Development of Long-Life Lithium/Sulfur-Containing Polyacrylonitrile Cells

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University of California, San Diego

June 25th, 2021

Project ID # bat509

BATTERY 500 CONSORTIUM

Overview

Timeline

- Project start date: Oct. 2016
- Project end date: Sept. 2021
- Percent complete: 90%

Budget

- Total project funding
  - DOE share $ 50 M
  - Contractor share
- Funding for FY 2020: $ 10 M
- Funding for FY 2021 (if available): $ 10 M

Barriers

- Barriers addressed
  - 500 Wh/kg Li-S battery
    - High loading sulfur cathode
  - Cycle life
    - Stable, high efficiency lithium anode
    - Solid electrolyte for lithium protection
    - Electrolyte for stable sulfur cycling

Partners

- Project Lead
  - PNNL
- National Laboratories
  - PNNL, INL, Brookhaven, SLAC/Stanford
- Academia
  - Binghamton, U. Washington, U. Texas

Relevance

- **Overall Battery 500 Objective**
  – Develop commercially viable Li battery technologies with a cell level specific energy of 500 Wh/kg through innovative electrode and cell designs that enable utilization of maximum capacity of advanced electrode materials
- **Chemistry**
  – Utilize a L**i metal anode** combined with a compatible electrolyte system, and either
    - A nickel-rich NMC or **S**
- **Keystone project (2): Electrode Architecture**
  – Leverages materials and chemistry advances from Keystone (1): Materials and Interfaces to enable stable, high loading anode and cathode
  – Provides component and materials support for Keystone (3) Cell Design and Integration
  – Focuses on architectures for both Li and cathodes

Milestones: Keystone 2 and UCSD

End date	12/31/2020	03/31/2021	06/30/2021	09/30/2021
Keystone Project 2 Electrode Architecture	Compare new Li anode architecture with 50 micron Li anode using protocols for 350 Wh/kg cells **Completed**	Measure solid or semisolid (oxides, polymer or composites) electrolyte performance using protocols for 350 Wh/kg cells **Completed**	Compare pan-S cathode with benchmark S cathode using protocols for 300 Wh/kg cells with 50 cycles **In Progress**	Propose strategies to incorporate Li anode, Li protection for practically implementing into pouch cells **In Progress**
UCSD	Structural characterization of coated NMC with benchmark NMC using protocols for 350 Wh/kg cells **Completed**	Develop understanding of SPAN structure and reaction mechanisms **Completed**	Compare SPAN cathode with benchmark S cathode using protocols for 300 Wh/kg cells with 50 cycle **In Progress**	Propose strategies to incorporate Li anode, Li protection for practically implementing into pouch cells **In Progress**

Keystone 2 Challenges and Approaches

3D Hosts for Lithium

UNIVERSITY of WASHINGTON

Modeling

UC San Diego

Analysis

SLAC NATIONAL ACCELERATOR LABORATORY

Solid Electrolytes

THE UNIVERSITY OF TEXAS AT AUSTIN

STANFORD UNIVERSITY

3D architecture

Pacific Northwest NATIONAL LABORATORY

UC San Diego

A combined experiment, modeling, and characterization effort to:

- Understand how lithium is lost
- Model and experimentally investigate effect of pressure
- Develop new solid electrolytes and coatings to protect Li
- *Design new 3D architectures to achieve high efficiency and long cycle life*

Thick cathode architecture > 6 mAh/cm^2 SPAN

UC San Diego

Pacific Northwest NATIONAL LABORATORY

BROOKHAVEN NATIONAL LABORATORY

Engineer high-loading SPAN electrode to maximize cell energy density

- Understand SPAN working mechanisms
- Develop electrolyte formulations that enable both Li and SPAN
- *Optimize binder, porosity, and electrode conductivity*
- *Demonstrate performance in pouch cells*

