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Development of High Energy Lithium-Sulfur Batteries

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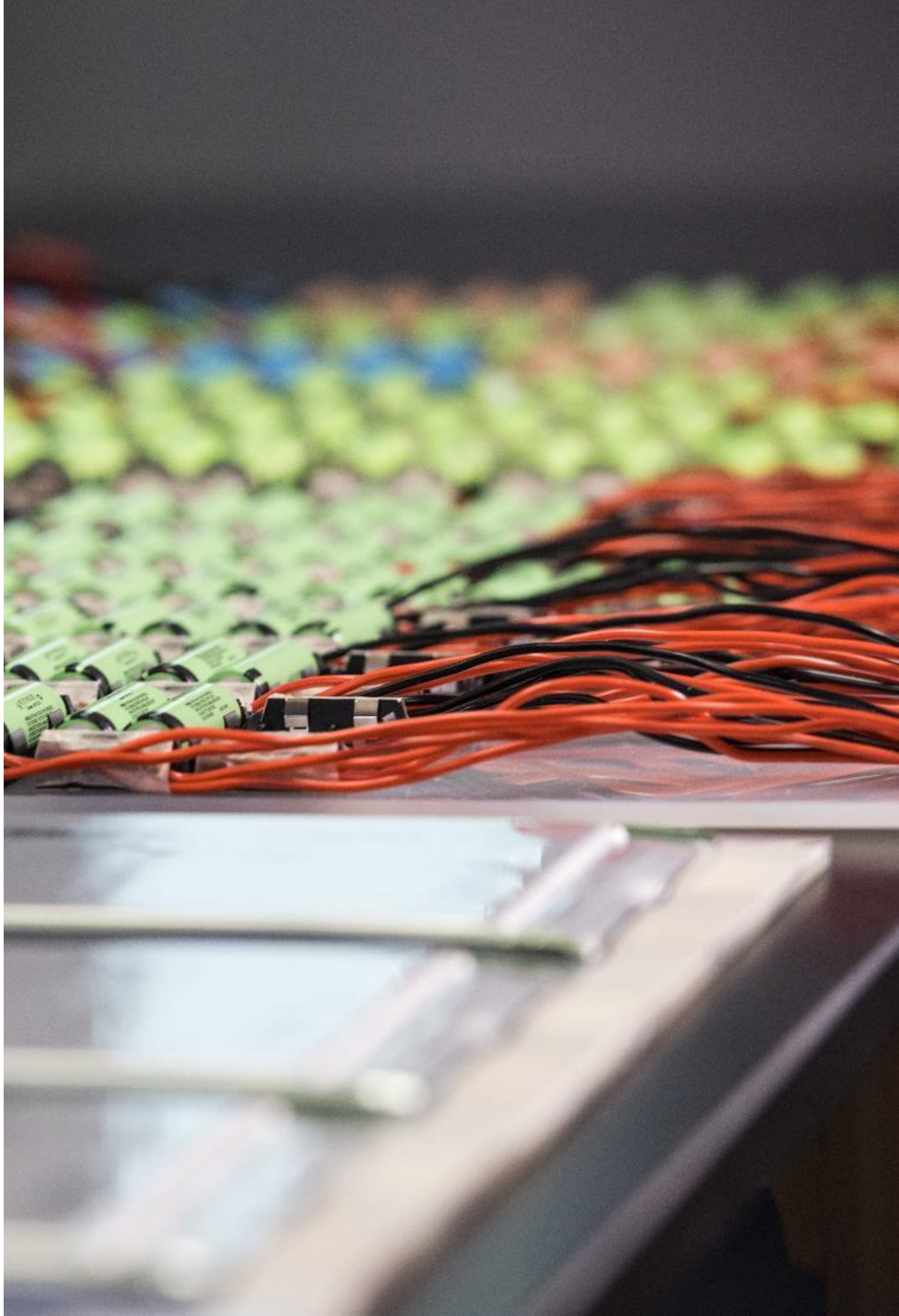

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Relevance/Objectives

- Advance the fundamental understanding of key factors that affect Li-S cell lifespan at realistic high-loading cathode and lean electrolyte amount conditions.
- Realize preparation and application of low porosity sulfur cathodes to boost both specific energy (Wh/kg) and energy density (Wh/L).
- Construct a robust and high Li^+ conductive network to enhance sulfur conversion kinetics at lean electrolyte conditions.
- Project efforts are directly aimed at barriers of low practical energy density, shuttle effect, low rate capability, and limited cycling life of Li-S batteries.

