PURDUE CHEMICAL ENGINEERING

ViPER Vilas Pol Energy Research

Batteries: Fundamentals, Recent Advances, and Inherent Safety Aspects

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Fall 2023

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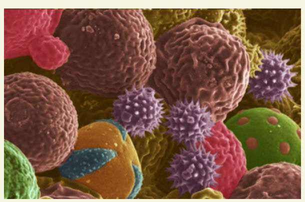
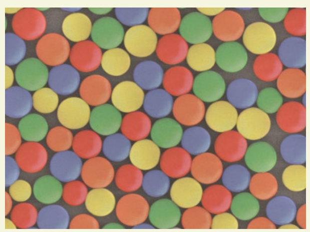
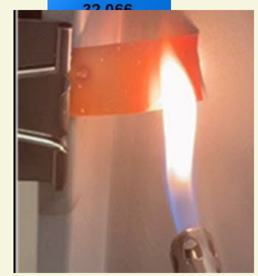
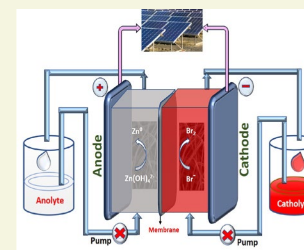
Prof. Vilas G. Pol

PURDUE
ENGINEERING
CHEMICAL ENGINEERING

Research Areas

Lithium-ion	Sodium ion	Potassium ion	Li-S/Solid state	Flow
3 Li Lithium 6.941	23 Na SODIUM 11	19 K Potassium 39.0983	16 S	30 Zn Zinc 65.37
				

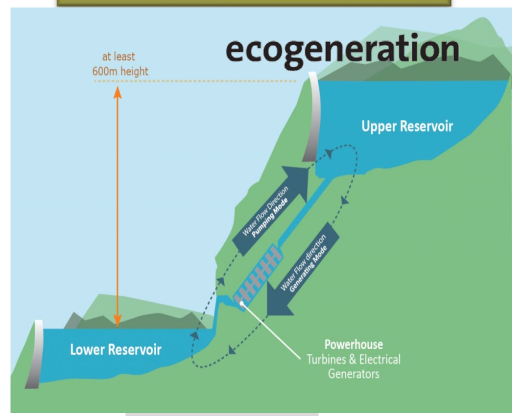
ARMY RESEARCH OFFICE · NASA · ONR Science & Technology · NSF SBIR/STTR · PURDUE UNIVERSITY · P2SAC · Mosaic

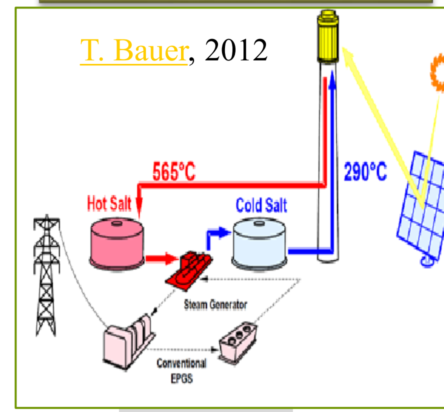
NEPTUNE · U.S. DEPARTMENT OF ENERGY · NSF · PURDUE RESEARCH FOUNDATION · VALGOTECH · TIMKEN · BRIGHTVOLT

260+ Publications; H index 55, 150+ invited talks
19 issued US patents, 20+ pending, 40+ awards

Types of Energy Storage

Electrochemical | **Mechanical** | **Thermal**





Rechargeable Batteries | **Pumped Hydro** | **Molten Salt**

	Rechargeable Batteries	Pumped Hydro	Molten Salt
Discharge Time	1 min – 8h	4-16h	hours
Lifetime	1,000 – 10,000	30-60 years	30 years
Energy Density (Wh/L)	200-400	0.2-2	70-200
Efficiency	85-95%	70-85%	80-90%
Cost	High	Low	Low

Classes of battery

Primary vs. Secondary Batteries

Primary:

- Cell reaction is irreversible
- Must be discarded after use
- Have relatively short shelf life
- They cannot be used as storage devices
- Can not be recharged
- e.g. Dry cell.

Secondary:

- Cell reaction is reversible
- May be recharged
- Have long shelf life
- They can be used as energy storage devices
- They can be recharged.
- e.g. Li-MnO_2 battery, Lead acid, Ni-Cd battery.

Standard Modern Primary Batteries

- Zinc-Carbon: used in all inexpensive AA, C and D dry-cell batteries. The electrodes are zinc and MnO_2-carbon, with an acidic paste between them that serves as the electrolyte. (disposable)

- Alkaline: used in common Duracell and Energizer batteries, the electrodes are zinc and manganese-oxide, with an alkaline electrolyte (KOH).

$$Zn_{(s)} + 2OH^{-}_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^{-}\ [e° = 1.28\ V]$$
$$2MnO_{2(s)} + H_2O_{(l)} + 2e^{-} \rightarrow Mn_2O_{3(s)} + 2OH^{-}_{(aq)}\ [e° = +0.15\ V]$$

Overall reaction:

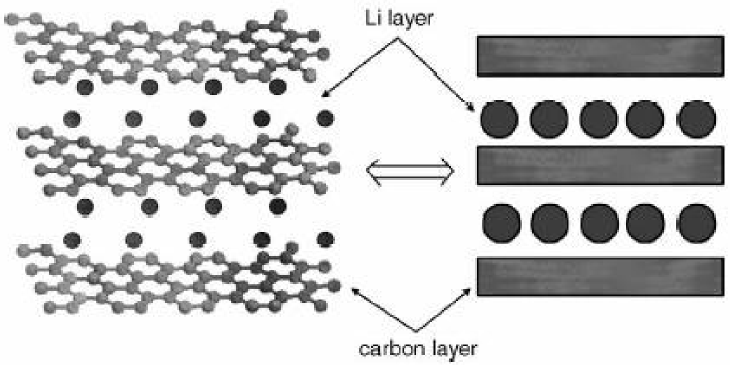
$$Zn_{(s)} + 2MnO_{2(s)} \rightarrow ZnO_{(s)} + Mn_2O_{3(s)}\ [e° = 1.43\ V]$$

- **CANNOT BE RECHARGED**

Theoretical Capacity of Materials

- From Faraday's 1st Law of Electrochemistry $1Q = [6.241 \times 10^{18}$ electrons$]$
  - 1 gm. equivalent wt. of materials will deliver 96487 Coulombs

Thus, 96487 / 3600 = 26.8 Ah



- At # of C is 6 x 2 = 12 (atomic mass)

Forming LiC_6 structure 6 x 12 = 72

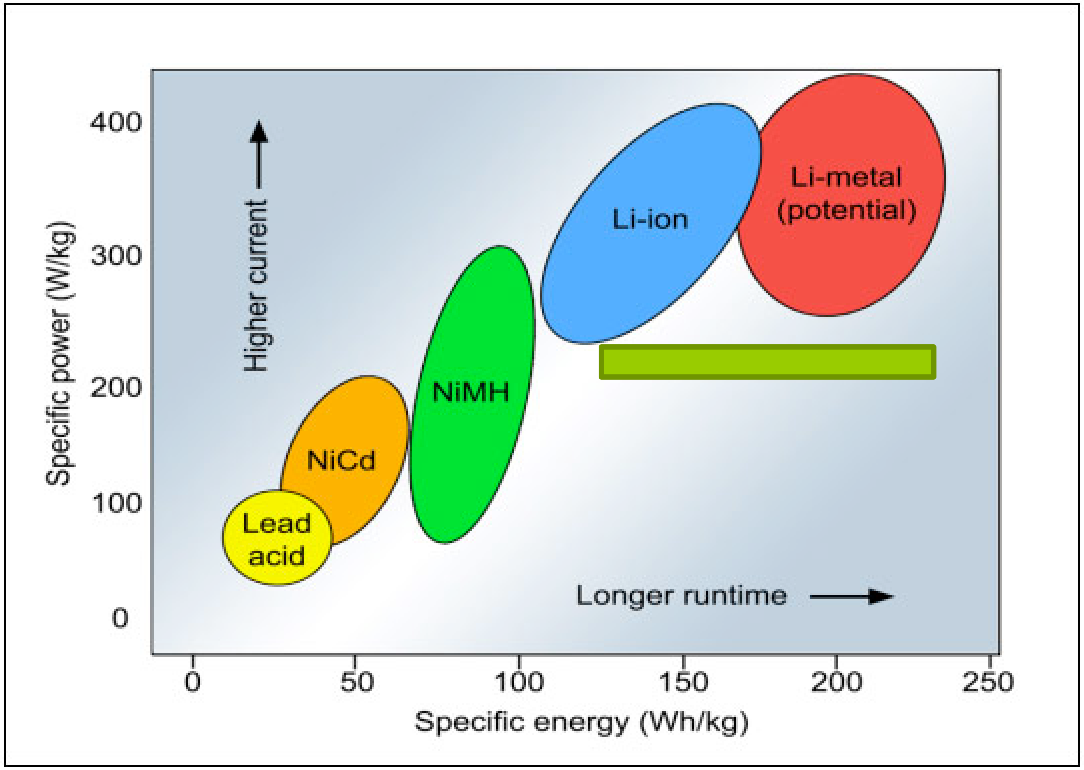
- Theoretical specific capacity of Graphite
  = 26.8/72

= 0.372 Ah/g

= 372 mAh/g

Existing Battery Types

Ragone Plot



Higher power and energy are driving the Li Ion battery growth

Specific energy is the total energy a battery can deliver in watt-hours per kilogram (Wh/kg)

Specific power is the battery's ability to deliver power in watts per kilogram (W/kg).

History of Li-ion batteries

1970: M. S. Whittingham – Proposed Li ion battery (SUNY, USA).

1980 : J. Goodenough - Layered $LiCoO_2$ material as cathode (Oxford University, Now at UT)

1991 : SONY Commercialized Li ion battery ($LiCoO_2$ as cathode, Japan).

Chevrolet Volt (GM)

EV Range : 50 miles per charge
Battery Type : 16kW.h Lithium Ion
Cost of Battery : $11,000

