High-Energy Solid-State Lithium Batteries with Organic Cathode Materials

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Project ID: bat511

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

Overview

Timeline

- Project start date: 10/1/2017
- Project end date: 12/31/2021
- Percent Complete: 87%

Barriers

- Barriers addressed
  - Inflated price of Co and environmental impact of Co-mining
  - Co-free high-Ni cathode cycling instability

Budget

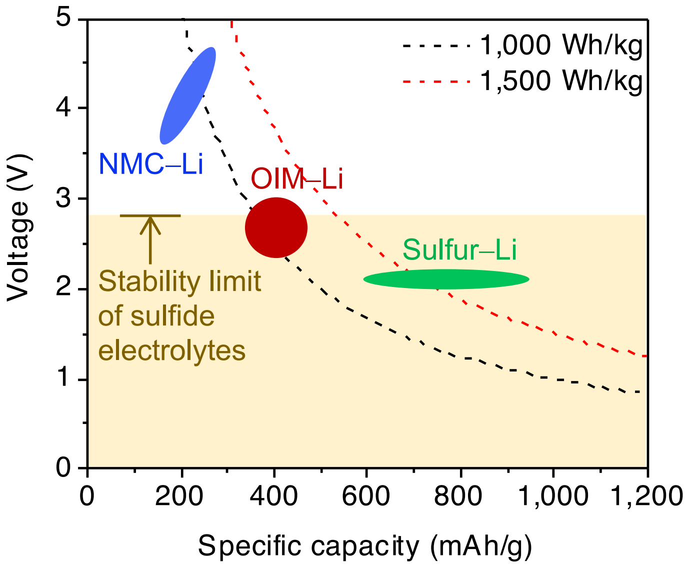
- Total project funding
  - $1.2 M from DOE
  - $128,884 cost share
- Funding for FY18-FY19 $400K
- Funding for FY20 $400K
- Funding for FY21 $400K

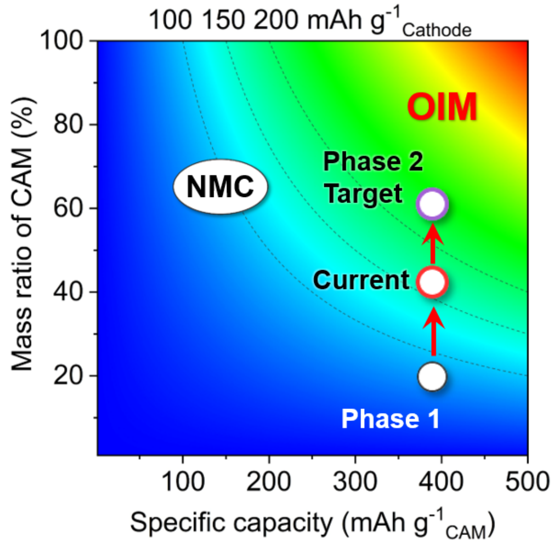
Partners

- This is a seedling project of Battery500
- Collaboration
  - Battery500 Core Team
  - PNNL, BNL
  - Solid Power, TESCAN, Ampcera

Project Objective and Relevance

- Research and develop metal-free multi-electron organic insertion materials (OIMs) for solid-state lithium batteries capable of achieving the energy and cycle life targets set by Battery500 Consortium.
- In Phase 1, we achieved a reversible specific capacity of 400 mAh/g (98% active material utilization) with a capacity retention of 61% after 1000 cycles.
- In Phase 2, we target to significantly increase the active material fraction in cathode composite to translate high material-level specific energy to cell-level specific energy.
- In Phase 2, we also design, synthesize and integrate OIMs with higher energy (1200 Wh/kg) into solid-state cells.
- This project is directly aimed at developing Co- and Ni-free cathode materials for all-solid-state Li batteries (ASSBs).