Milestones

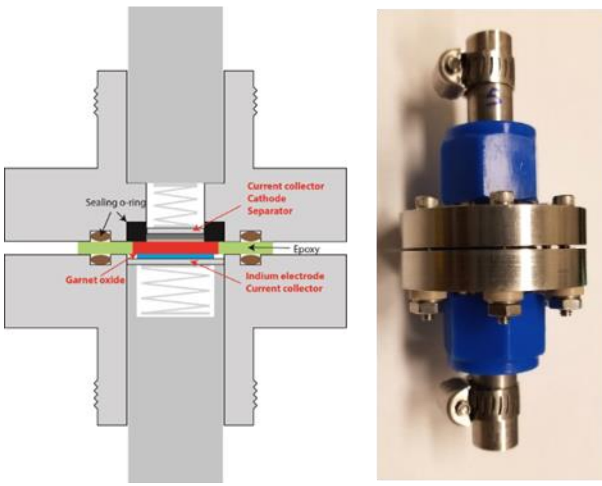
Date	Milestones and Go/No-Go Decisions	Status
Dec. 2018	Demonstration of high Li^+ conductivity sulfur cathodes enabled by sulfide based Li^+ conductors with room temperature conductivity > 1 mS/cm.	Completed
March 2019	Development of electrode preparation method for sulfur/ Li^+-conductor cathodes with sulfur mass loading > 4 mg/cm^2 and sulfur >70 wt. % in whole electrode.	Completed
June 2019	Complete electrode composition and architecture optimization for low porosity sulfur electrodes (electrode density >1 g/cm^3).	On track
Sept. 2019	Complete electrochemical evaluation of the high loading sulfur electrodes (> 4 mg/cm^2) at low electrolyte/sulfur ratio (E/S<3 μL/mg) and identify compatible liquid electrolytes with the cathodes.	On track

Approach

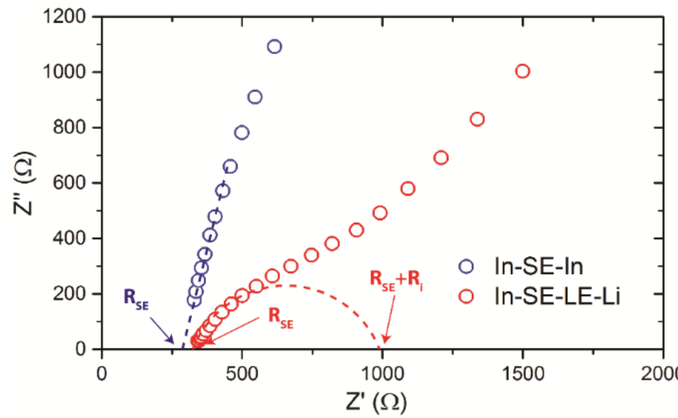
- Design of a garnet oxide/liquid electrolyte hybrid cell set-up for focused fundamental studies of the sulfur cathode.
- Identifying limiting factors of Li-S cell life at practical conditions.
- Preparation of highly conductive sulfide based Li^+ conductors to improve the ionic conductivity of the sulfur cathode.
- Dry-processing approach to prepare the high-loading and low-porosity sulfur cathode to reduce the E/S (electrolyte/sulfur) ratio.
- New sulfur cathode architecture enabled by the solid/liquid mixing Li^+ conduction.

Technical Accomplishments

Garnet/liquid electrolyte hybrid cell design to decouple the interferences of Li for focused studies of sulfur cathodes



Design and assembly of hybrid cell



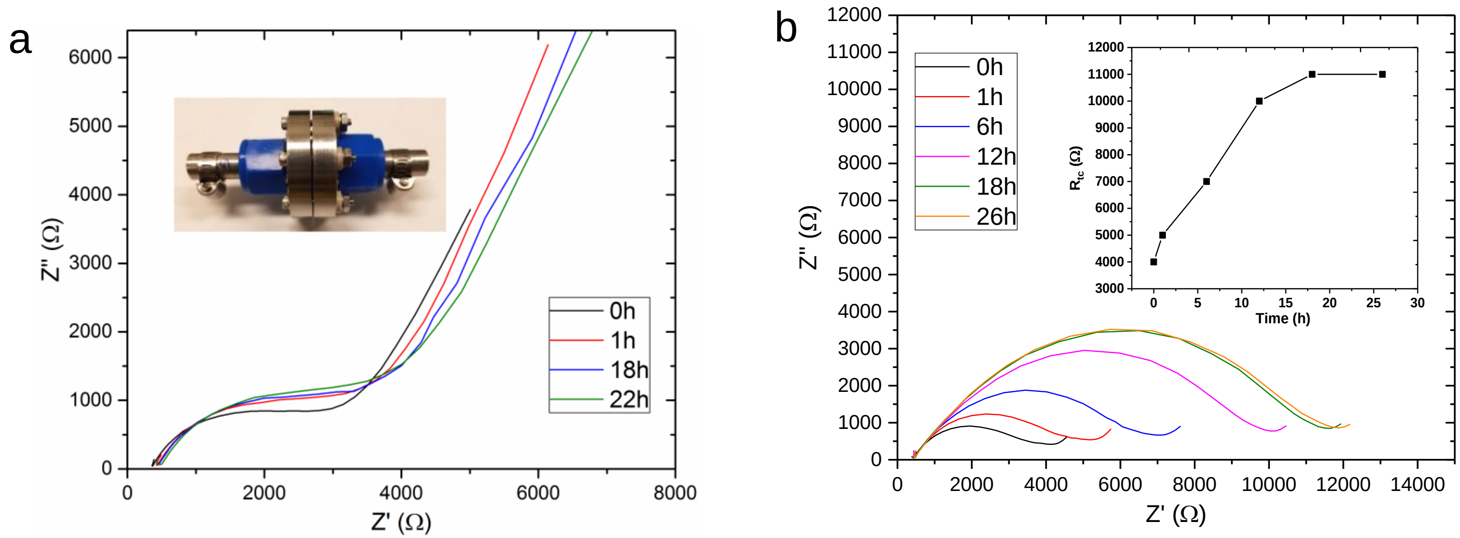
In-indium
SE-solid electrolyte
LE-liquid electrolyte
SS-stainless steel

