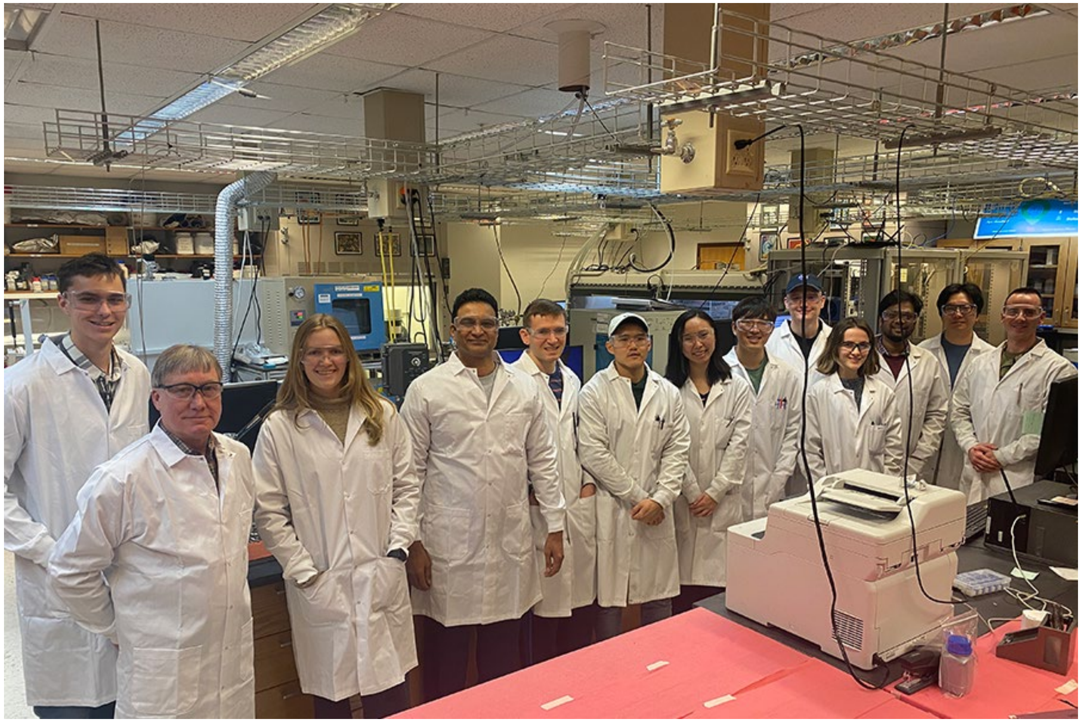
Towards Making Li-ion Batteries Inherently Safer
&
Operable at Extreme Temperatures

Vilas G. Pol

Professor of Chemical Engineering



What’s new?

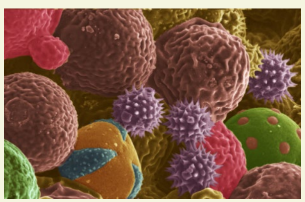
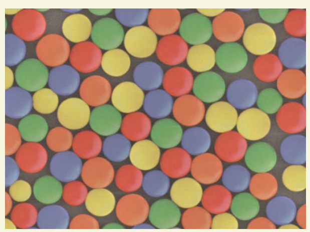
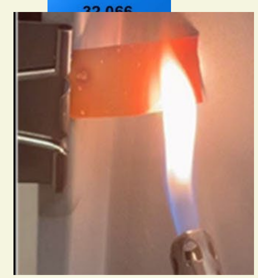
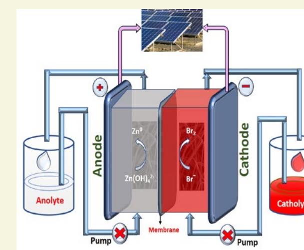
1. Can we avoid battery fire?

2 Can we stay on Mars?

Prof. Vilas G. Pol

PURDUE
ENGINEERING
CHEMICAL ENGINEERING

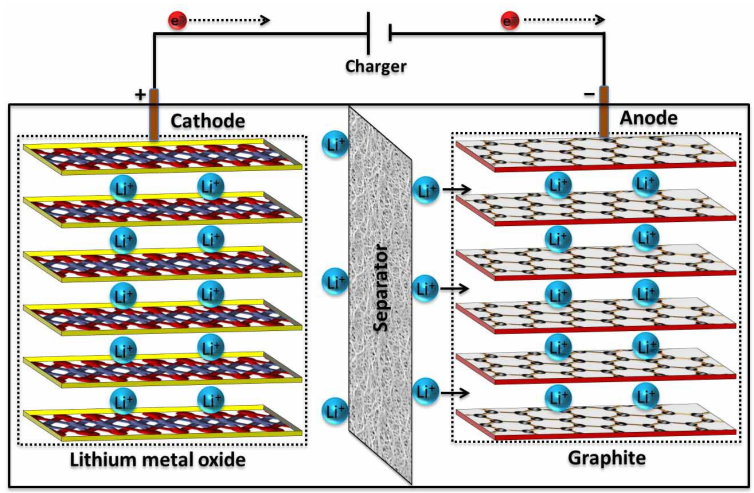
Research Areas

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
				

270+ Publications; H index 57, 160+ invited talks
20 issued US patents, 20+ pending, 40+ awards

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

200 mAh/g

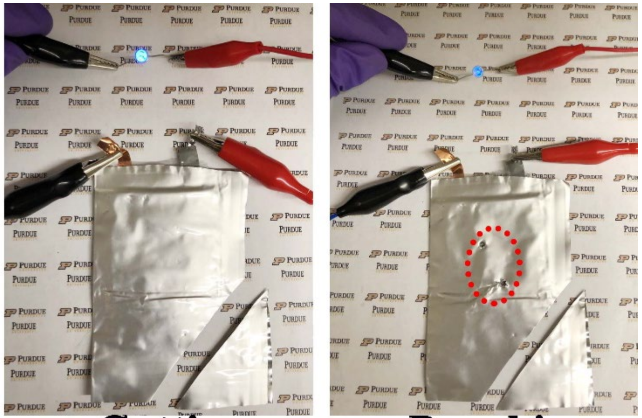


- Graphite: 372 mAh/g
- Li metal: 3840 mAh/g

Li-ion battery with liquid electrolytes

Energy density ~ 250 Wh/kg

Solid-state battery

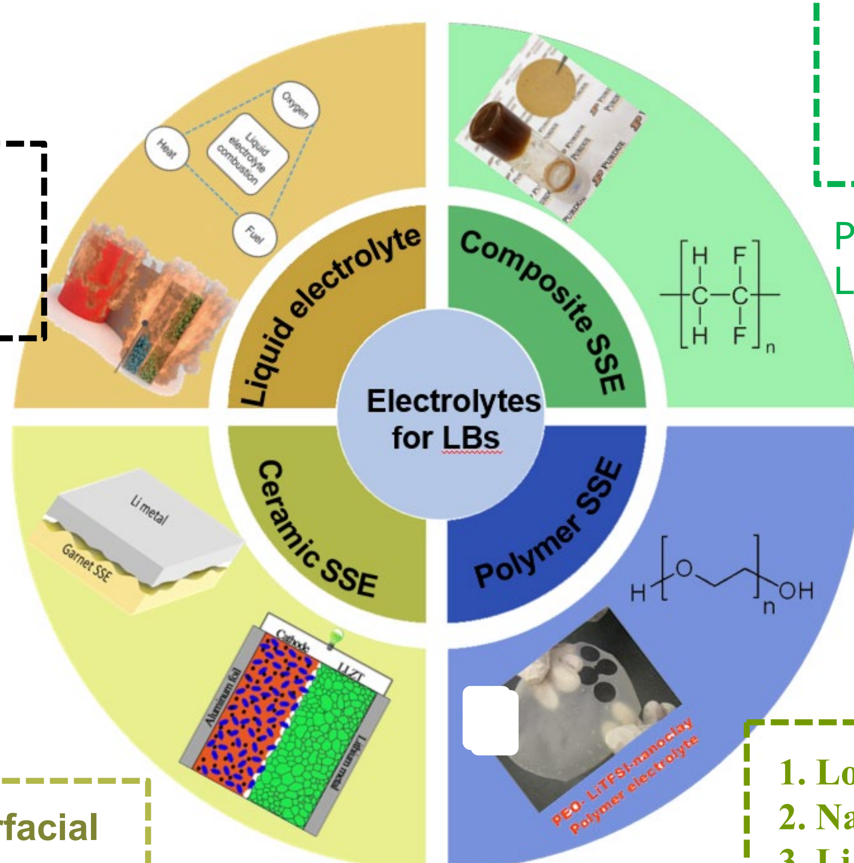


Cutting **Punching**

Energy density ~ 450 Wh/kg

Purdue's Advanced Solid-state Battery Technology

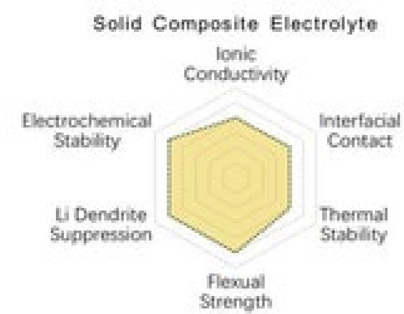
1. Flammable
2. Leak
3. Li dendrite



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)**



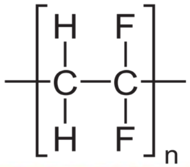
1. High interfacial resistance
2. Li dendrite

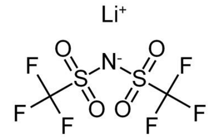
1. Low ionic conductivity
2. Narrow voltage window
3. Li dendrite

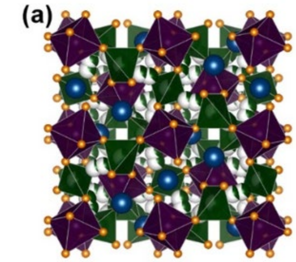
Poly(ethylene oxide) (PEO)

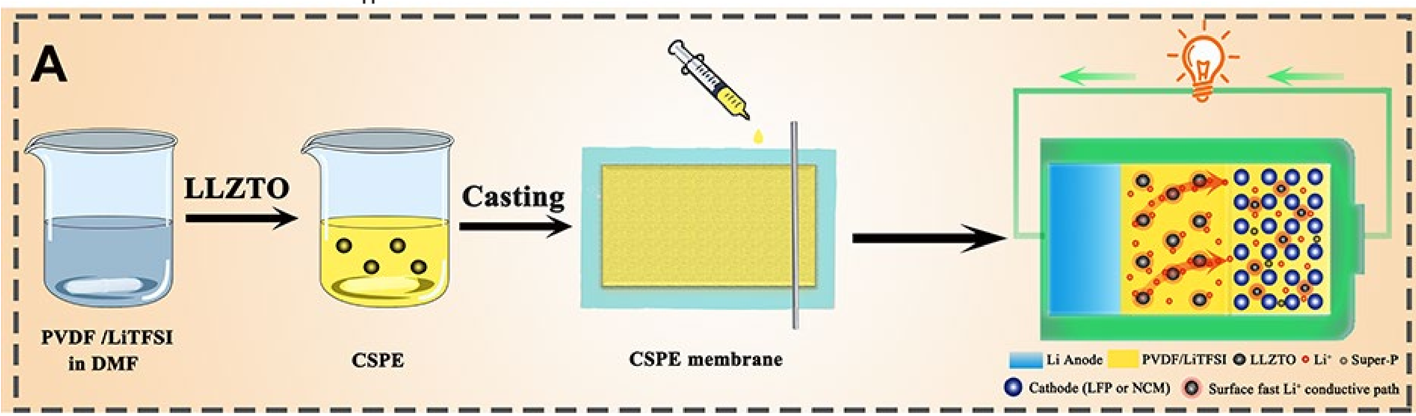
Scalable Fabrication of SS Composite Electrolyte