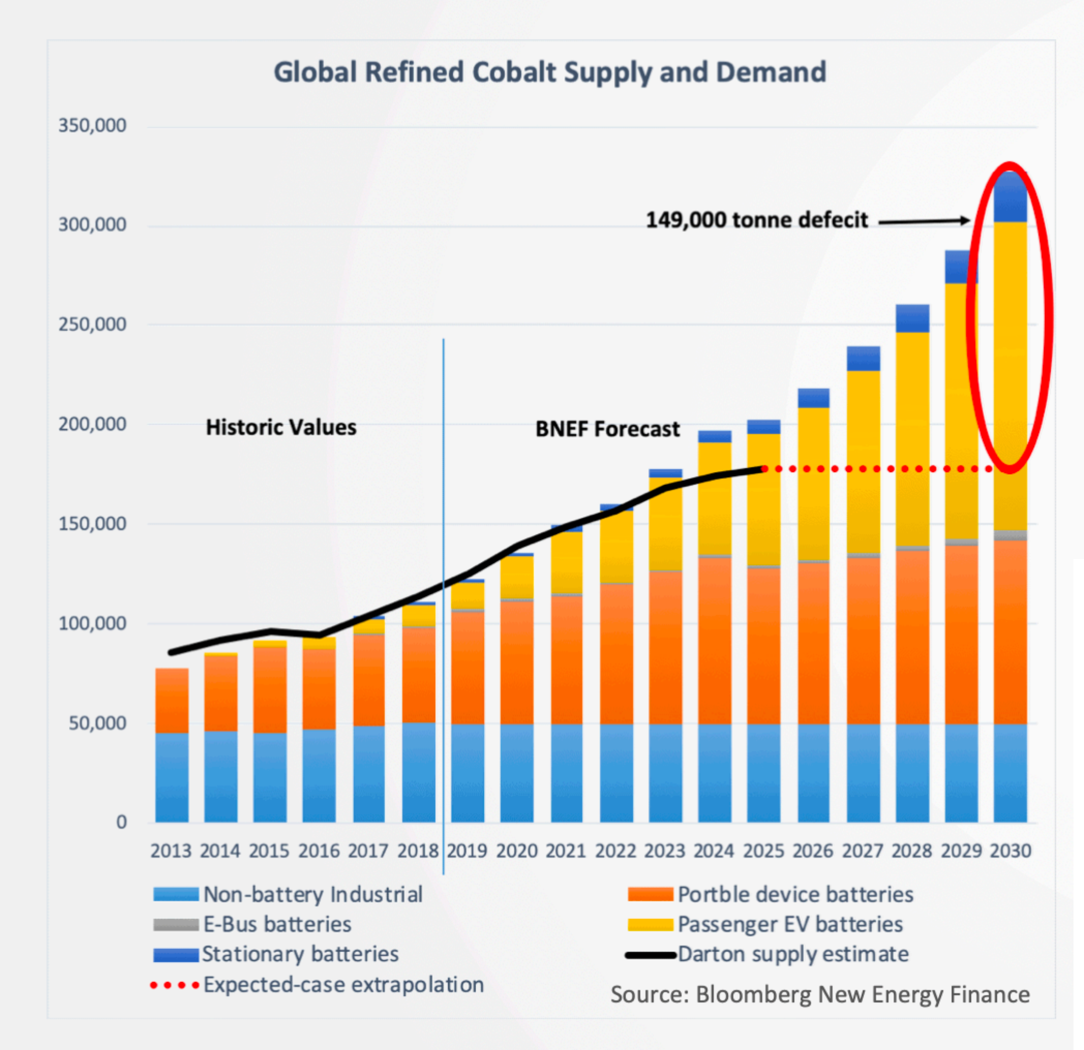


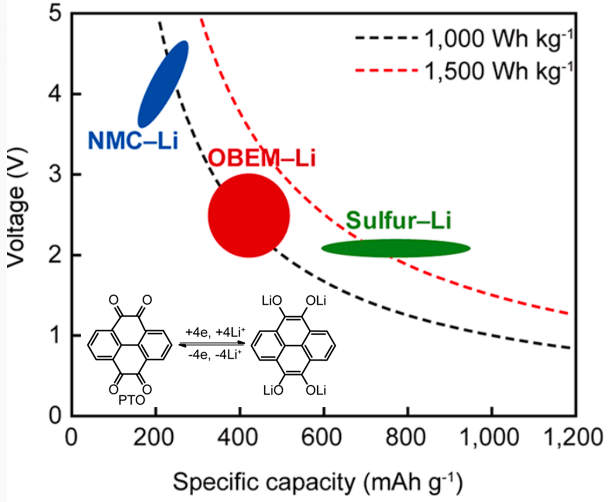
Milestones for FY20 and FY21

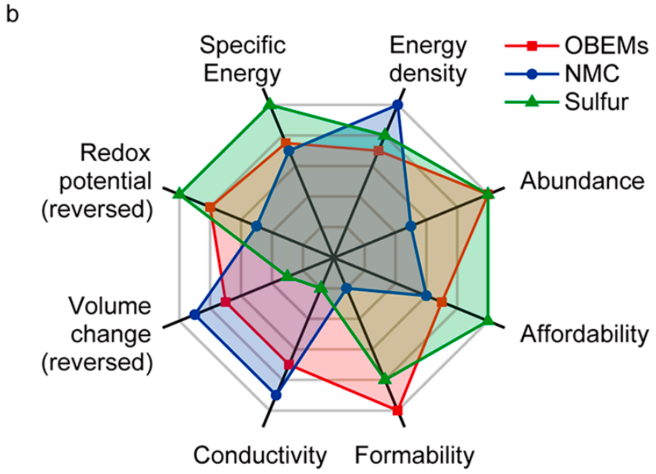
Month/Year	Description of Milestones	Status
Jun. 2020	**Synthesis of soft electrolyte precursors** − Synthesized soft electrolyte precursor by solution process and determined its modulus to be lower that of PTO.	*Completed*
Sep. 2020	**Synthesis and characterization of new OIMs** − Synthesized new OIMs and demonstrate its capacity to be over 440 mAh/g with a voltage of 2.6 V vs Li^+/Li.	*Completed*
Dec. 2020	**Integration of soft electrolyte into OIM cathode** − Characterized the cathode microstructure formed with soft electrolyte, revealing better percolation for charge transport. Achieved electrode-level specific energy of 300 Wh kg^{-1}.	*Completed*
Dec. 2021*	**Integration of new OIMs into solid-state cells** − Integrate high-capacity OIM into cell and achieve electrode-level specific energy of 500 Wh kg^{-1}.	*Ongoing*

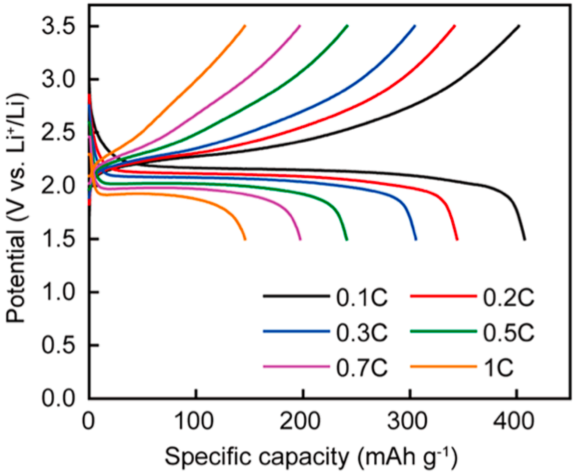
* No-cost extension was requested and approved due to postdoc leaving and slow replacement during COVID.

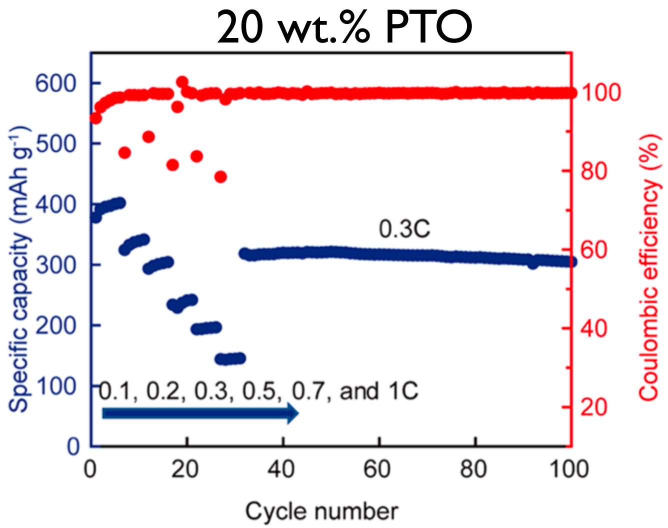
Approach – Cobalt-free Cathode for ASSLBs





