Safety Evaluation of Next-generation Solid-State Li-ion Battery

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Acknowledgement of Funding & Project Objective

Funded by

Project Objective: Generate experimental database to access the safety (*thermal, electrical and environmental*) level in solid-state Li-ion compared to liquid electrolyte based Li-ion.

UDRI Lithium Battery Research and Team Contribution

- Synthesis / Solid State Electrolytes
- Interface study
- Bulk and thin-film Li batteries
- Cell fabrication & tests (electrochemical & safety)
- Safety tests: Thermal, electrical, mechanical, Impact (high-speed impact)

Mr. Liu Tongjie (Ph.D. Student)
Solid state Lithium batteries

Mr. Kum Lenin Wung (Ph.D. Student)
Solid electrolyte/electrode interface, and solid-state lithium batteries

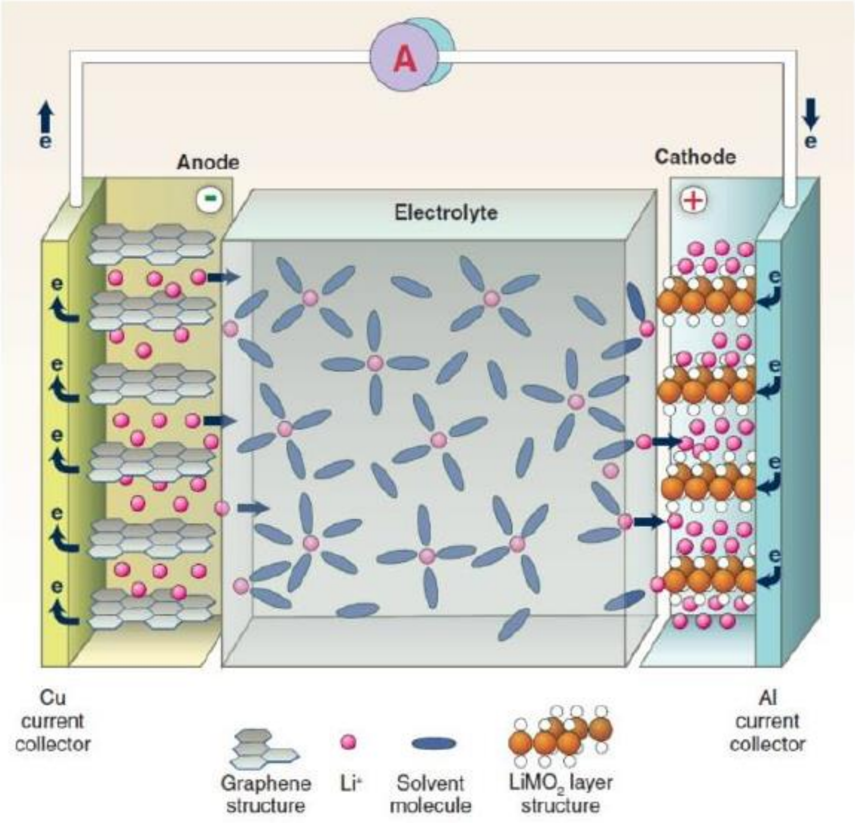
Mr. Nick Vallo (Ph.D. Student)
Dendrite sensing, Heat sensing, Wireless BMS; LIBs safety

Deependra Kumar Singh, Ph.D.
Thin-film solid-state battery, materials characterization

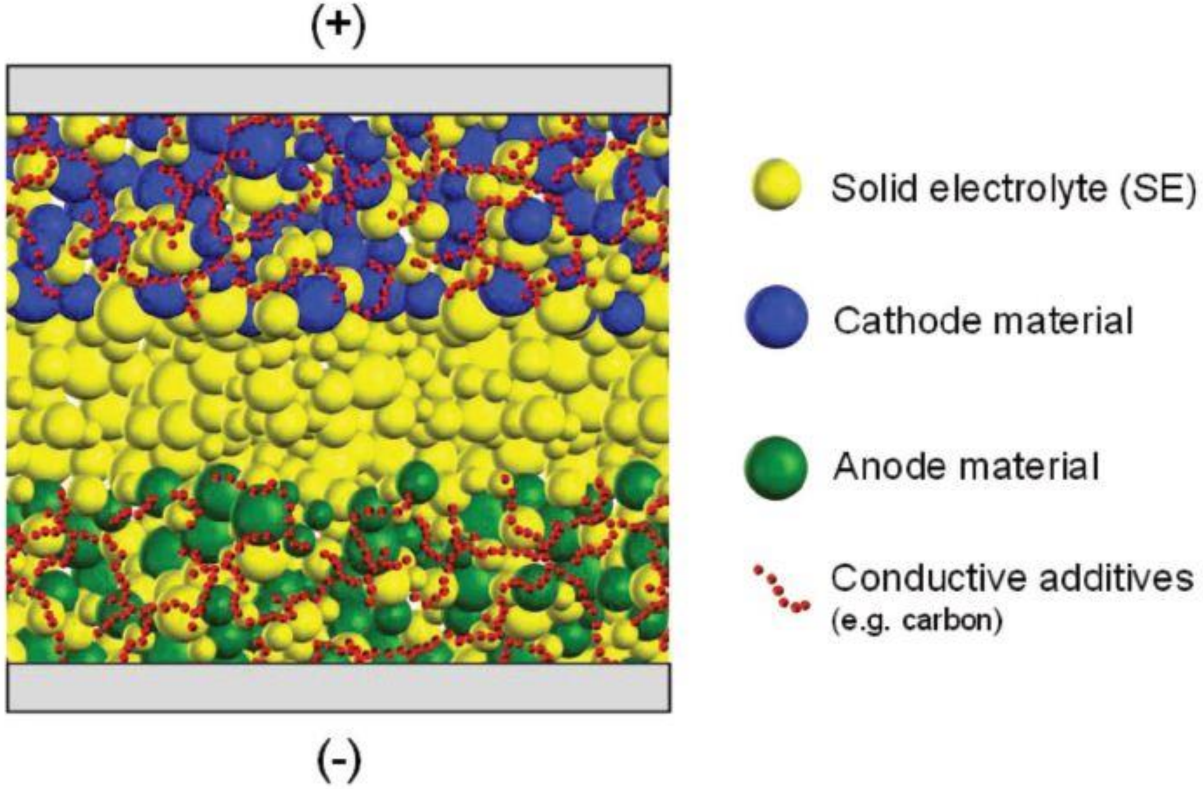
What we need from future battery?

