Li-ion Batteries: Need, Safety and Low Temperature Performance

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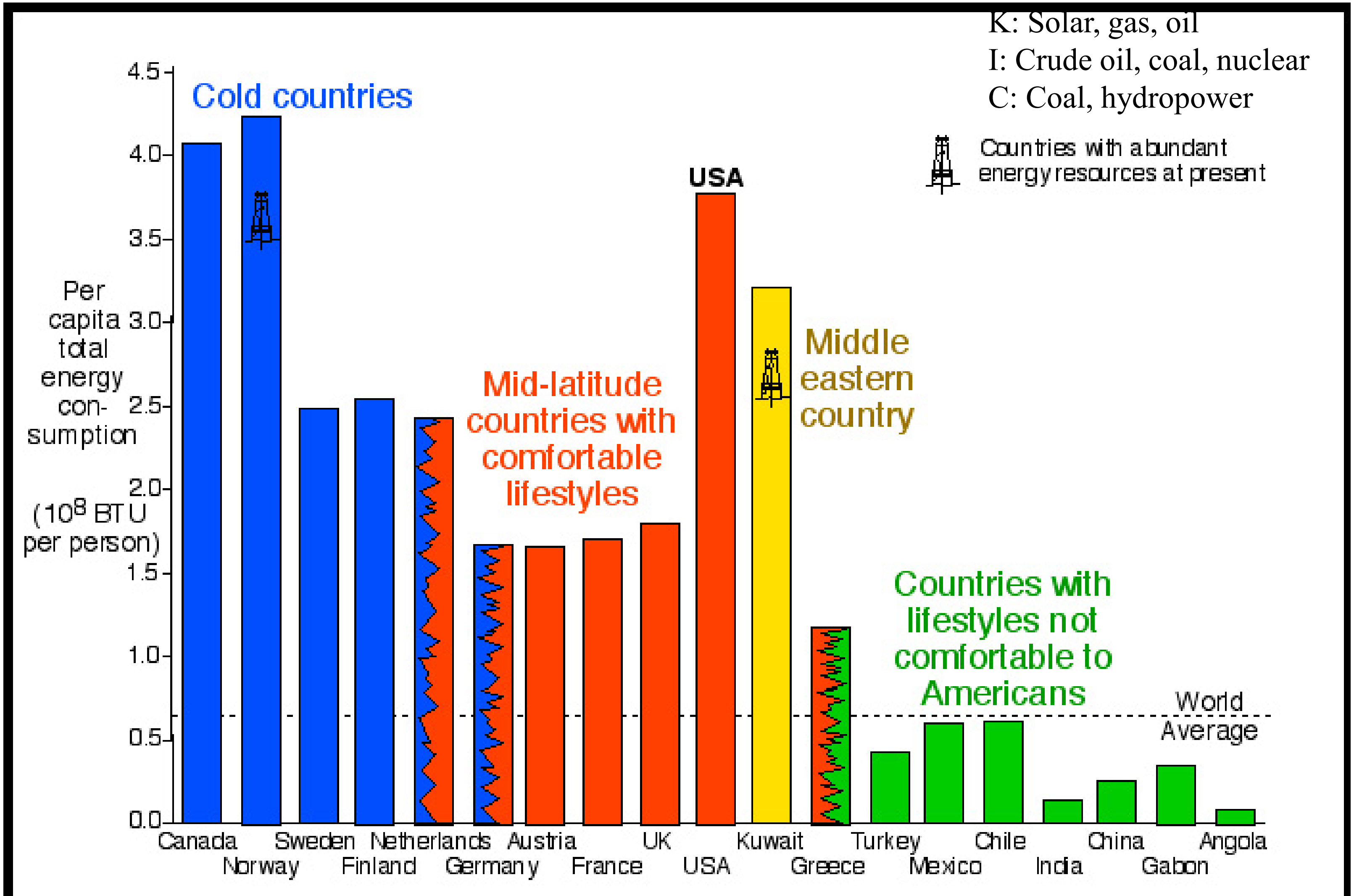
https://engineering.purdue.edu/ViPER/pol.html

World consumption of energy

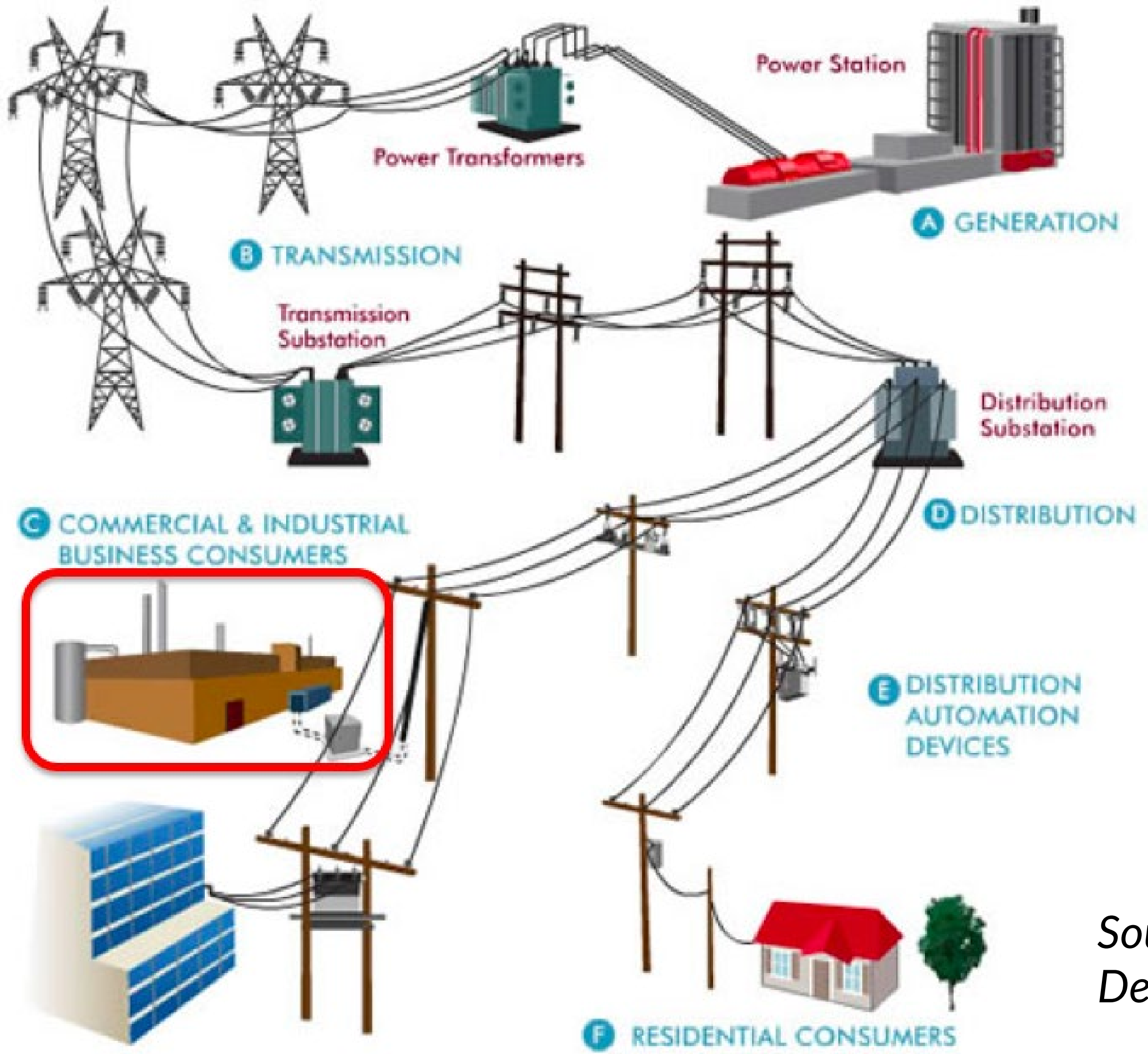
N:Hydropower
C: Natural gas
U: Gas, coal
K: Solar, gas, oil
I: Crude oil, coal, nuclear
C: Coal, hydropower



1BTU =1KJ

http://americanhistorylinks.com/GlobalWarming.htm

Conventional grid - It is a unidirectional grid in which power generates at one end and then it is transmitted to the areas which requires the power. After the long transmission it is then distributed to each specific customer using distribution transformer to lower down the voltage at consumer level.