Currently, >90 % of Li-ion cells are manufactured in Japan, Korea, China

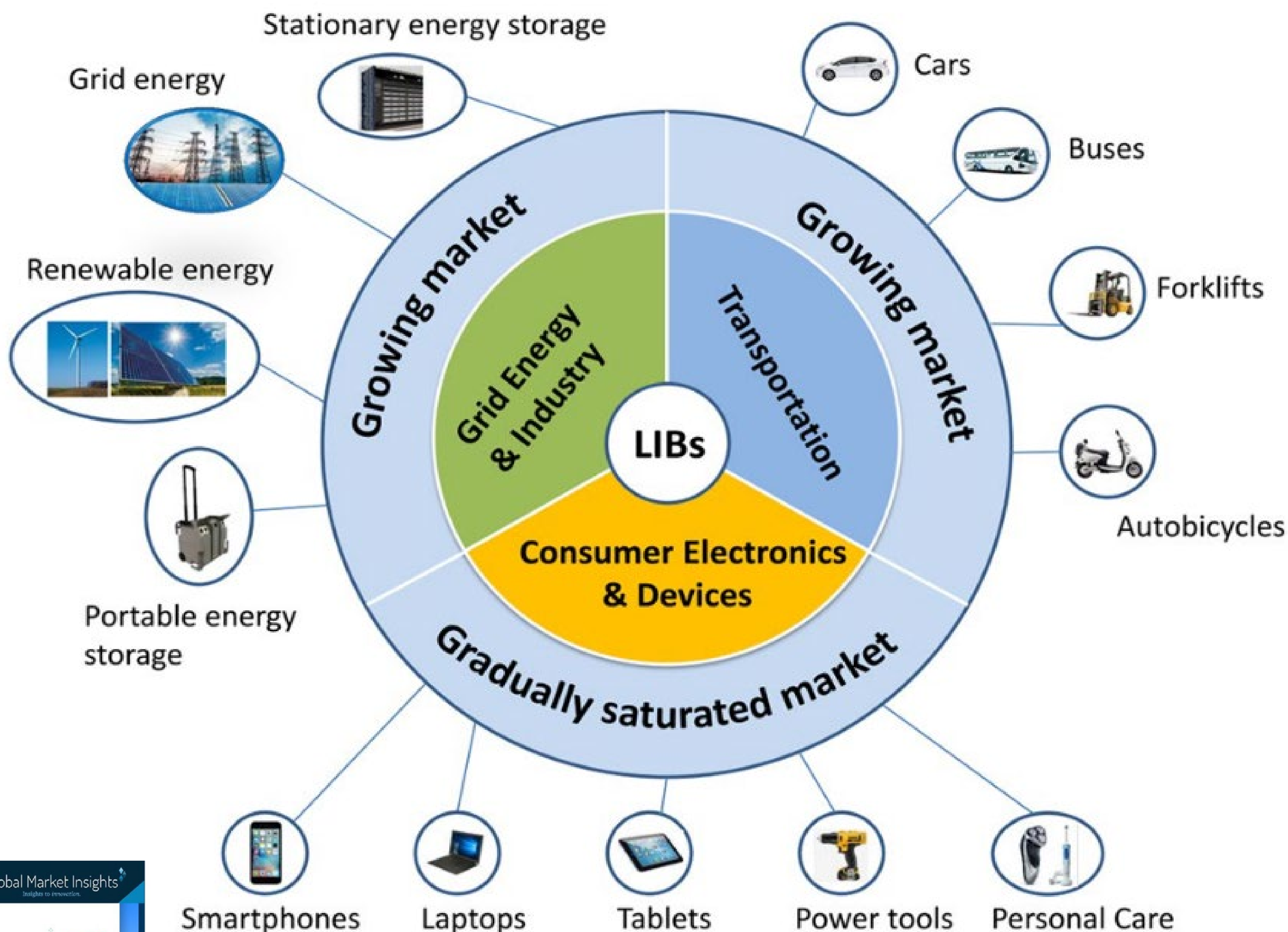
We are not trading our dependence on foreign oil to a dependence on foreign batteries

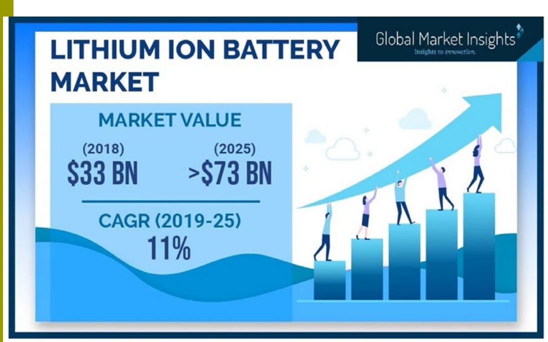
How many batteries are required to run your EV?

A 90 kWh *battery* built with Panasonic 3.4 Ah 18650 *cells* will require about ***9000 cells***

18650

Lithium ion Batteries are Everywhere!





Ding et al., *Electrochem. Energy Rev.* 2019

Li-ionBattery Research Challenges

New

- **Cost**

  Current projected cost (25 kW battery) ~ \$1000

  - Target cost (25 kW battery) ~ \$500

- **Safety**

  Inherently safe batteries needed

  - Overcharge protection circuitry expensive

- **Life**

  Current technology ~ 5 to 10 years

  - Target ~ 15 years

- **Low Temperature Performance**

  Current technology ~ Sluggish < 0 ºC

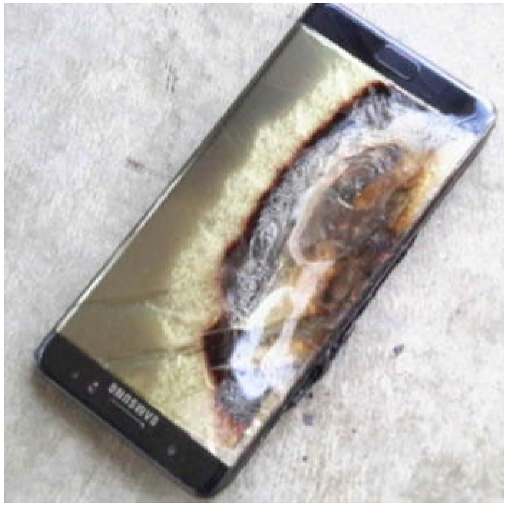
  - Target ~ -30 ºC (cold cranking)

John B. Goodenough *et al.*, *Chemistry of Materials* **(2010)** *22*, 587

Safety Concerns of Lithium-ion Batteries

Boeing 787, Dec. 2014 [(1)]

Tesla Model S, Aug. 2016 [(2)]



Samsung Note 7, Sept. 2016 [(3)]

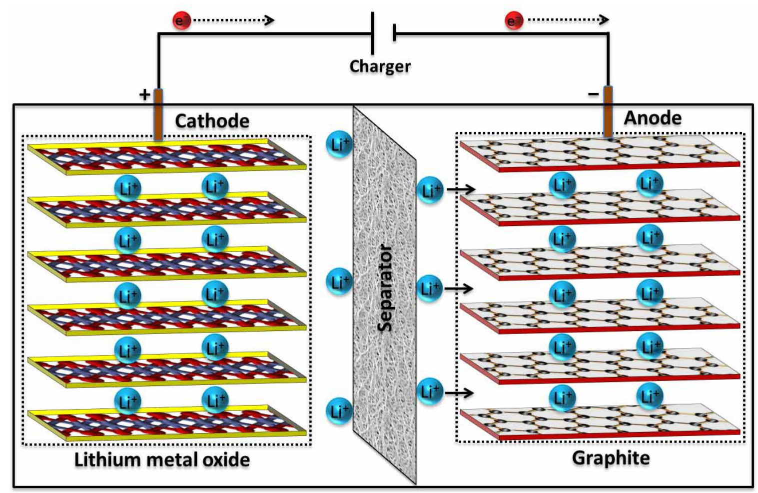
- LIBs dominate rechargeable energy storage market due to high energy density
- Safety incidents still occurring for mature Li-ion battery technology
- Susceptible to thermal runaway: can occur by overcharging, cell puncture, dendrites

Motivation: Improve understanding of thermal runaway and how to mitigate for rechargeable battery

(1)https://www.scientificamerican.com/article/how-lithium-ion-batteries-grounded-the-dreamliner/
(2)https://electrek.co/2016/08/15/tesla-model-s-catches-fire-test-drive-france/
(3)http://www.cbsnews.com/news/samsung-galaxy-note-7-batteries-fires-faa-warnings-passengers-worldwide-rec

Need: High safety, high energy density solid-state Li metal batteries required for electric vehicles, electronics and defense applications

200 mAh/g

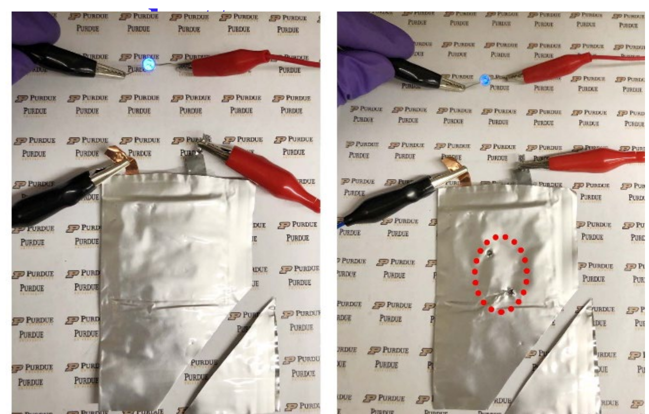


- **Graphite: 372 mAh/g**
- **Li metal: 3840 mAh/g**

Li-ion battery with liquid electrolytes

Energy density ~ 250 Wh/kg

Solid-state

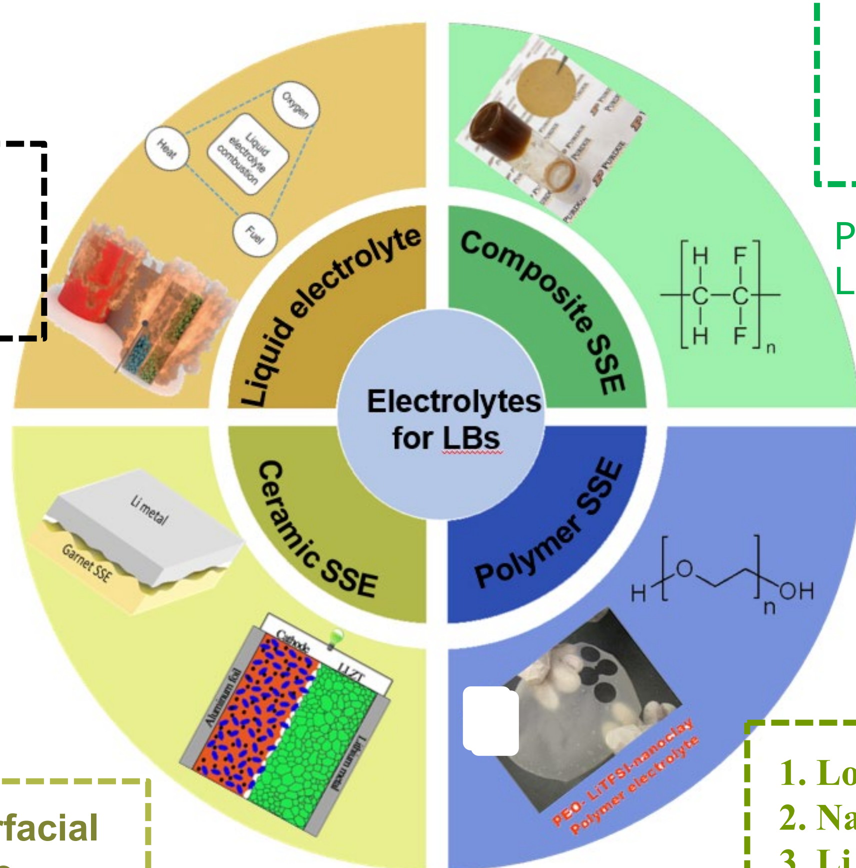


Cutting **Punching**

Energy density ~ 450 Wh/kg

Purdue's Advanced Solid-state Battery Technology

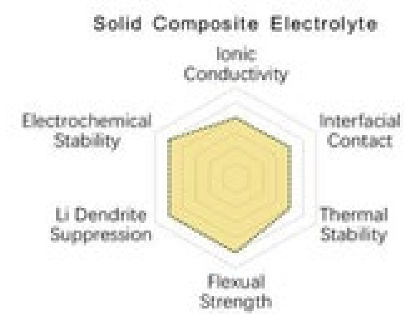
1. Flammable
2. Leak
3. Li dendrite



Purdue Innovation

1. High ionic conductivity
2. Wide voltage window
3. Thermal Safe
4. Li Dendrite free

Polyvinylidene fluoride **(PVDF)**
$Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ **(LLZTO)**



1. High interfacial resistance
2. Li dendrite

1. Low ionic conductivity
2. Narrow voltage window
3. Li dendrite

Poly(ethylene oxide) (PEO)

Purdue's Generation I

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Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Room-temperature, high-voltage solid-state lithium battery with composite solid polymer electrolyte with *in-situ* thermal safety study ✔