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



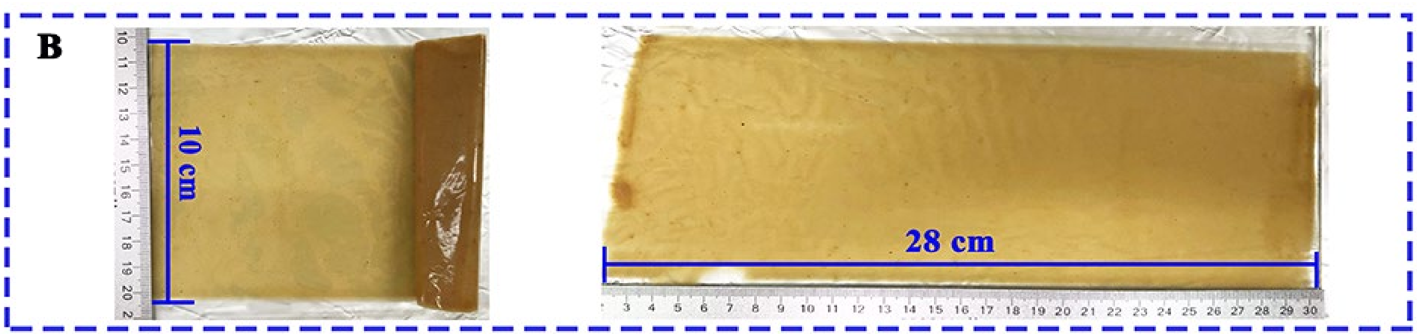






The synthesis of composite solid polymer electrolyte

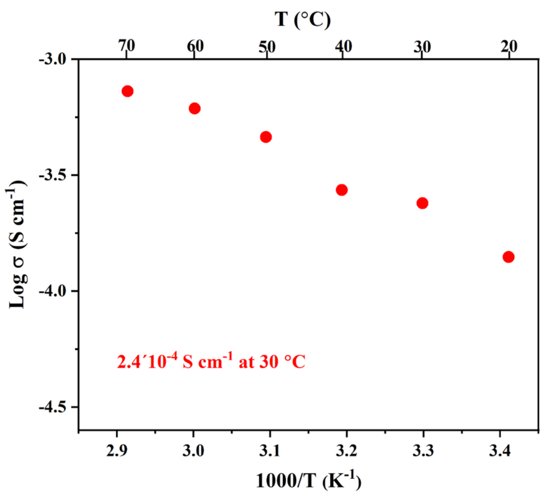
- ✓ Facile synthesis
- ✓ Operation at room temperature

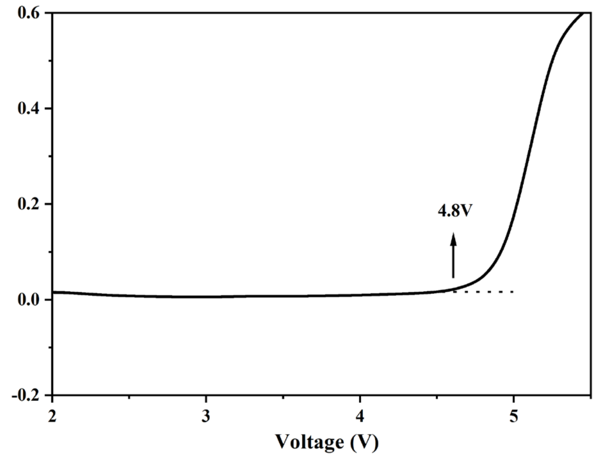


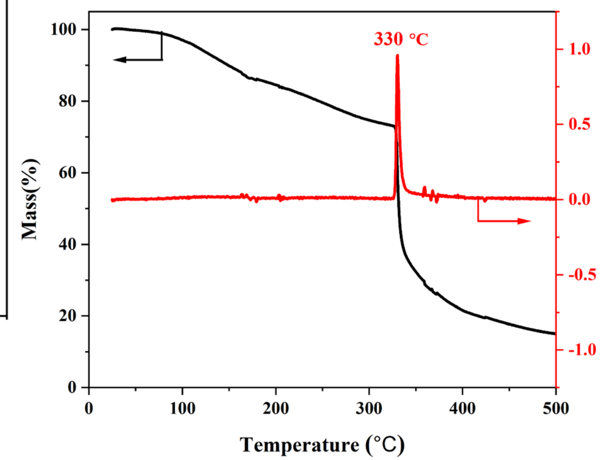
Pictures of as-prepared composite solid polymer electrolyte

- ✓ 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 ℃)

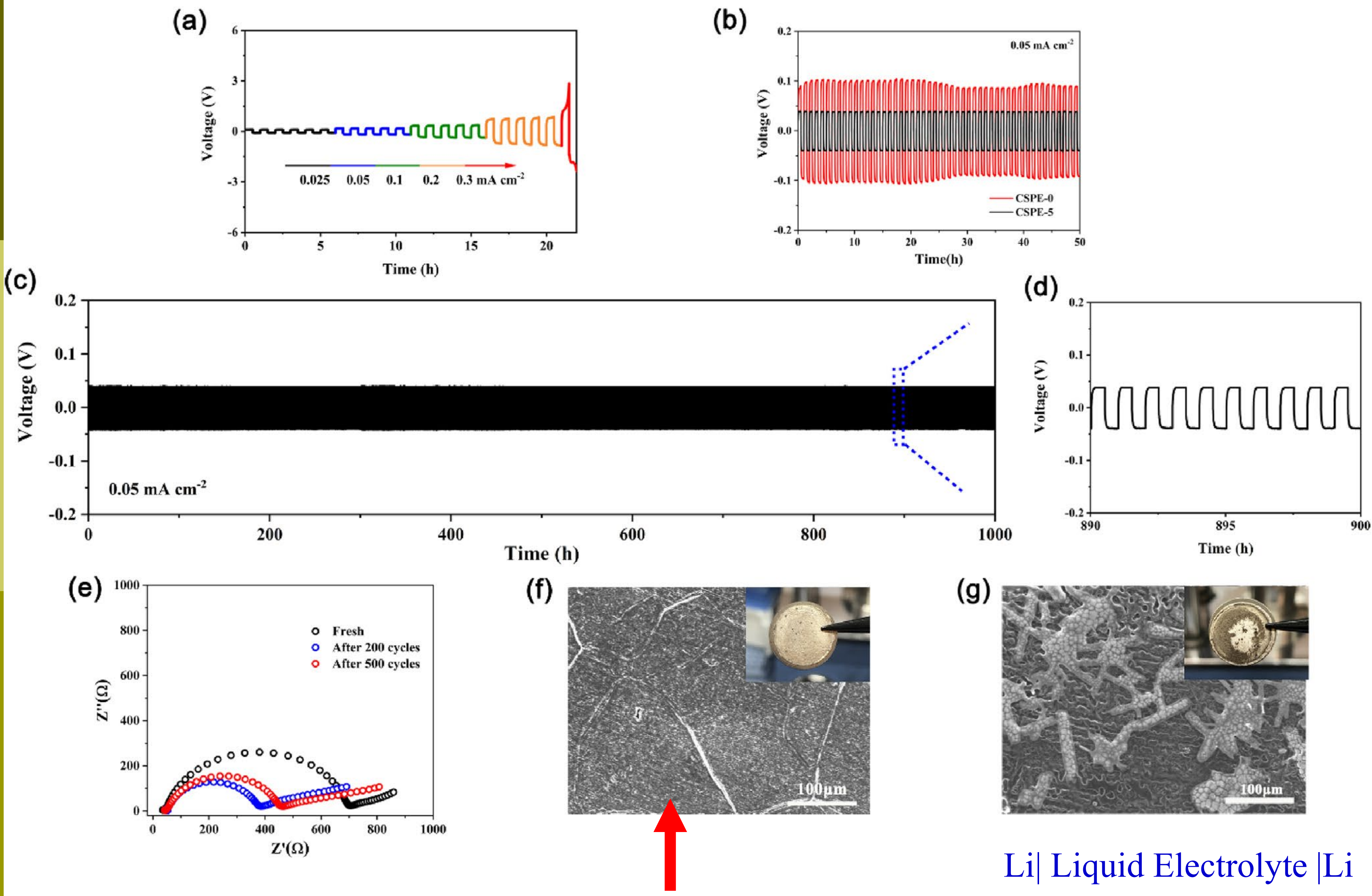
Purdue's Composite solid polymer electrolyte