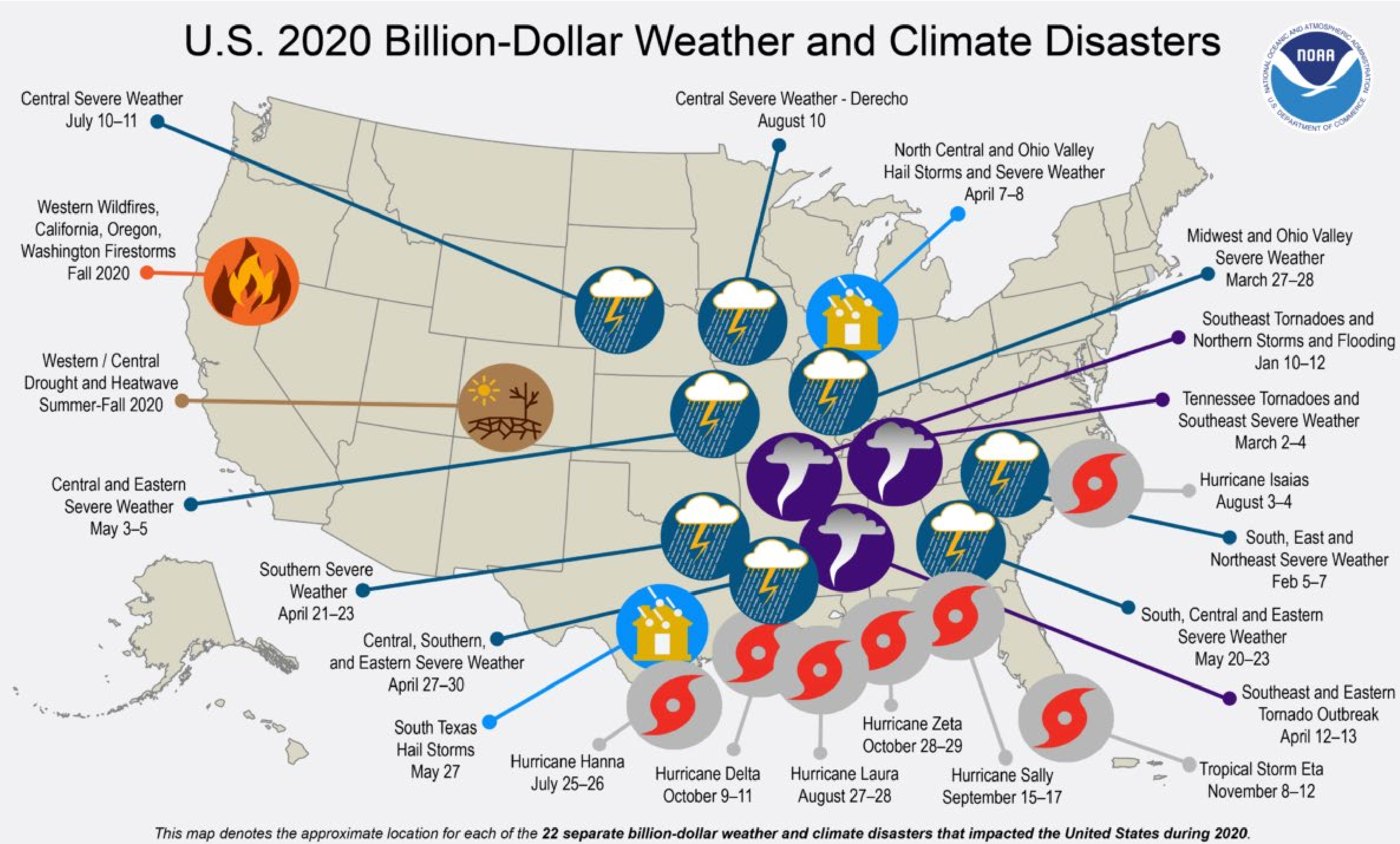
Source: Oncor Electric Delivery Company

Microgrid - It is a grid which can work with the connection of conventional grid and also it can work isolated which is known as islanded mode and its bidirectional

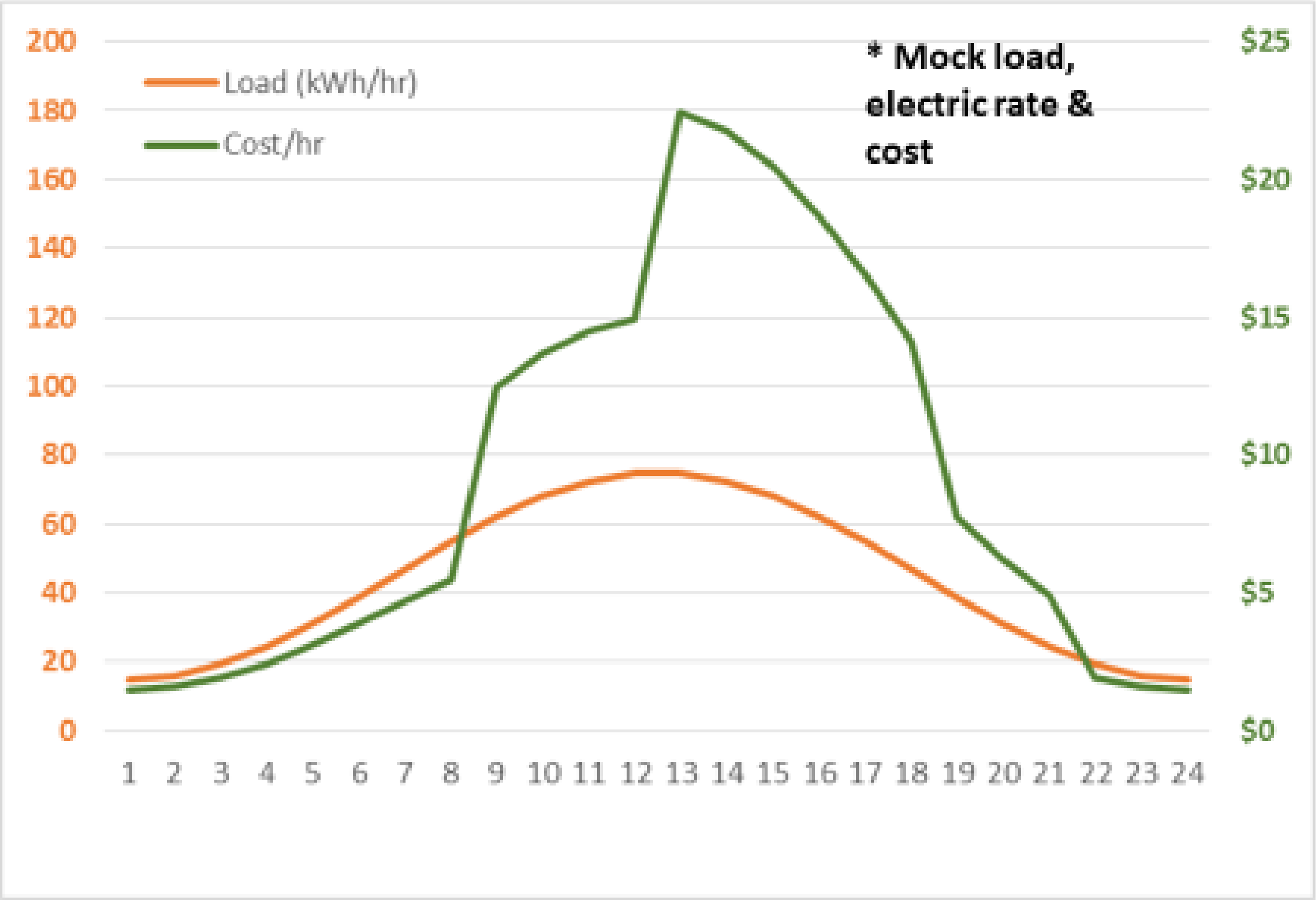
Source: https://clean-coalition.org/community-microgrids/

Why do we need Community Microgrids?

- US power system is century-old technology, vulnerable to extreme weather event
- Since 1980, the US has experienced over 280 weather disasters
- 262 people died in the 2020 events and total cost of $1 billion.