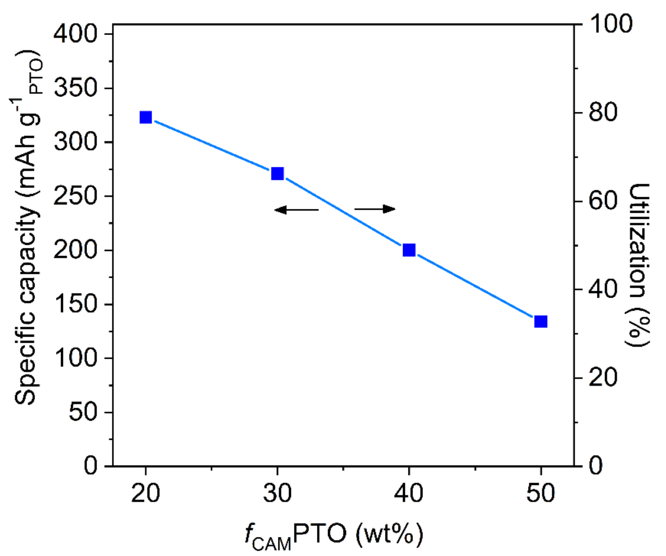


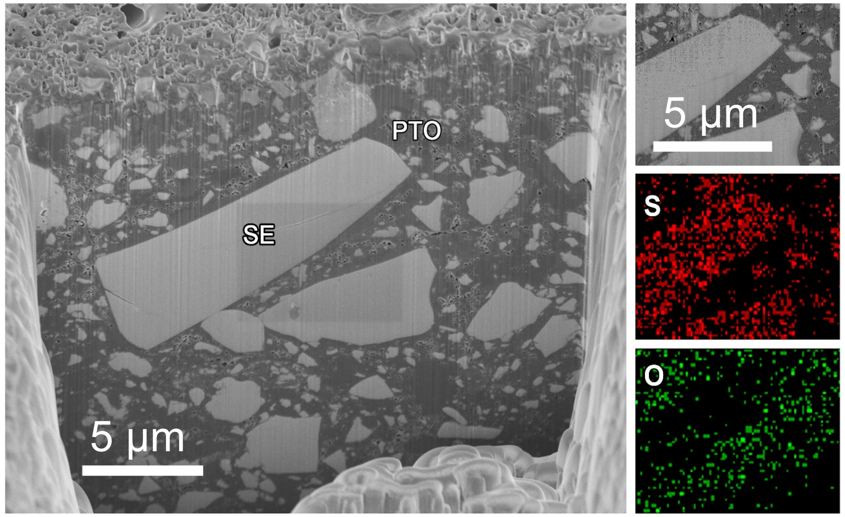




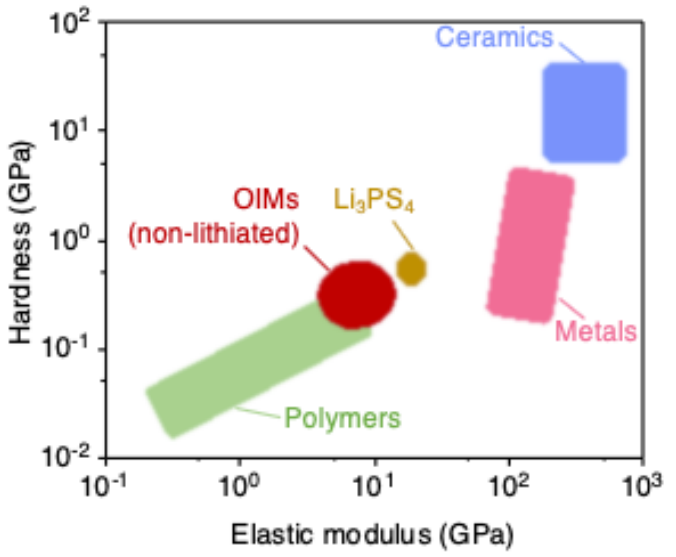
Fang, Liang, Yao, et al. *ACS Energy Lett.* 6, 201 (2021)

Approach – Origin of low active material utilization





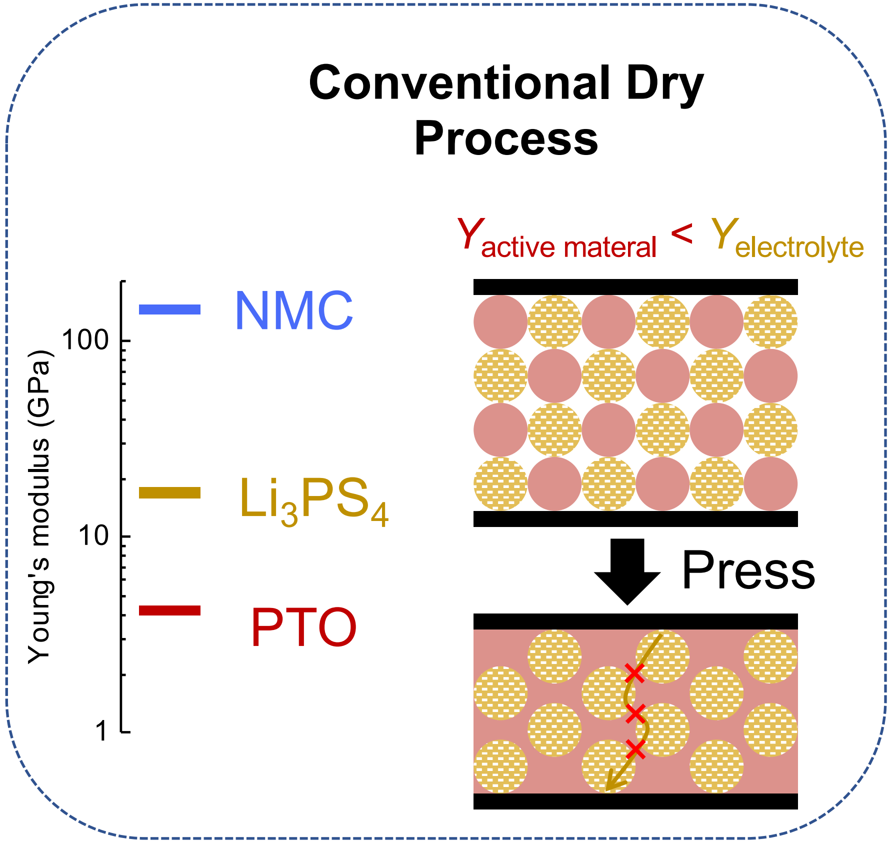
electrolyte-in-active material

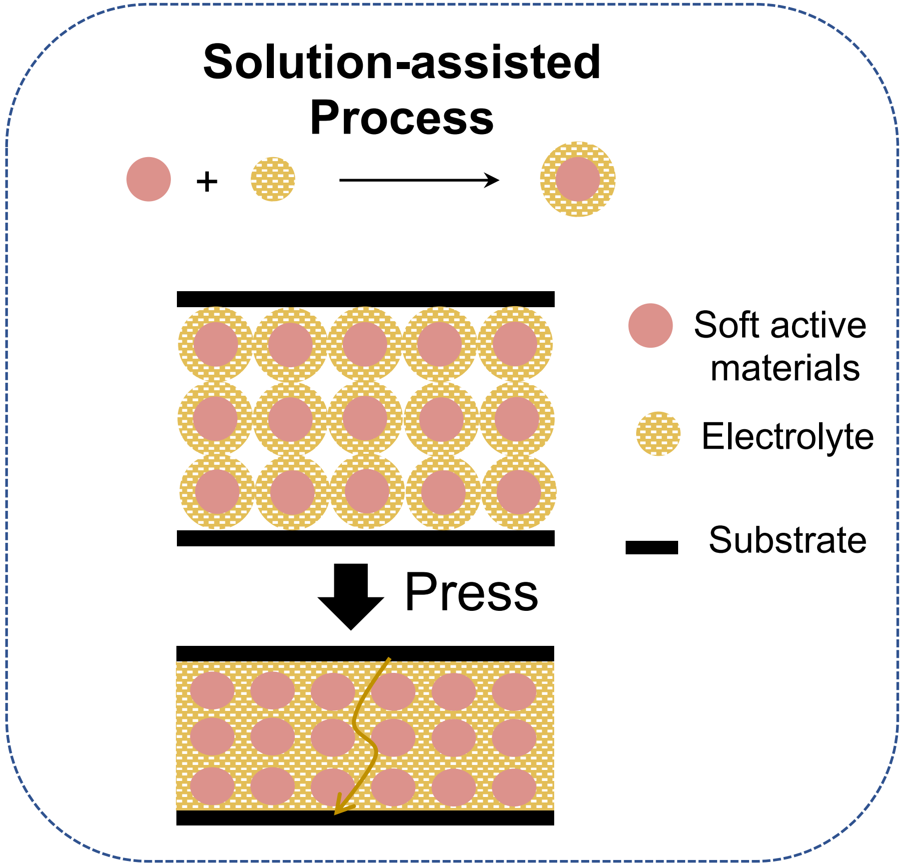


- When increasing active material ratio in cathode composites, both specific capacity and material utilization decease.
- Such a decrease originates from the non-ideal phase separation as revealed by FIB-SEM, where solid electrolyte is surrounded by PTO (OIM), because PTO is mechanically softer than Li_3PS_4 and deforms first during the powder compacting fabrication process.