VS

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

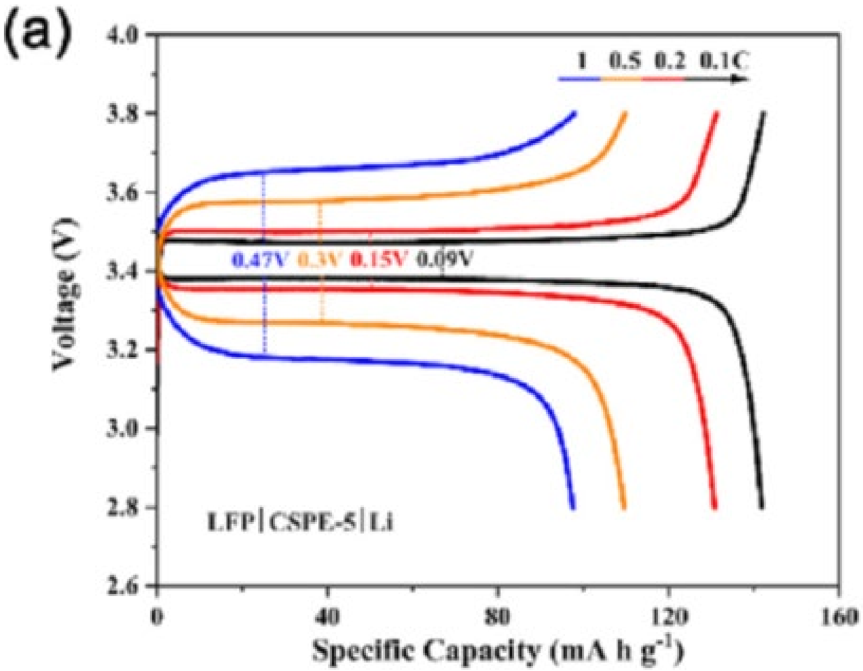
Typical PEO-based polymer electrolyte

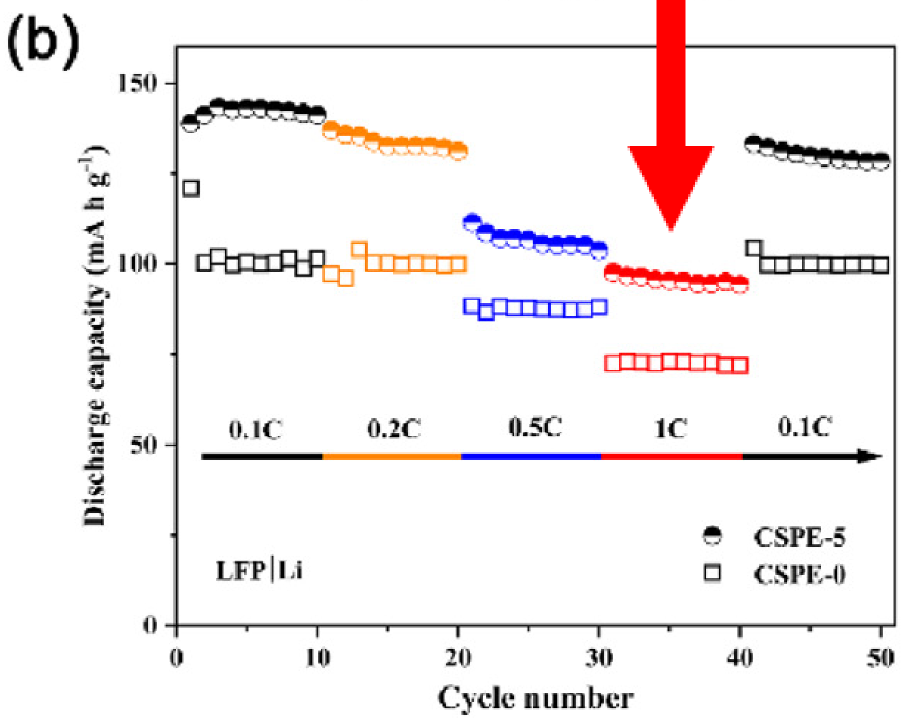
Li|CSPE-5|Li symmetric cell



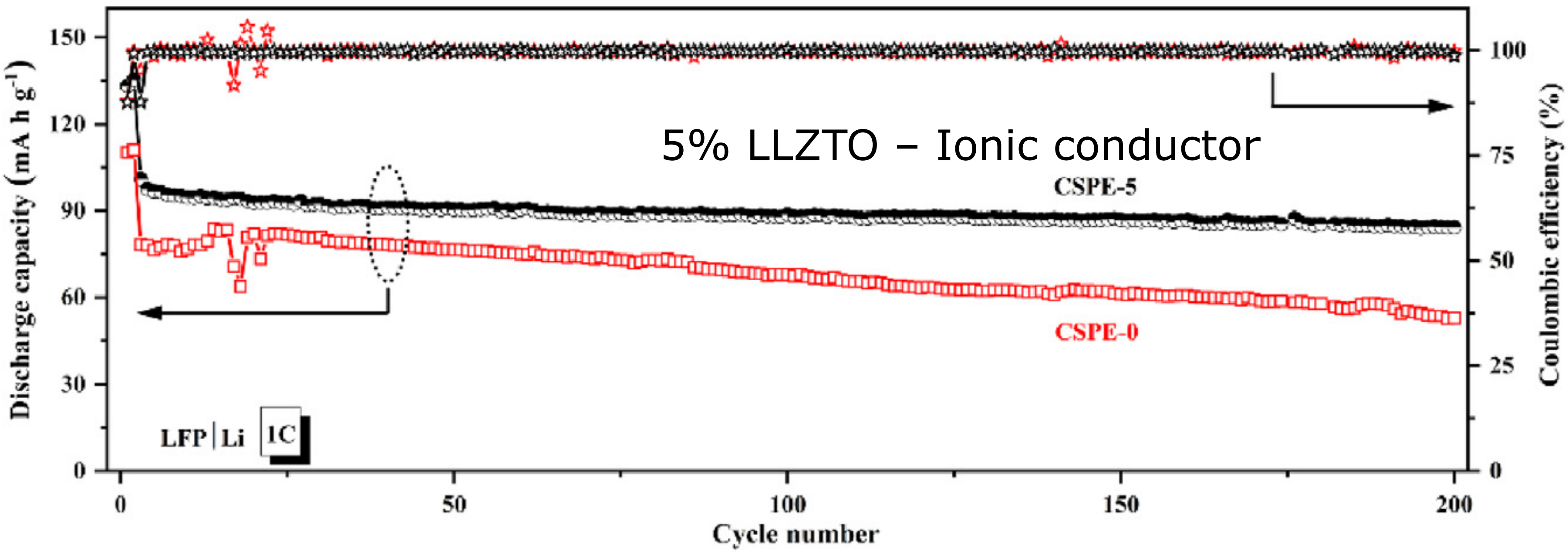
Li| Liquid Electrolyte |Li

Rate studies



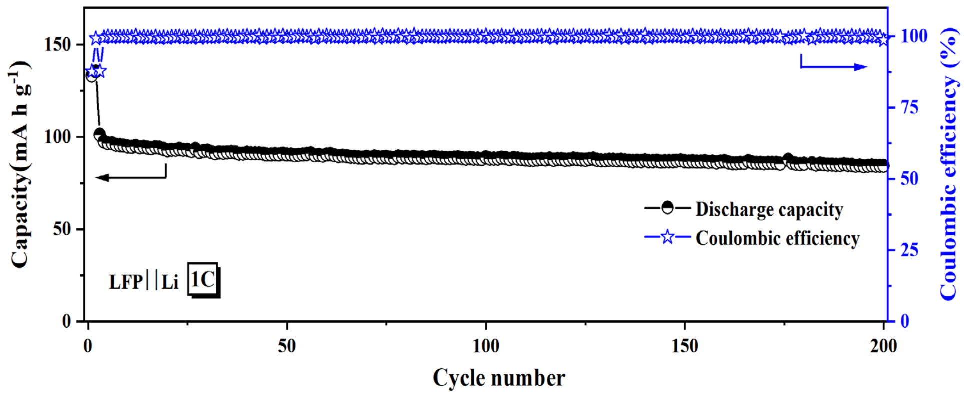


Long-term cycling stability of the LFP|Li cell using CSPE-0 and CSPE-5

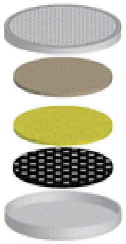


✓ Purdue's Gen. I Composite solid polymer electrolyte does have stability once combines polymer, ionic conductor, salt etc. with remaining solvent DMF

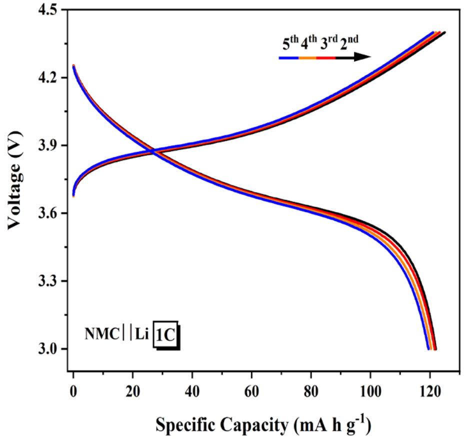
Electrochemical Performance of Solid-state Full Cell

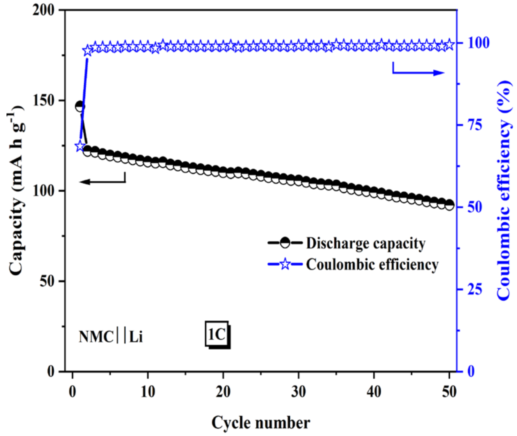


$LiFePO_4$
2.8 ~ 3.8 V



Room Temperature





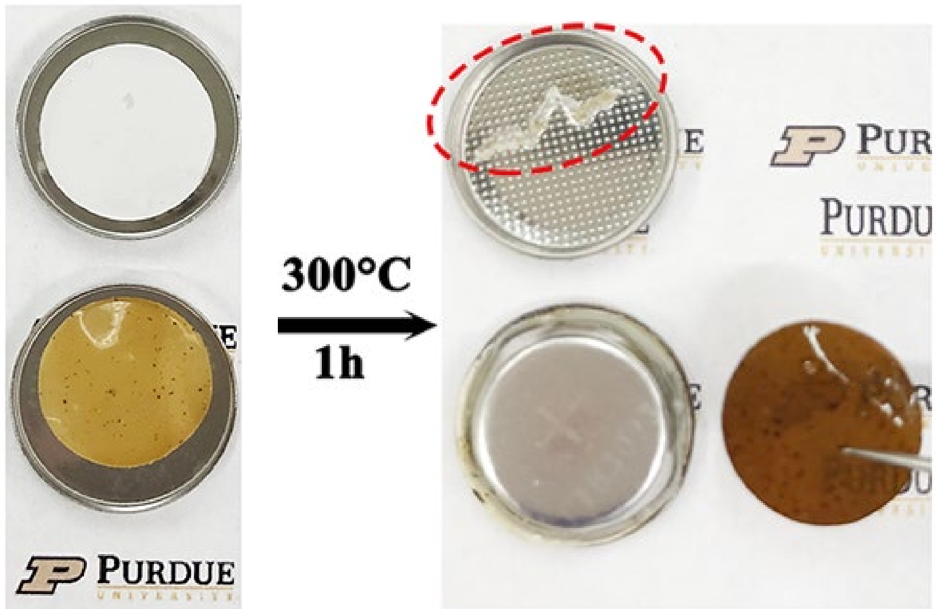
$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
3 ~ 4.4 V