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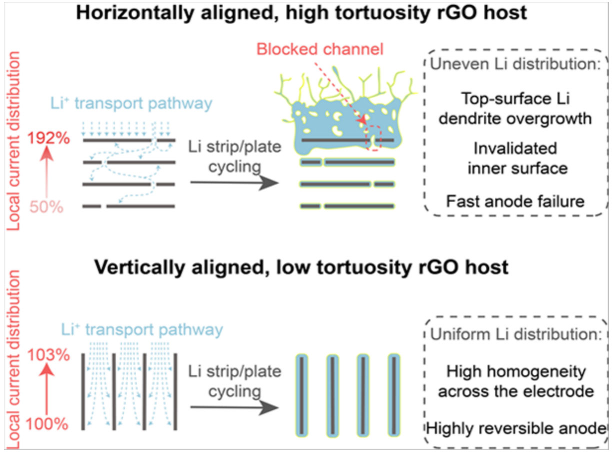
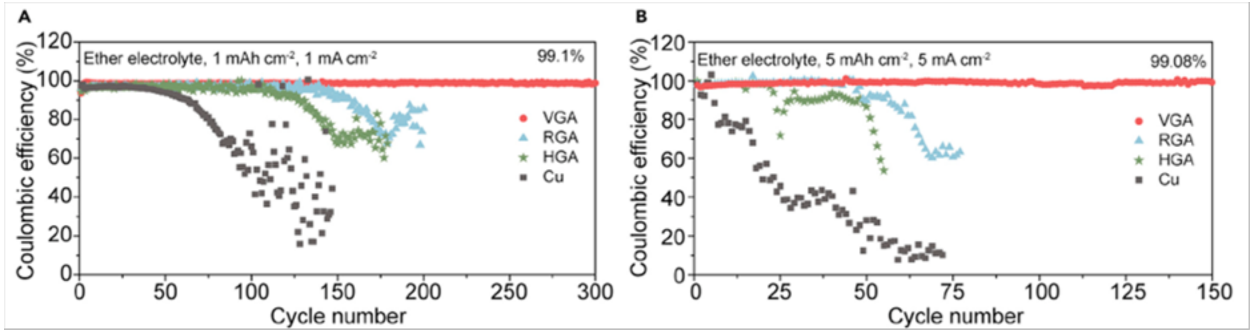
Technical Accomplishments: New 3D Li Architecture-1

Cui STANFORD UNIVERSITY



Vertically aligned, low tortuosity host is highly beneficial

H. Chen, A. Pei, J. Wan, D. Lin, R. Vila, H. Wang, D. Mackanic, H.-G. Steinruck, W. Huang, Y. Li, A. Yang, J. Xie, Y. Wu, H. Wang, and Y. Cui, "Tortuosity Effects in Lithium-Metal Host Anodes" *Joule* (2020) DOI: 10.1016/j.joule.2020.03.008



Technical Accomplishments: New 3D Li Architecture-2

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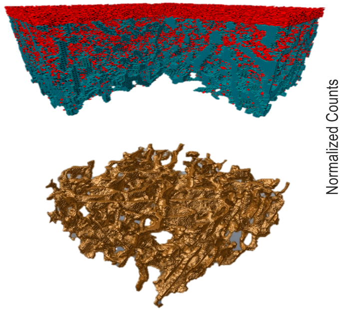