More energy
More Power
More cycle-life
Higher safety
Faster charge
Lower Cost

Li ion battery construction: Liquid vs. solid state



Liquid electrolyte: $LiPF_6$ in organic carbonate electrolyte



Solid electrolyte: sulfides or oxides or phosphates

Potential Solid electrolytes for Li batteries

Candidate	Advantage	Disadvantage
Sulfide based (LPS, LPSX; X = Cl, Br, I)	• High Li^+ ion conductivity at RT • High interfacial stability with Li anode • Soft and Compressible	• Not stable in air • Low voltage stability
Oxide (LiLaZrO, LiAlGeP, and derivatives) Phosphates (LAGP, LATP and derivatives)	• High stability at high voltage • More stable in air	• Lower conductivity • Brittle

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Manufacturing sulfide solid electrolyte (SSE): Commercial vs UDRI

Method used in literatures

Quartz tube furnace

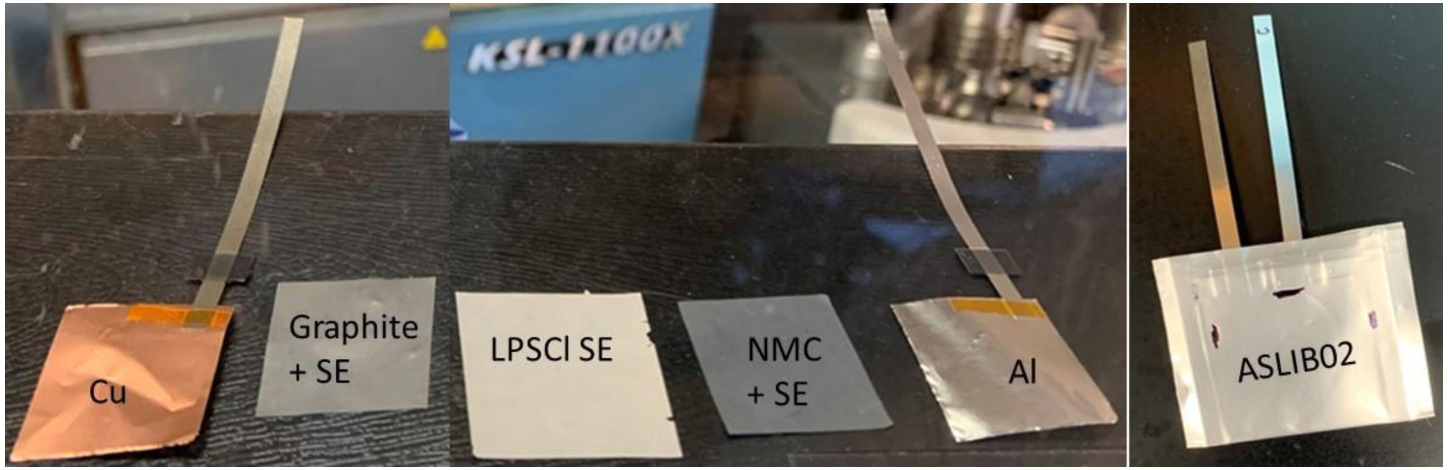
- Small quantity
- Material could encounter with air and moisture