Check for updates

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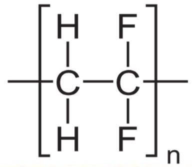
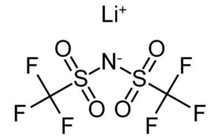
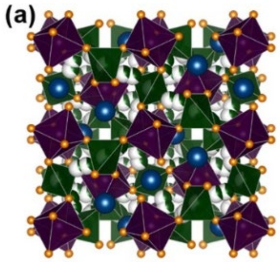
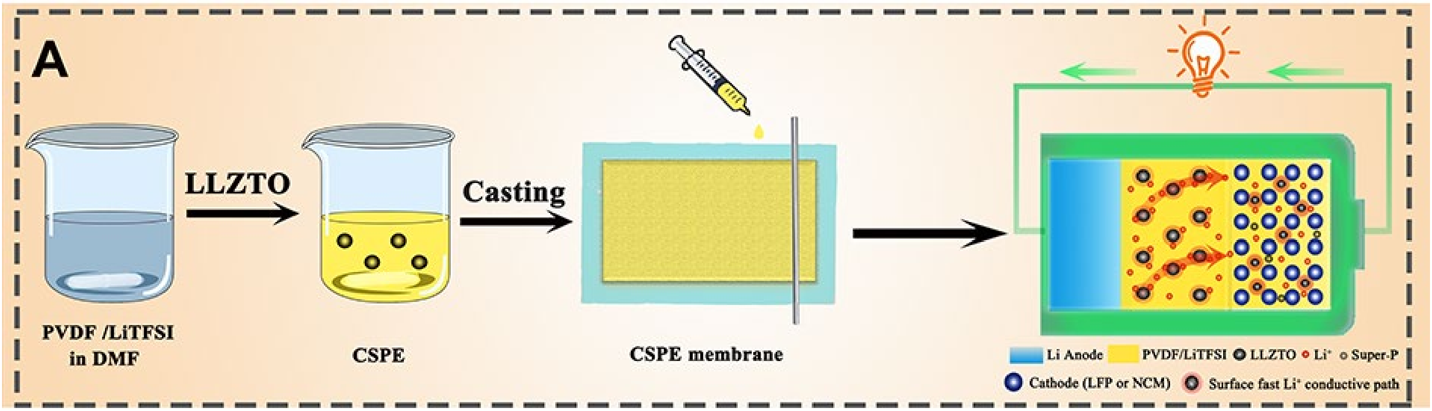
Scalable Fabrication of SS Composite Electrolyte

PVDF – Polymer Matrix; LiTFSI – Li salt; LLZTO – ceramic nanoparticles



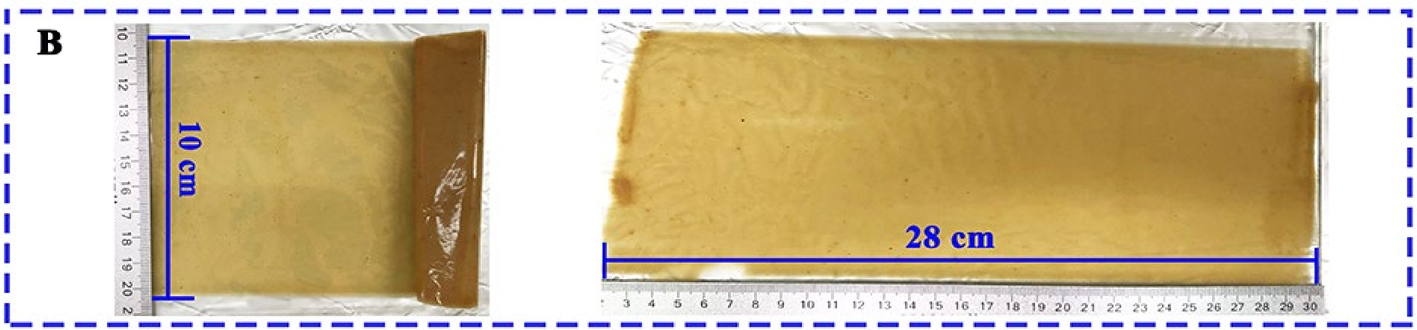






The synthesis of composite solid polymer electrolyte

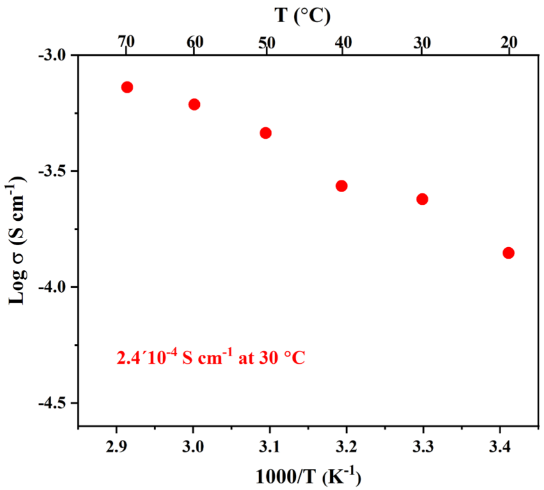
- ✓ **Facile synthesis**
- ✓ **Operation at room temperature**

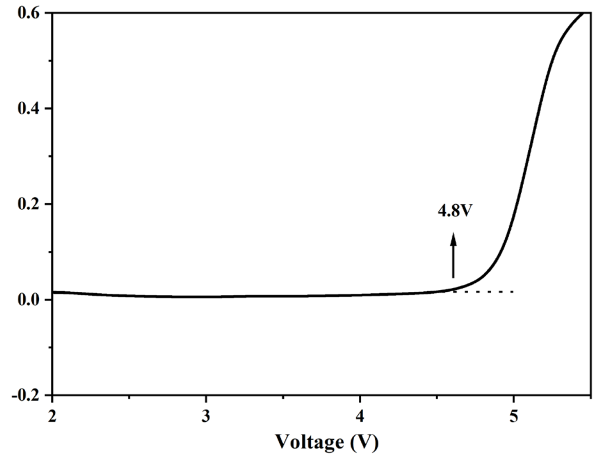


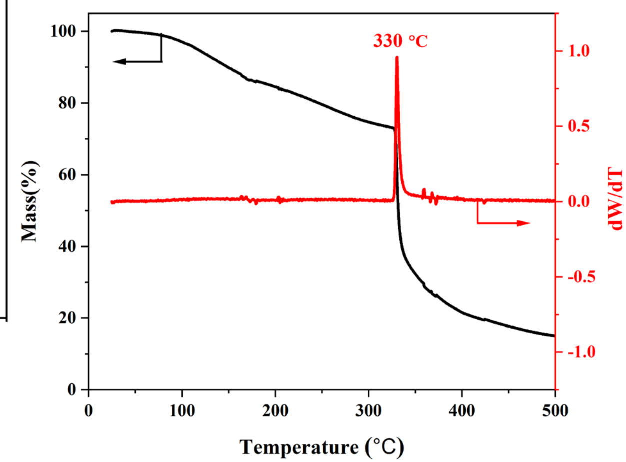
Pictures of as-prepared composite solid polymer electrolyte

- ✓ **Flexible**
- ✓ **Free standing**
- ✓ **Scalable**

Ionic Conductivity, Voltage Window, Thermal Stability







- ✓ High room-temperature ionic conductivity (2.4×10^{-4} S cm^{-1})
- ✓ Wide voltage window (~ 4.8 V)
- ✓ Excellent thermal stability (~ 330 ℃)

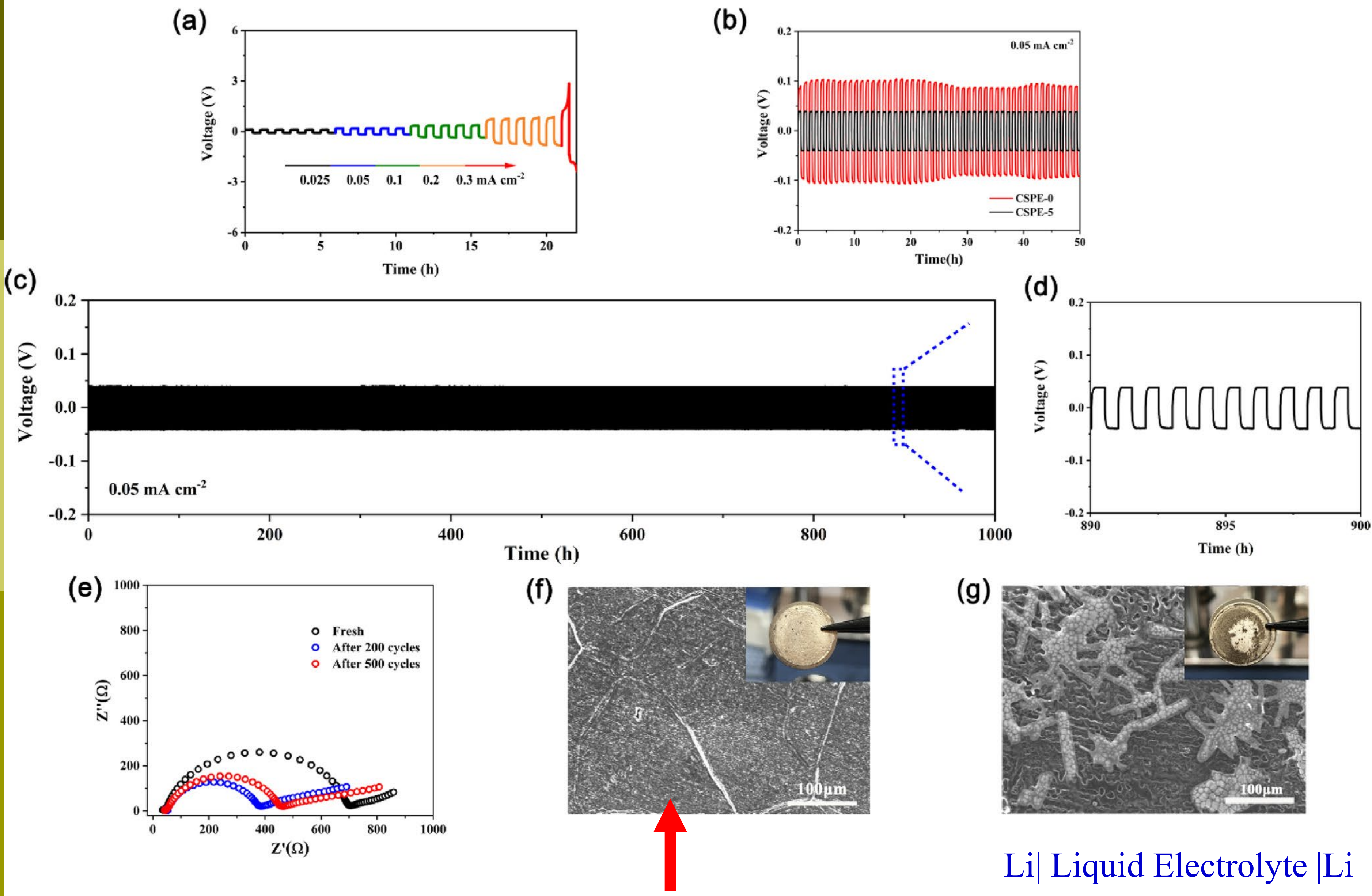
Purdue's Composite solid polymer electrolyte

VS

- ✗ Low room-temperature ionic conductivity (10^{-7} -10^{-5} S cm^{-1})
- ✗ Narrow voltage window (~ 3.8 V)
- ✗ Inferior thermal stability (~ 230 ℃)