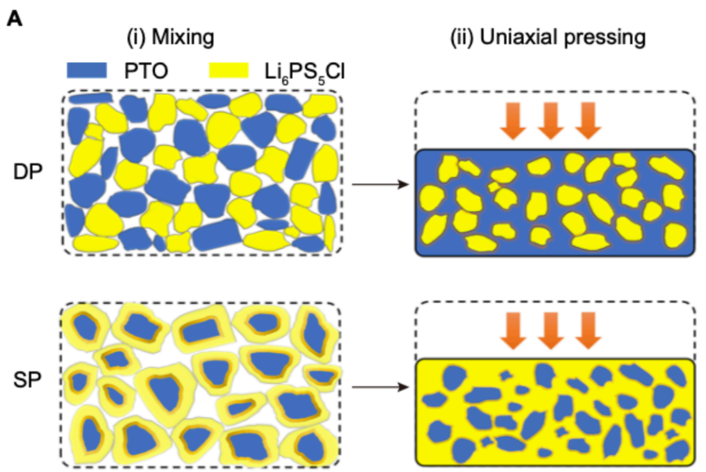
Approach – Strategy

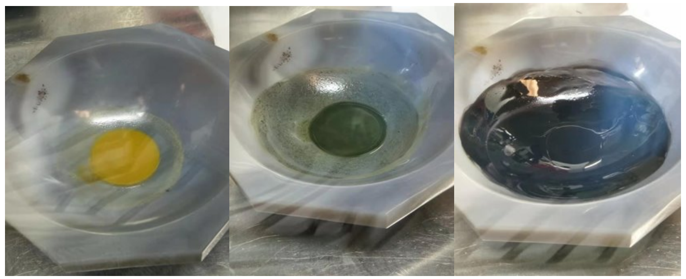
To circumvent the modulus-dependent microstructure formation, we propose a solution-assisted process to form electrolyte-coated OIM core-shell structures that could be later compacted into an ideal microstructure and increase cathode active material (CAM) fraction.



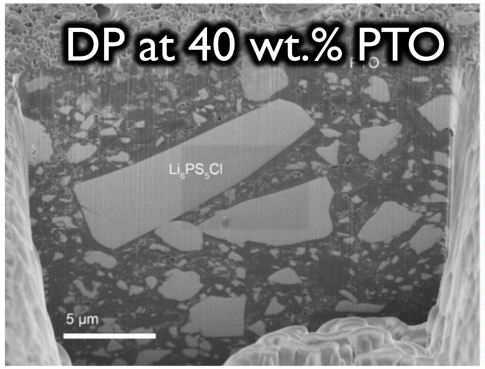


Previous Accomplishment – Solution process increases CAM fraction

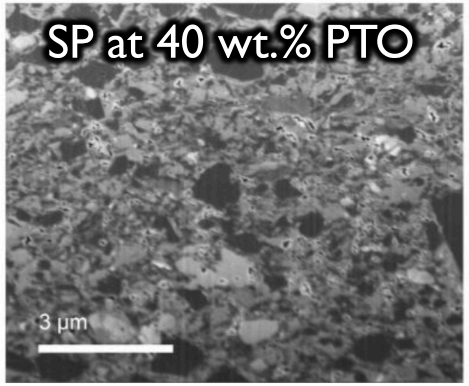




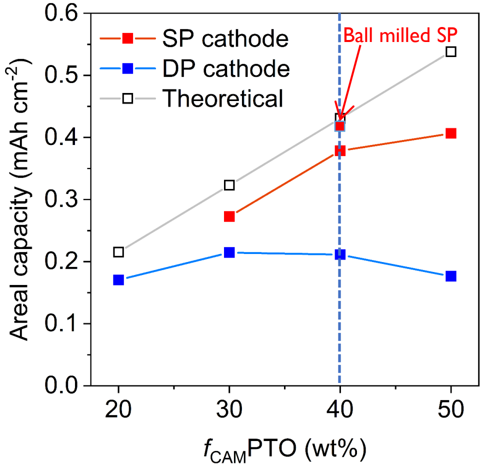
PTO in EtOH | Add Carbon | Add Li_6PS_5Cl