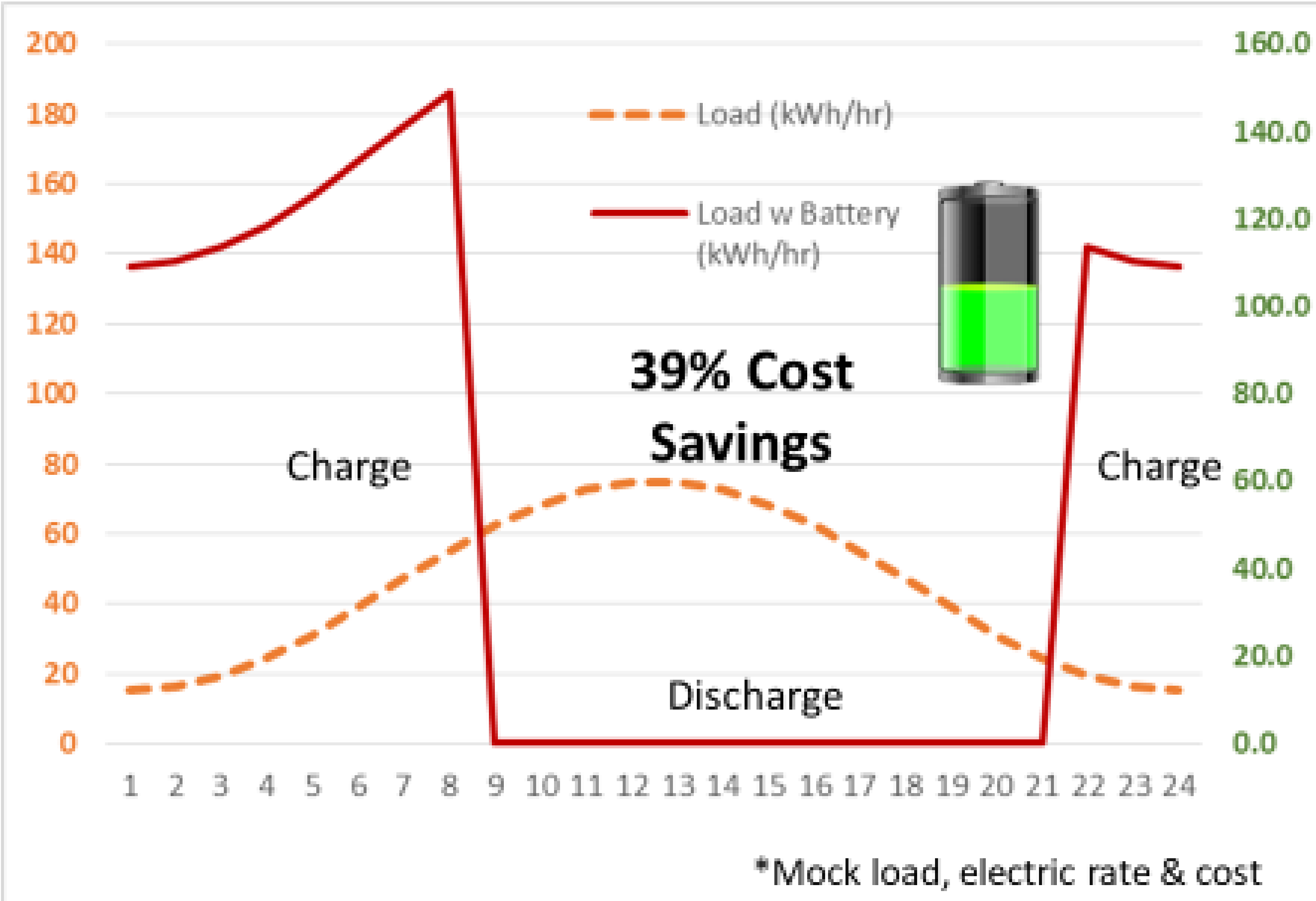


Customer Load Management



Energy Construction & Utilities
California Community Colleges
Workforce & Economic Development

Customer Load Management, cont.

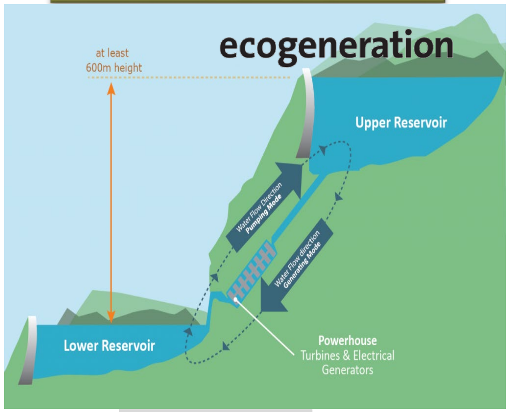


Types of Energy Storage

Electrochemical

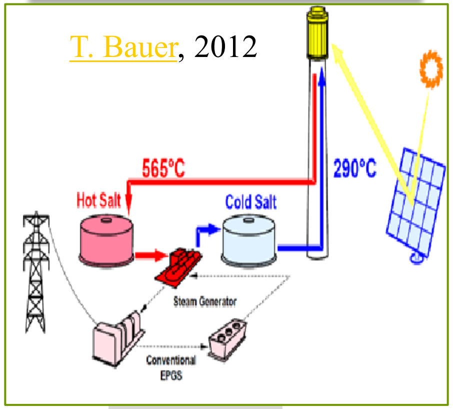
Rechargeable Batteries

Mechanical



Pumped Hydro

Thermal



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

Technology Towards Commercial Na-ion Batteries

Upcycling

$$$

FARADION UK

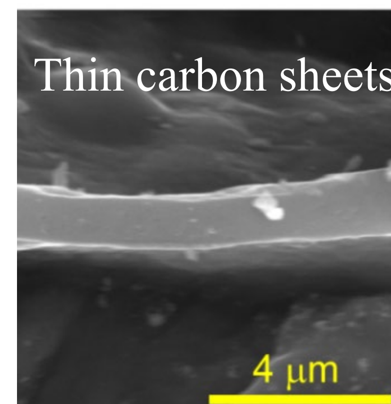
SURE CARBON, TN

Waste

Facile Precursor Loading

Proprietary Pyrolysis
Batch Reactor

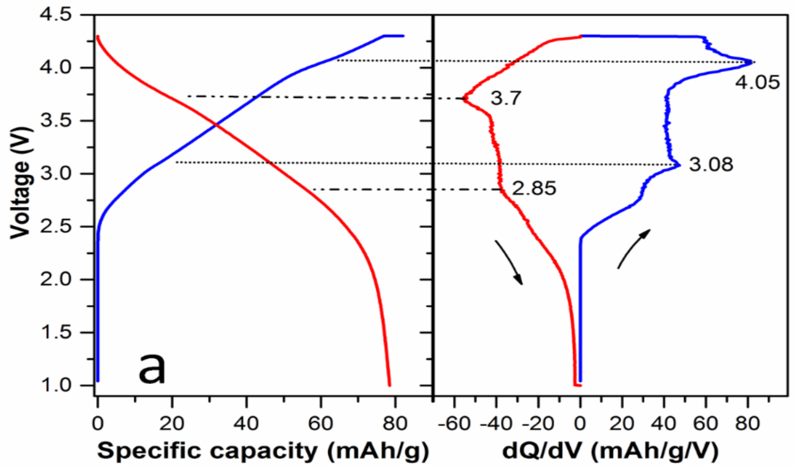
Milling/Bottling of
Carbon Microsheets



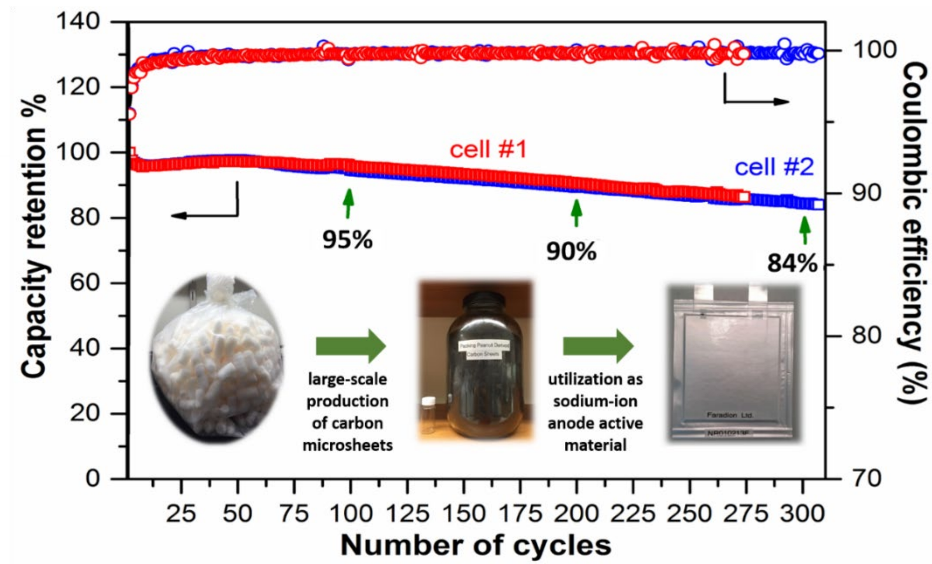
US Patent

Etacheri et al, Environmental Science and Tech., 2015, 49, 11191−11198

Carbon Sheets vs $Na_aNi_{1-x-y}Mn_xM_yO_2$



FARADION



✓ **Carbon sheet is scalable product does provide 85% capacity after 300 cycles**

J. Tang, J. Barker, V. G. Pol, Energy Technology, 2018, 6, 213-220

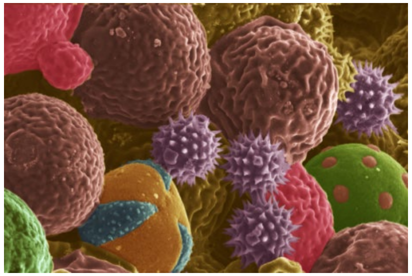
Trask Innovation Funds, 2018

What ViPER Group Does?

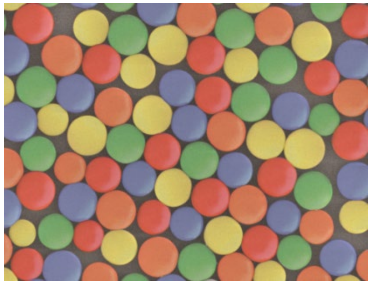
Interest: Battery Safety, Extreme Temperature Batteries, Next Gen.

Lithium-ion | Sodium ion | Potassium ion | Li-S/Solid state

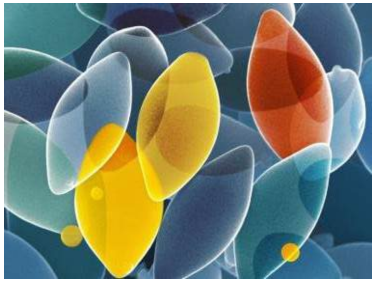
3
Li
Lithium
6.941



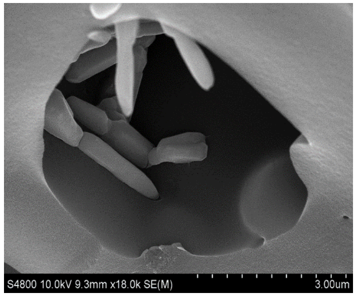
23
Na
SODIUM
11



19
K
Potassium
39.0983



16
S
32.066



Discovery, Characterization and Testing of Energy Storing Materials

250+ publications, 14 issued US Patents, 20 applications, 4 book chapters

Classes of battery

Primary vs. Secondary Batteries

Primary	Secondary
Cell reaction is irreversible	Cell reaction is reversible
Must be discarded after use	May be recharged
Have relatively short shelf life	Have long shelf life
They cannot be used as storage devices	They can be used as energy storage devices
Can not be recharged	They can be recharged.
e.g. Dry cell.	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).