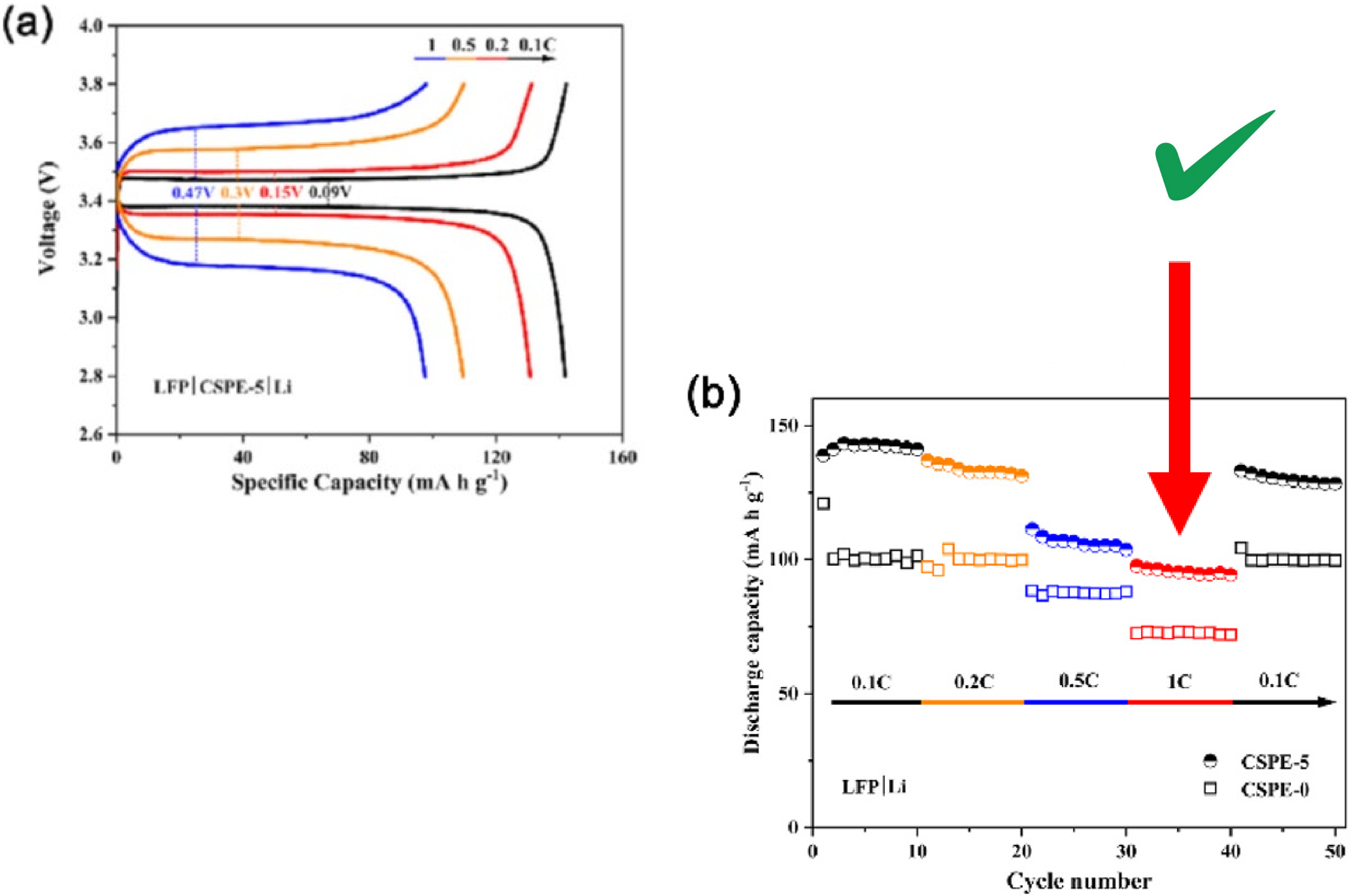
Typical PEO-based polymer electrolyte

Li|CSPE-5|Li symmetric cell

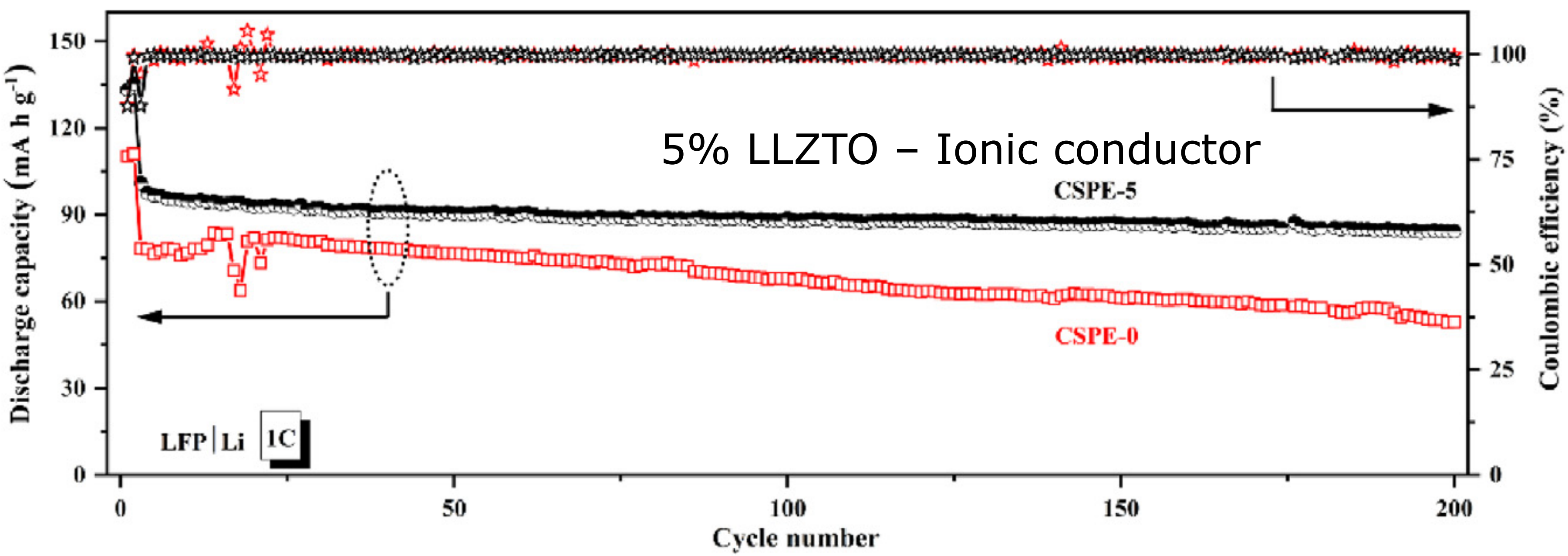


Li| Liquid Electrolyte |Li

Rate studies

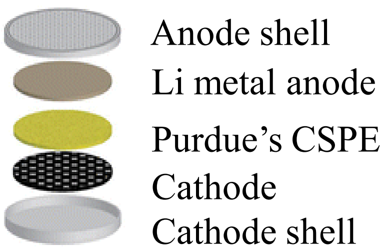


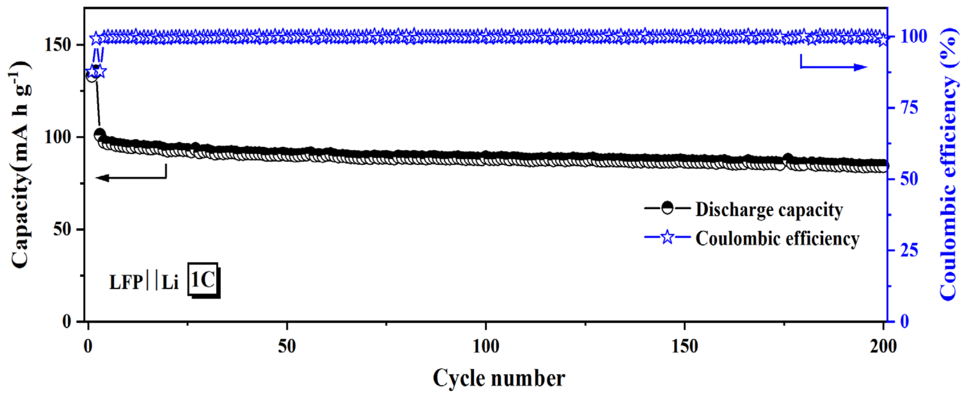
Long-term cycling stability of the LFP|Li cell using CSPE-0 and CSPE-5



- ✓ Purdue's Gen. I Composite solid polymer electrolyte does have stability once combines polymer, ionic conductor, salt etc. with remaining solvent DMF

Electrochemical Performance of Solid-state Full Cell

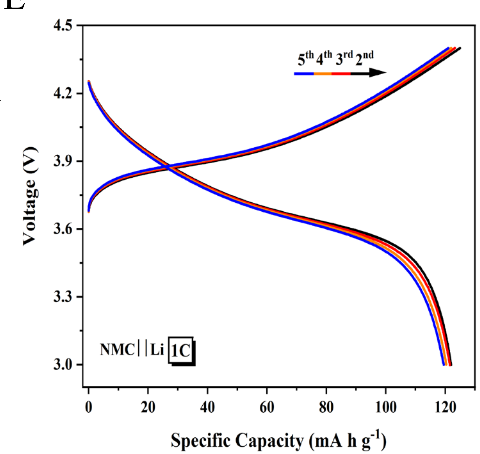


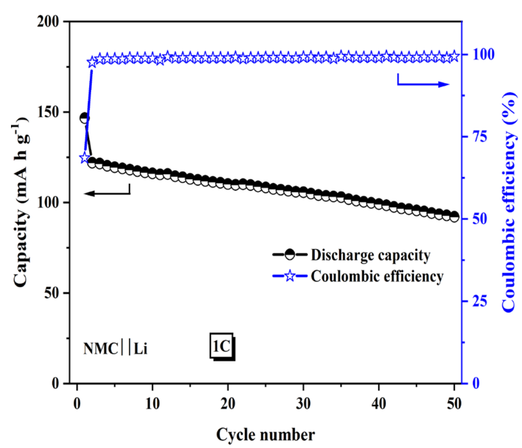


$LiFePO_4$

2.8 ~ 3.8 V

Room Temperature





$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

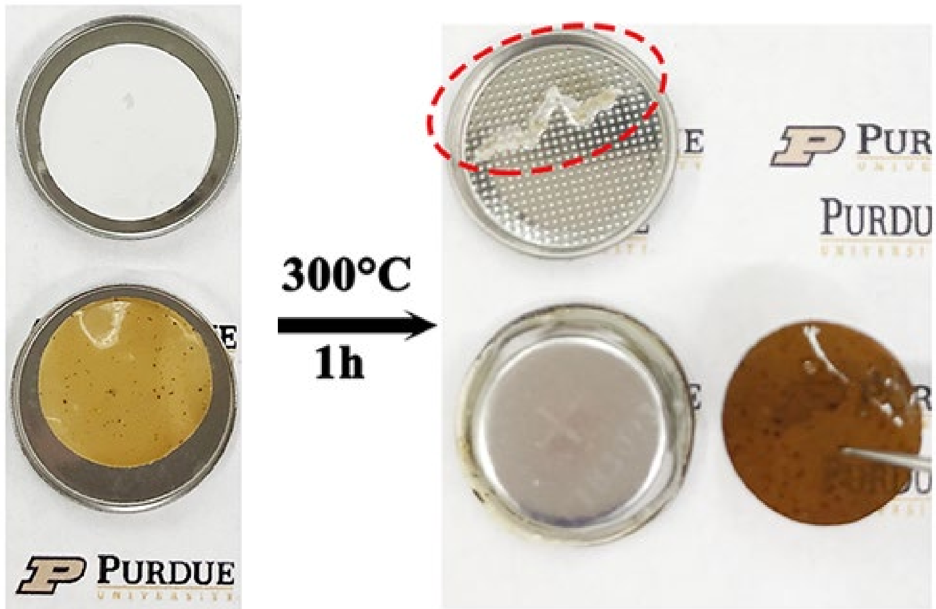
3 ~ 4.4 V

✓ Purdue's Gen I composite solid polymer electrolyte does work with various cathodes