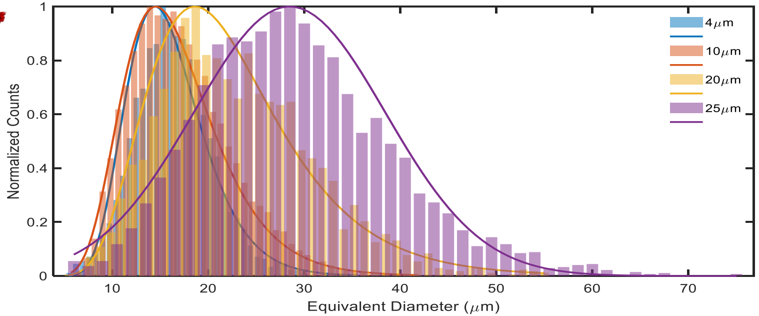

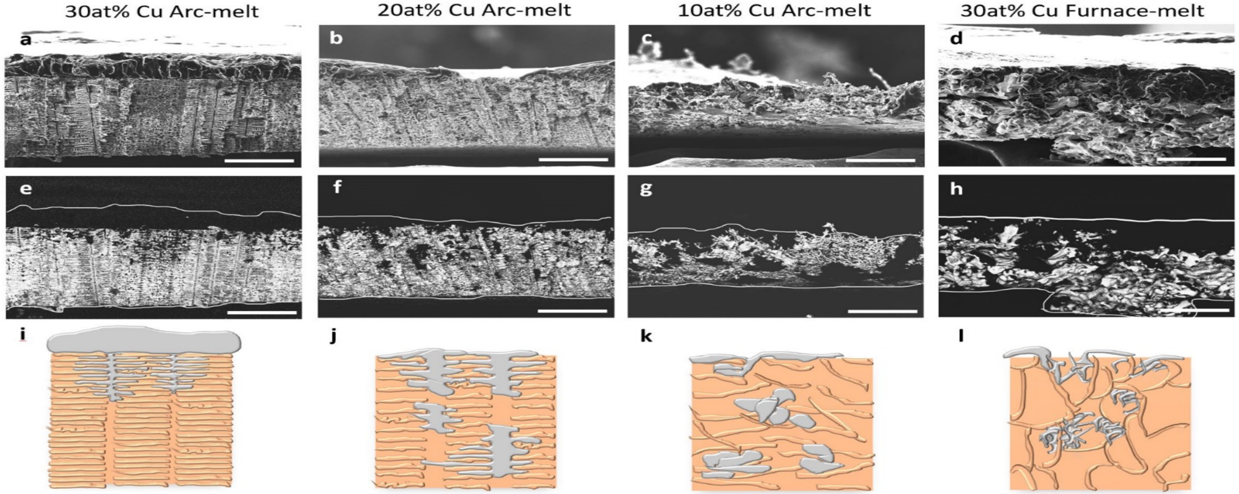

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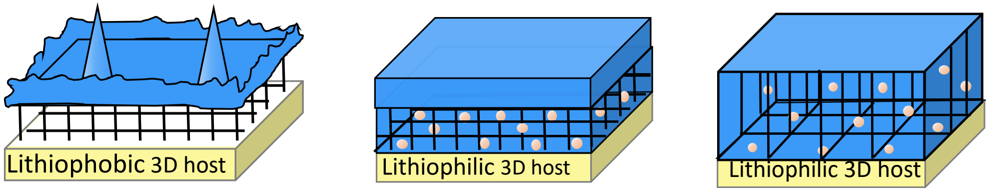
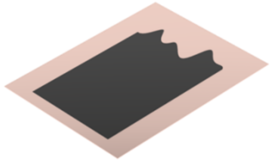
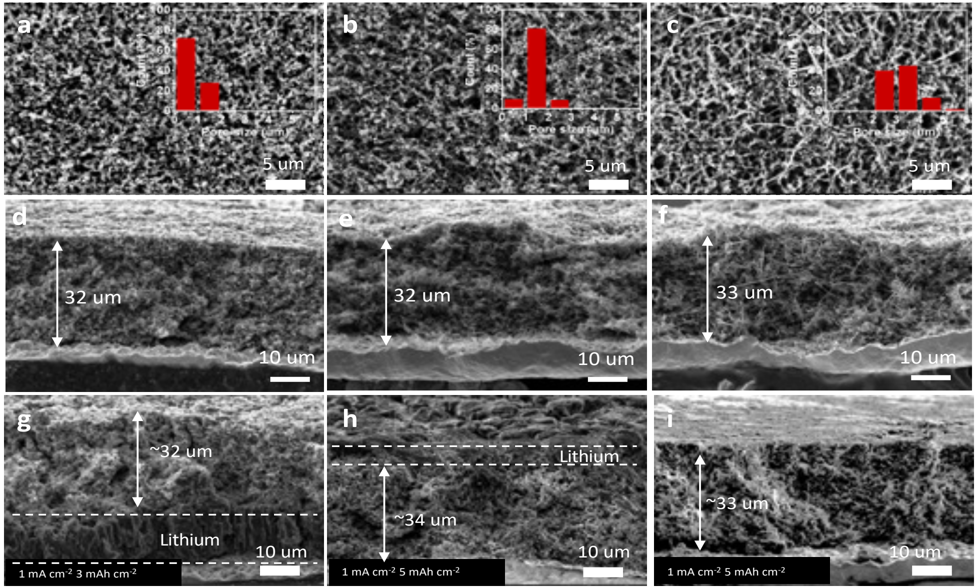
Imaging provides quantitative description of 3D hosts