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

Thermal Stability

Commercial PP separator

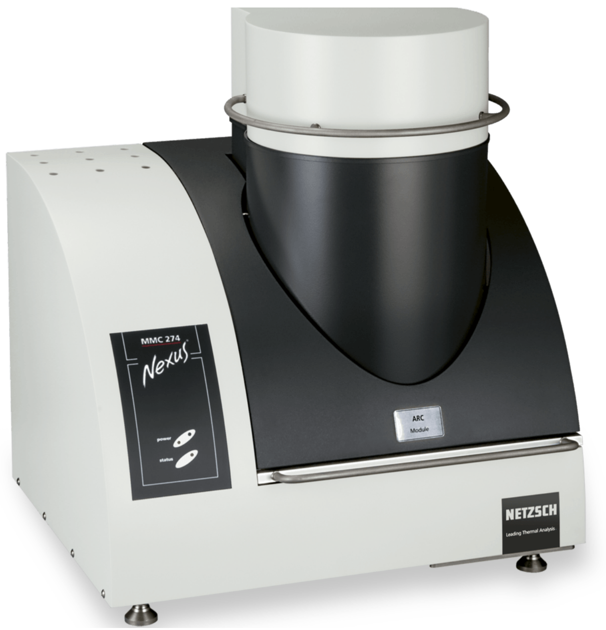
Purdue's CSPE

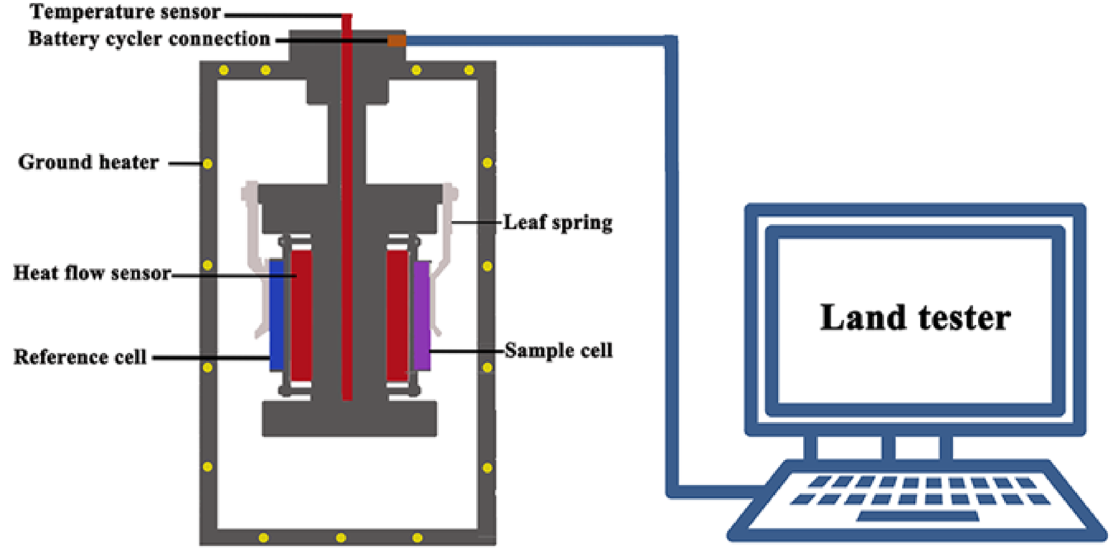


× Melt and shrink

✓ Maintain its structure

Schematic of multiple module calorimeter

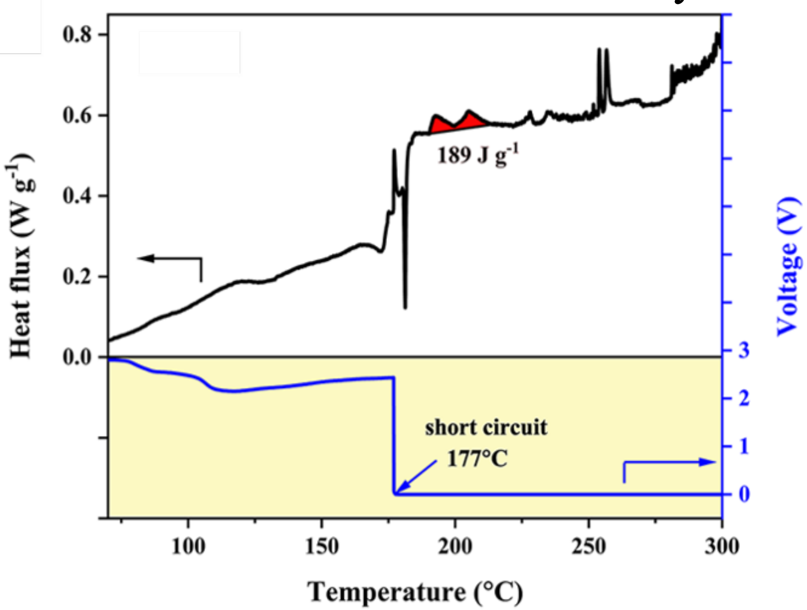




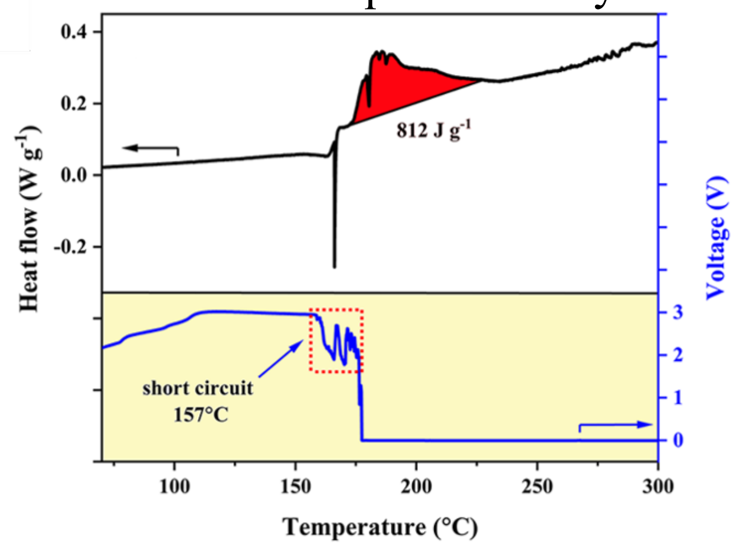
- Different from DSC and ARC
- **MMC** can **in-situ** investigate the thermal behavior of an **entire coin cell** instead of individual components

Thermal Safety Performance

Purdue's solid-state battery



Traditional liquid electrolyte battery



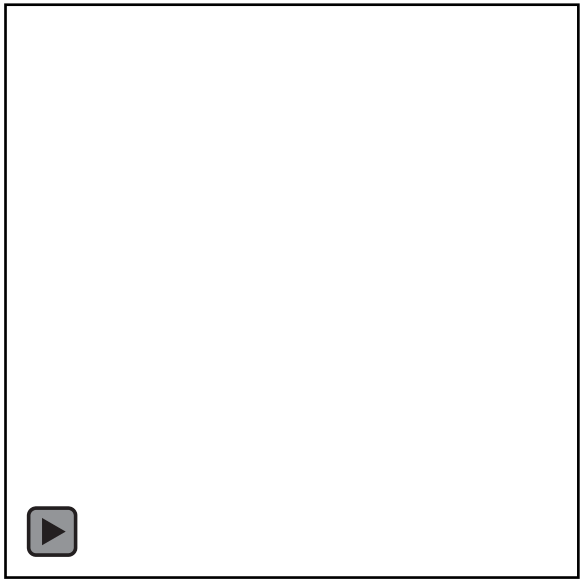
Thermal stable window:	✓ up to 177 °C	*VS*	× up to 157 °C
Heat generation:	✓ 189 J g^{-1}		× 812 J g^{-1}

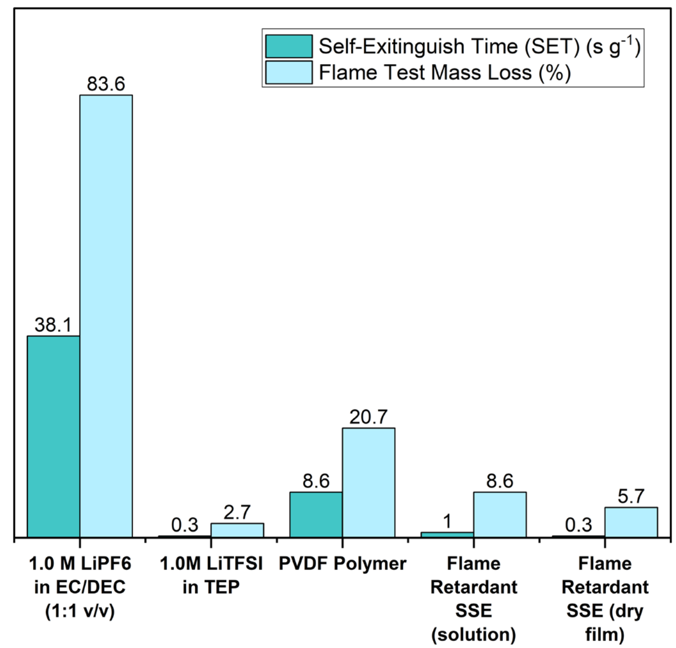
Can we do opposite to avoid battery fire?

1
2
3
4
5

1
2
3
4
5

Fire retardant molecule as solvent and plasticizer

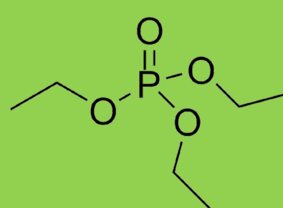




$$PO\bullet + H\bullet \rightarrow HPO$$
$$PO\bullet + OH\bullet \rightarrow HPO_2$$
$$HPO + H\bullet \rightarrow H_2 + PO\bullet$$
$$OH\bullet + H_2 + PO\bullet \; r\!\rightarrow H_2O + HPO$$
$$HPO_2\bullet + H\bullet \rightarrow H_2O + PO$$
$$HPO_2\bullet + H\bullet \rightarrow H_2 + PO_2$$
$$HPO_2\bullet + OH\bullet \rightarrow H_2O + PO_2$$

Schartel *et al. Materials* 3, 10 (2010): 4710–45.

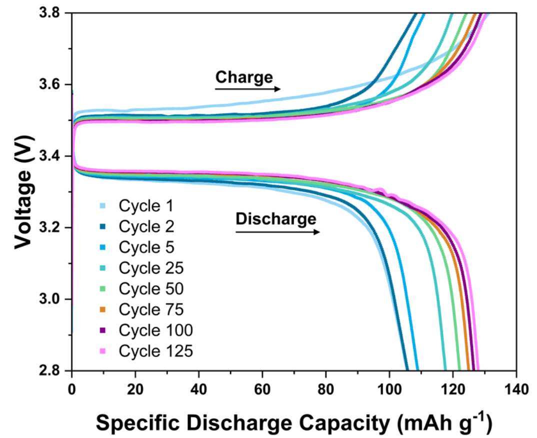
Triethyl Phosphate (TEP)

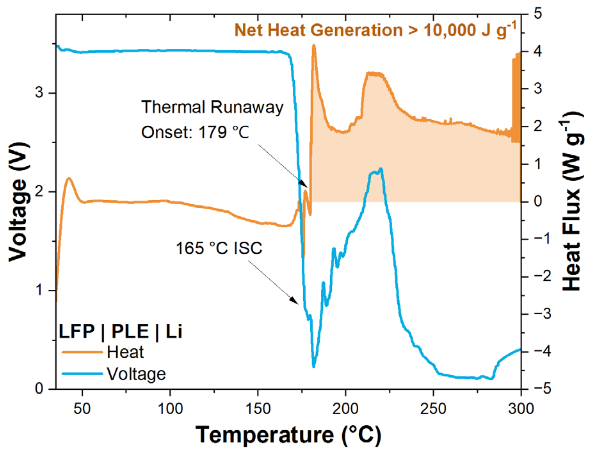


- Green and nontoxic liquid
- Excellent solubility with lithium salts and polymer
- Excellent oxidative stability

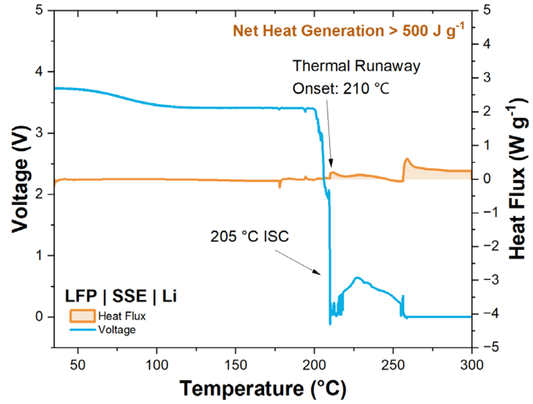
Does the Li-ion Battery works having retardant inside?