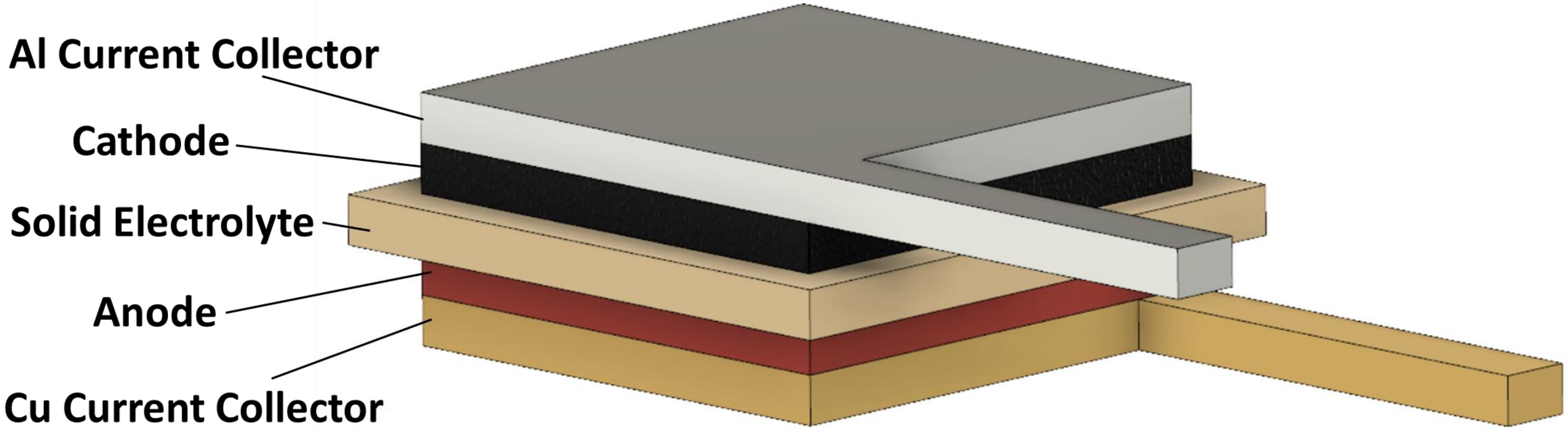
Our method

Furnace in Ar glovebox

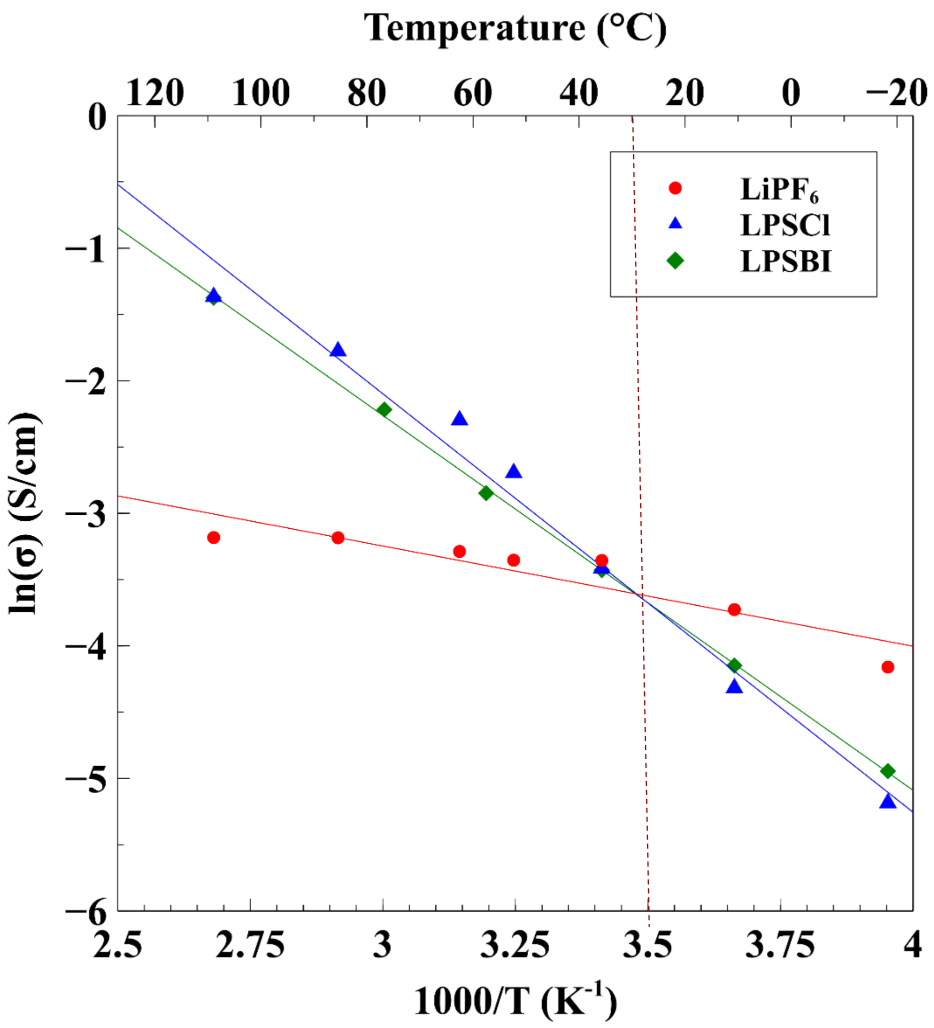
- Large quantity
- Material always operated in Ar atmosphere