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

Overall reaction:

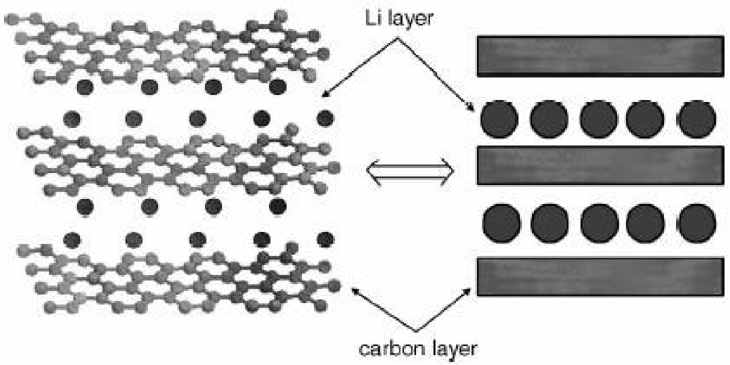
$$Zn_{(s)} + 2MnO_{2(s)} \rightarrow ZnO_{(s)} + Mn_2O_{3(s)} \; [e° = 1.43 \text{ V}]$$

- **CANNOT BE RECHARGED**

Theoretical Capacity of Materials

- From Faraday's 1st Law of Electrochemistry 1Q = [6.241×10^{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

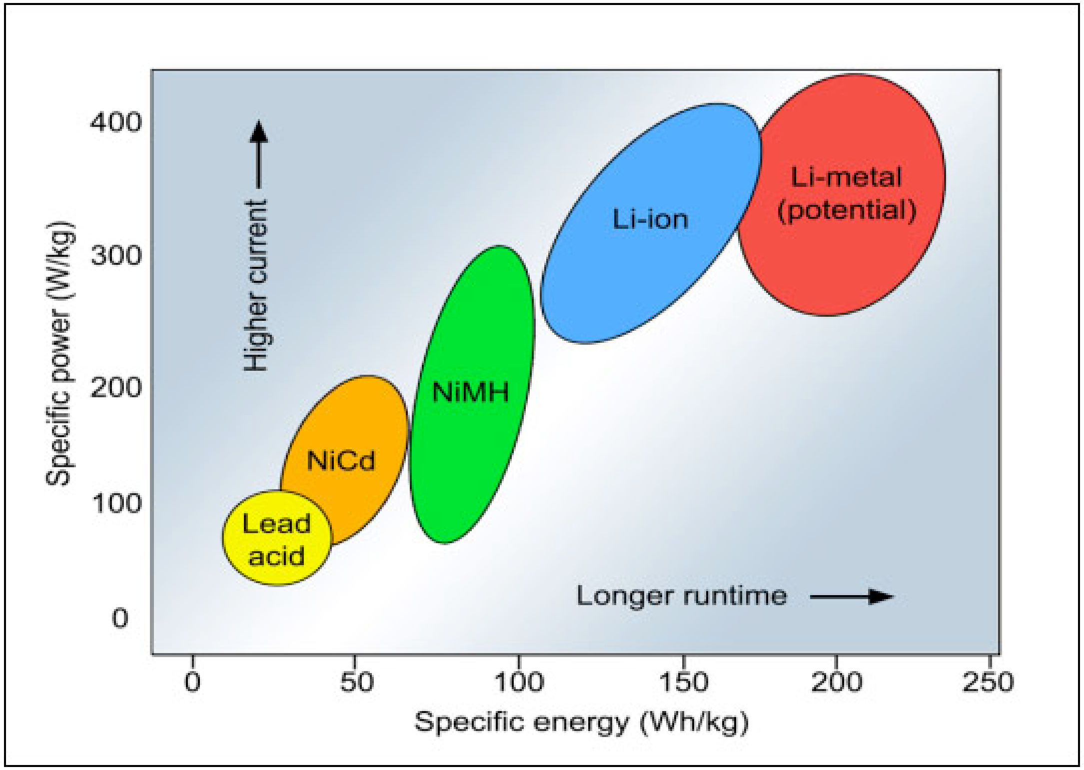
= 26.8/72

= 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

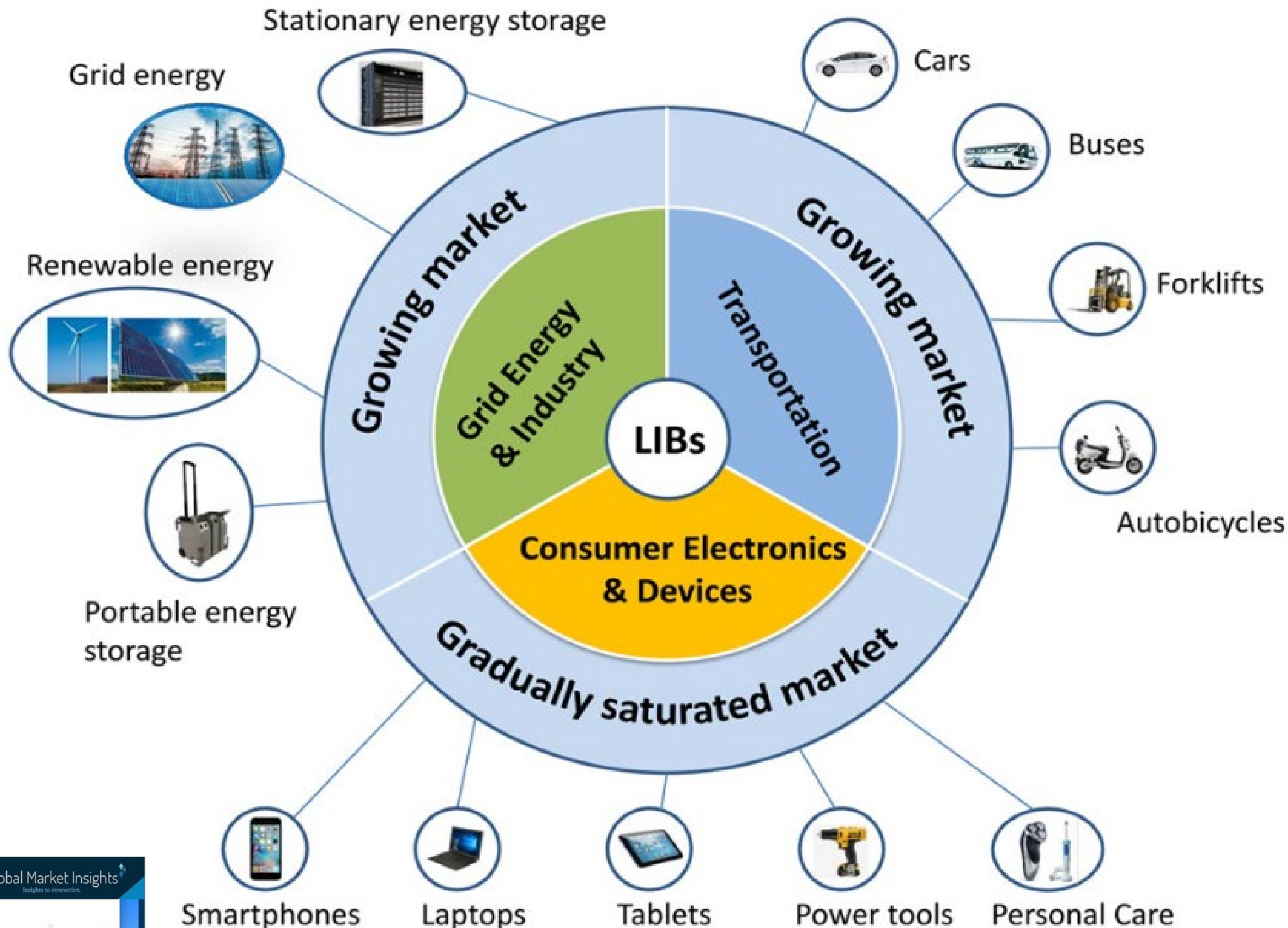
We are not trading our dependence on foreign oil to a dependence on foreign batteries

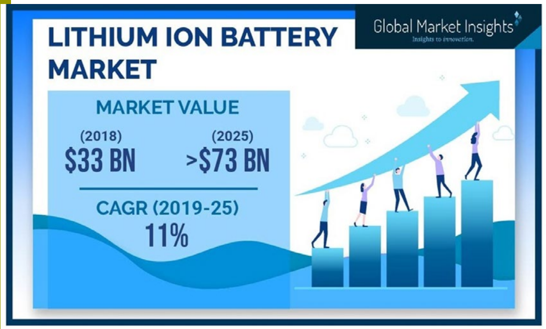
How many batteries are required to run your TESLA?