- Stable cyclability of high-energy Li-ion battery





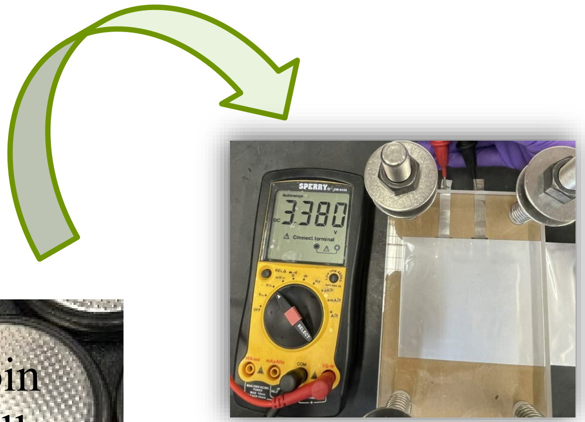
Traditional liquid electrolyte battery



Purdue's nonflammable solid-state battery

Is it scalable?

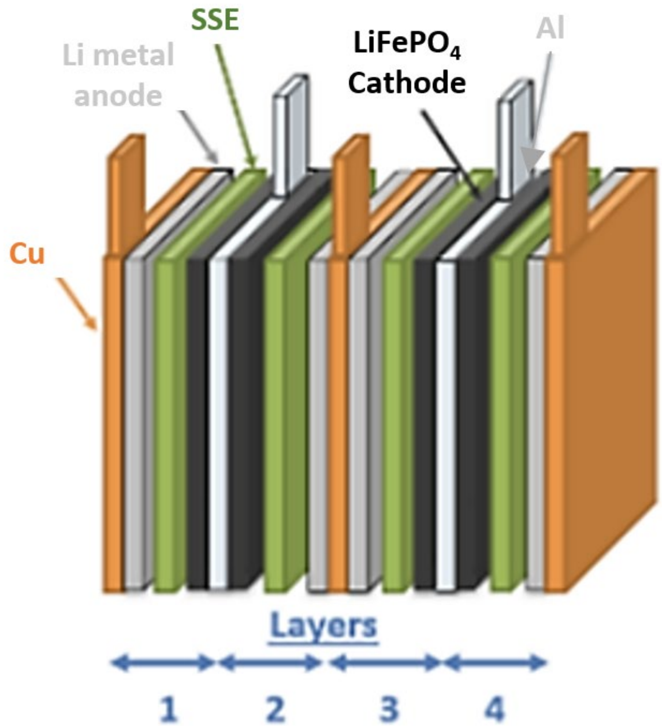
12x Scaleup into Pouch Cell

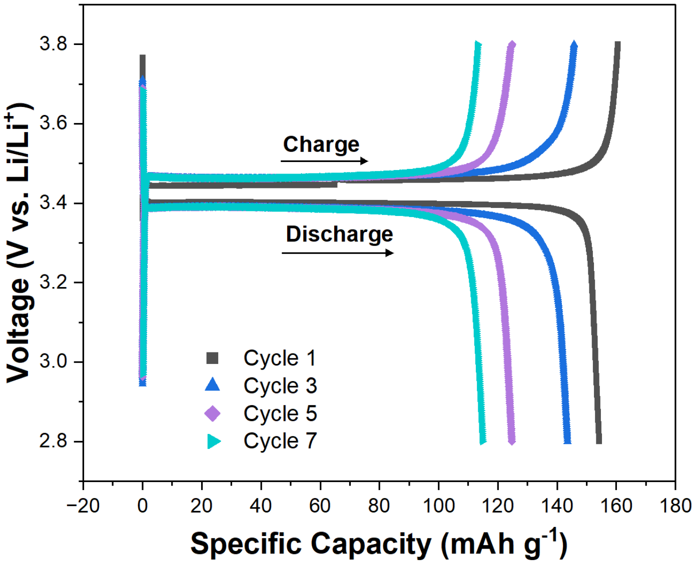


120 mAh

10 mAh

Successful scale-up from laboratory coin cell scale to multilayer Li metal pouch cell





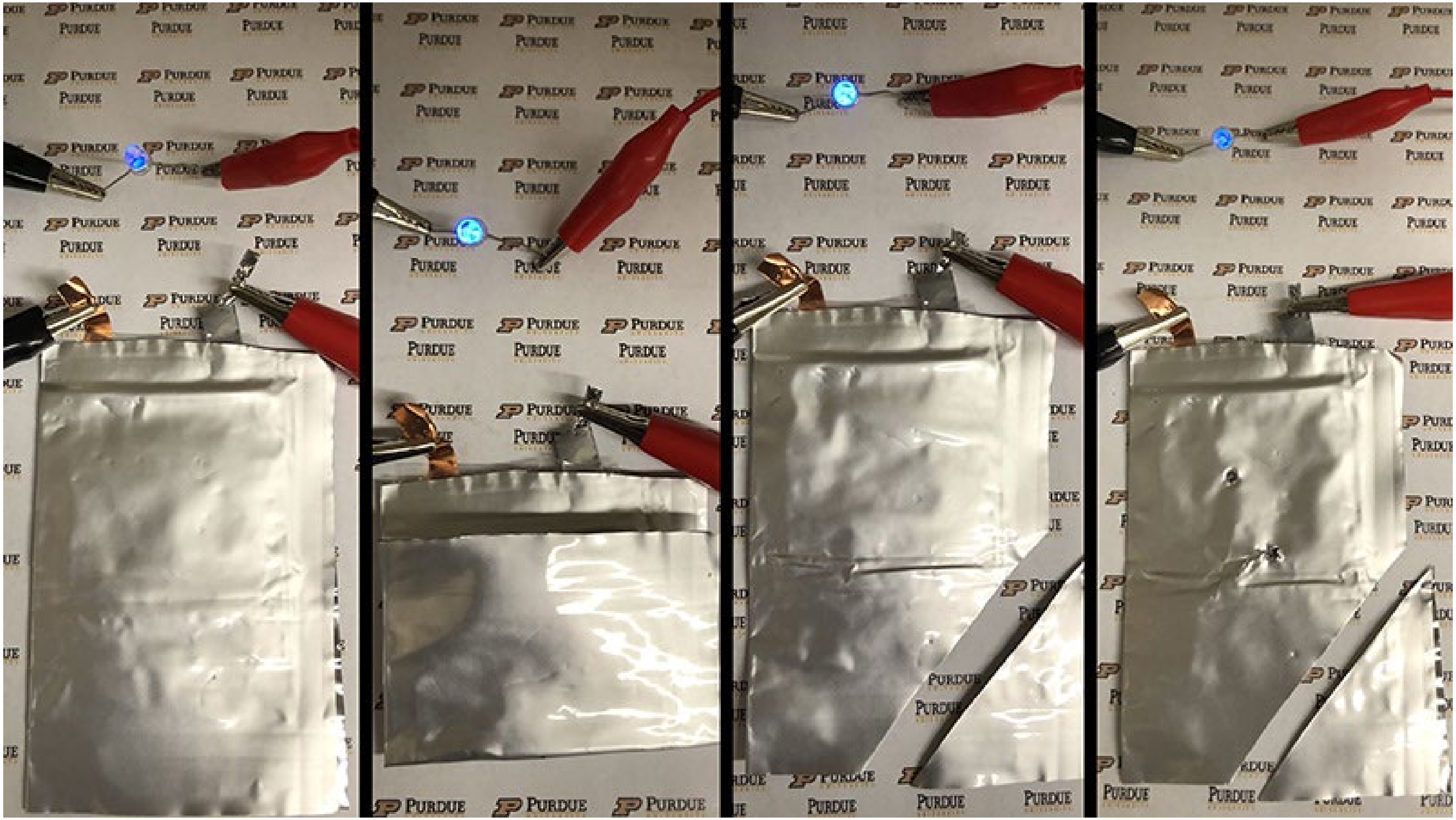
Does it really make battery safer?

Ballistic Testing of <u>100% SOC</u> Multilayer Pouch Cell

- Collaborative ballistic testing courtesy of Cornerstone Research Group (CRG) in Ohio
- **Cell configuration**:
  - 120 mAh; 5-layer pouch
  - LFP Full Cell | fire retarding electrolyte | Li anode
- **Testing Protocol**
  - Precycled and fully charged
  - Shot with 7.62x39mm round (cartridge size of AK-47)
  - Visual/IR monitoring for smoke, flame, or temperature increase

Bullet Type	Velocity (m/s)	Energy (J)	Time of Impact (s)	Temperature Increase from impact to 10s
8.0 g FMJ	738.0 m/s	2,179 J	2.20 s	None detected by IR