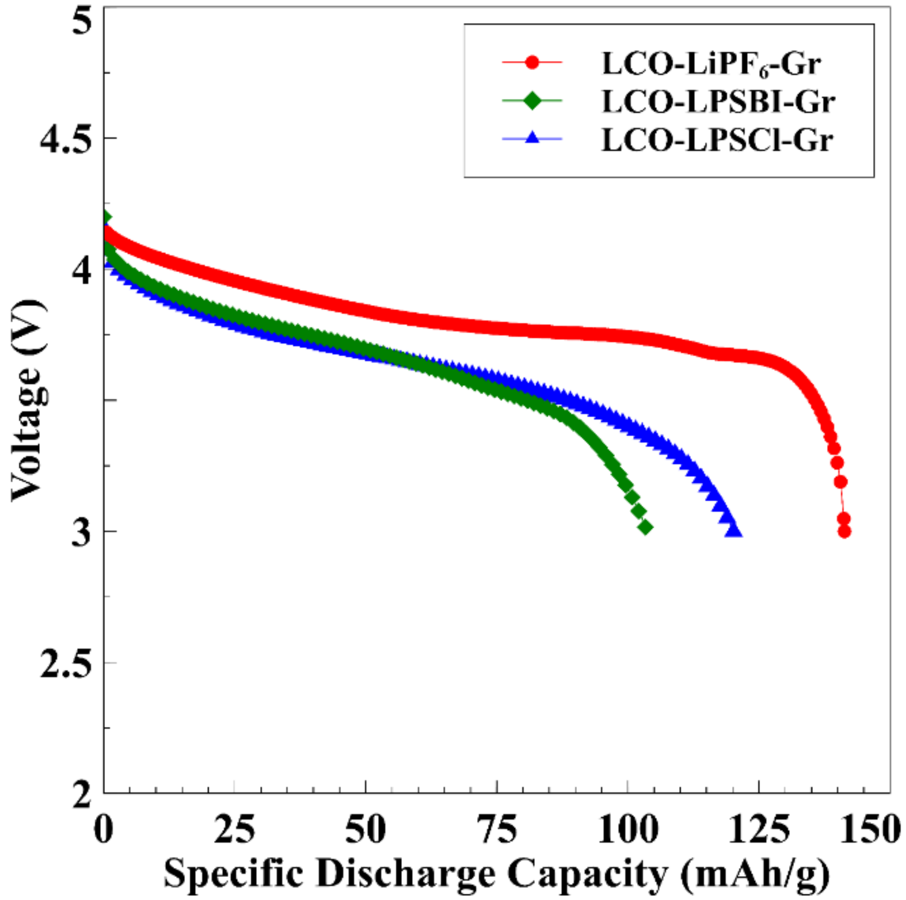
Fabrication of components and pouch ASLIB





Electrical and electrochemical performance: Sulfide SE vs LE





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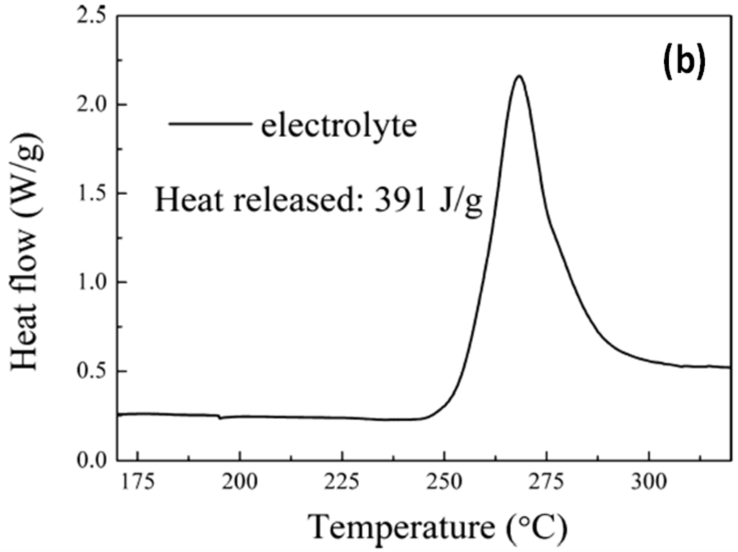
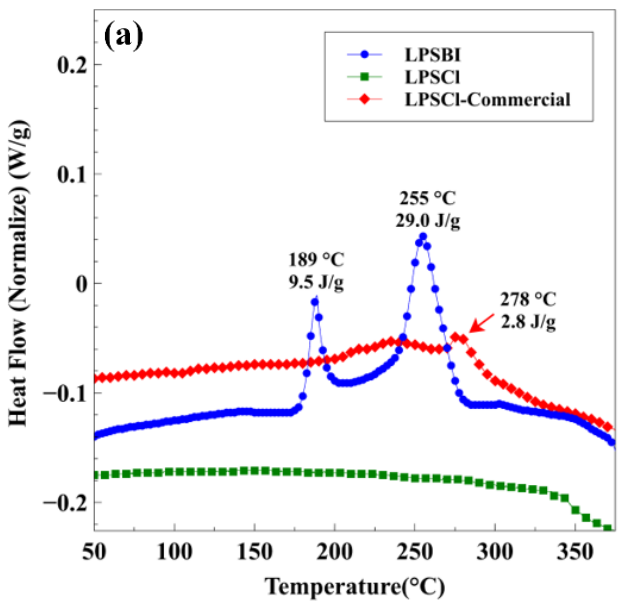
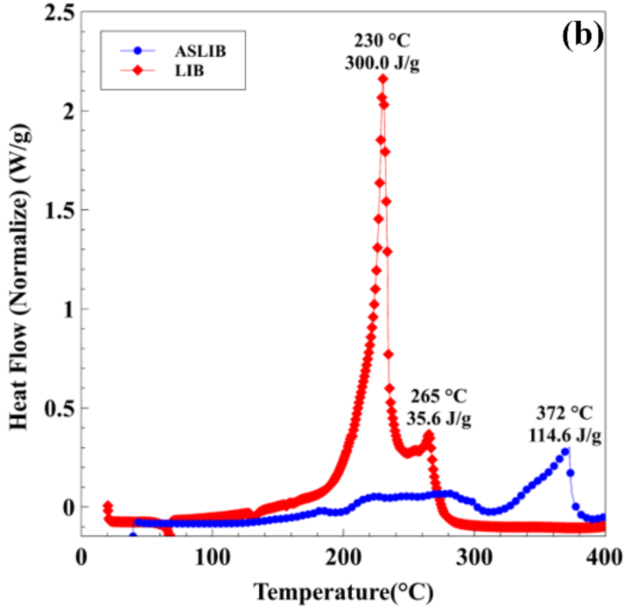
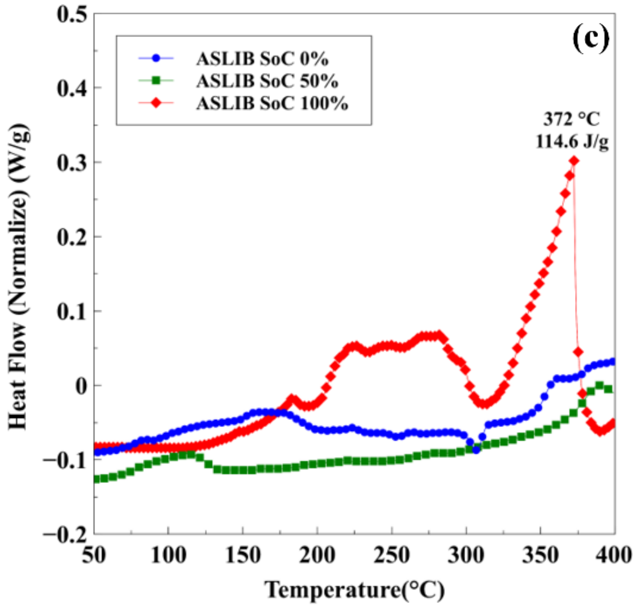
Heat release characteristic (DSC): sulfide SE vs LE