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

Battery Research Challenges

- Cost

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

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

- Safety

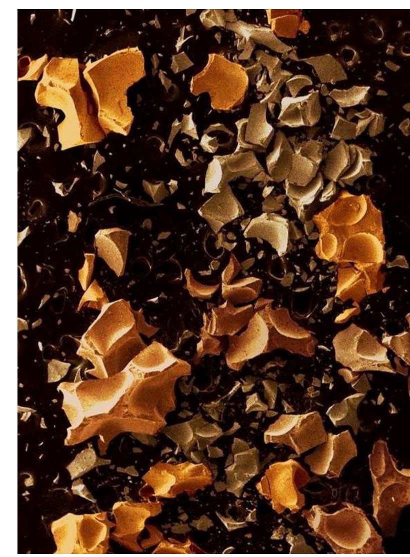
  Inherently safe batteries needed

  - Overcharge protection circuitry expensive

- Life

  Current technology ~ 5 to 10 years

  - Target ~ 15 years



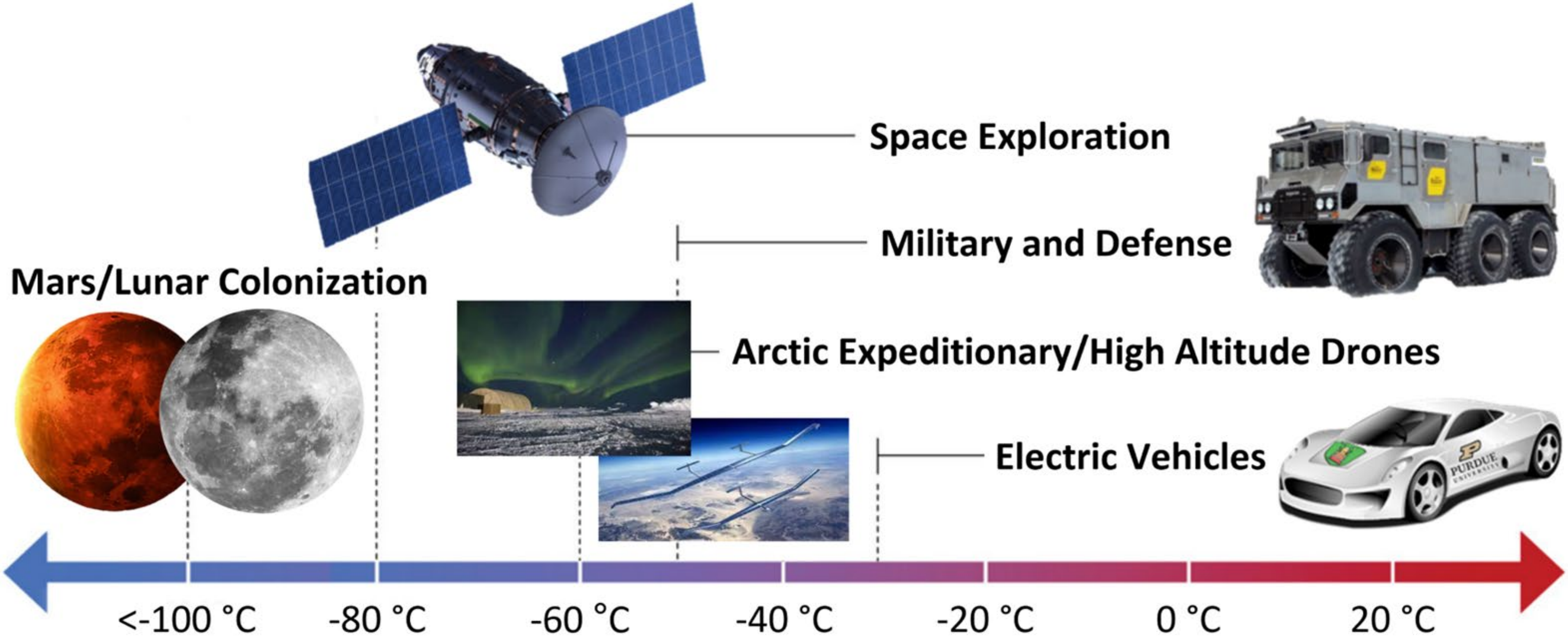
- Low Temperature Performance

  Current technology ~ Sluggish < 0 ºC

  - Target ~ -30 ºC (cold cranking)

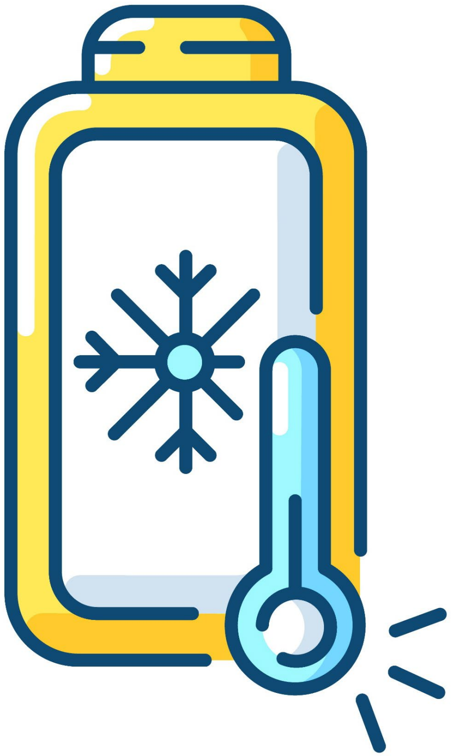
John B. Goodenough *et al.*, *Chemistry of Materials* **(2010)** *22*, 587

Low Temperature Battery Applications



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

Major Two Challenges in Current Systems



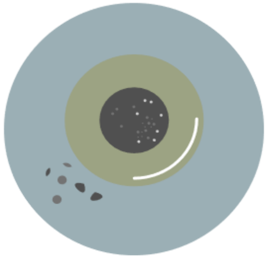
Electrolyte issue

- **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.

Li-ion Battery Low Temperature Challenges



Solid Electrolyte Interphase (SEI)

Instability

Dendrite growth at high rate or cycles

Kinetic limitations for charging speeds

Small optimal temperature operating window

(0°C to 40°C)

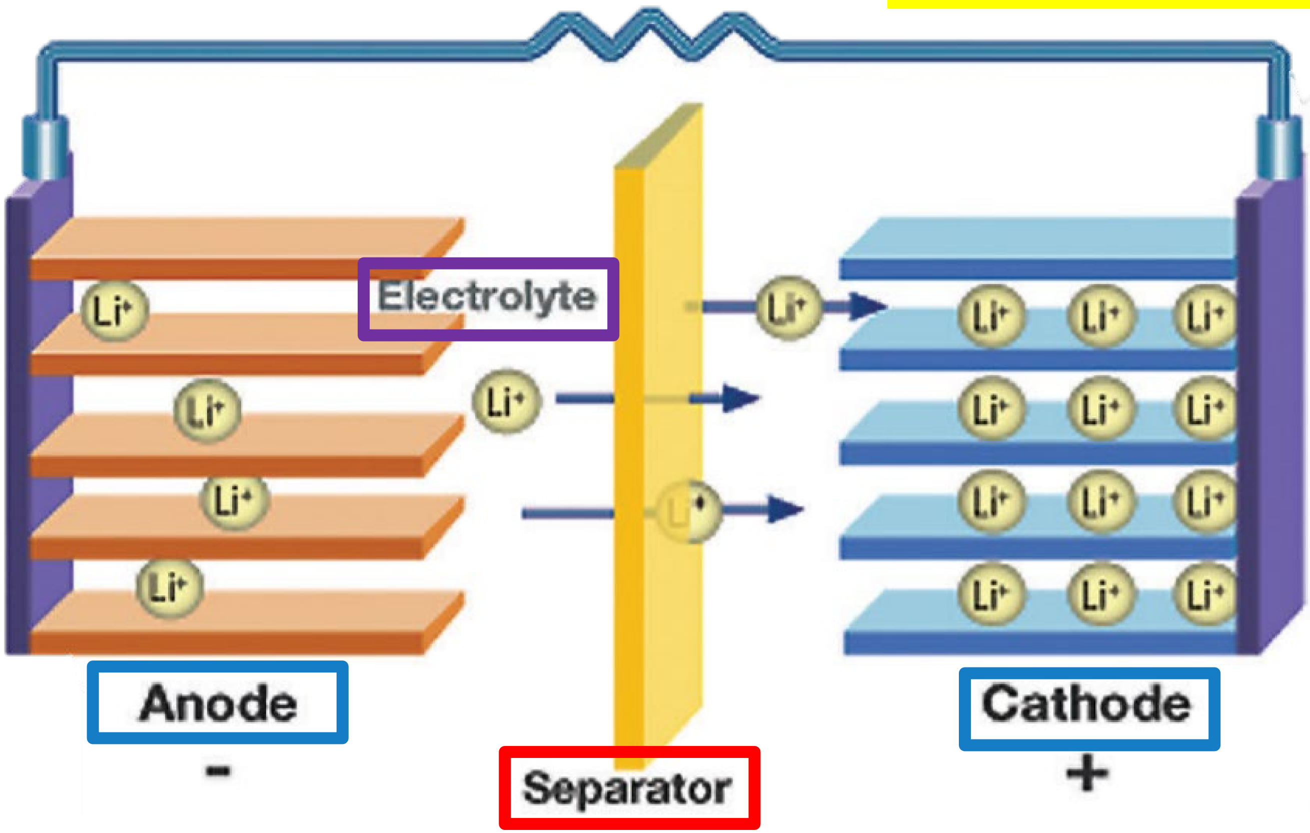
Unsafe

Low Temperature Limitations

4 Main Areas of Focus

Resistance

Reduced Li ion conductivity



Lithium plating

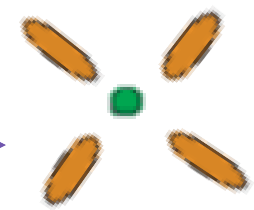
Charge transfer resistance at interphase