Electrochemical impedance spectroscopy (EIS) *of In-SE-In and In-SE-LE-Li (5 mv, 10^5-10^{-1} Hz)*

- Completely separated two electrode chambers by garnet oxide membrane.
- Sealing mechanism and meticulously designed sealing parts ensure stable electrochemical operations outside the glovebox.

Technical Accomplishments

Identified slow electrode wetting process of high loading sulfur cathodes

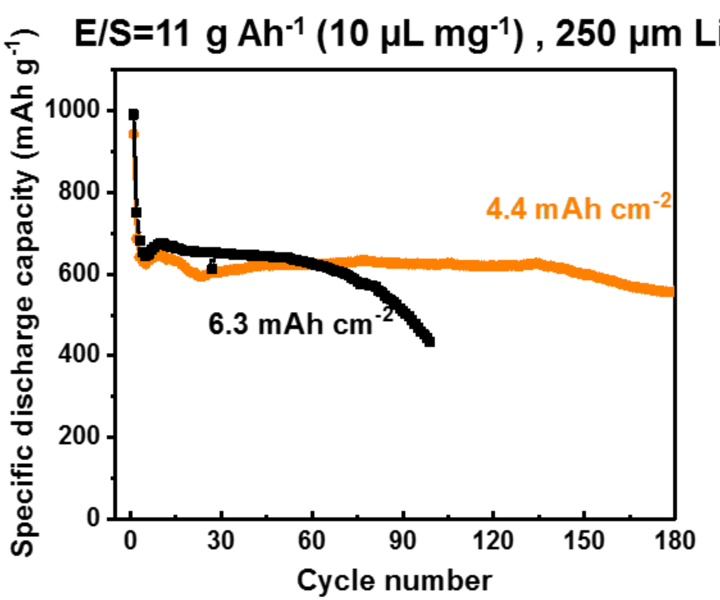


EIS of InLi/SE/LE/SS cells (a) without and (b) with a sulfur cathode (LE:1 M LiTFSI/DOL, EIS: 5 mv, 10^5-10^{-1} Hz) indicates slow electrode wetting in the high loading cathodes.

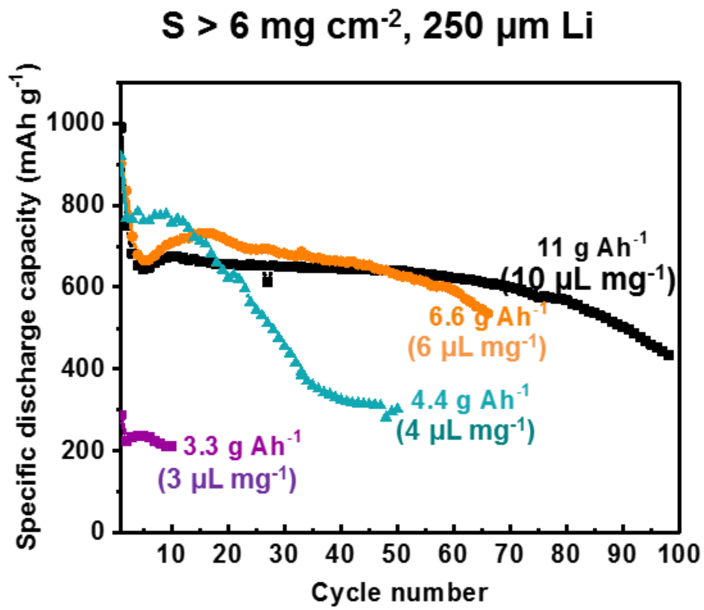
- The garnet/LE hybrid cell was used to study sulfur electrode wetting with different electrolytes and at different E/S ratios.
- Slow electrode wetting process was observed for high-loading sulfur cathodes at lean electrolyte conditions.

Technical Accomplishments

Limiting factors of Li-S cell cycle life at practical conditions



Higher sulfur loading cathode leads to shorter cycle life.