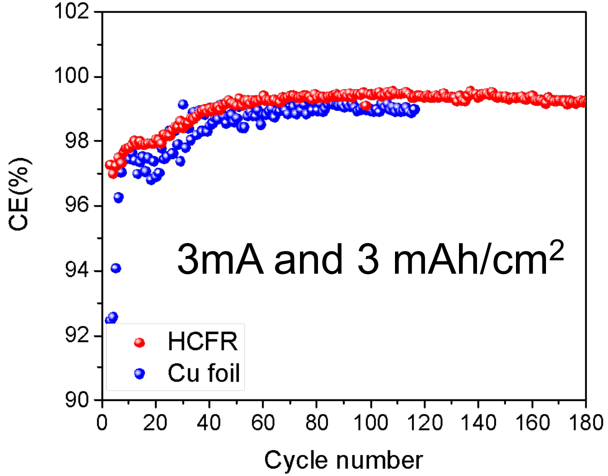
Technical Accomplishments: New 3D Li Architecture-3

Liu UC San Diego









Carbon nanofiber enables 80% porosity and 2000 mAh/g capacity

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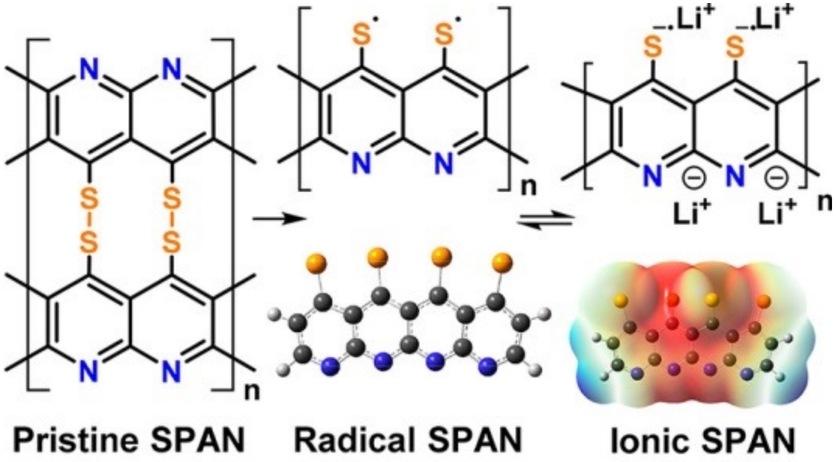
Technical Accomplishments:
Towards Stable 250-300 Wh/kg Li/SPAN Pouch Cell



Wang, ACS Energy Lett. 3, 289

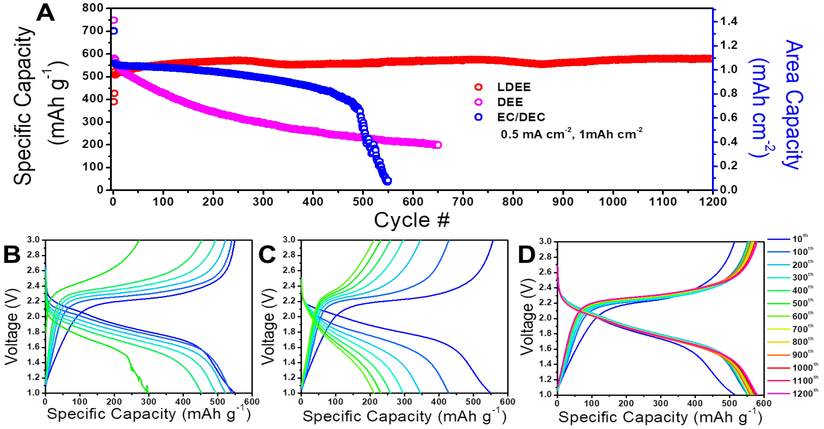
Advantages:

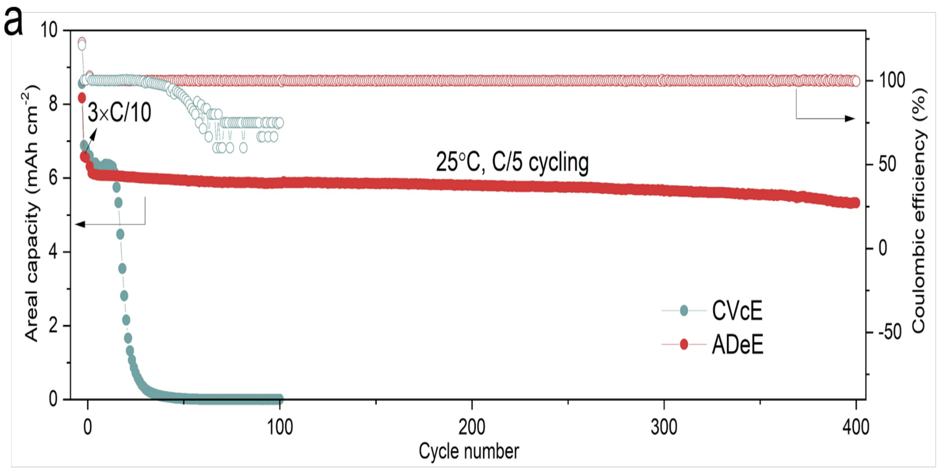
- SPAN is a low-cost, highly stable S-based cathode
- In certain electrolytes, SPAN has no S dissolution with very long cycle life

Main questions:

- What is the structure and the reaction mechanism?
- What electrolyte will maximize cycle life for both Li and SPAN?
- Can we develop high loading cathode that works in lean electrolyte conditions?

New Electrolytes That Enable Both Li and SPAN





UCSD: LDEE: 1.8 M LiFSI/DEE-BTFE

PNNL: ADeV, LiFSI-1.2DME-3TTE;

CVcE: 1M LiPF6-EC/EMC (3:7 by wt.) + 2 wt.% VC

Liu, H., Holoubek, J., Zhou, H., Chen, A., Chang, N., Wu, Z., Yu, S., Yan, Q., Xing, X., Li, Y. and Pascal, T.A., 2021. Ultrahigh coulombic efficiency electrolyte enables Li|| SPAN batteries with superior cycling performance. *Materials Today*, *42*, pp.17-28.

W. Xu

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LHCE is ideal for both Li and SPAN stability

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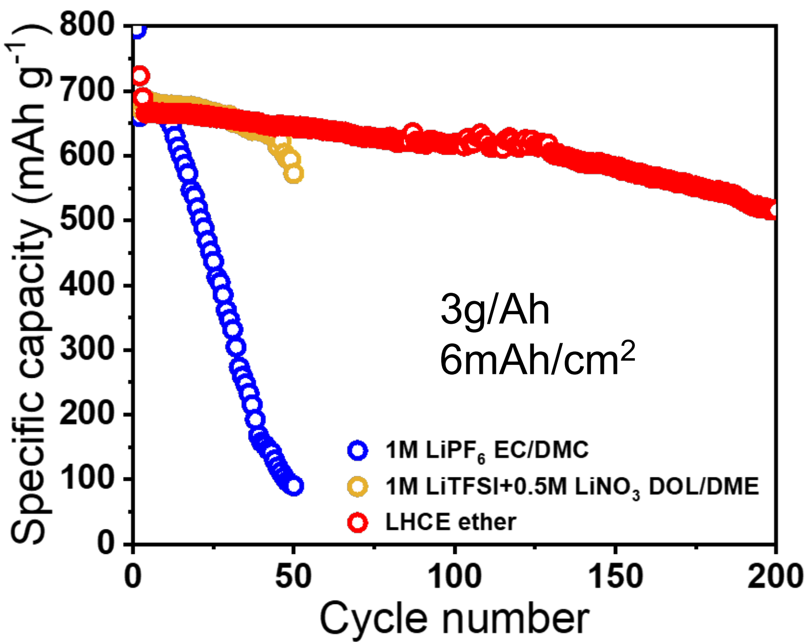
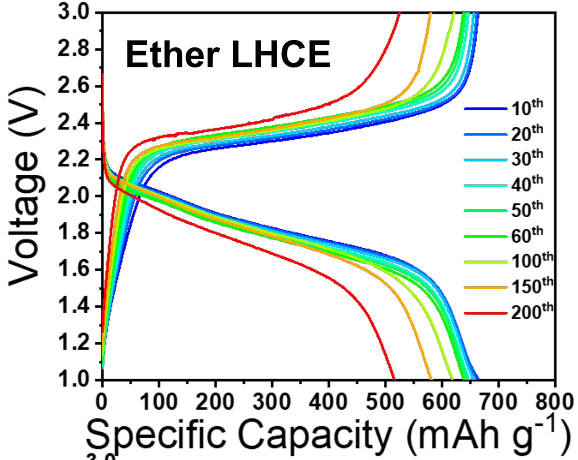
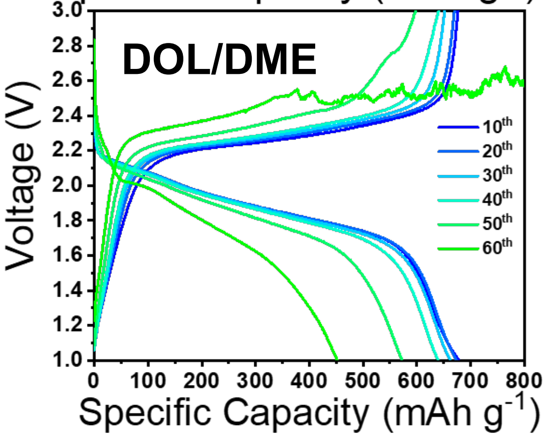
Technical Accomplishment
Cycling Stability Under Lean Electrolyte Test