N Chawla, *Batteries* (2019)

Electrolyte Solvation Mechanism for Reduced Charge Transfer

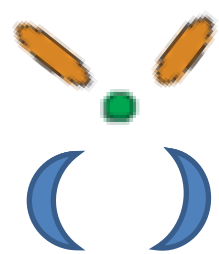
Typical Solvent Shell

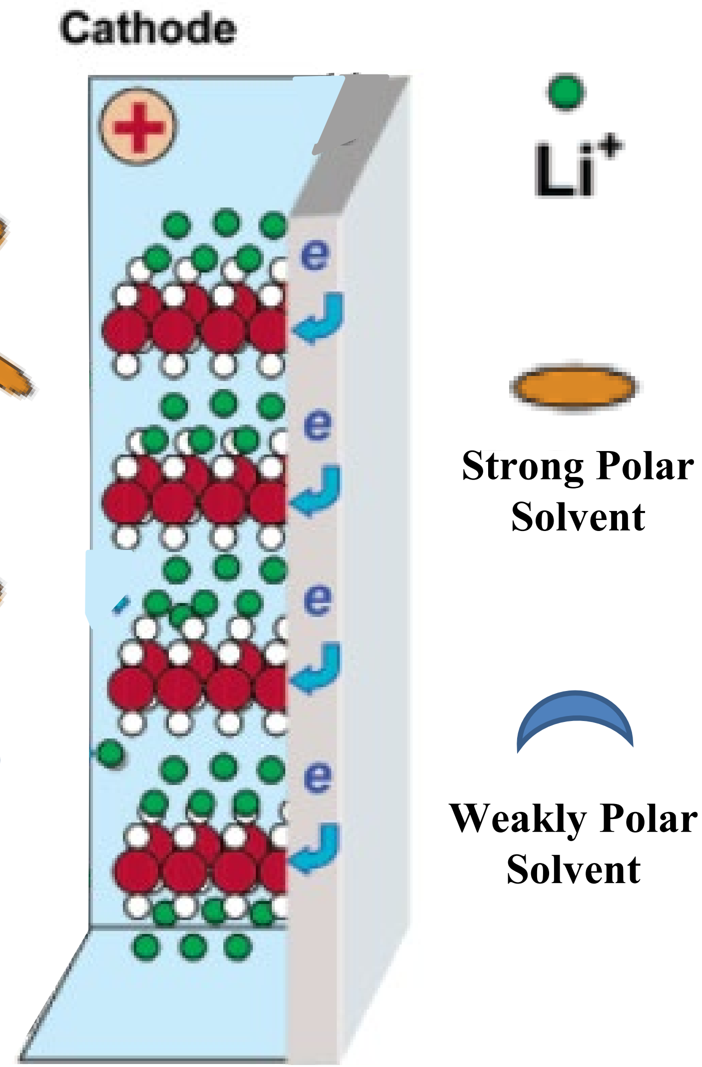
- Desolvation shell **strongly held together**
  - High affinity between solvent molecule and Li^+



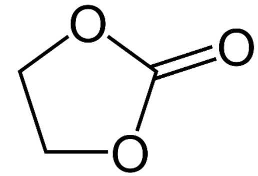
Our Solvent Shell

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

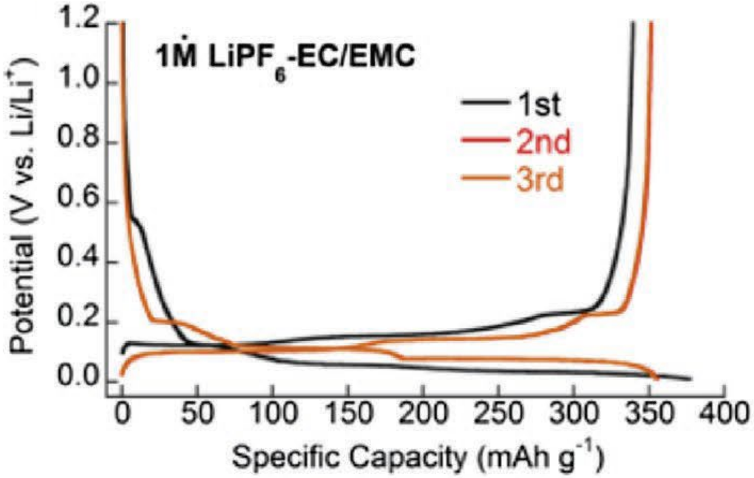


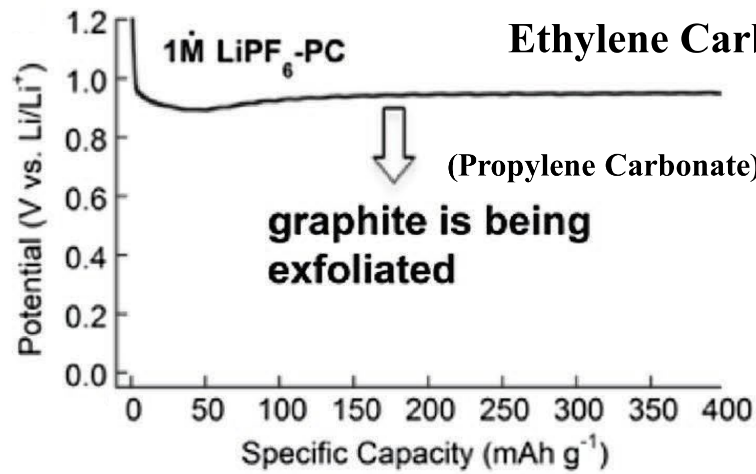


Current EC-based Electrolytes



Ethylene Carbonate (EC)