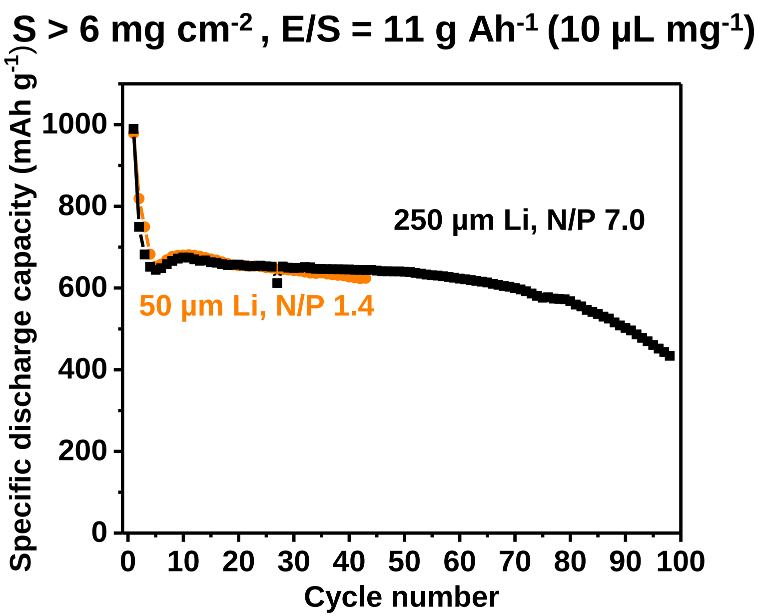


Lower E/S ratio leads to shorter cycle life.

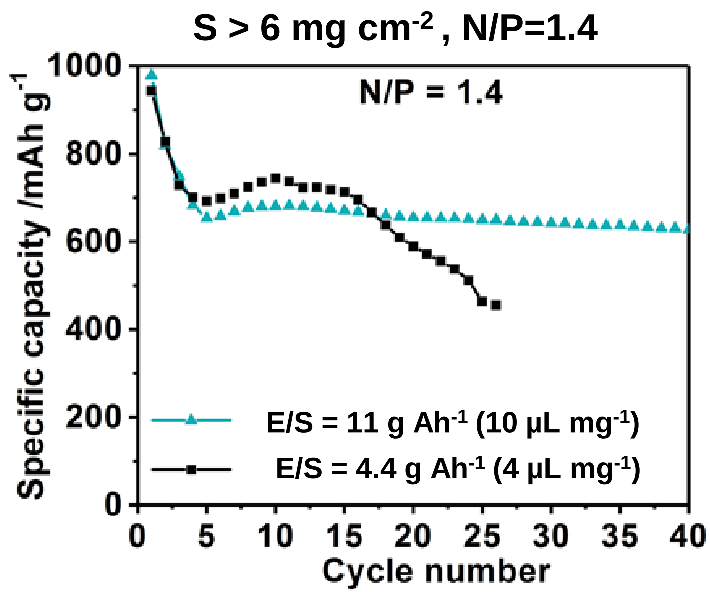
- Sulfur cathode loading plays a key role in cell cycle life at conditions of excess amounts of electrolyte and Li anode.
- Cell cycle life is highly dependent on the E/S ratio at the same level of cathode loading and N/P ratio.

Technical Accomplishments

Limiting factors of Li-S cell cycle life at practical conditions



Lower N/P ratio results in shorter cycle life.