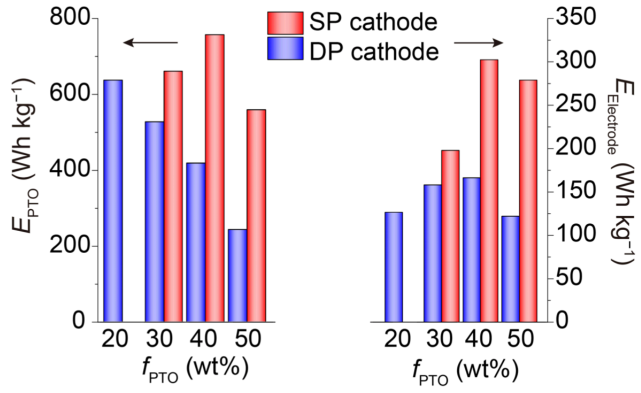


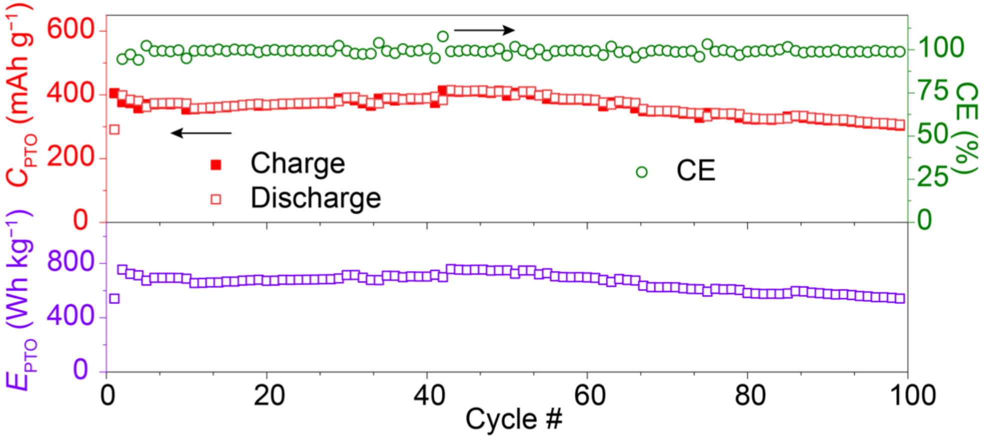
electrolyte-in-active material



active material-in-electrolyte





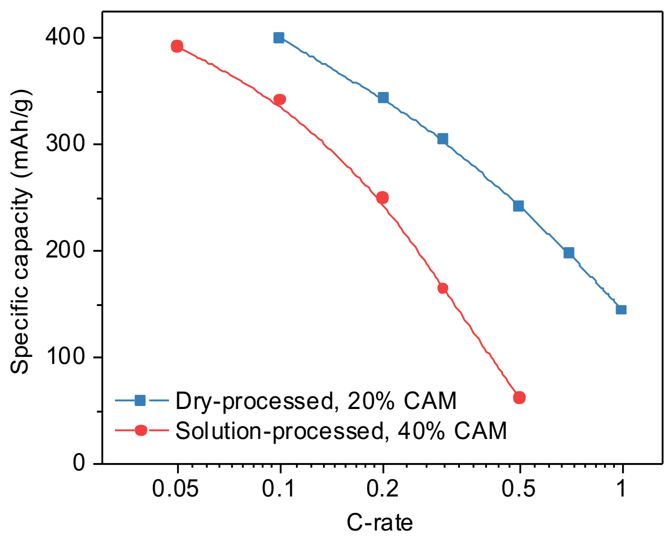


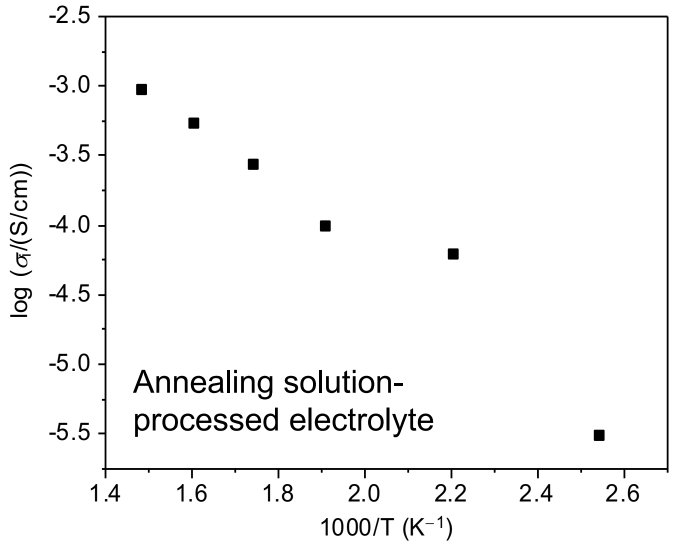
- Non-ideal microstructure leads to low cathode active materials (CAM) utilization in dry-processed samples.
- Solvent-assisted process reverses microstructure and results in 95% utilization at 40 wt.% CAM fraction.

Zhang, Yao, et al. *Joule,* 2021, accepted

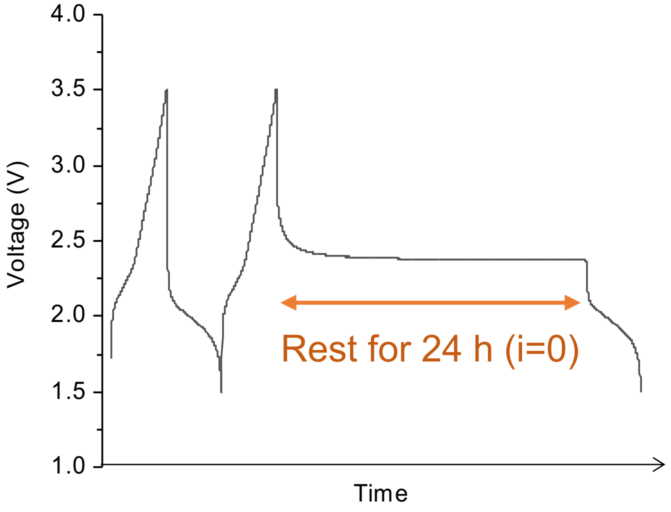
Accomplishment – Rate capability and self-discharge

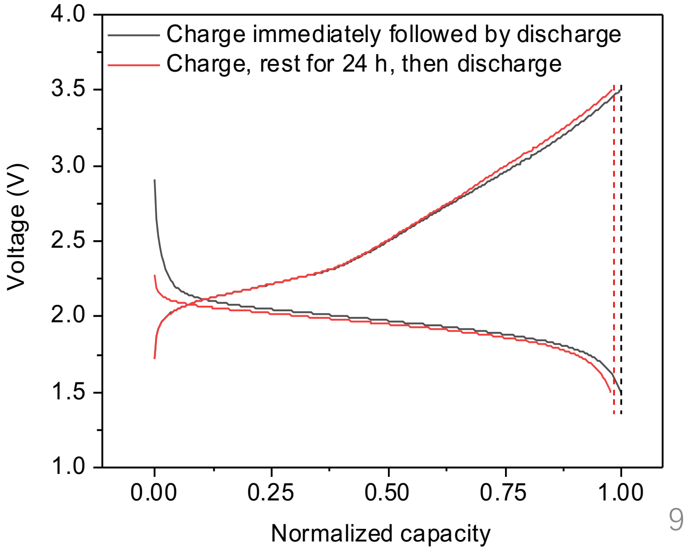
- Solution-processed OIM cathodes show compromised rate capability;
- Annealing solution-processed electrolytes will help restore their conductivity and thus rate capability.



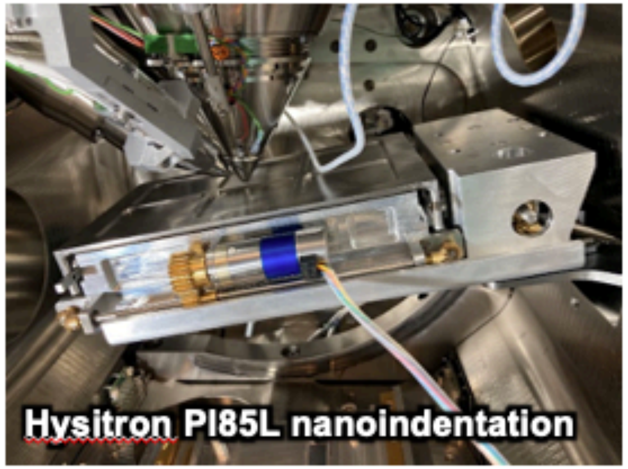


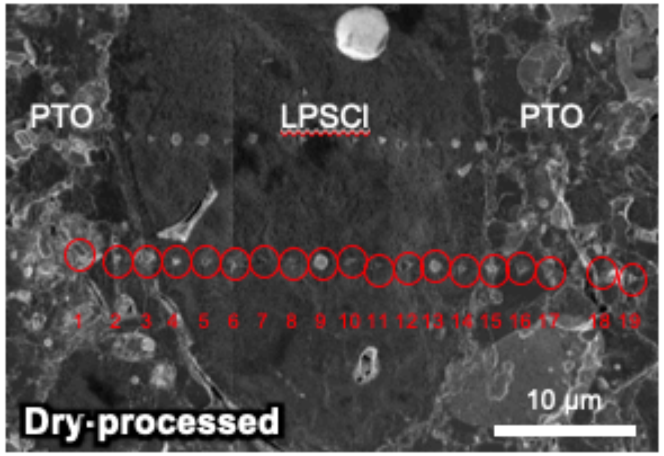
- OIM cathodes, regardless of processing method, show no noticeable self-discharge when resting at the fully charged state.