Commercial liquid electrolyte:
Exothermic peaks at *269°C*
Heat release: *391 J/g*







(d)

Sample/Property	Heat Flow (J/g)	Temperature (°C)
LPSBI	9.5	189
	29	255
LPSCl	–	–
LPSCl - commercial	2.8	278
1 M $LiPF_6$ in EC/DMC (1:1 v/v)[ref]	588	273
LIB	300	230
	35.6	265
ASLIB	114.6	372
ASLIB SoC 0%	–	–
ASLIB SoC 50%	–	–
ASLIB SoC 100%	114.6	372

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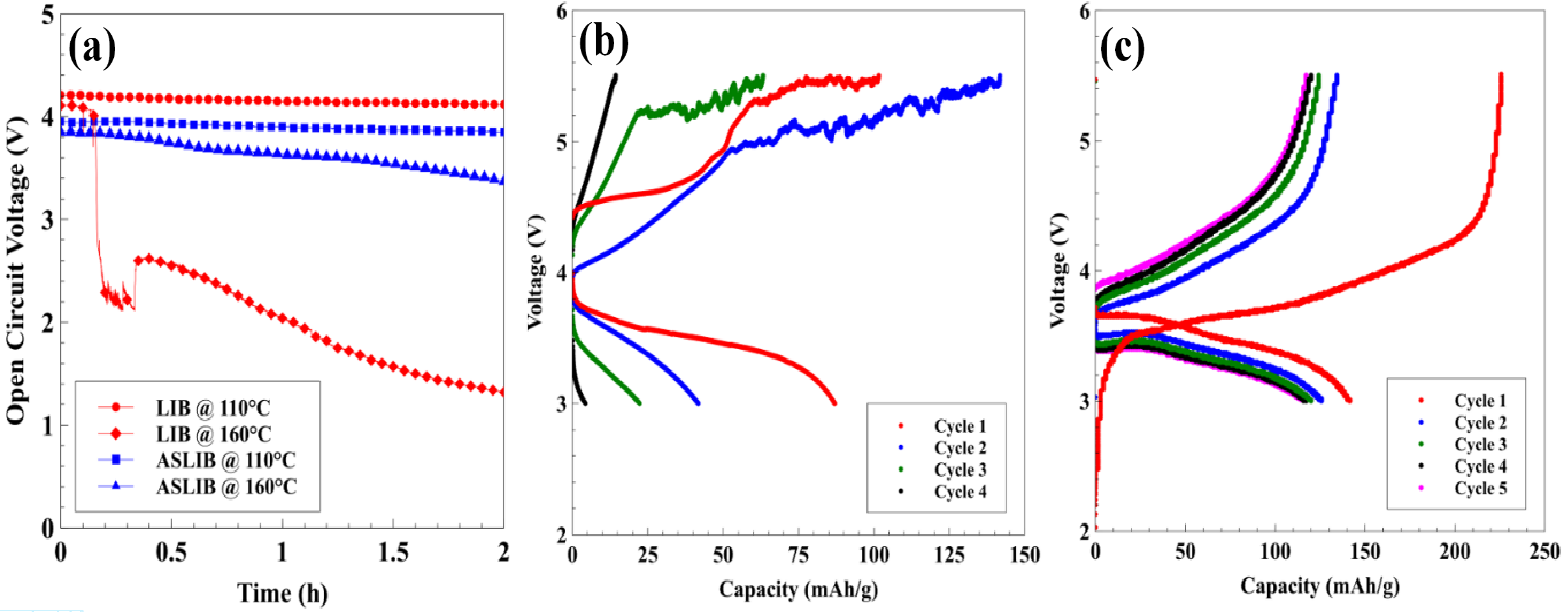
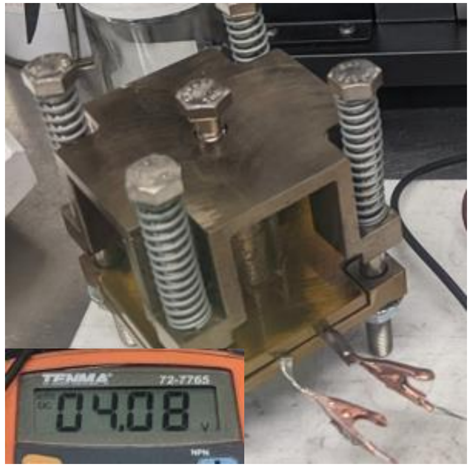
Electrical safety: Temperature, voltage