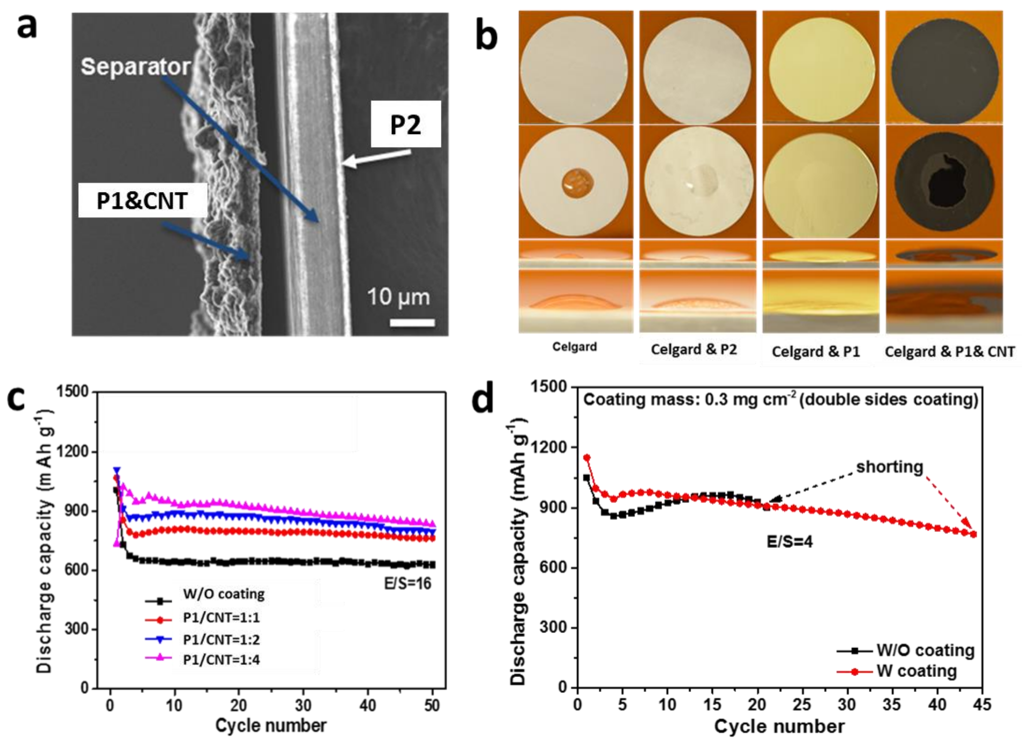


E/S ratio plays a more critical role in cycle life compared to N/P ratio.

- The N/P ratio (negative/positive capacity) affects cell cycle life at the same level of sulfur loading and excess amounts of electrolyte.
- At the same N/P ratio, the E/S ratio plays a more dominant role in cell cycle life.

Technical Accomplishments

Functional separator coating to extend cell cycle life at realistic conditions



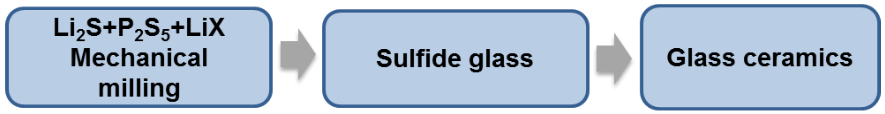
Functional coating of separator (Celgard 2500) improves separator wetting and cell performance (Sulfur loading: 4 mg/cm^2).

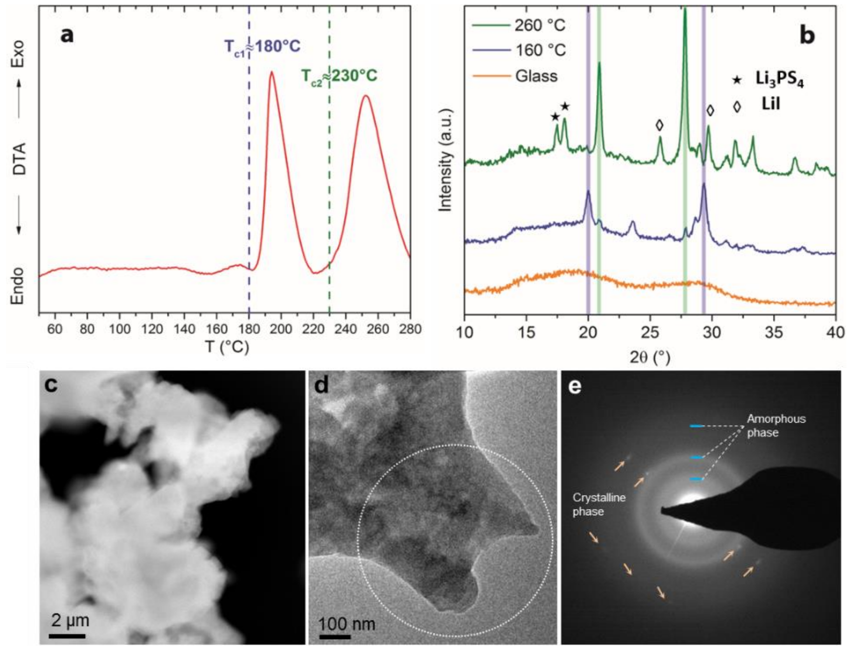
- Double-side functional coating (< 0.3 mg/cm^2) was applied onto separator.
- The separator coating shows significant improvement for sulfur utilization rate and cell cycle life at lean electrolyte conditions (E/S=4 μL mg^{-1}).

Technical Accomplishments

Preparation of highly conductive Li^+ conductor ($Li_7P_2S_8Br_{0.5}I_{0.5}$) to enhance cathode conductivity

Mechanochemical synthesis of $Li_7P_2S_8Br_{0.5}I_{0.5}$





- Low temperature phase of $Li_7P_2S_8Br_{0.5}I_{0.5}$ (LT-LPSBI) was formed below 180 ℃.
- Presence of crystalline and amorphous phases.