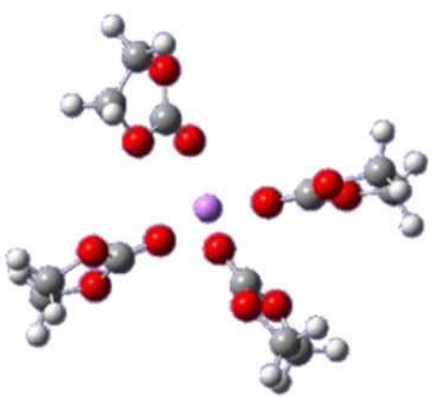




Nano. Lett. **2017**, 17, 1602-1609

⇒ Essential solvent of EC for stable SEI layer

$Li^+(EC)_4$

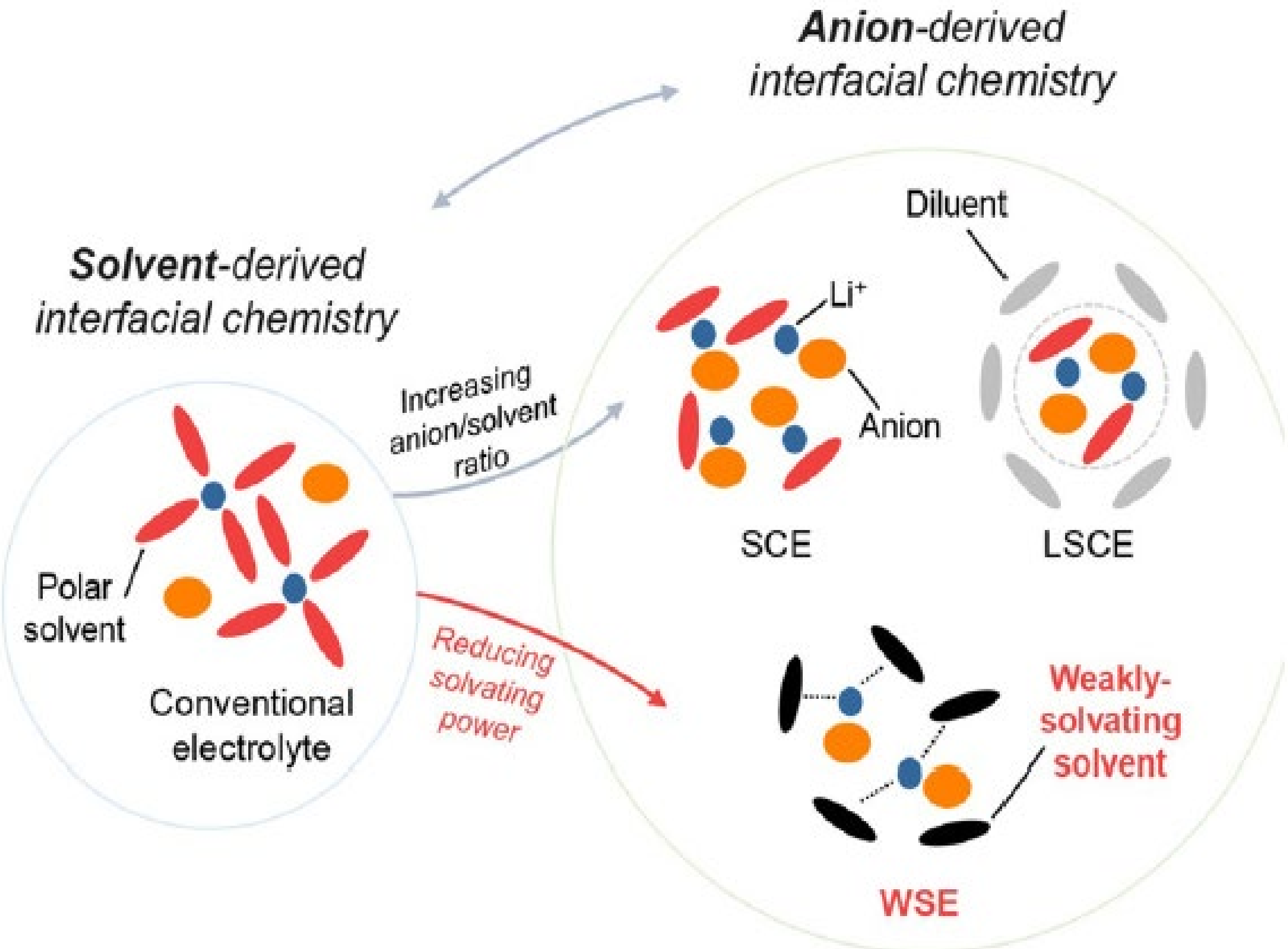


Limitations for Li^+ kinetics

- Tight solvation shell surrounding Li^+ in solution
- Presenting an intrinsically high desolvation barrier
- High freezing (melting) point (36 °C)

J. Electrochem. Soc., **2014**, 161, A1415-1421

EC-free + Anion-derived Solvation Structure



* **SCE:** Superconcentrated Electrolyte
LSCE: Localized Superconcentrated Electrolyte
WSE: Weakly Solvating Electrolyte

Angew. Chem., **2021**, 133, 4136-4143

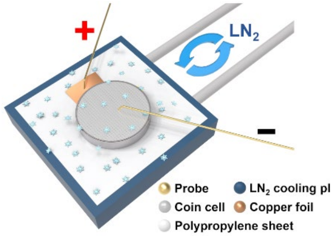
Solution to Electrolyte Issues

Approach 1 - Cyclopentyl Methyl Ether (CPME) based WSE

Approach 2 - Tetrahydrofuran (THF) based SCE

Solution to Battery evaluation system issue

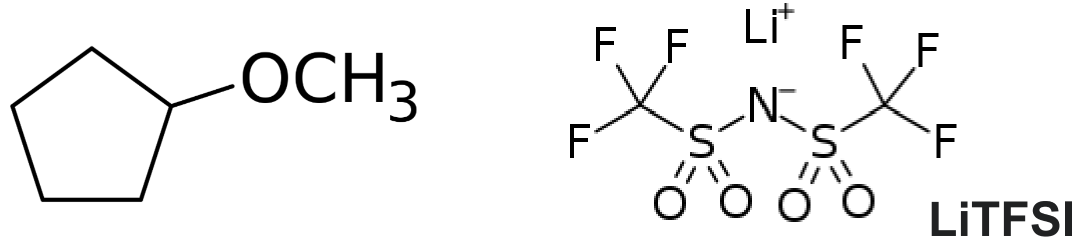
Purdue's Ultra Low Temperature Test Facility



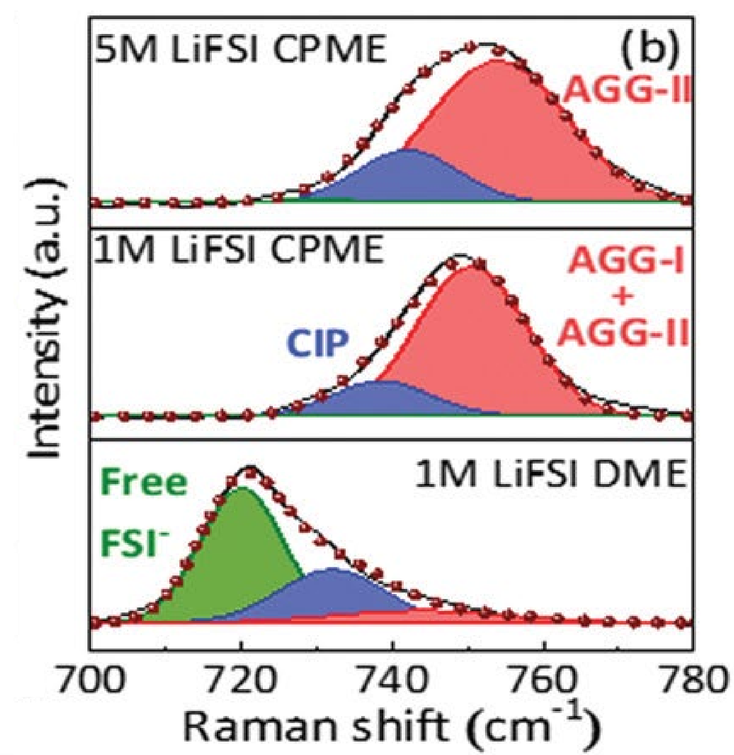
Coin cell

3 cm x 3 cm Pouch cell

Approach 1- Cyclopentyl Methyl Ether (CPME) based WSE

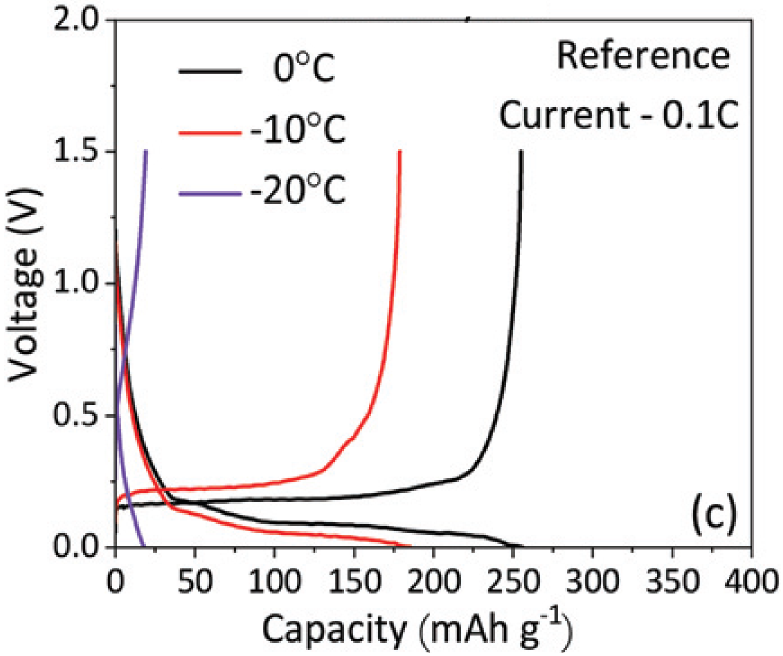


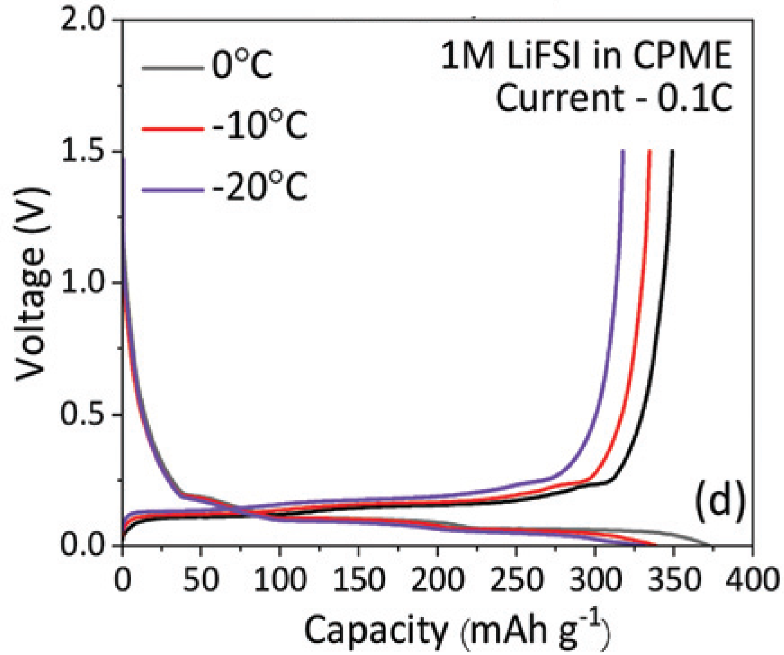
- CPME (B.P: 106 °C and M.P: -140 °C)
- High solubility of the salt (7M)
- Environmentally safe and economically feasible CPME solvent
- Unique solvation structure consisting of CIPs and AGGs
- AGG-I → An FSI^- bonded with 2 Li^+, AGG-II → An FSI^- bonded with 3 Li^+



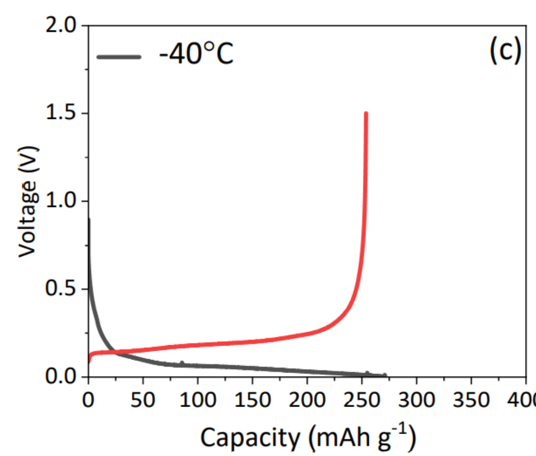
Pol et al. Chem. Commun. **2022**, 58, 5124

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.