Thermal Stability

Commercial PP separator

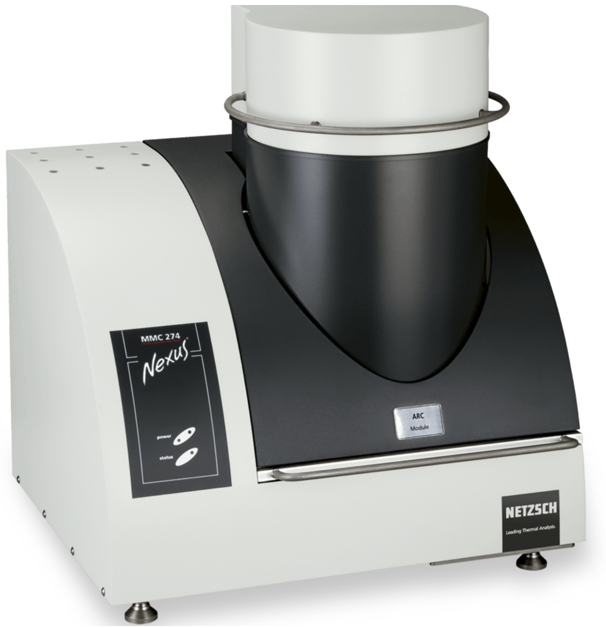
Purdue's CSPE

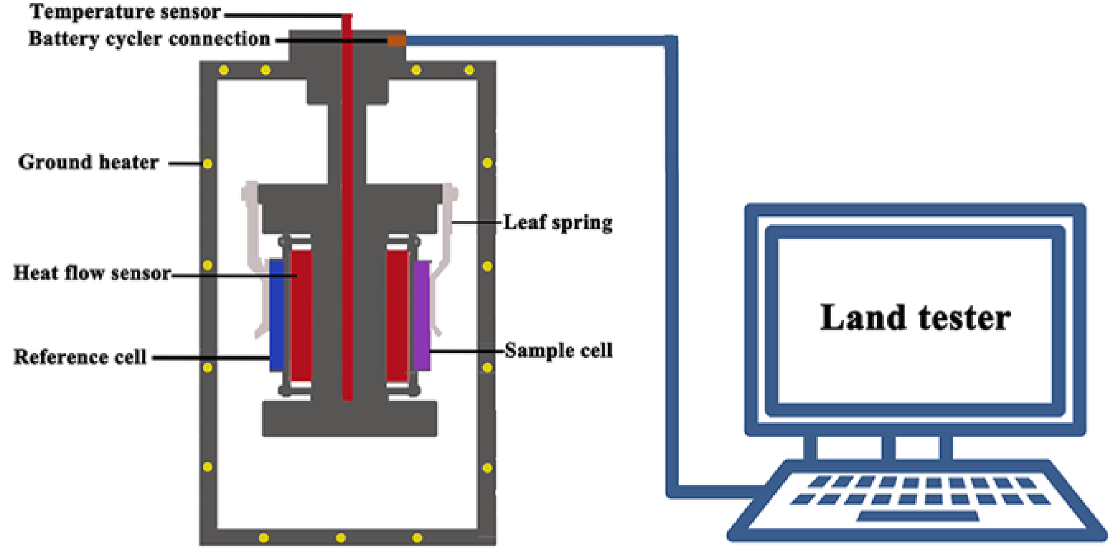


× Melt and shrink

✓ Maintain its structure

Schematic of multiple module calorimeter

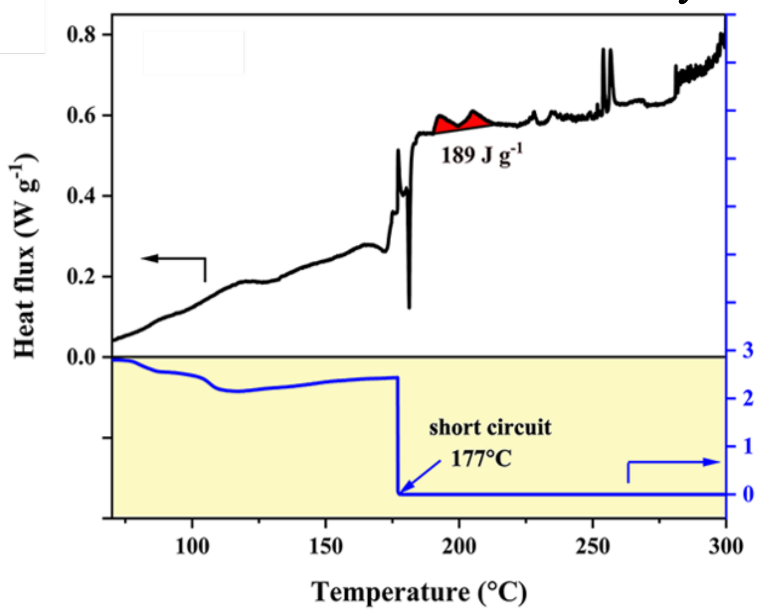




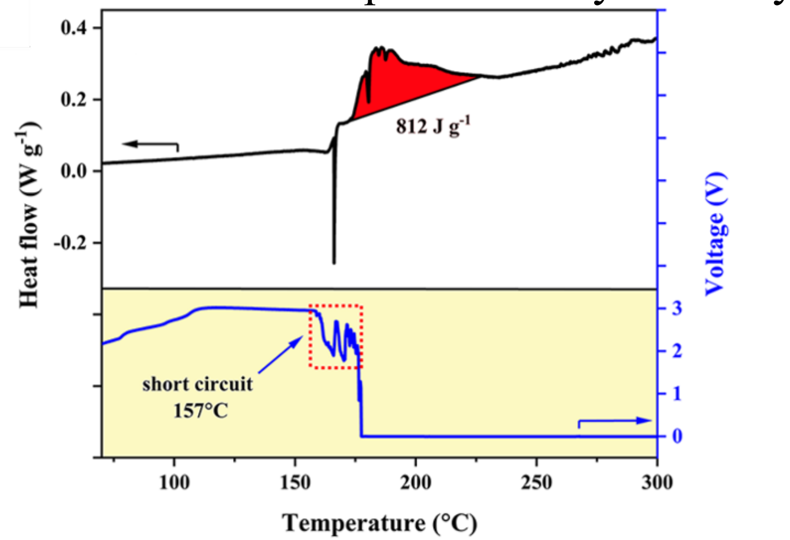
- Different from DSC and ARC
- **MMC** can **in-situ** investigate the thermal behavior of an **entire coin cell** instead of individual components

Thermal Safety Performance

Purdue's solid-state battery



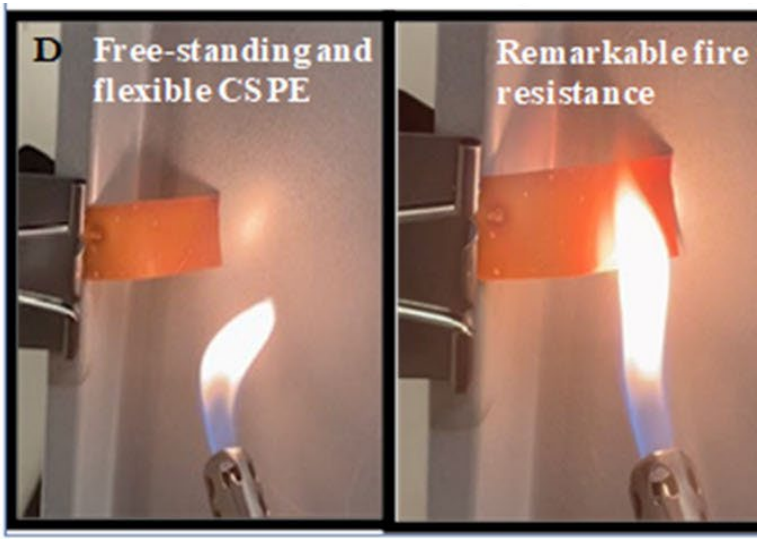
Traditional liquid electrolyte battery

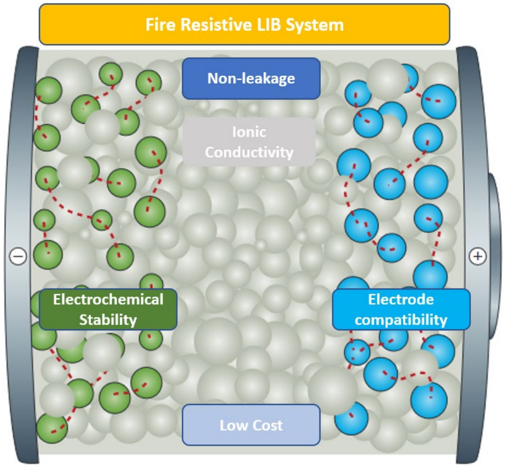


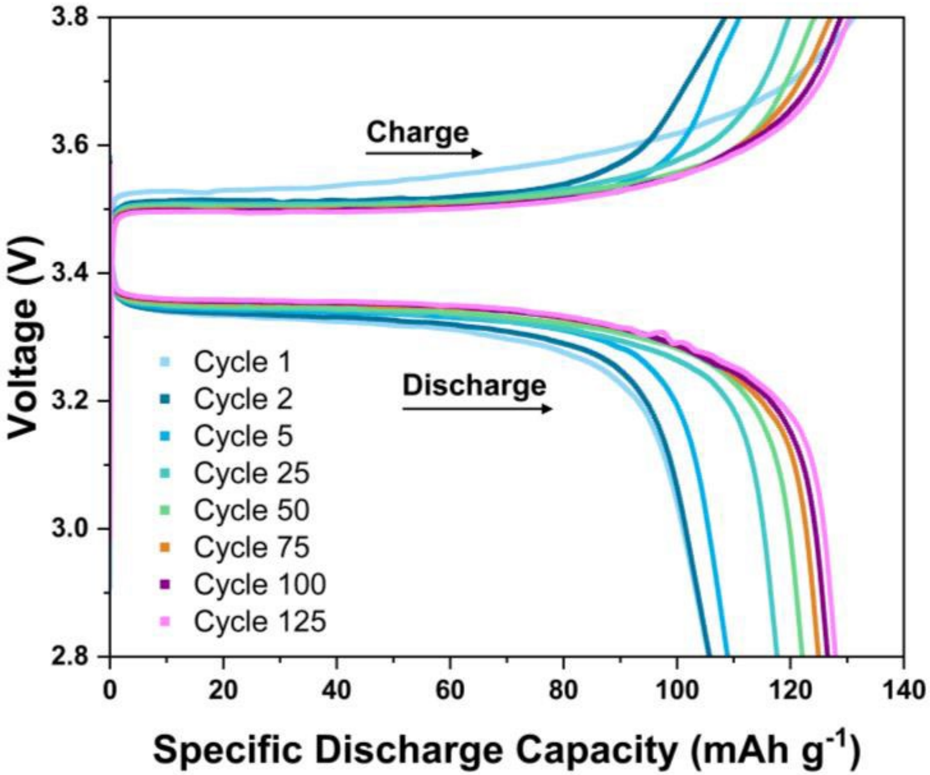
Thermal stable window: ✓ **up to 177 °C** *VS* ✗ **up to 157 °C**