LIB electrically short around 160 degC, ASLIB remain stale beyond 160 degC

LIB quickly develop micro-short below 5V, ASLIB remain stable beyond 5V

Mechanical safety: Cutting nail penetration



Under pressure

No pressure

Cut

Penetrated

Nail removed

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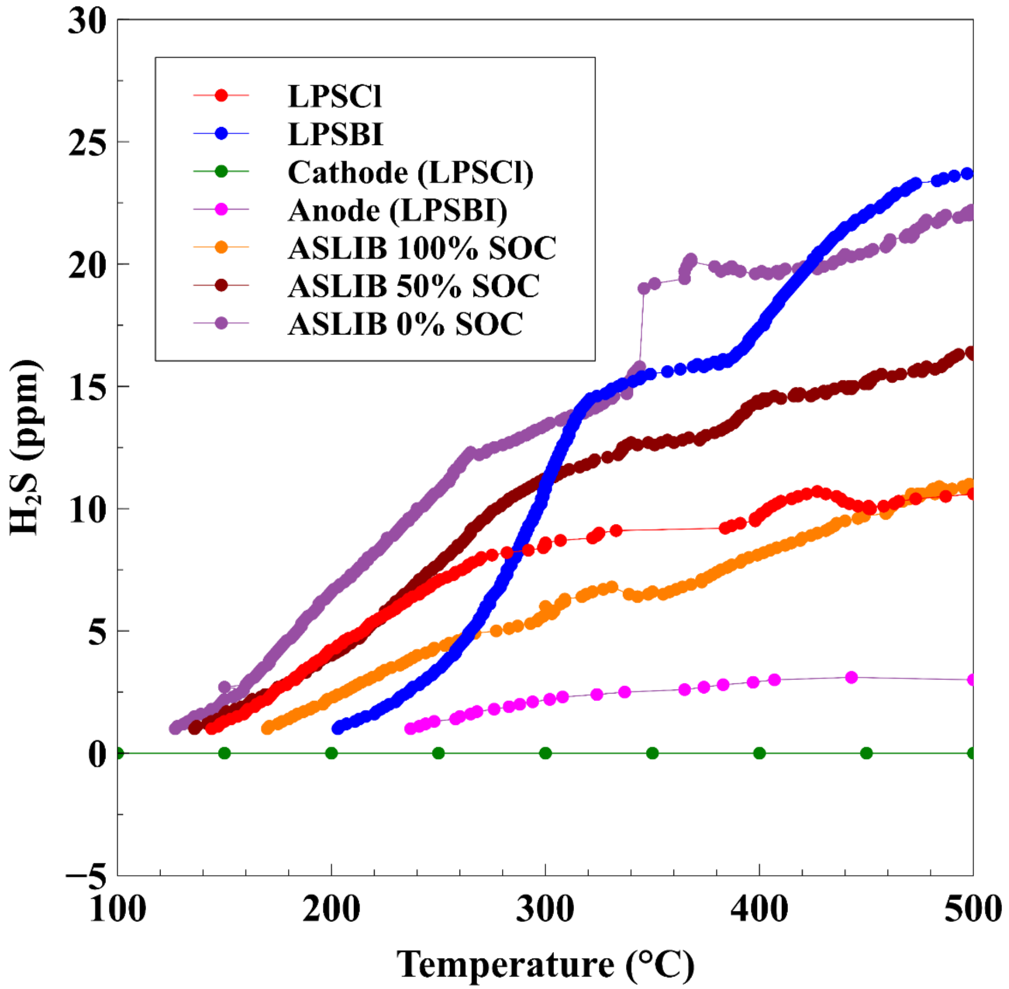
Gas generation measurement in ASLIBs

Main hazardous gas from battery fire: hydrogen fluoride (HF - 20 and 200mg/Wh) and phosphoryl fluoride (POF3 - 15–22mg/Wh), CO, CO2



Tube volume: 60cm * (43.9mm / 2)^2 * 3.14 = 907.7 cm^2
Box volume: 18cm * 22cm * 13cm = 5148 cm^2
Total volume = 6055.7 cm^2