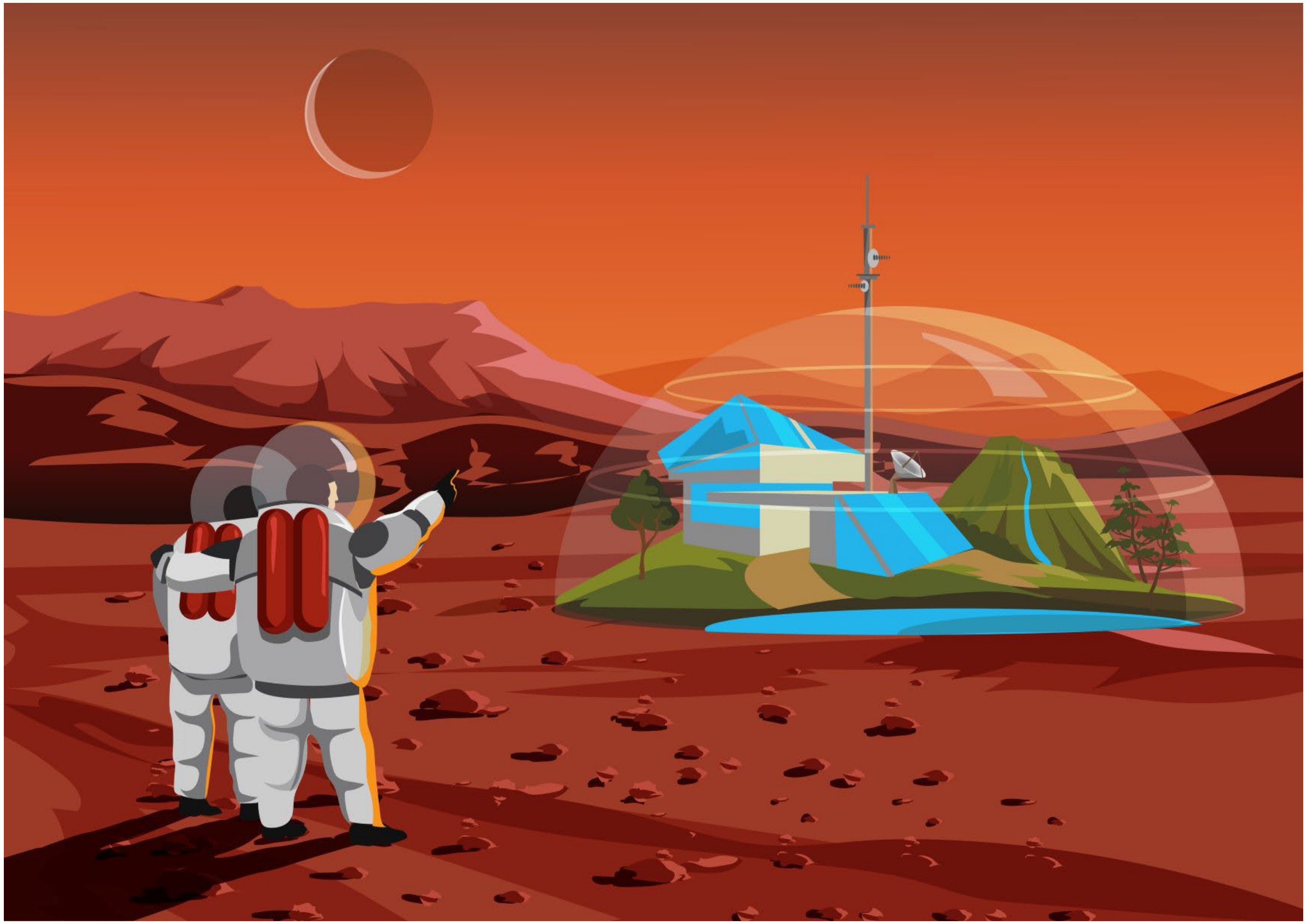
Cutting, nail penetration and operation tests



Why we are not going on Mars (Yet)?

Cold

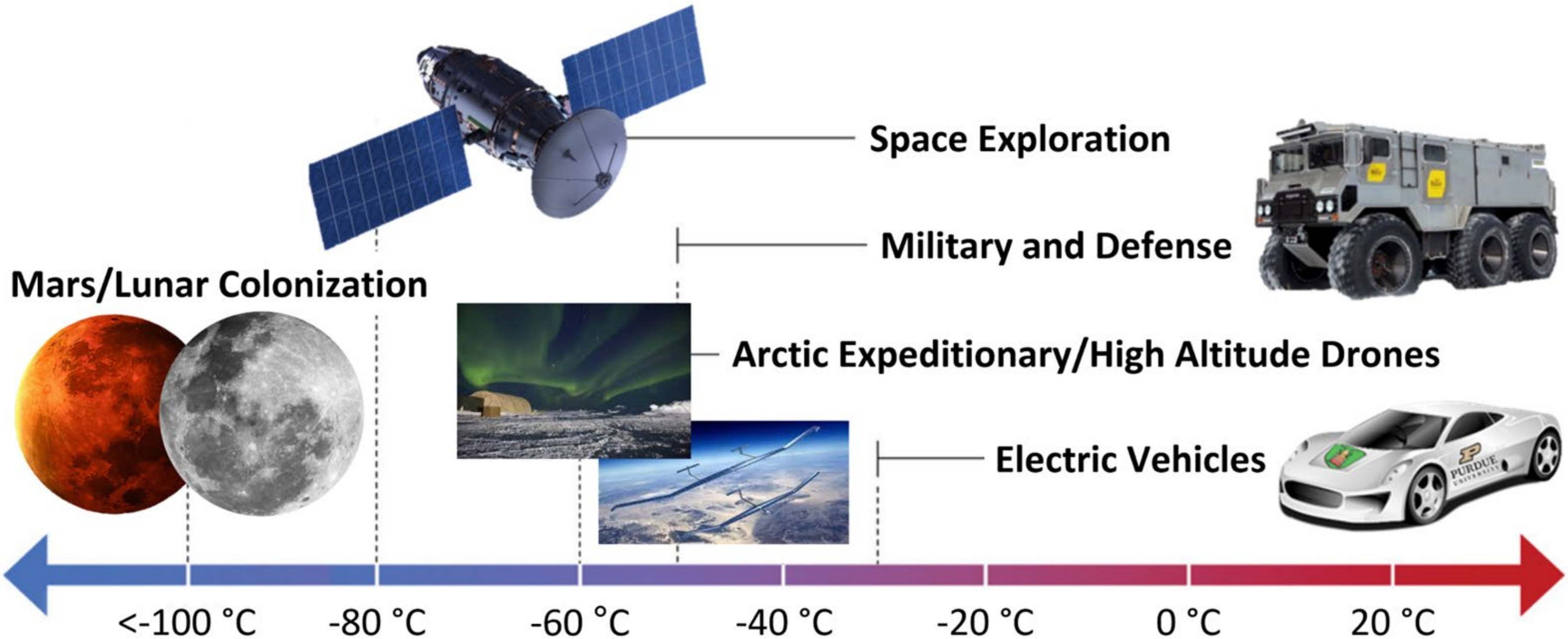
Energy



Water

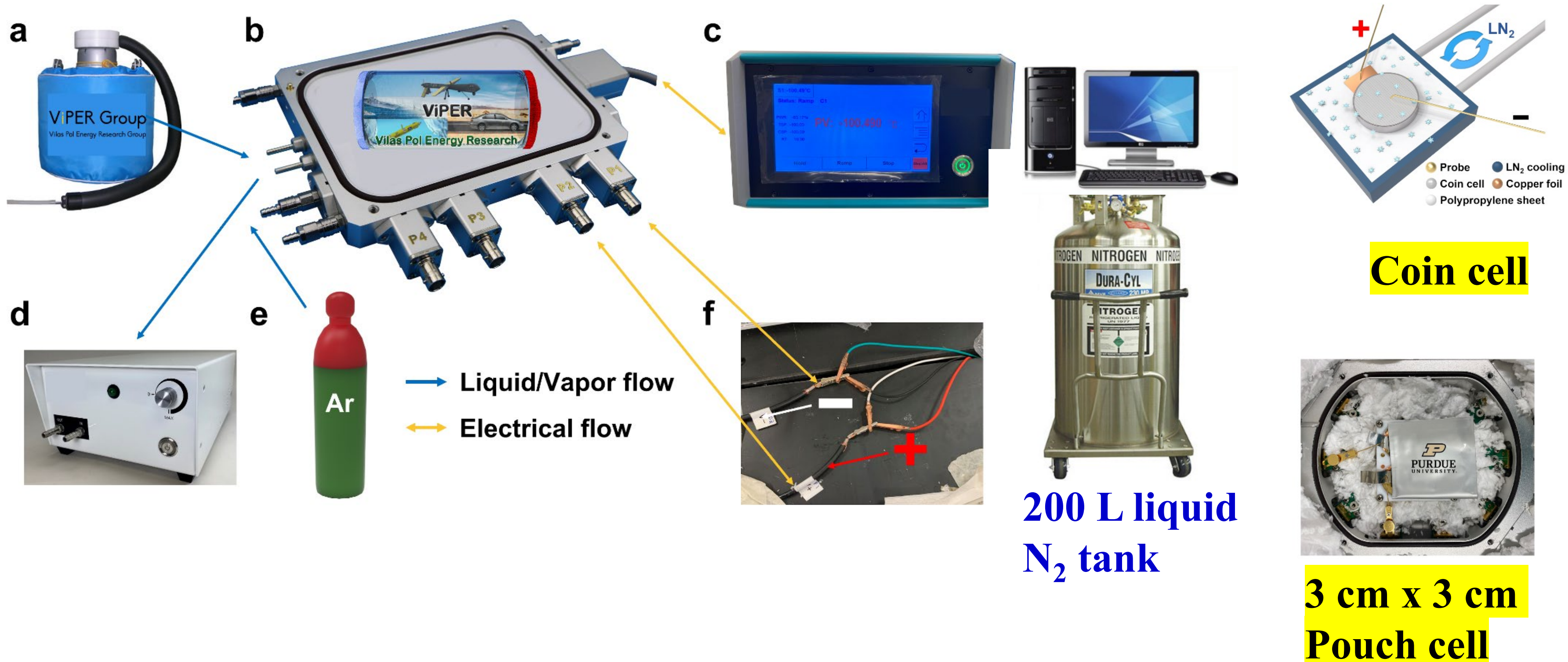
Food

Low Temperature Battery Applications



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

Purdue's Ultra Low Temperature Test Capability



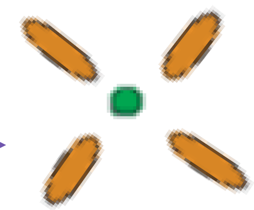
Affordable cost and accurate/reliable electrical measurement

- 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

Electrolyte Solvation Mechanism for Reduced Charge Transfer

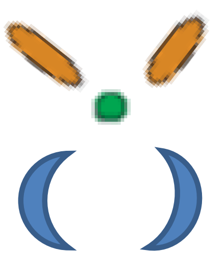
Typical Solvent Shell

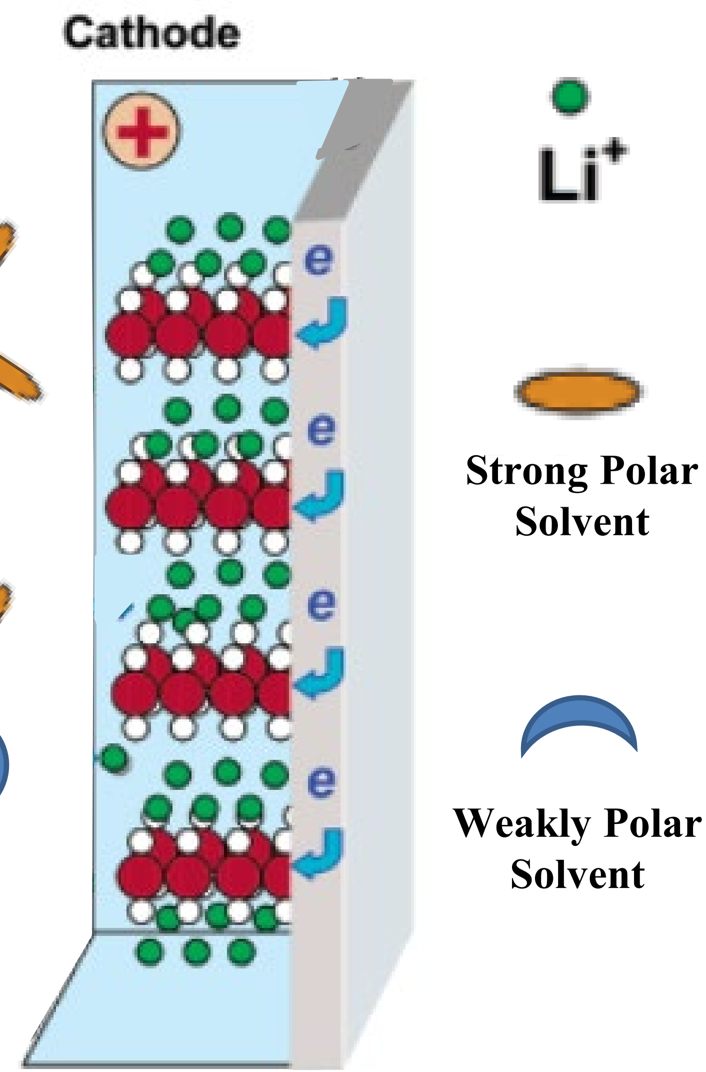
- Desolvation shell **strongly held together**
  - High affinity between solvent molecule and Li^+