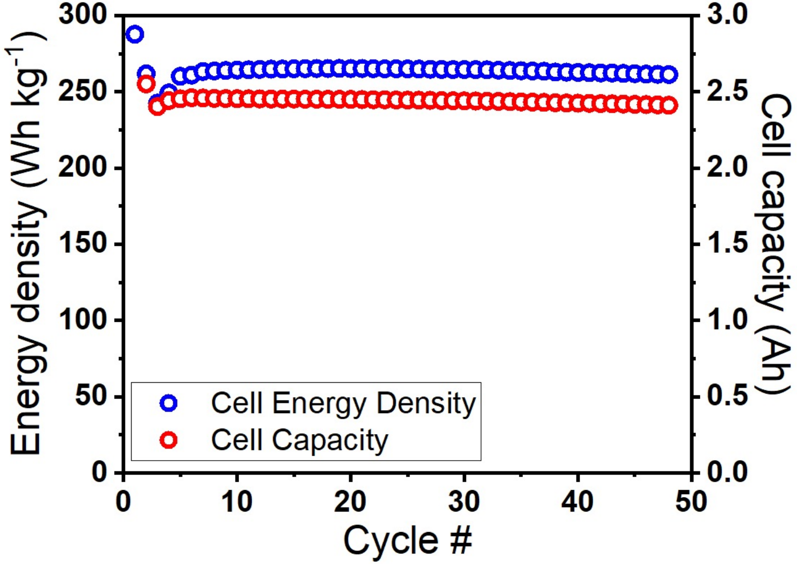


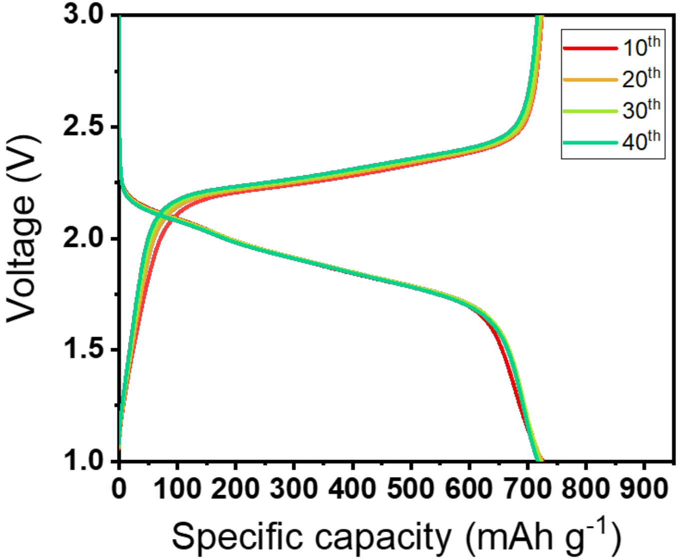




LHCE is the only electrolyte providing sustained cycling stability

Technical Accomplishment -2 Ah Li/SPAN Pouch Cell Performance





100 um Li, 1x excess, 8 mAh/cm^2

Thanks to the entire PNNL pouch cell team!