Heat generation: ✓ **189 J g^{-1}** *VS* ✗ **812 J g^{-1}**

Purdue's Generation II:
Fire retardant molecule as solvent and plasticizer

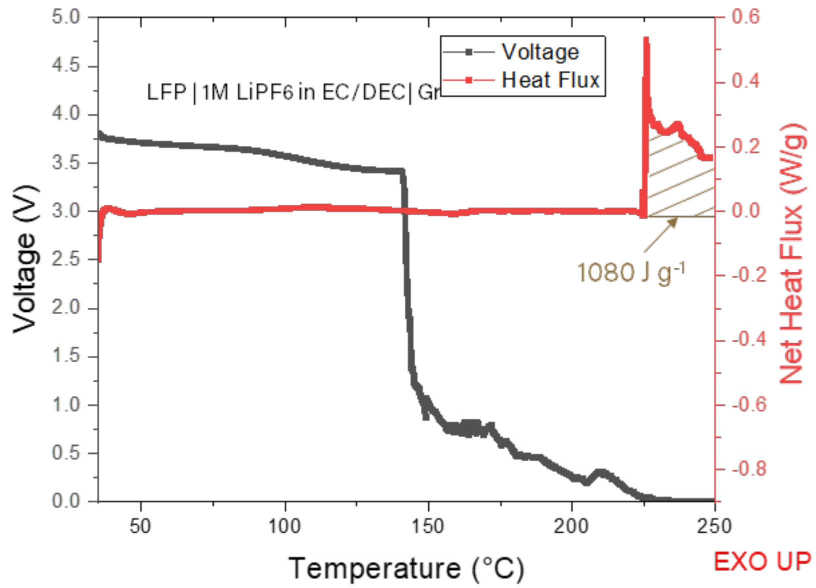




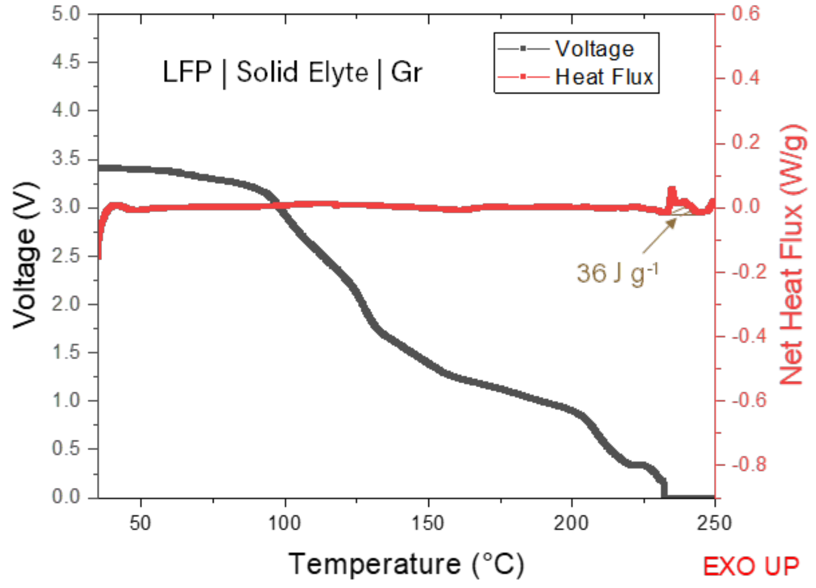


Exothermic heat measurements - MMC

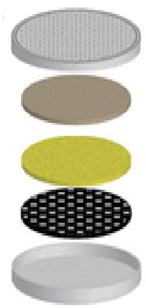
Conventional



Quasi-solid state



A scalable quasi-solid state battery



Anode shell

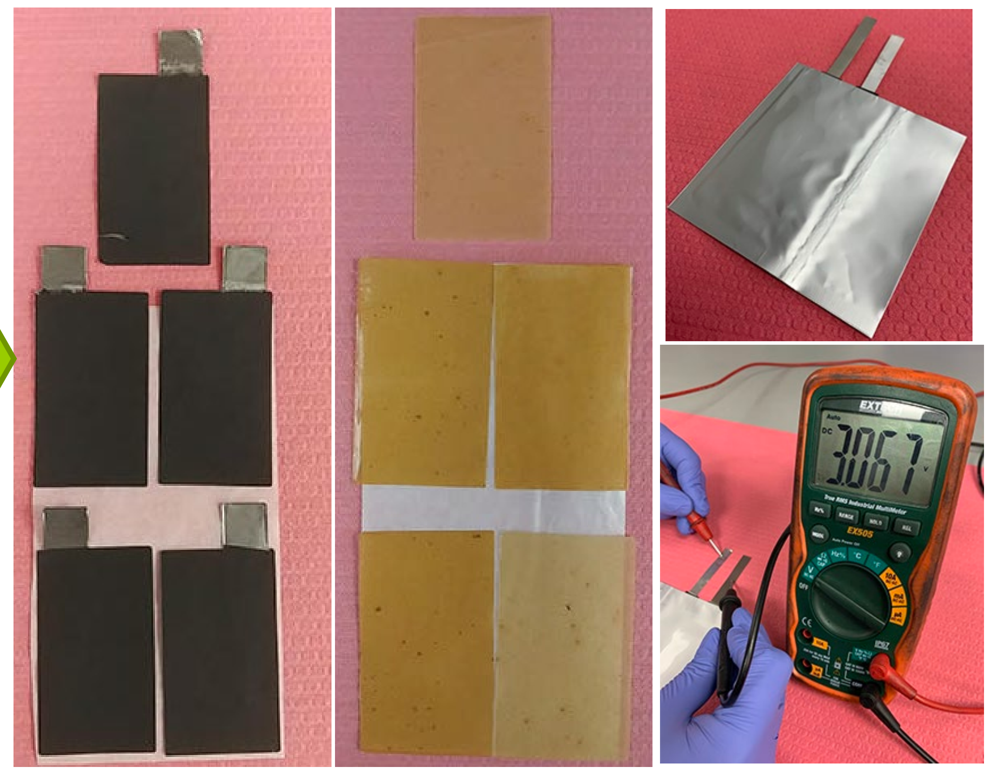
Li metal anode

Purdue’s CSPE

Cathode

Cathode shell

Small scale coin cell



Large scale, single-layer pouch cell

Abuse testing with functionality

Original Bending Cutting Punching

- Apart from various abuse tests still functional

nature communications

Article

https://doi.org/10.1038/s41467-023-36647-1

Non-polar ether-based electrolyte solutions for stable high-voltage non-aqueous lithium metal batteries

Received: 21 July 2022

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Check for updates

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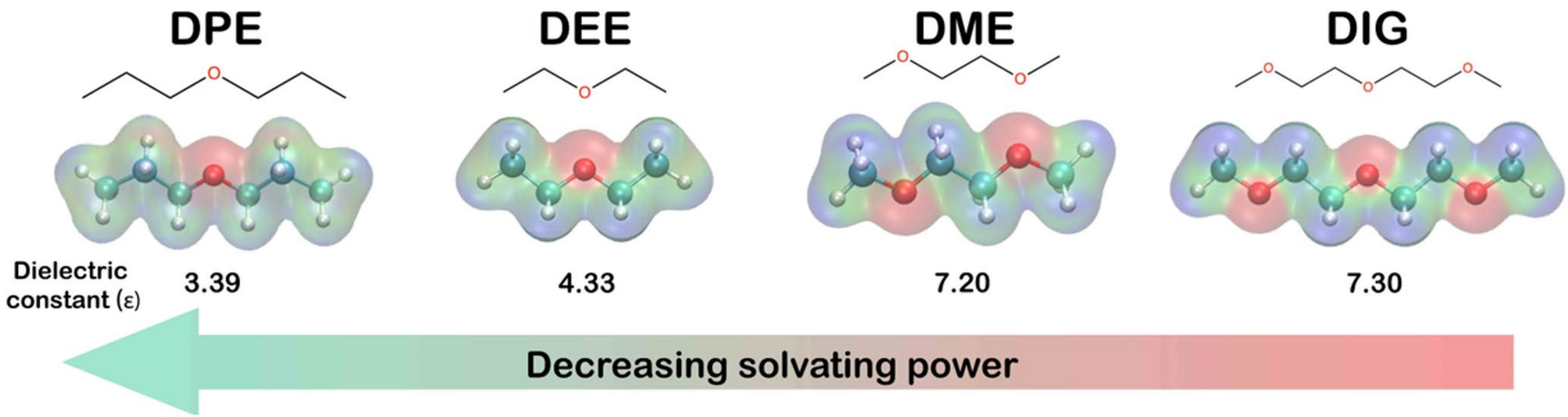
The electrochemical instability of ether-based electrolyte solutions hinders their practical applications in high-voltage Li metal batteries. To circumvent this issue, here, we propose a dilution strategy to lose the Li^+/solvent interaction and use the dilute non-aqueous electrolyte solution in high-voltage lithium metal batteries. We demonstrate that in a non-polar dipropyl ether (DPE)-based electrolyte solution with lithium bis(fluorosulfonyl) imide salt, the decomposition order of solvated species can be adjusted to promote the Li^+/salt-derived anion clusters decomposition over free ether solvent molecules. This selective mechanism favors the formation of a robust cathode electrolyte interphase (CEI) and a solvent-deficient electric double-layer structure at the positive electrode interface. When the DPE-based electrolyte is tested in combination with a Li metal negative electrode (50 µm thick) and a $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$-based positive electrode (3.3 mAh/cm^2) in pouch cell configuration at 25 °C, a specific discharge capacity retention of about 74% after 150 cycles (0.33 and 1 mA/cm^2 charge and discharge, respectively) is obtained.

Solvation structure-dependent stability

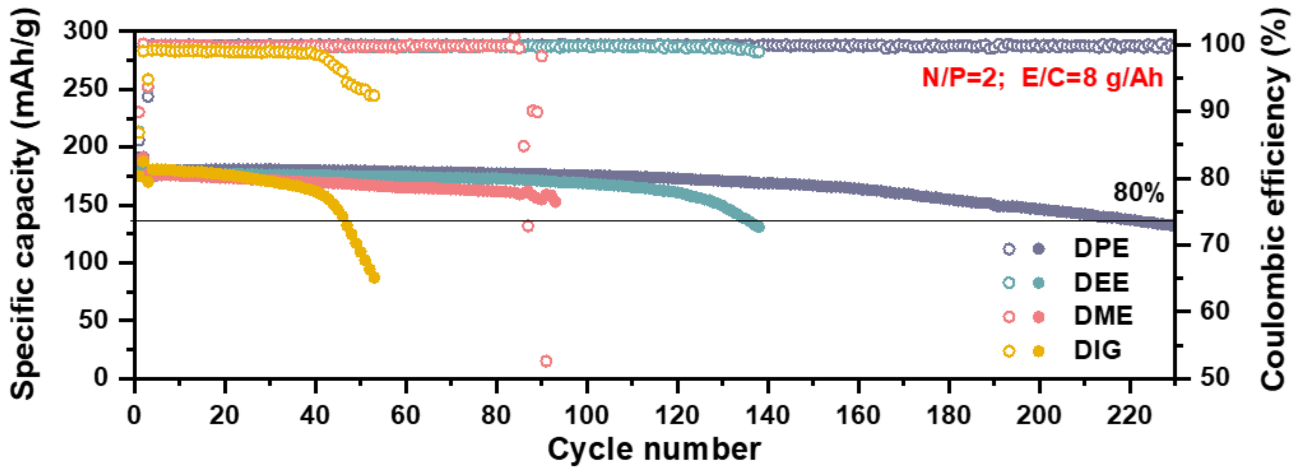
Ethers are inherently more stable on Li metal surface, which enables higher cycling efficiency than carbonates. However, they are extremely unstable at high operating potential

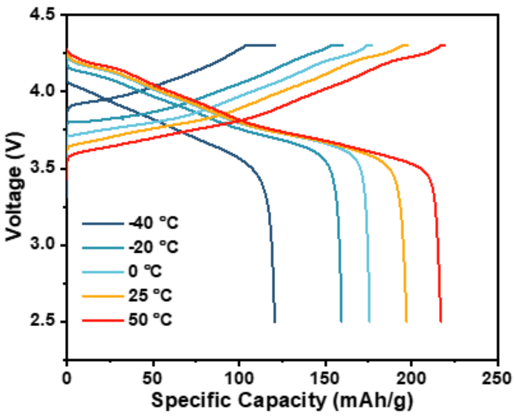


- ✓ Modulating the solvating power of ether solvents is hypothesized to change the interfacial stability via selectively forming a protective anion-derived CEI and kinetically stabilized the interface, because the solvation structure controlled by solvent strength governs the electrolyte decomposition pathways and the CEI composition.

