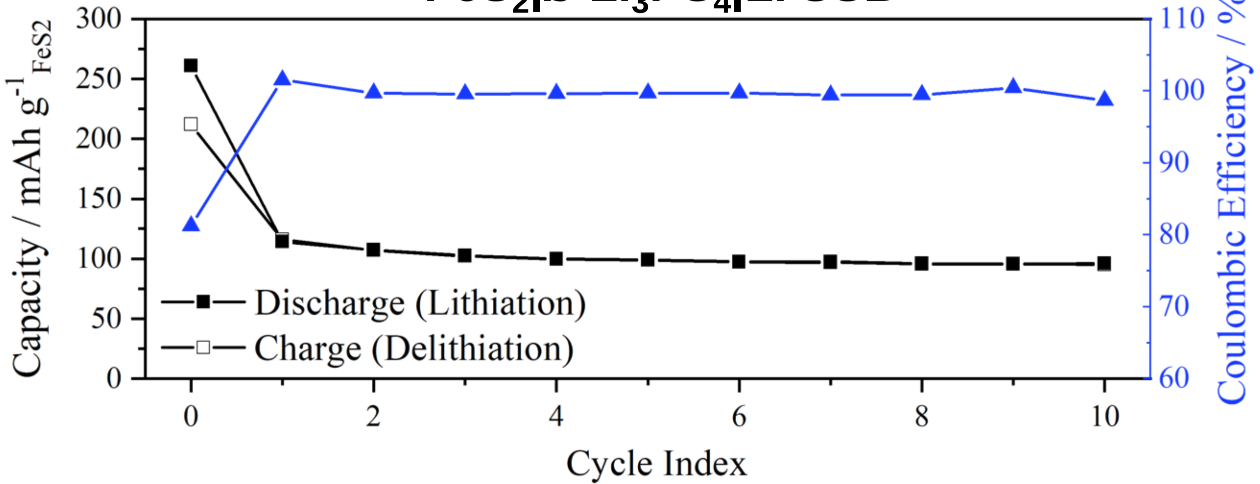
- Developed procedures to benchmark the performance of SSBs containing Li anodes, sulfide SE separators, and composite cathodes
- Designed *in-operando* setup to monitor stack pressure in SSBs

Accomplishments:

- Established structure/function correlations for Li_3PS_4-based SEs using ssNMR and neutron scattering. Li^+ mobility is strongly correlated with P-S coordination.
- Identified oxidative stability limit of Li_3PS_4 SE using composite electrodes containing high surface area carbon
- Demonstrated good cycling stability of FeS_2 solid-state cathode



FeS_2|*ß*-Li_3PS_4|Li SSB



Ongoing Work:

- Optimize performance of Li-free conversion cathodes (e.g., FeS_2, FeF_3, and S).
- Develop tape-casting procedures to produce thin sulfide SE separators (<50 µm).
- Explore mechanochemical synthesis routes to produce new sulfide SE phases (e.g., Li_6PS_5OH).