265 Wh/kg demonstrated, > 300 Wh/kg for active stack

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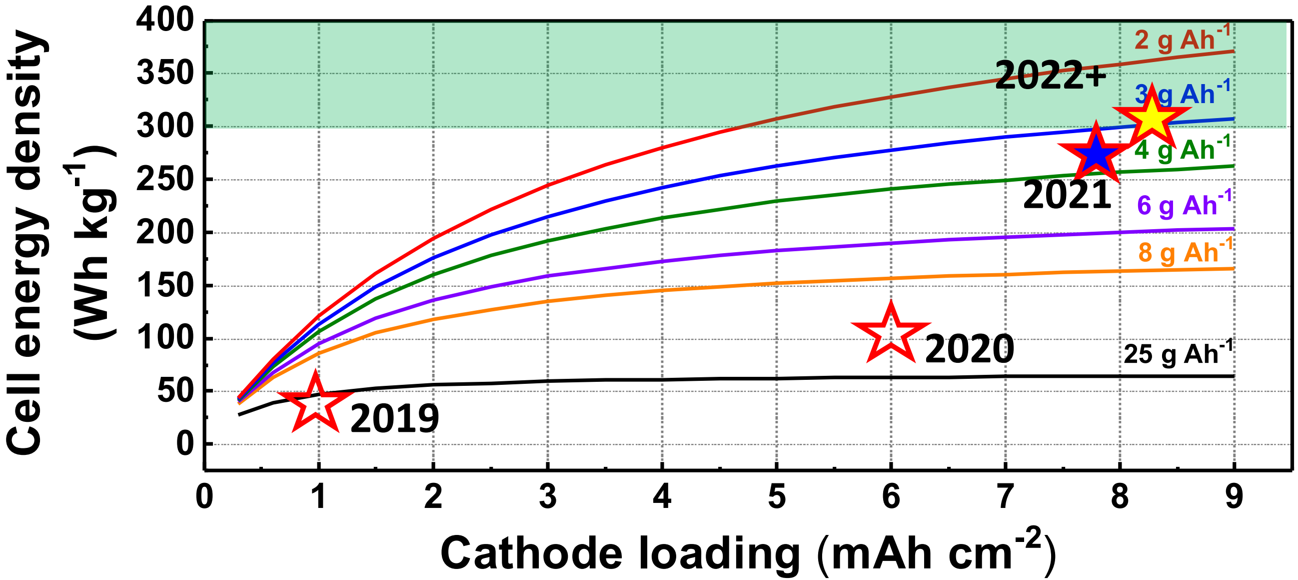
Conclusions

- Ether-based LHCE-electrolytes enable stable cycling for Li and SPAN cathode.
- With the right binder, thick SPAN cathodes with > 6 mAh cm^{-2} can cycle in 3g Ah^{-1} electrolyte.
- Preliminary results on Li||SPAN pouch cells are promising.



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Responses to Previous Year Reviewers' Comments

- This project's goal of 300-350 Wh/kg looked concerning to the reviewer, considering where the Li metal/NMC cell currently is. Hopefully, there is a clear path to reaching 500 Wh/kg.
- Yes, the team agrees that reaching 500 Wh/kg is still the eventual goal. However, achieving long cycle life at even 300 Wh/kg remaining a daunting challenge. We think this is a good intermediate target and the recent concern with regard to resource constraint makes a 300 Wh/kg Li-S cell itself appealing.
- During the discharge of SPAN, does any S become dissolved?
- No. The essence of the SPAN idea is to relay on a solid-solid reaction to avoid S dissolution
- The reviewer indicated that it should not be necessary to cycle a cell 900 times to determine that the CE is too low to be commercially viable
- It is indeed true the CE requires further improvement. However, recent work indicates that such CE value, while important, does not exactly translate to the same value in a full cell. On the other hand, ensuring a stable efficiency is important over a long cycling regiment since the build up of dead lithium can deteriorate the value.
- But the reviewer thought that the Battery500 program would benefit from additional cathode R&D beyond or instead of the high Ni NMC. That work is likely reaching diminishing returns, and S is extremely difficult (but very worth pursuing).
- We agree. The consortium is dramatically increasing its effort in S.