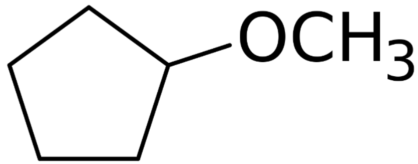
Our Solvent Shell

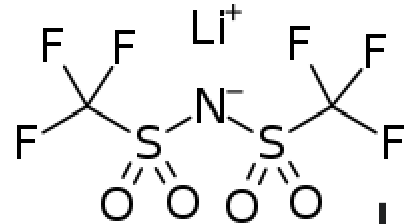
- Desolvation shell weakly held together
  - Diff polarity solvents cause shell to have **weaker interaction**



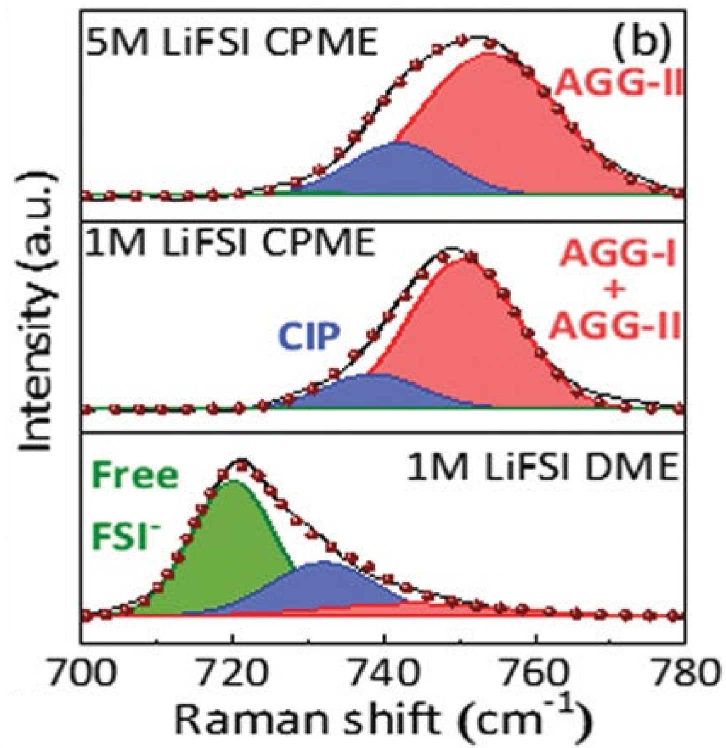


Approach 1- Cyclopentyl Methyl Ether (CPME) based WSE



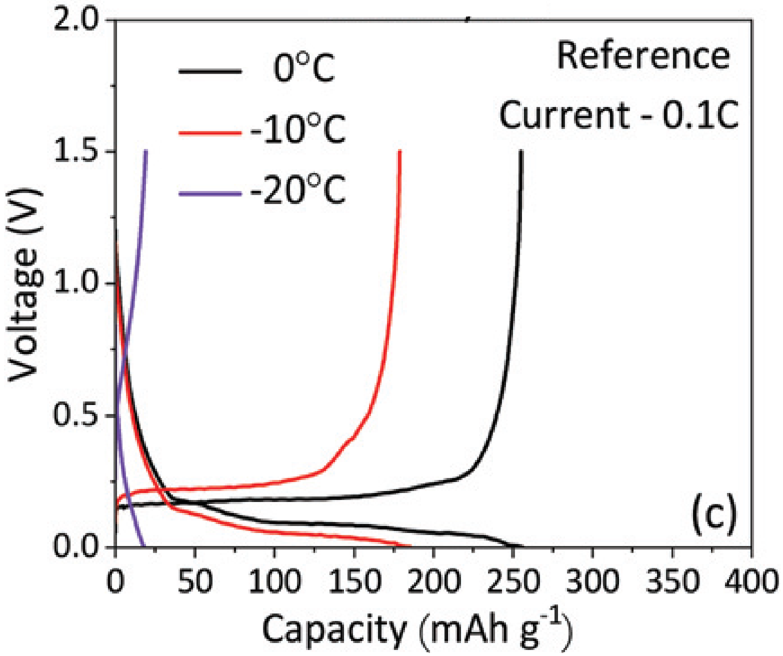


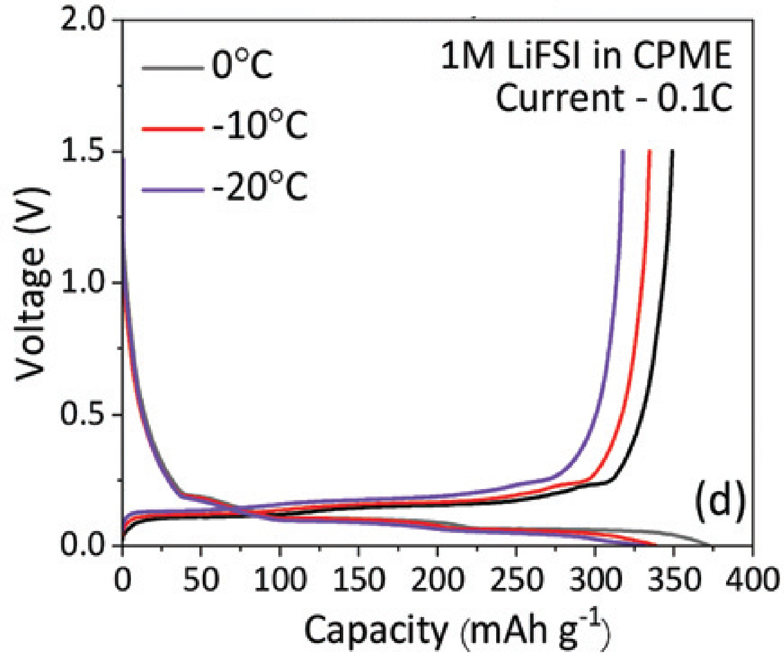
- CPME (B.P: 106 °C and M.P: -140 °C)
- High solubility of the salt (7M)
- Environmentally safe and economically feasible CPME solvent
- Unique solvation structure consisting of CIPs and AGGs
- AGG-I → An FSI^- bonded with 2 Li^+, AGG-II → An FSI^- bonded with 3 Li^+

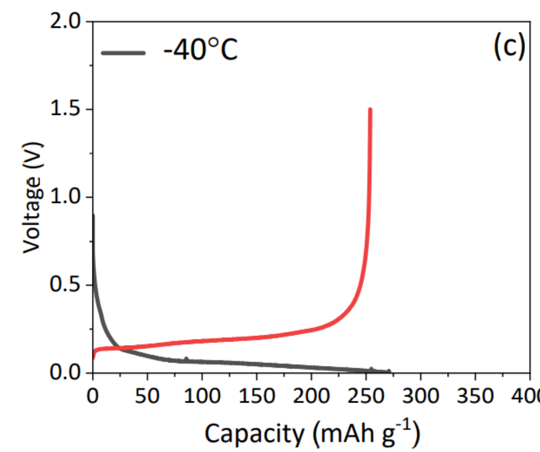


Pol et al. Chem. Commun. **2022**, 58, 5124

Low Temperature Electrochemical Performance







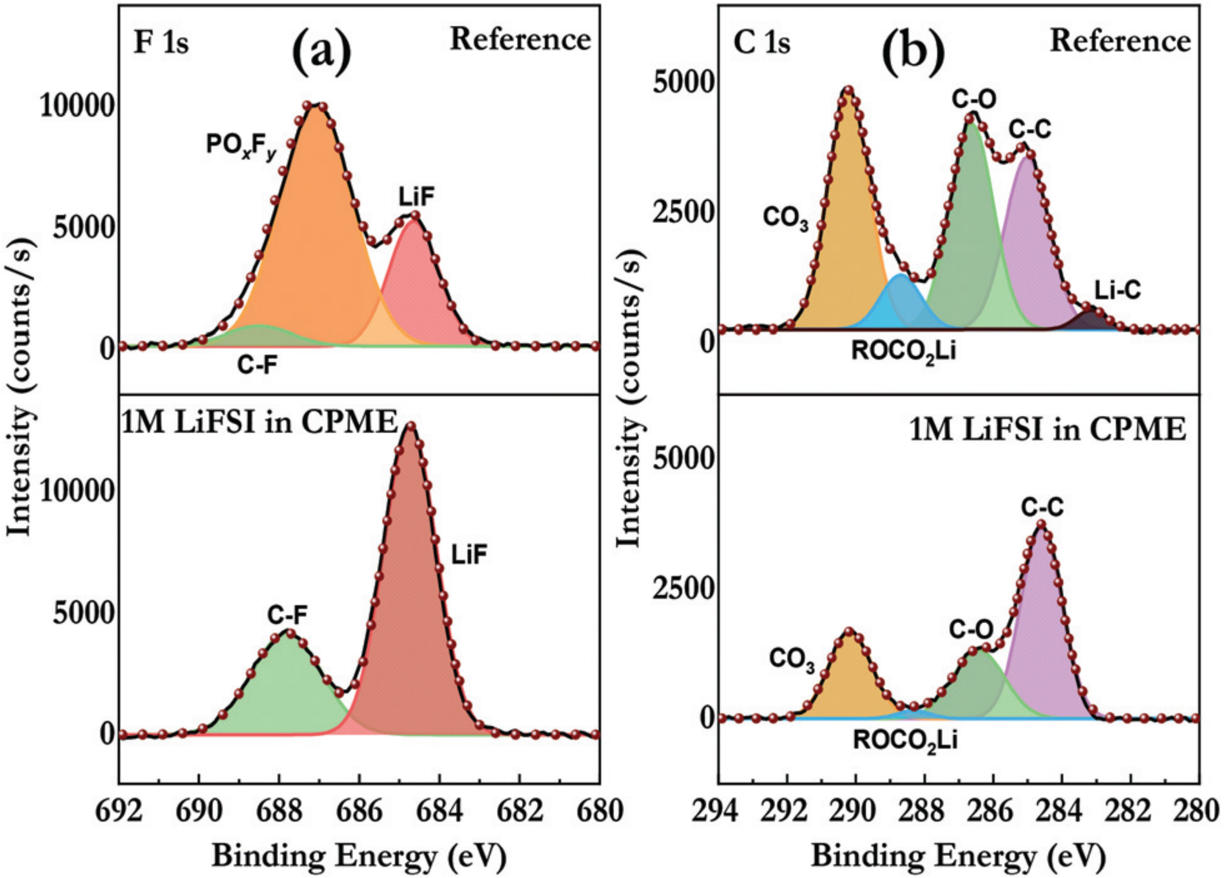
- Excellent low temperature performance of 370, 337, and 330 mAh g^{-1} at 0, -10, -20 °C, respectively.
- Even at -40 °C, the cell can deliver 274 mAh g^{-1} without electrolyte freezing.