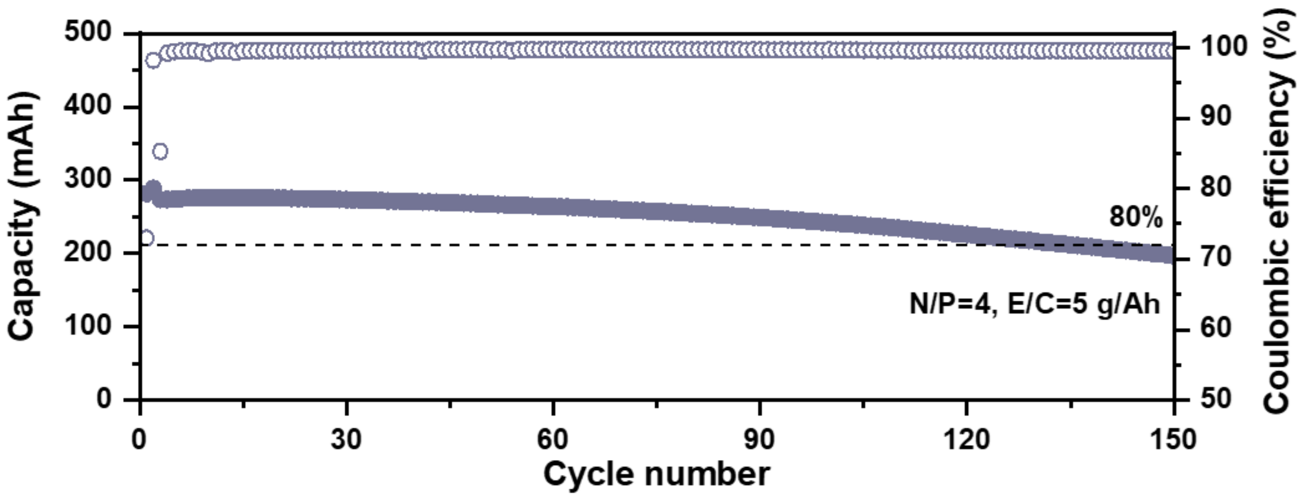
Long cycle performance in Practical LMBs

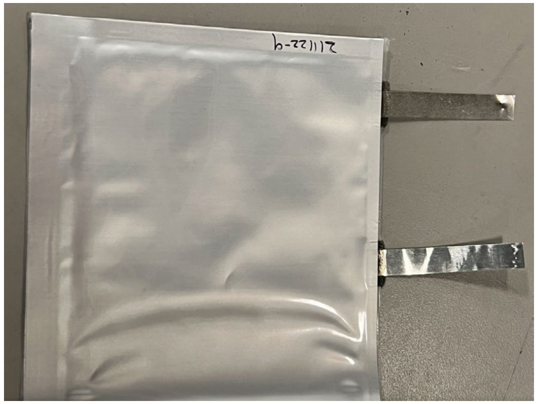
Coin cell with controlled amount of anode and electrolyte





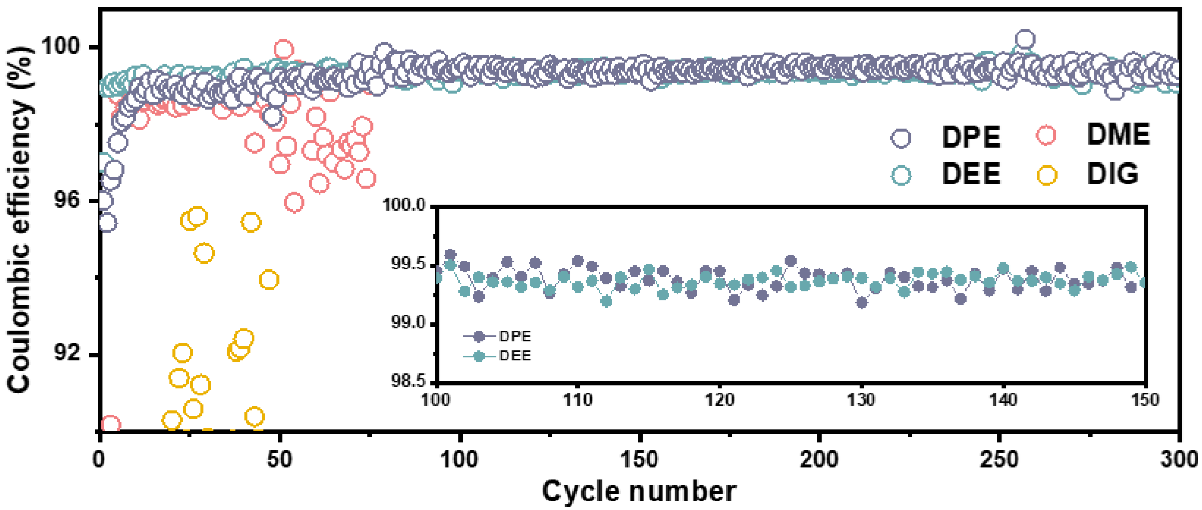
300 mAh pouch cell performance



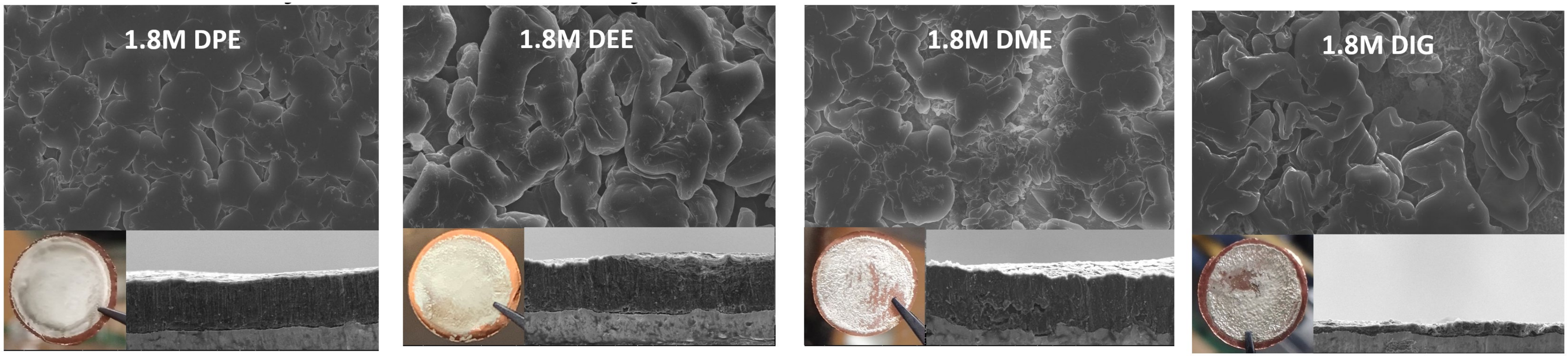


Compatibility to Li metal anode:

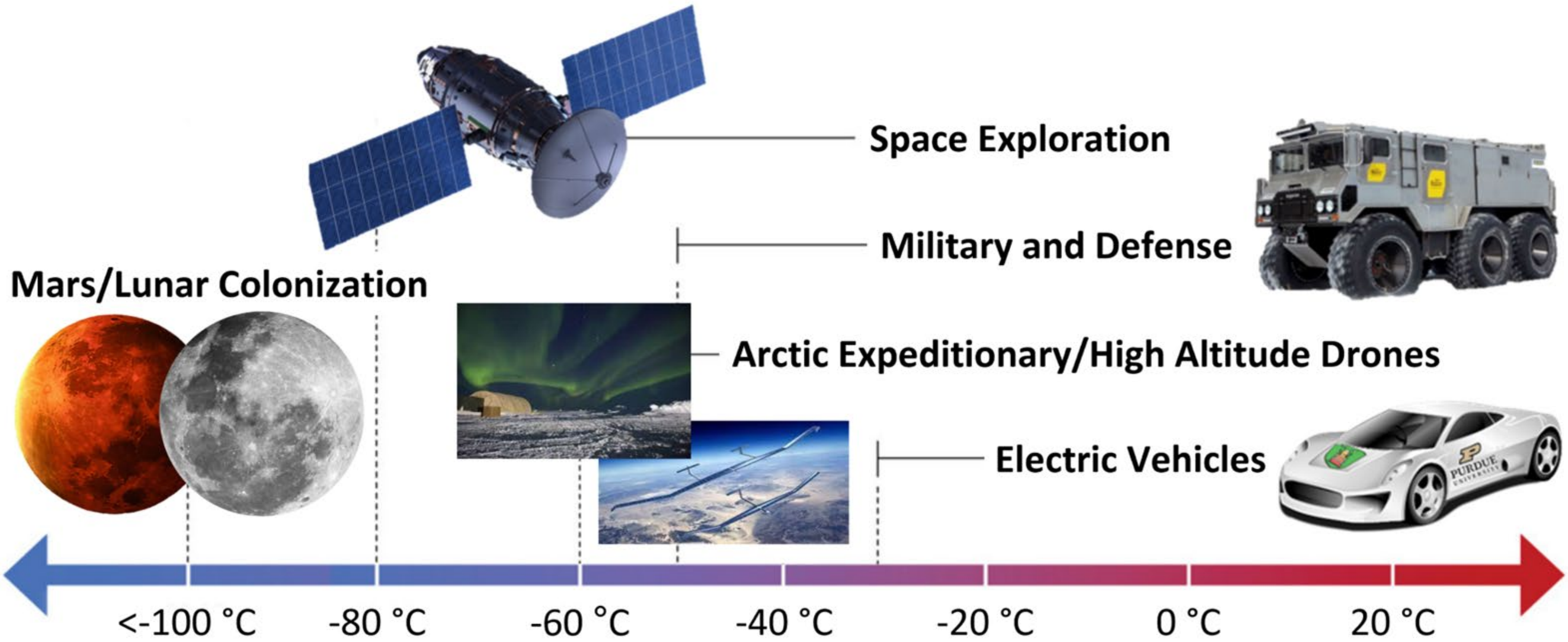
- High coulombic efficiency of 99.5% over 300 cycles



- Dense Li depositing morphology

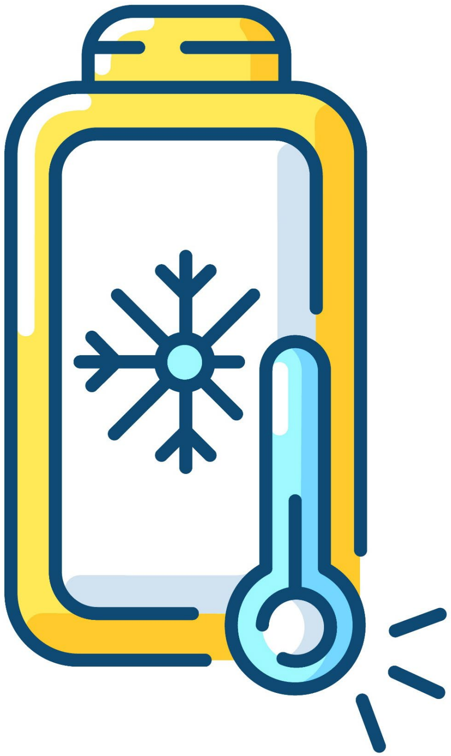


Low Temperature Battery Applications



- Space, defense, daily life applications of lithium-ion batteries

Major Two Challenges in Current Systems



Electrolyte issue

- **Electrolyte freezing and sluggish Li^+ reaction kinetics** originated from high melting point and Li^+ desolvation barrier of ethylene carbonate (EC).