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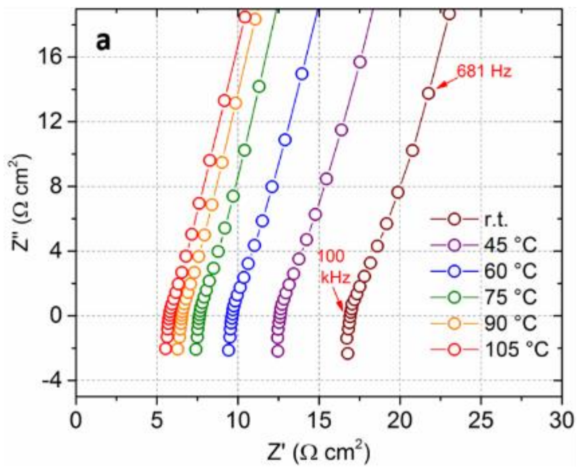
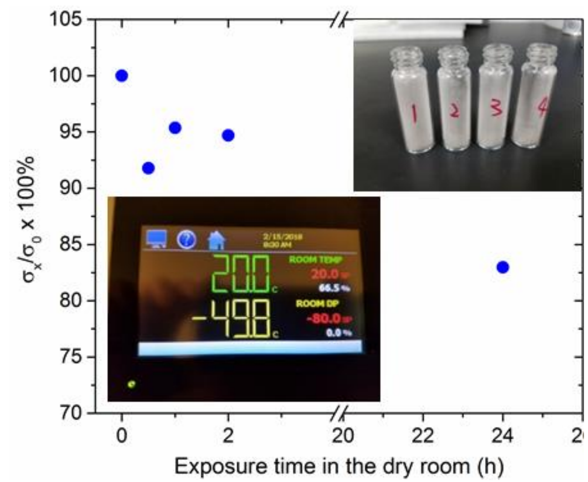
Technical Accomplishments

High conductivity and air stability of low temperature phase $Li_7P_2S_8Br_{0.5}I_{0.5}$



High conductivity was measured by EIS.

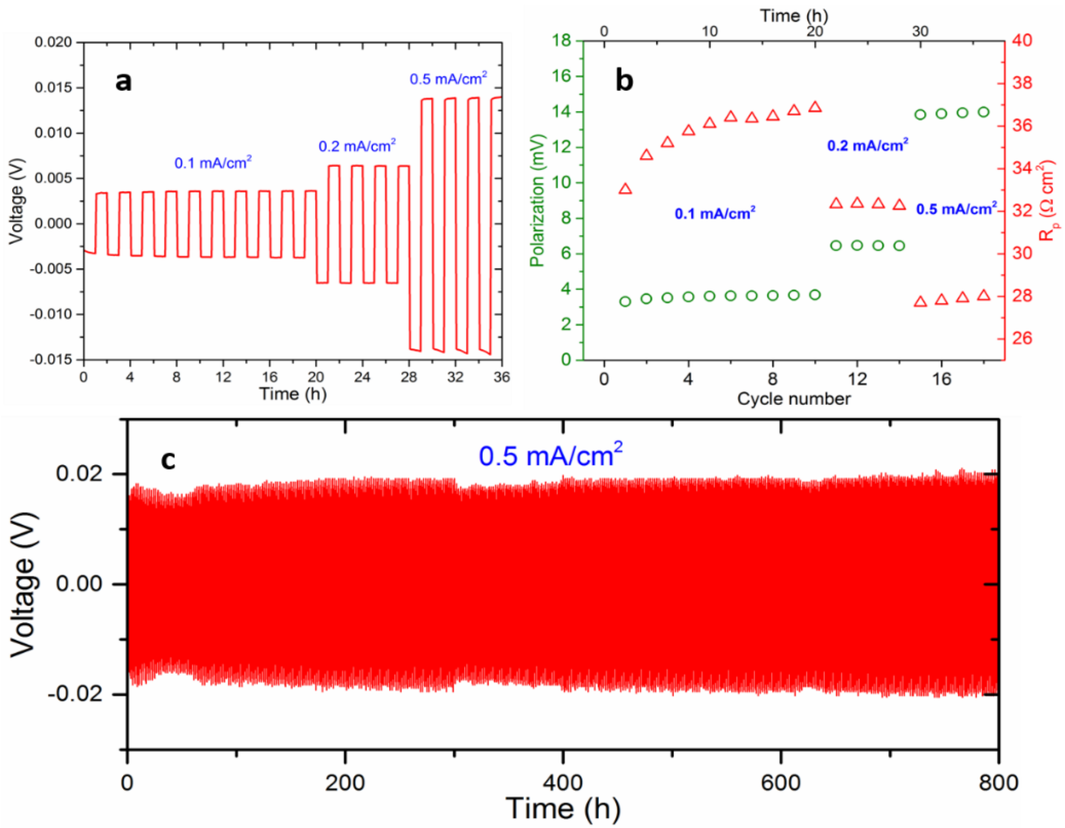


Dependence of conductivity on exposure time indicated decent air stability of the materials.

- High Li^+ conductivity (4.7 mS/cm) of the $Li_7P_2S_8Br_{0.5}I_{0.5}$ (LT-LPSBI) at room temperature.
- Decent air stability of the LT-LPSBI makes application of the material more practical.

Technical Accomplishments

Low and stable interfacial resistance of $Li_7P_2S_8Br_{0.5}I_{0.5}$ with Li anode enables long-term cycling stability



Li/SE/Li symmetric cell study proves high critical current density and long-term cycling stability of the materials with Li.

- Low and stable interfacial resistance (5 Ω cm²) with Li metal anode.
- Long-term cycling stability at high current densities (0.5 mA/cm²).