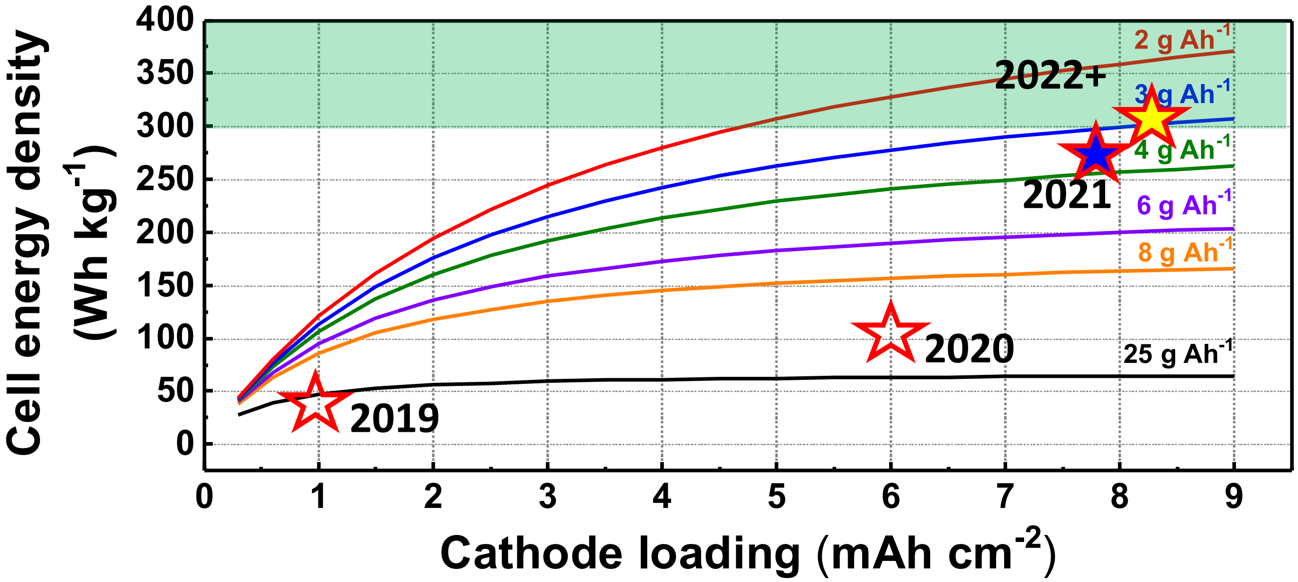
UCSD Partners and Collaborators

- Brookhaven National Laboratory: in-situ XRD and PDF
- Pacific Northwest National Laboratory: Pouch cell design, fabrication, and testing
- Texas A&M University: Computational study of SPAN structures
- University of Washington: Electrochemical modeling of advanced electrode architectures
- Binghamton University: NMC811 data exchange
- UT-Austin: synthesis of NMC811 materials

Remaining challenges for Keystone 2-Li metal

- **Will 3D Li electrodes make a difference in pouch cells?**
  - Do they have to be prelithiated or can be fabricated Li free?
  - Are 3D anodes scalable?
- **Can solid electrolyte/protective coating push Li efficiency higher in a pouch cell?**
  - Is protective coating method scalable? Does their benefit translate to full cell performance?
  - Does protective layer slow down electrolyte consumption in the pouch cell?
  - What is the thinnest we can use?

Remaining Challenges Keystone 2-Li/Thick SPAN



Credit: PNNL

Based on 800 mAh/g capacity

- Reduce electrolyte further
- Understand SPAN structure and raise capacity
- Increase loading further

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Proposed Future Work-Keystone 2

- Continue to optimize and scale up 3D Li anodes and evaluate them in pouch cells with lean electrolyte and high areal loading to support cell-level energy density targets;

- Fabricate ion-conducting, electrolyte impermeable protective coating layers and implement in pouch cells;

- Understand the structure and operating mechanism of SPAN; Continue to raise S content; Determine the maximum areal loading for operation under lean electrolyte conditions; Optimize pouch cell performance.

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

Keystone 2 Summary

- Qualitative and quantitative design rules have been developed for 3D Li anodes including the role of tortuosity and pore size;
- Several localized high concentration electrolytes have been shown to enable stable cycling of both Li and SPAN electrodes;
- Optimization of binder and electrode fabrication enables high loading SPAN to cycle stably in lean electrolyte conditions;
- A 2 Ah Li/SPAN pouch cell has demonstrated promising cycling stability