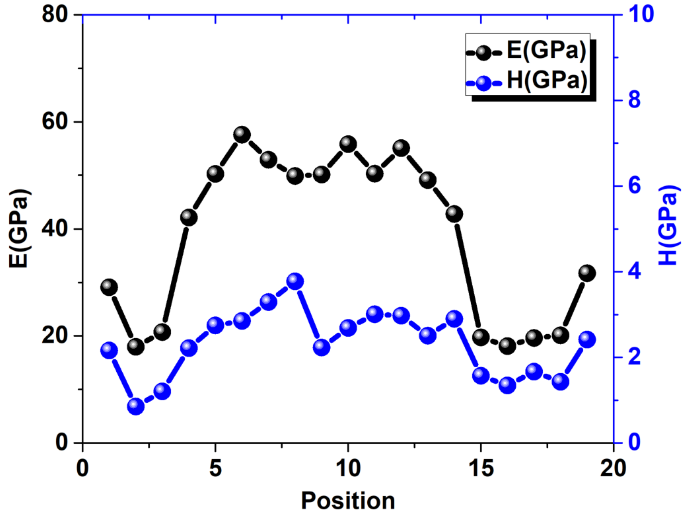


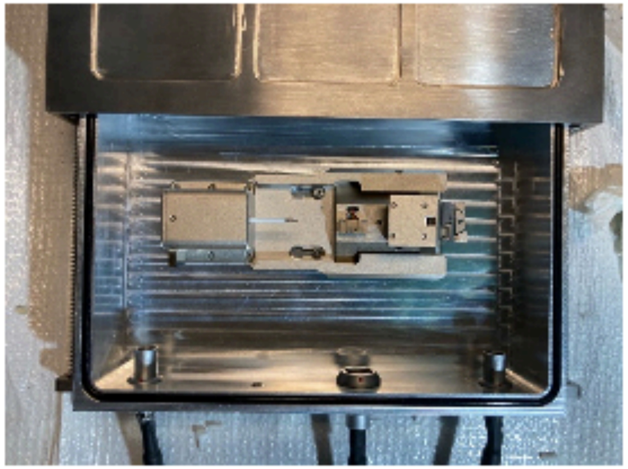


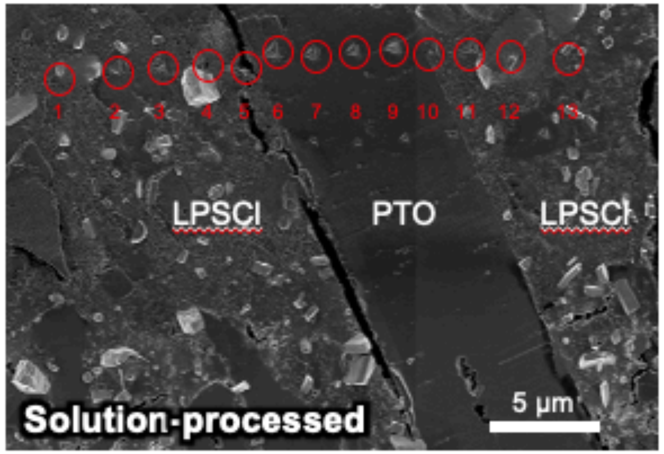
Accomplishment – Understanding origin of structure inversion