Technical Accomplishments

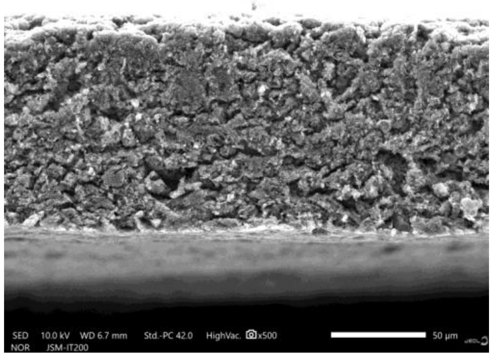
A new approach for preparation of high-energy cathode

	Electrode parameter
Active material	C/S
Sulfur content	>70% (in whole cathode)
Sulfur loading	>5 mg cm^{-2}
Areal capacity	>6 mAh cm^{-2}
Thickness	< 110 µm
Density	>0.8 g/cm^3

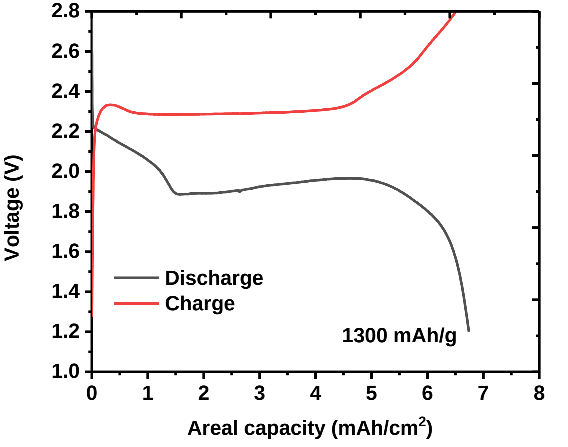
- A dry-processing method enables scalable preparation of sulfur cathodes with practically high **loading**, high **sulfur content** and high **calendering density**.

Technical Accomplishments

A new approach for preparation of high-energy cathode



Sulfur loading: > 5 mg/cm^2
Sulfur content:>73%
Binder content: 1%
Electrode density: 0.8g/cm^3



Dense and uniform sulfur electrode as characterized by the cross-section SEM

>1300 mAh/g for 5.2 mg/cm^2 sulfur cathode at E/S=4 μL/mg and i=0.35 mA/cm^2

- High-loading electrode with increased sulfur content and reduced parasitic weights.
- Realized high sulfur utilization rate at lean electrolyte conditions (E/S=4 μL/mg).

Collaboration and Coordination with Other Institutions

- Brookhaven National Laboratory: reaction mechanism study
- General Motors: material/electrode test
- The Chemours Company: separator development
- University of Wisconsin–Milwaukee: electrolyte/additive study
- Environmental Molecular Sciences Laboratory/ Pacific Northwest National Laboratory: materials characterization and electrochemical in-situ study

Remaining Challenges and Barriers

- Low sulfur utilization rate of high-loading and low-porosity sulfur electrode
- Long-term cycling stability of Li-S battery with high-loading sulfur cathodes and lean amount of electrolyte
- Durable electrolyte/additives for long-term cell cycling
- Instability of Li metal anode

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Future Work – FY19

- Scale-up preparation of sulfur cathode with high mass loading (>5 mg S/cm^2), high sulfur content (>70% of electrode) and high calendering density (>1 g/cm^3).
- New design of cathode architecture to enable high sulfur utilization rate (>1300 mAh/g) in the high-loading cathodes at very lean electrolyte (E/S<3 μL/mg) conditions.
- Fundamental understandings of the sulfur/polysulfide reaction pathway, electrode structural evolution, and cathode degradation mechanism at practical conditions through advanced in-situ/ex-situ techniques.
- Comprehensive approaches of new electrolyte/additives, separator coating, and Li protection to extend the cycle life of Li-S cells.

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

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Summary

- A garnet oxide/liquid electrolyte hybrid cell set-up was designed and employed for focused fundamental studies of sulfur cathodes; slow wetting process of high-loading sulfur cathodes was identified at lean electrolyte conditions.

- At practical conditions, Li-S cell life is highly dependent on cathode loading, electrolyte amount, and Li thickness, among which lean electrolyte amount is a dominant factor.

- Low-temperature phase $Li_7P_2S_8Br_{0.5}I_{0.5}$ with high conductivity of 4.7 mS/cm^2 was synthesized to improve the ionic conductivity of a sulfur cathode.

- Dry-processing approach was developed for high-loading and low-porosity sulfur cathode preparation; a sulfur utilization rate of 1300 mAh/g was realized for a high loading cathode (5.2 mg/cm^2) at lean electrolyte conditions (E/S=4 μL/mg).