Hazard: H2S gas

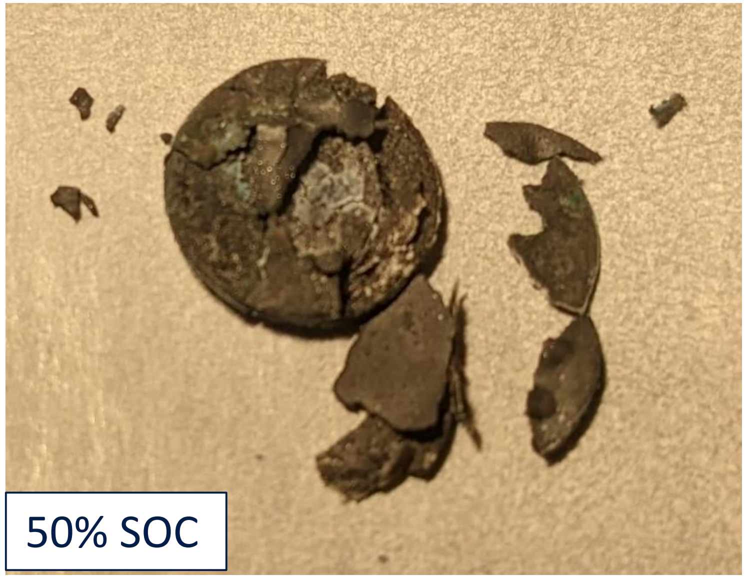
https://www.osha.gov/hydrogen-sulfide/hazards

Concentration (ppm)	Symptoms/Effects
0.00011-0.00033	Typical background concentrations
0.01-1.5	Odor threshold (when rotten egg smell is first noticeable to some). Odor becomes more offensive at 3-5 ppm. Above 30 ppm, odor described as sweet or sickeningly sweet.
2-5	Prolonged exposure may cause nausea, tearing of the eyes, headaches or loss of sleep. Airway problems (bronchial constriction) in some asthma patients.
20	Possible fatigue, loss of appetite, headache, irritability, poor memory, dizziness.
50-100	Slight conjunctivitis ("gas eye") and respiratory tract irritation after 1 hour. May cause digestive upset and loss of appetite.
100	Coughing, eye irritation, loss of smell after 2-15 minutes (olfactory fatigue). Altered breathing, drowsiness after 15-30 minutes. Throat irritation after 1 hour. Gradual increase in severity of symptoms over several hours. Death may occur after 48 hours.
100-150	Loss of smell (olfactory fatigue or paralysis).
200-300	Marked conjunctivitis and respiratory tract irritation after 1 hour. Pulmonary edema may occur from prolonged exposure.
500-700	Staggering, collapse in 5 minutes. Serious damage to the eyes in 30 minutes. Death after 30-60 minutes.
700-1000	Rapid unconsciousness, "knockdown" or immediate collapse within 1 to 2 breaths, breathing stops, death within minutes.
1000-2000	Nearly instant death

OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION

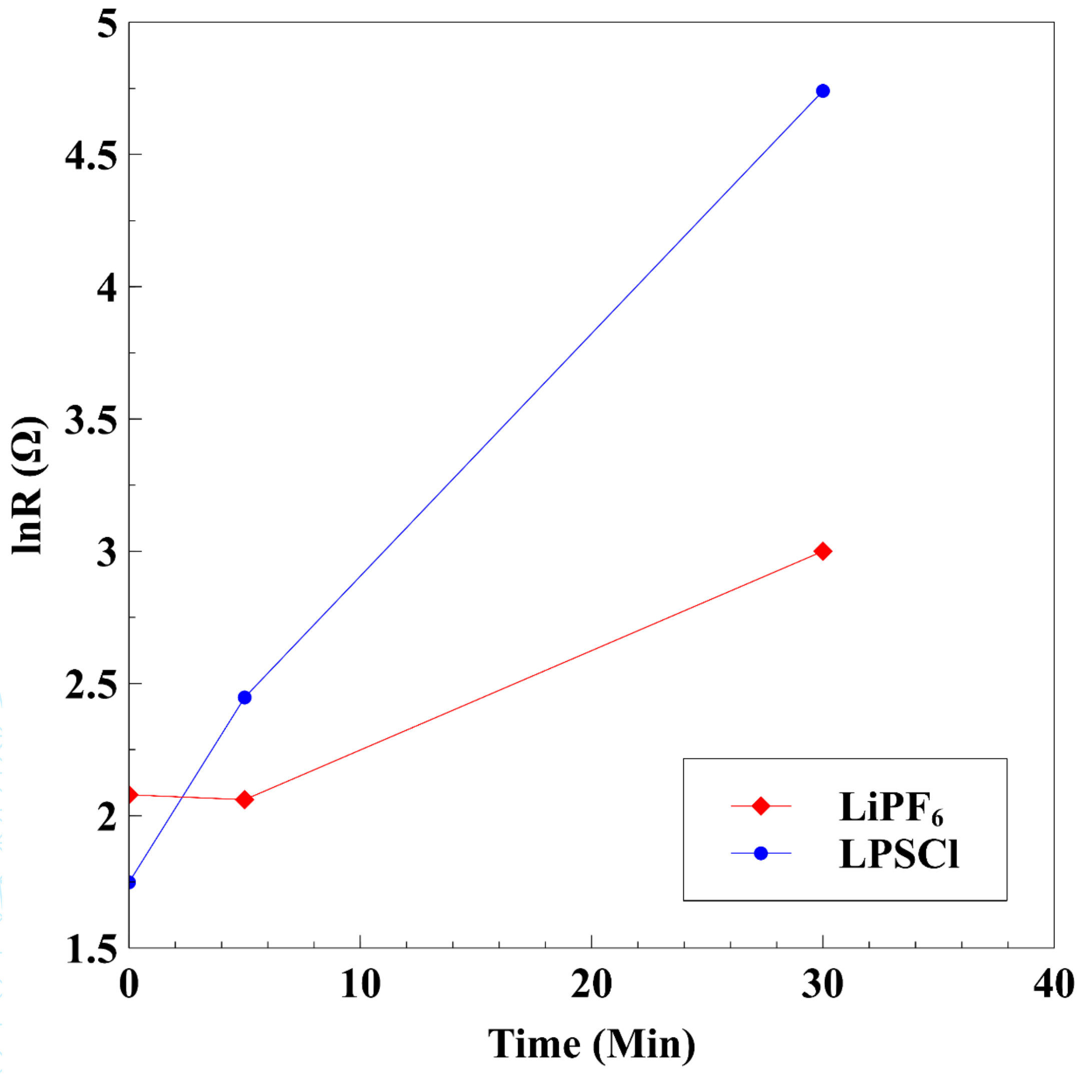
Worker Exposure Limits
NIOSH REL (10-min. ceiling): 10 ppm
•OSHA PELs:General Industry Ceiling Limit: 20 ppm •General Industry Peak Limit: 50 ppm (up to 10 minutes if no other exposure during shift) •Construction 8-hour Limit: 10 ppm •Shipyard 8-hour limit: 10 ppm
NIOSH IDLH: 100 ppm
IDLH: immediately dangerous to life and health (level that interferes with the ability to escape) (NIOSH) **PEL:** permissible exposure limit (enforceable) (OSHA) **ppm:** parts per million **REL:** recommended exposure limit (NIOSH)