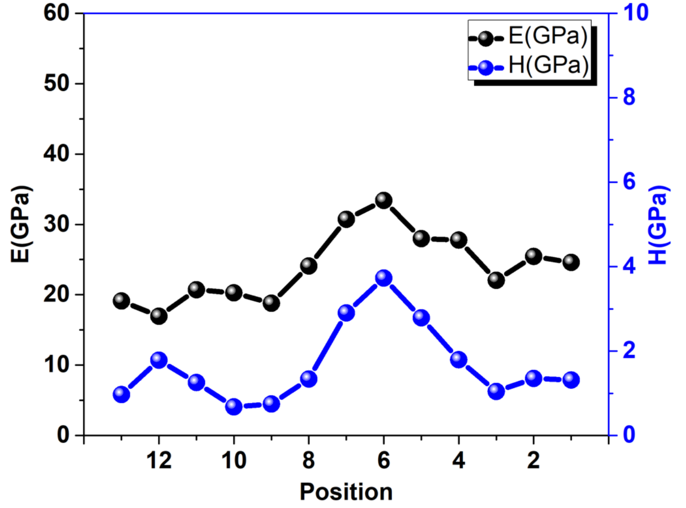






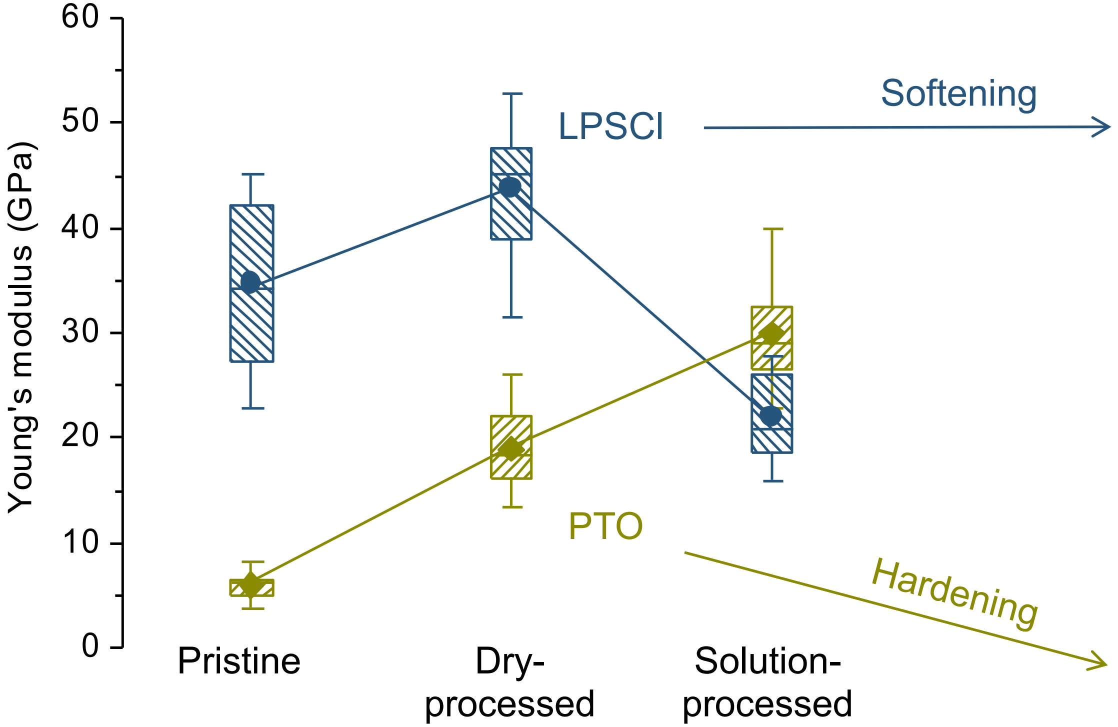


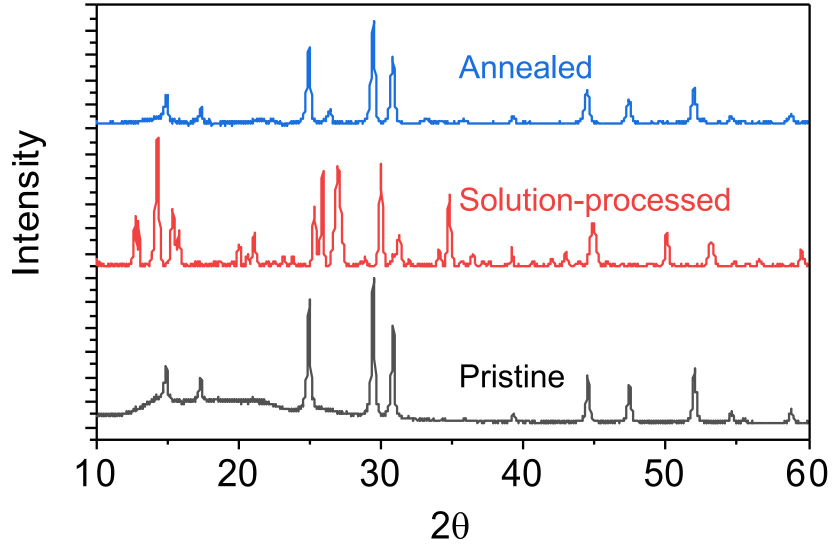


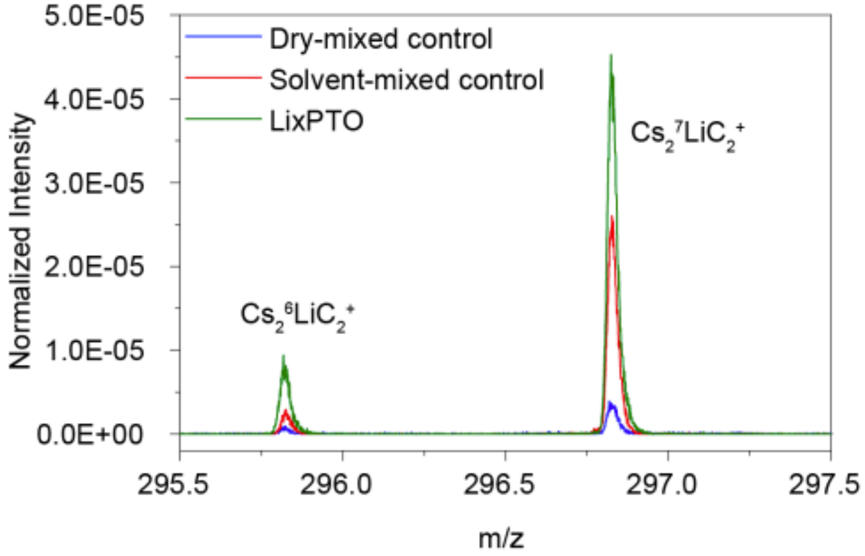


Nanoindentation reveals mechanical property changes of the PTO and LPSCl domains, which causes the structure inversion.

Accomplishment – Understanding origin of structure inversion



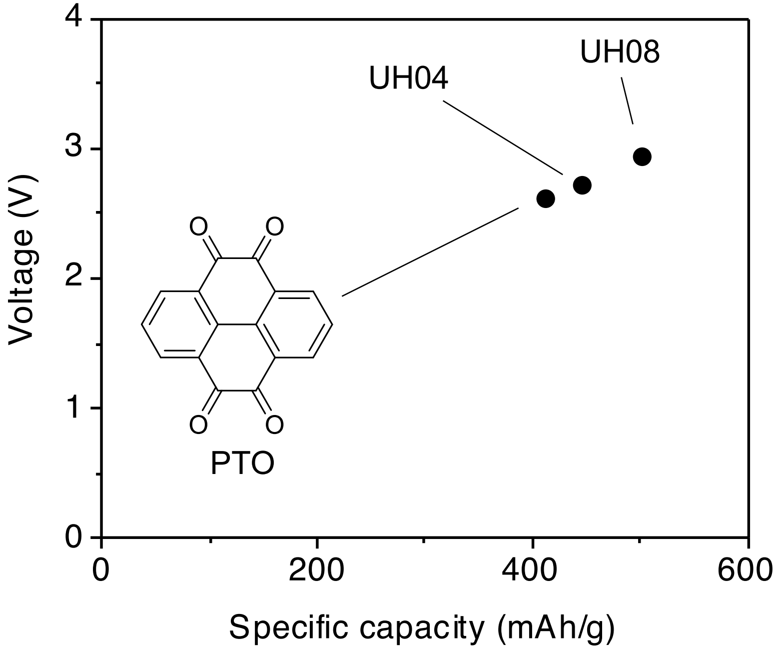




Multi-technique characterizations of the processed PTO and LPSCl reveal chemical and structural evolution of both materials, shedding light on the underlying mechanism of mechanical property changes and microstructure formation.

RICE

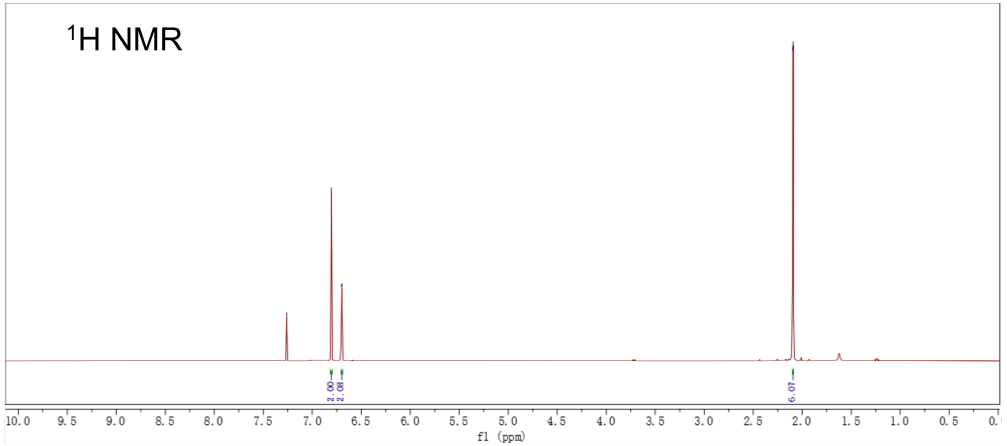
Accomplishment – Synthesis of OIM with higher energy

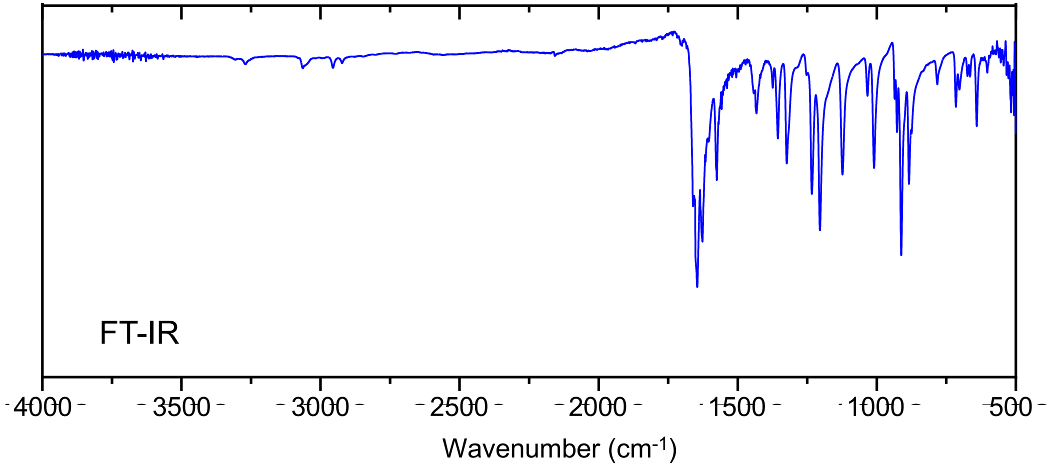


	Specific capacity (mAh/g_{OIM}) (theoretical)	Voltage (V)	Specific energy (Wh/Kg)	Status
PTO–Li	409	2.6	957	Demonstrated in all-solid-state cells.
UH04–Li	445	2.7	1072	Demonstrated in cells with liquid electrolytes; being implemented in all-solid-state cells.
UH08–Li	501	2.9	1285	Synthesis initiated.

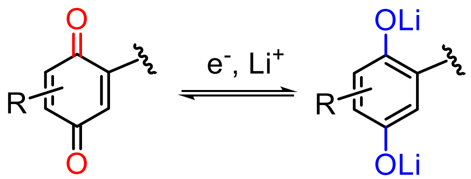
Electrochemical parameters of identified OIMs for higher specific capacity and voltage, and the status of work on each material.