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

Why Enhanced Low Temperature Electrochemical Performance?

- Graphite||Li cell in the CPME based WSE

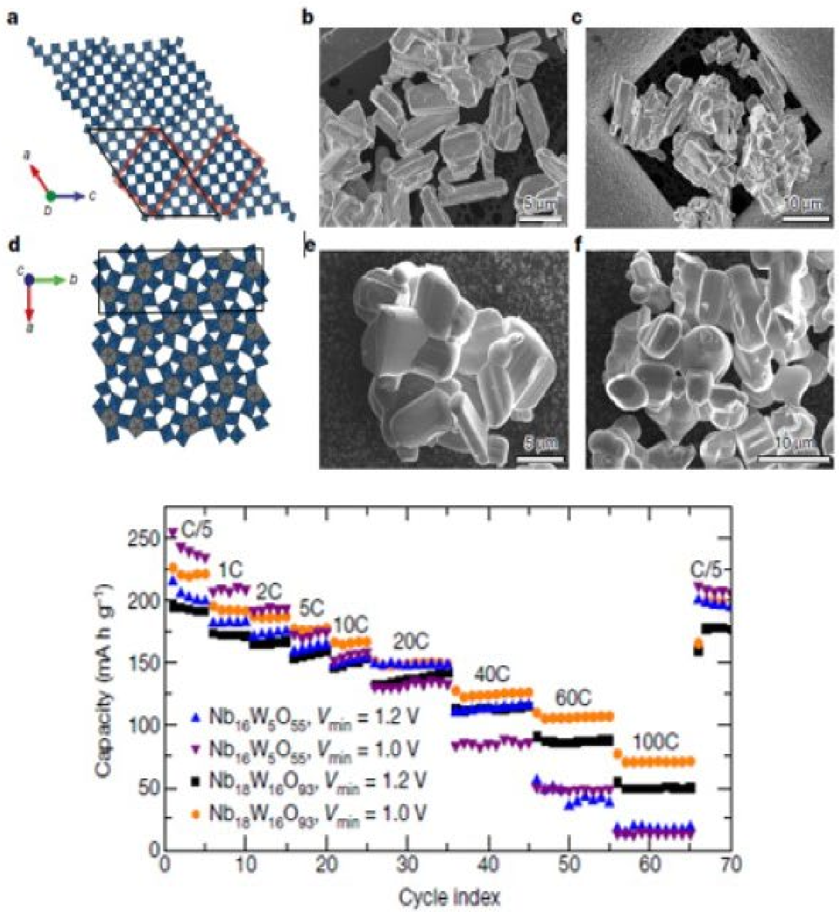
XPS analysis for SEI



- Inorganic LiF-rich SEI would helps in overcoming the main bottleneck of the high Li^+ desolvation energy.

Fast Charging Batteries

Research Backgrounds (NbWO)



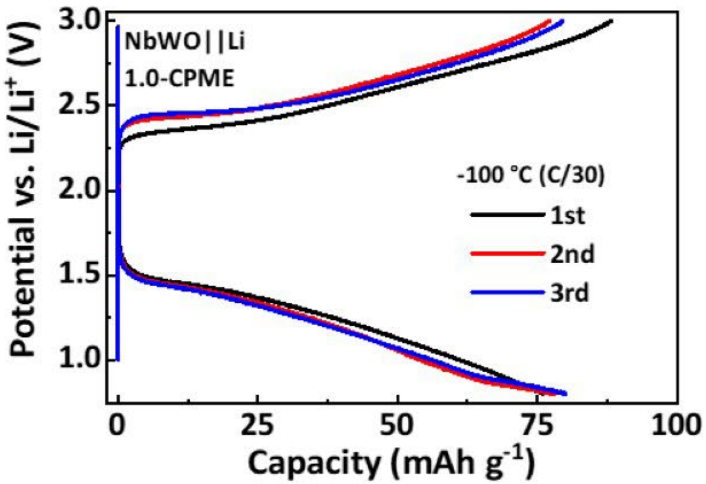
Nature **2018**, 559, 556-563

Niobium Tungsten Oxides

- Excellent fast charge-discharge ability
- Multielectron redox (Nb^{5+}/Nb^{4+} and W^{6+}/W^{5+})
- Open framework (fast solid-state diffusion)
- Randomly distributed Nb and W (prevent Li ordering)
- Pseudocapacitive property

-100 °C Tests (NbWO||Li)

-100 °C (C/30) test (0.8-3.0V)



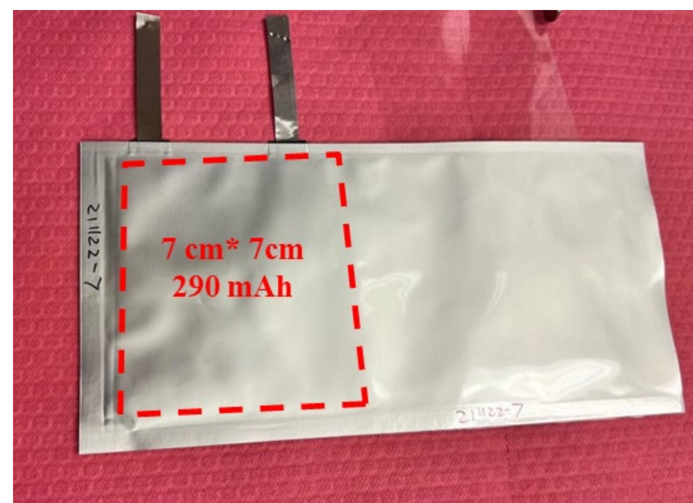
~75 mAh g^{-1} @ -100 °C

-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)



PURDUE UNIVERSITY | Davidson School of Chemical Engineering

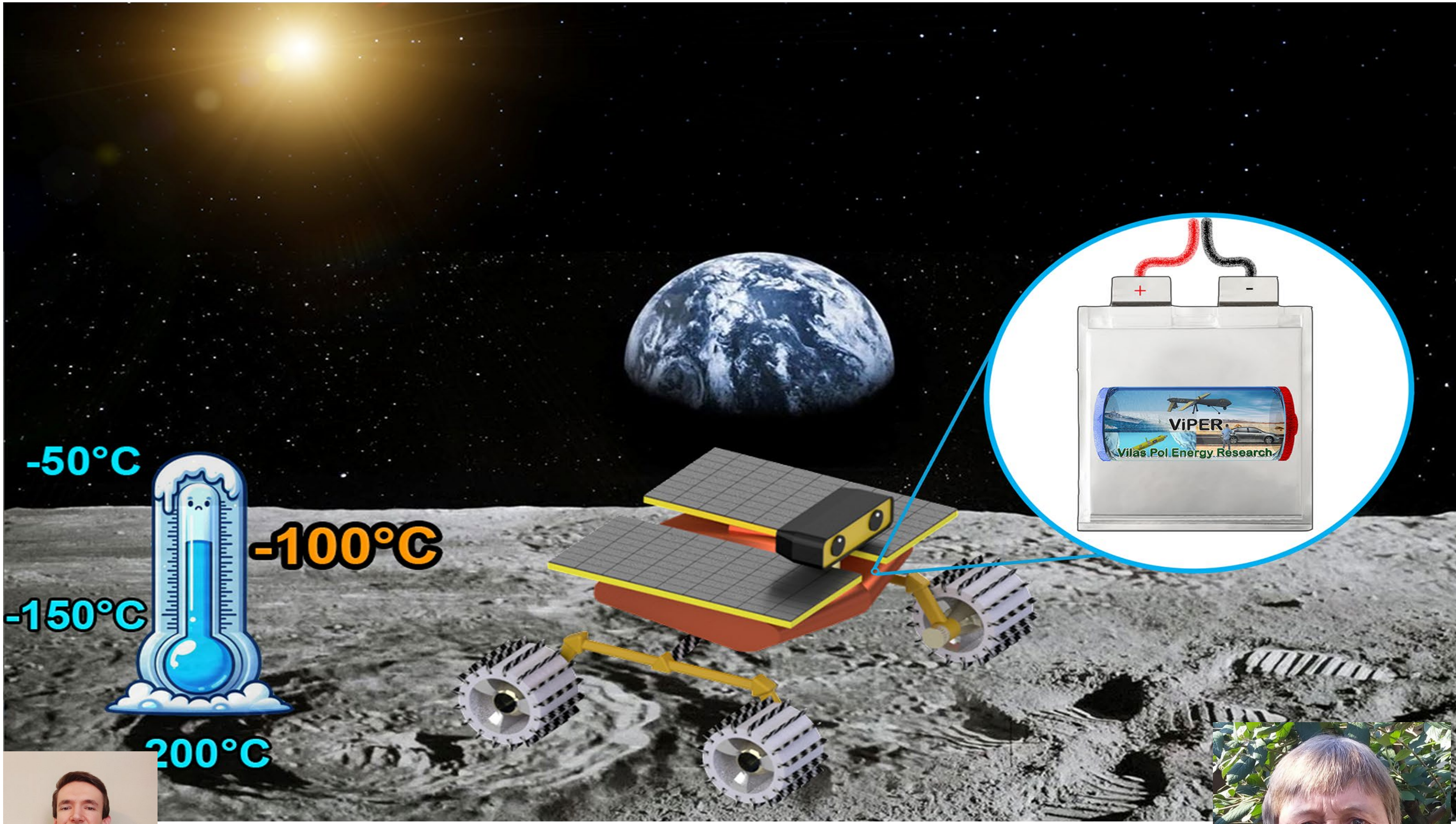
Purdue's ViPER group sets GUINNESS WORLD RECORDS^{TM} title for the lowest temperature, -100 degrees Celsius, to charge a lithium-ion battery

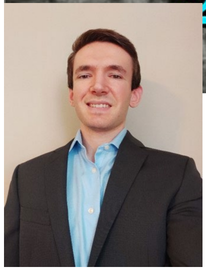
2018

2022

Purdue graduate, Neil Armstrong stepped on the moon for the first time; ***Advanced lithium-ion batteries could be next – Vilas G. Pol***

Energy Harvesting and Storage at Extreme Temperatures





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

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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.

Summary

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

2. Recent electrolyte is towards making quasi-solid state battery that would not catch fire with any abuse!

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

4. Lithium metal batteries are VERY promising with DPE-based electrolyte.

5. Fast charging batteries are possible with NbWO cathode