ASLIB weight loss after 500 degC in air



LPSBI: 100mg – 117mg
LPSCl: 100mg – 60mg
LCO cathode: 10mg – 10mg
Gr Anode: 10mg – 6mg
ASLIB 100 SOC: 120mg – 138mg
ASLIB 50 SOC: 120mg – 135mg
ASLIB 0 SOC: 120mg – 135mg

Environmental degradation upon air exposure: LIBs vs. ASLIBs



- Sulfide SE degrades much faster than liquid electrolyte upon air exposure
- Fast impedance growth (chemo-resistive) in SSE can be beneficial for quick shut-down of battery functioning
- A combination of protection with high thermal stability and quick shut-down can make the ASLIB completely explosion- and fire-safe.
- Need to determine behavior at cell level.

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Summary

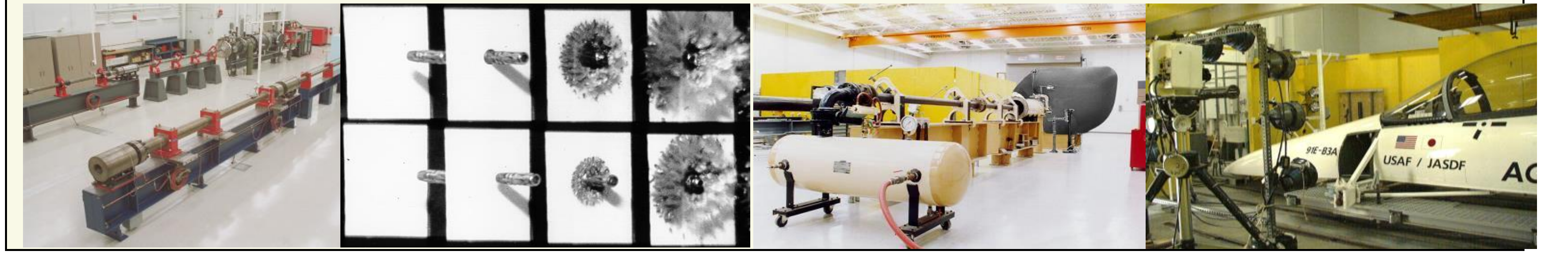
At small cell format ASLIB is clearly safer (thermally, electrically, environmentally) compared to liquid electrolyte based LIB but data need to be generated at large format cells and later at module and pack level.

Li-ion Battery Safety under High-Speed Impact: Diagnosis, Prognosis and Risk Mitigation

Objectives

- Battery response under aircraft speed impact conditions
- New methods of quickly de-energize LIBs to minimize thermal runaway risks
- Machine learning (ML) to equip BMS in making self-corrective

System	Characteristics	Typical Uses
Compressed-gas Guns	Bores up to 12 in., Package weights to 115 lb., Velocities to 1,600 fps	Foreign Object Damage impact testing with Soft and hard body FOD. Testing of aircraft full-scale and component level structures
2 and 3-stage light-gas guns	50/20 mm and 75/30 mm guns, Velocities to 33,000 fps	Orbital debris and micrometeoroid impact damage, Penetration mechanics, Armor tests
Powder-Guns	Barrel bore sizes to 50mm, Velocities to 7,200 fps	Armor Testing, Penetration, and Blast frag. studies, Shock physics, Dynamic prop's, Ballistic limits



Questions / suggestions

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