Battery evaluation system issue

- **Several limitations to test batteries below -70 °C** with commercially available chambers and battery cyclers.

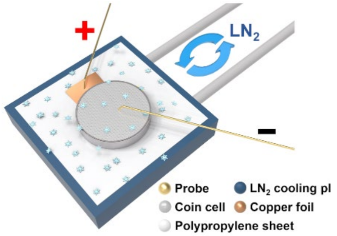
Solution to Electrolyte Issues

Approach 1 - Cyclopentyl Methyl Ether (CPME) based WSE

Approach 2 - Tetrahydrofuran (THF) based SCE

Solution to Battery evaluation system issue

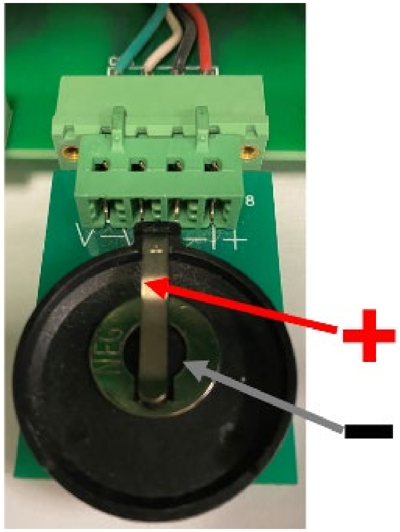
Purdue's Ultra Low Temperature Test Facility



Coin cell

3 cm x 3 cm Pouch cell

Limitations for Low Temperature Battery Testing



Expensive infrastructure is required

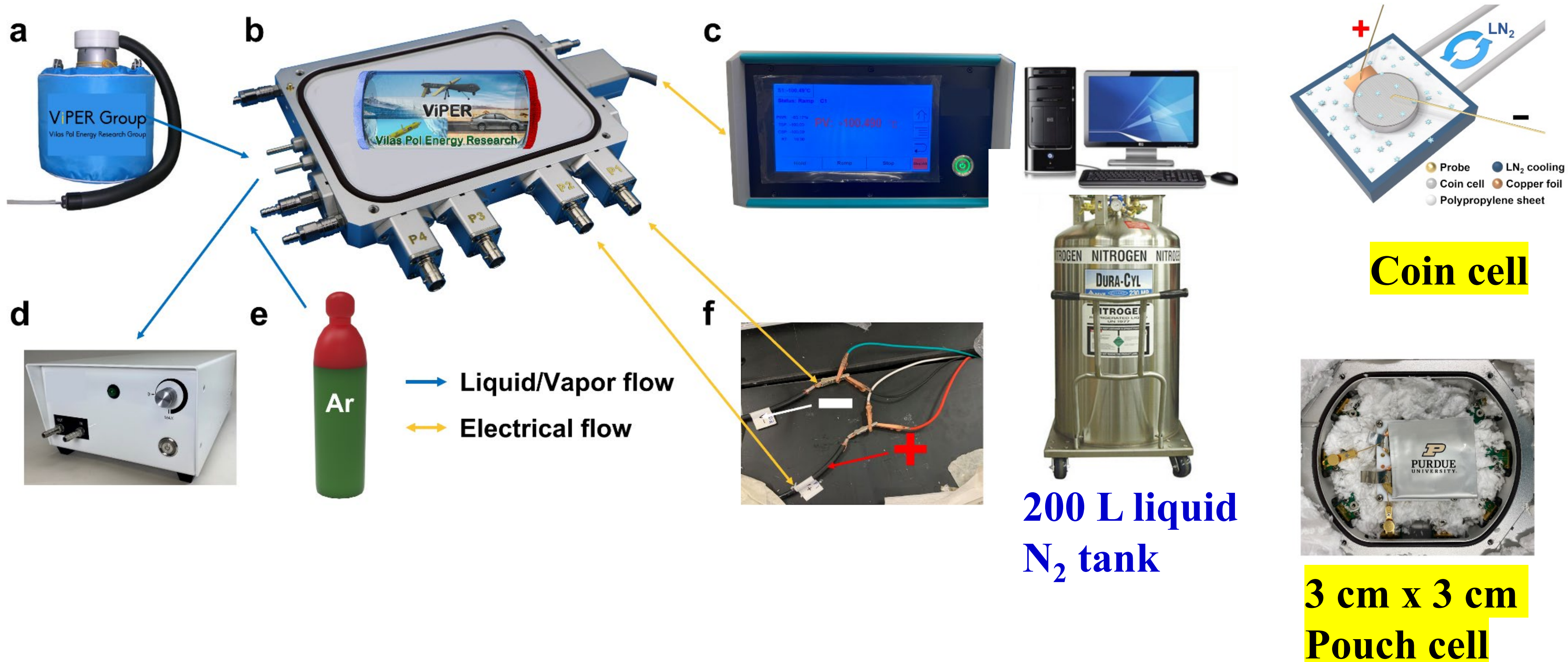
It is difficult to create a cooling system capable of -100 °C or below without LN_2.

Commercial systems has high LN_2 consumption rates (6 to 30 L hr^{-1}).

Resistance issue on commercial cell holder at low temperature

Arbin battery cycler cell holders are only rated to operate down the -20 °C with negligible resistance change.

Purdue's Ultra Low Temperature Test Capability

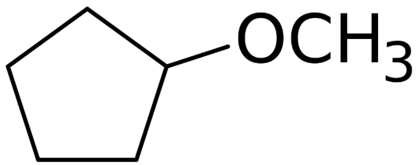


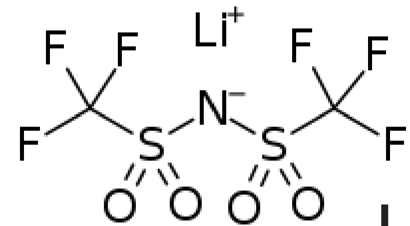
Affordable cost and accurate/reliable electrical measurement

- Available temperature → Up to -175 °C, Simulating extremely cold temperature environment (Lunar, Space, High Altitude, and Polar regions)
- Efficient LN_2 flow to minimize LN_2 usage (0.63 L hr^{-1}),
- Suppressed frost buildup by Ar purging

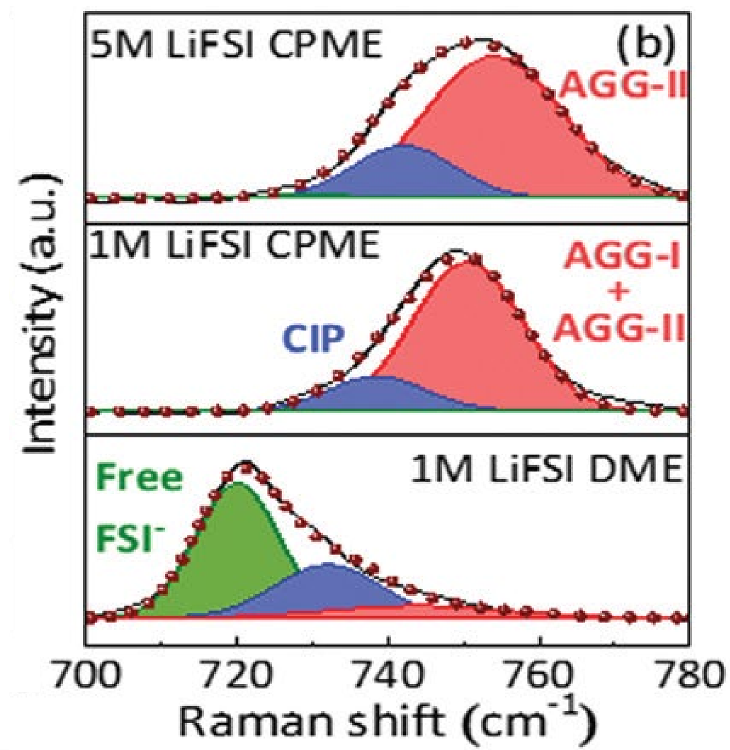
Pol et al, Energy Technol., **2022** 2200799.

Approach 1- Cyclopentyl Methyl Ether (CPME) based WSE



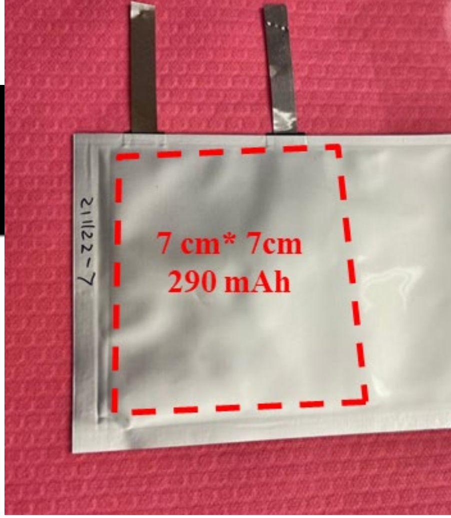


- CPME (B.P: 106 °C and M.P: -140 °C)
- High solubility of the salt (7M)
- Environmentally safe and economically feasible CPME solvent
- Unique solvation structure consisting of CIPs and AGGs
- AGG-I → An FSI^- bonded with 2 Li^+, AGG-II → An FSI^- bonded with 3 Li^+

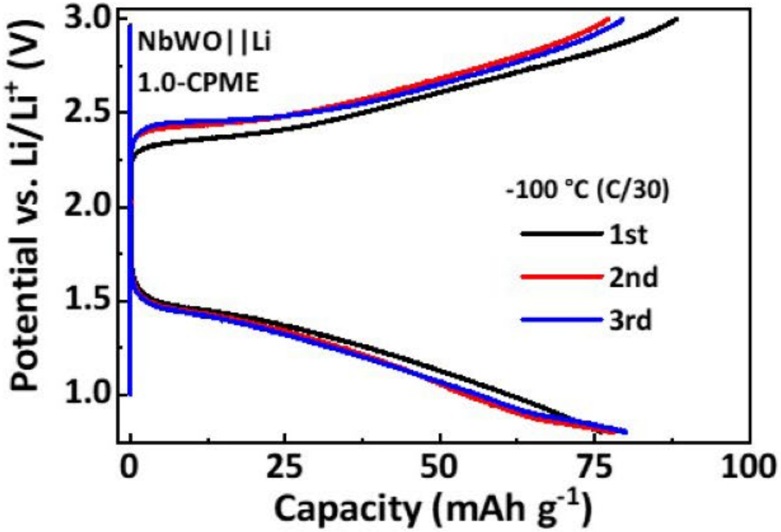


Pol et al. Chem. Commun. **2022**, 58, 5124

-100 °C Tests (NbWO||Li)



-100 °C (C/30) test (0.8-3.0V)



~75 mAh g^{-1} @ -100 °C

-100 °C tests with 1.0-CPME

- 1.0-CPME
  → Good low-temperature performance (graphite anode)
  → Charge-discharge ability at -100 °C with a small capacity and extremely slow current rate
- Finally, NbWO with 1.0-CPME achieved >75 mAh g^{-1} at C/30.
  → Much improved extreme low-temperature battery performance

1.0-CPME electrolyte (1M LiFSI in CPME)

CPME: cyclopentyl methyl ether (-140 °C)

Summary

1. Engineered composite quasi-solid state batteries could be safer than conventional Lithium ion batteries.

2. Gen III are towards making quasi-solid state battery that would not catch fire with any abuse!

3. Li-metal batteries are safe till 150 °C, separator and lithium metal melts after that causing huge exothermic heat.

3. Lithium metal batteries are VERY promising with DPE based electrolyte

P²SAC
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