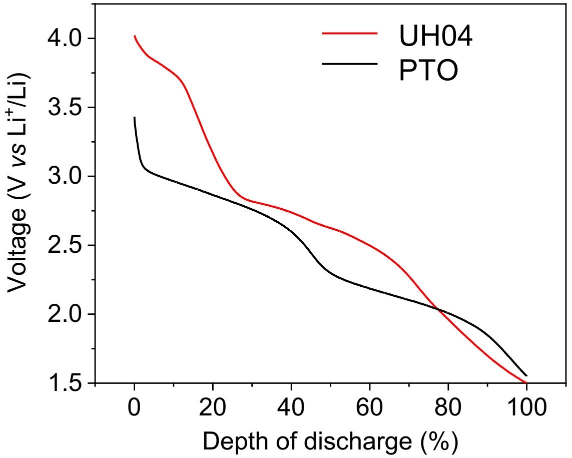
Accomplishment – Characterization of new OIM



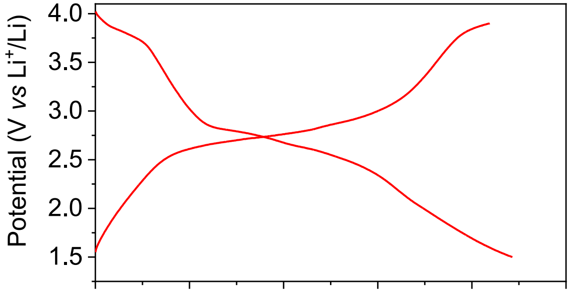


Charge storage mechanism of UH04

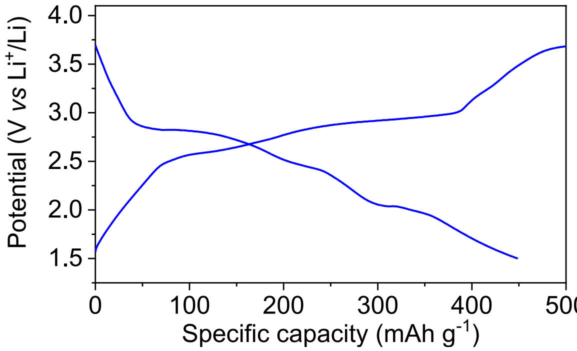




UH04 in ether-based electrolyte



UH04 in carbonate-based electrolyte



- Chemical characterizations and cell evaluation of new OIM UH04.
- UH04 shows both higher specific capacity and voltage than those of PTO.

Collaboration and Coordination

- **Characterizations**
  Dr. Jun Lou, Hua Guo, Tanguy Terlier (Rice)
  Dr. Chongmin Wang (PNNL)
  Dr. Xiaoqing Yang (BNL)
  Dr. Mike Craig (TESCAN)
  Dr. Venkat Selvamanickam (UH)

- **Solid electrolytes**
  Dr. Josh Buettner-Garrett (Solid Power)
  Dr. Ryan Du (Ampcera)

Pacific Northwest NATIONAL LABORATORY
BROOKHAVEN NATIONAL LABORATORY
RICE
TESCAN
Solid Power
Ampcera™

Proposed Future Research – Pathway to 500 Wh/kg

OIM cathode

Specific capacity	501	mAh/g
Active fraction	65	%
Average voltage (vs. Li)	2.9	V
Loading	12.2	mg/cm^2
Density	2.1	g/cm^3
Thickness	58.1	µm

Lithium anode

Loading	1.0	mg/cm^2
Thickness	17.4	µm

All-solid-state electrolyte

Thickness	20	µm
Density	1.56	g/cm^3

Current Collectors

	Thick (µm)	mg/cm^2
Cathode: aluminum	12	3.2
Anode: conductive coating	5	0.6

Material	Mass (mg/cm^2)	Thickness (µm)
Cathode	12.2	58.1
Anode	1.0	17.4
Separator	3.1	20.0
Cath. Curr. Collector	1.6	6.0
Anode Curr. Collector	0.3	2.5
Total	18.268	104.022

Maximum Performance

Stack Specific Energy	630.0	Wh/kg
Stack Thickness	104.0	µm
Capacity per Area	4.0	mAh/cm^2
Energy Density	1106.4	Wh/L
Capacity per Volume	381.5	mAh/cm^3
Density	1.8	g/cm^3

Packaging

Laminate	14	mg/cm^2
	100	µm

Cell-level Wh/kg with 80% packaging efficiency:
504.0 Wh/kg

Proposed Future Research

- Complete the synthesis of new OIM UH08; Integrate the new OIMs (UH04 and UH08) into all-solid-state lithium cells following procedures established for PTO.
- Elucidate the microstructure formation mechanism behind the solution-processing procedure for OIM cathode fabrication through more in-depth chemical and mechanical characterizations.
- Optimize the solution-processing procedure based on the understanding and apply the knowledge in cells based on new OIMs for increased active fraction in the cathode and higher areal capacity, an essential step towards 500 Wh/kg according to our cell design calculation.
- Collaborative research with US academic research institutions and industrial partners will be further expanded and strengthened. We received high-performance solid electrolytes from partners and will integrate them into OIM cells and use plasma FIB for cathode composite structure reconstruction.

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

Responses to Previous Year Reviewers' Comments

- One thing that PI may evaluate is the relevance of the focused materials toward the final energy target. The PI may have a big picture in mind. The reviewer wanted to know what the possible pathways are toward the final performance targets and what the applicable materials are to fulfill such requirements.
  - Response: Detailed cell design calculation has been performed based on the OIM–lithium, and a pathway towards 500 Wh/kg is identified.
- …more technical details need to be developed for the future plan.
  - Response: More actionable items with technical details have been proposed for Future Research.
- The reviewer commented that the study would benefit from a more in-depth analysis of the effect of discharge rate and shelf life on cell capacity. Response
  - Response: Discharge rate and shelf life have been studied; improvement strategies, where applicable, have been identified (see Accomplishment).
- To reach or approach the target cell energy, new OIMs with higher capacity and voltage are essential and would be the focus of the future research. To tackle the sluggish kinetics of both the active materials and OIM/SEI, stable and highly conductive solid electrolytes should be identified to support the cell-level integration.
  - Response: New OIMs with higher capacity and voltage have been synthesized, some already being evaluated for lithium cells. We have received high-performance solid electrolytes from partners and will integrate them into OIM cells with plasma FIB for cathode composite structure reconstruction.

Summary

- We explored organic electrode materials in ASSLBs to achieve the energy goal set by Battery500 Consortium.
- We investigated processing−microstructure−performance relationship for novel cathode materials which properties vastly different from inorganic ones.
- Solution-processed sulfides are softened precursors that allow formation of unique microstructures otherwise impossible. Nanoindentation and ToF-SIMS provide mechanical and chemical information that could lead to better understanding microstructure change and interfacial reactions.
- New OIMs with higher specific energy will be integrated into solid-state cells, combining high-rate cycling with thin solid electrolyte (less than 50um).

Acknowledgements

- U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (Program Managers: David Howell and Tien Duong)
- UH Contributors: Yan Yao, Yanliang Liang, Jibo Zhang, Zhaoyang Chen, Alae Eddine Lakraychi
- Rice Contributors: Jun Lou, Qing Ai, Hua Guo, Tanguy Terlier
- Yan Yao and Yanliang Liang co-founded LiBeyond LLC to commercialize cobalt-free solid-state lithium battery technologies spin-off from this project.