Acknowledgements

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- Team Members:

  Jie Xiao, Ji-Guang Zhang, Yuxing Wang, Lili Shi, Arthur Baranovskiy, Jian Qin

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Technical Backup Slides

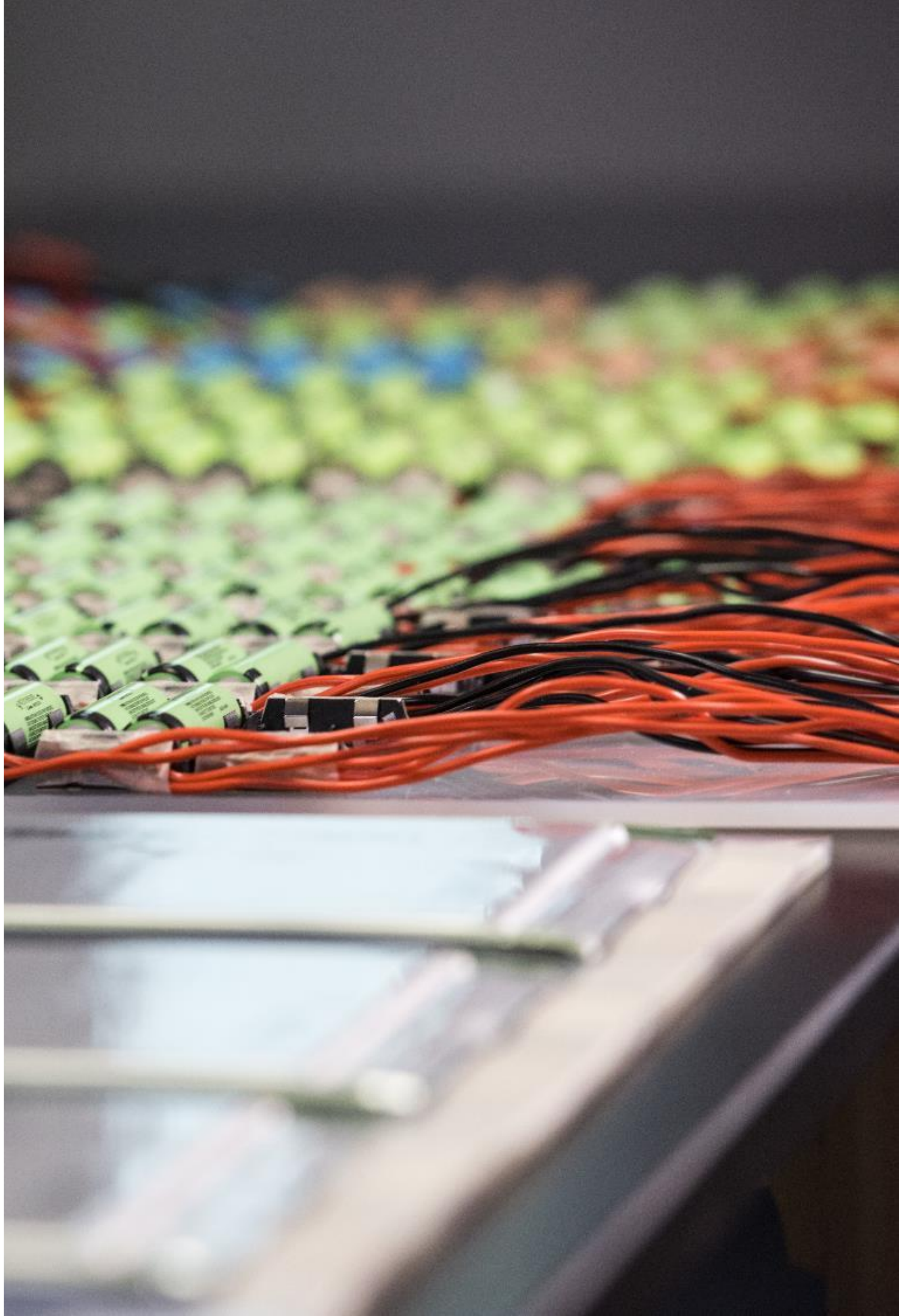

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Table 1. Design of a 350 Wh/kg Li-S Pouch Cell

	Prameters	Original Design 350 Wh/kg
Cathode	Material	S (80%)/C (20%)
	1st discharge capacity (mAh/g, based on S/C composite)	880
	Active material loading (S+C)	93.7%
	Total coating weight (mg/cm^2 each side)	7.8
	Areal Capacity (mAh/cm^2 each side)	6.4
	Electrode press density (g/cm^3)	1.1
	Electrode thickness (single side) (µm)	90
	Al foil thickness (µm)	12
	Layers	12
Anode	Cell balance (N/P ratio)	1.6
	Electrode thickness (single side) (µm)	50
	Cu foil thickness (µm)	6 (foil)
Electrolyte	Electrolyte/capacity ratio (g/Ah)	3.0
	Weight (g)	10.2
Separator	Thickness (µm)	20
Packet foil	Thickness (µm)	86
Cell	Voltage (V)	2.0
	Capactiy (mAh)	3410
	Energy density (Wh/kg)	350