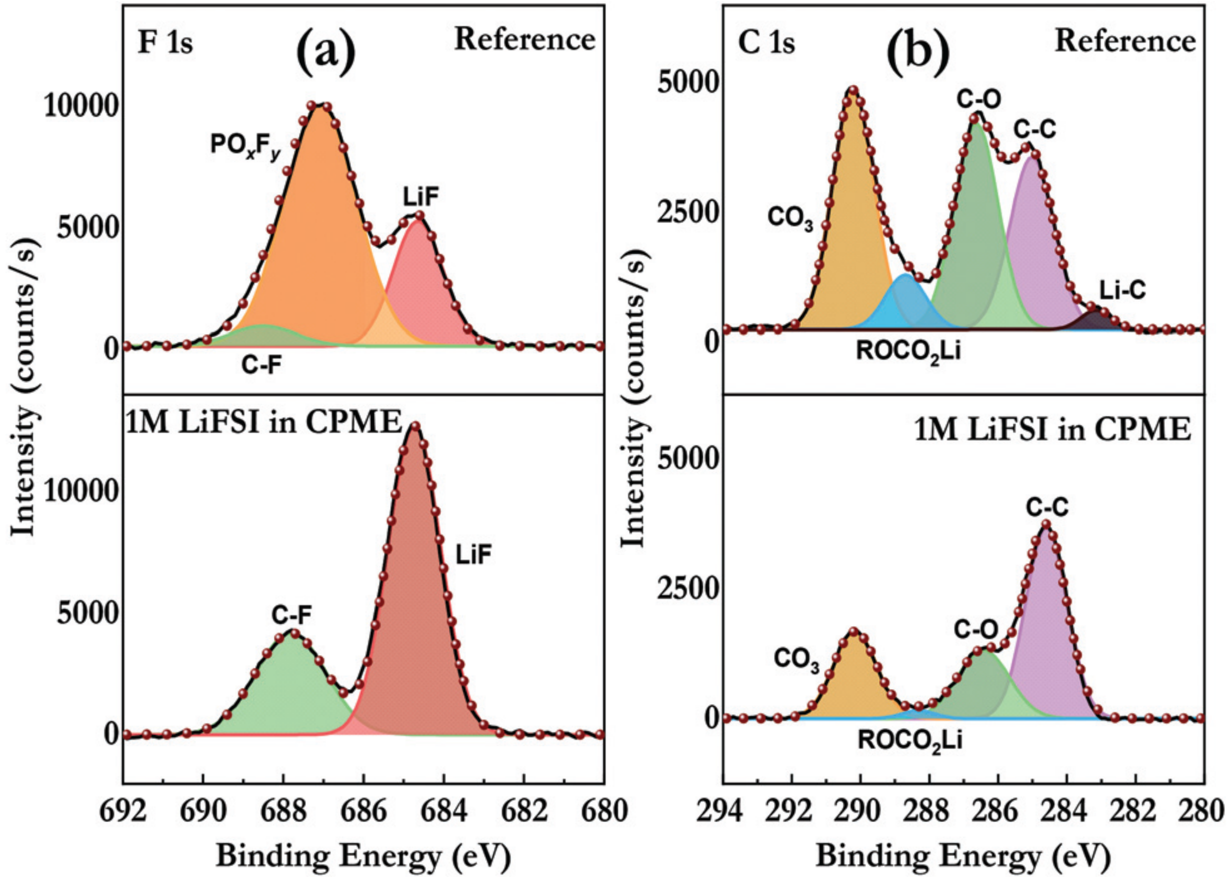


Pol et al. Chem. Commun. **2022**, 58, 5124

Why Enhanced Low Temperature Electrochemical Performance?

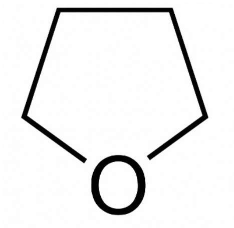
- Graphite||Li cell in the CPME based WSE

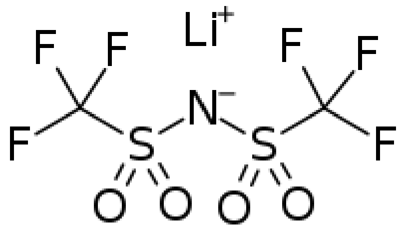
XPS analysis for SEI



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

Approach 2 - Tetrahydrofuran (THF) based SCE



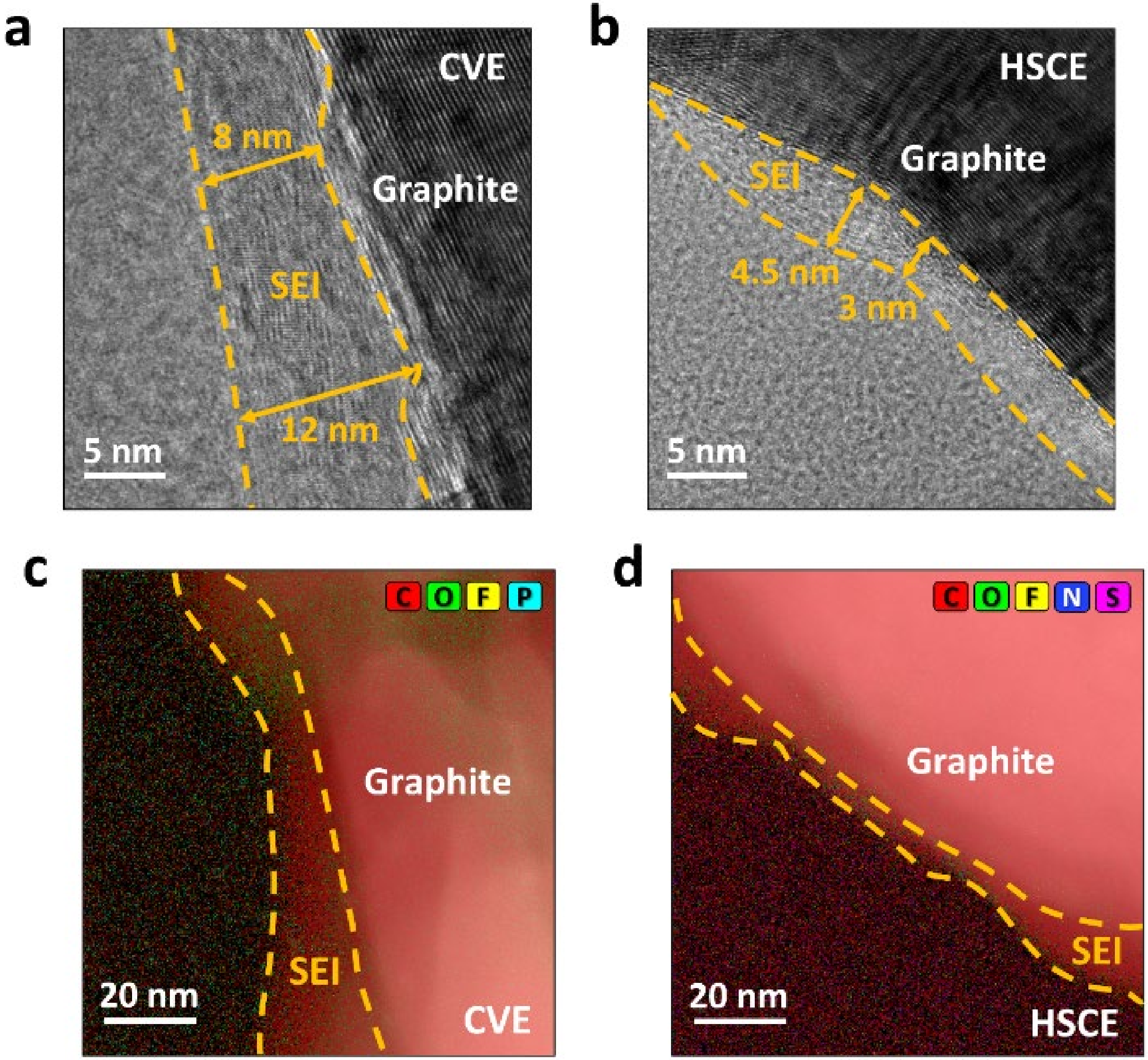


LiTFSI

- Low freezing (melting) point of THF (-109 ℃),
- Low viscosity (0.53 cP)
- Acceptable dielectric constant (7.5)

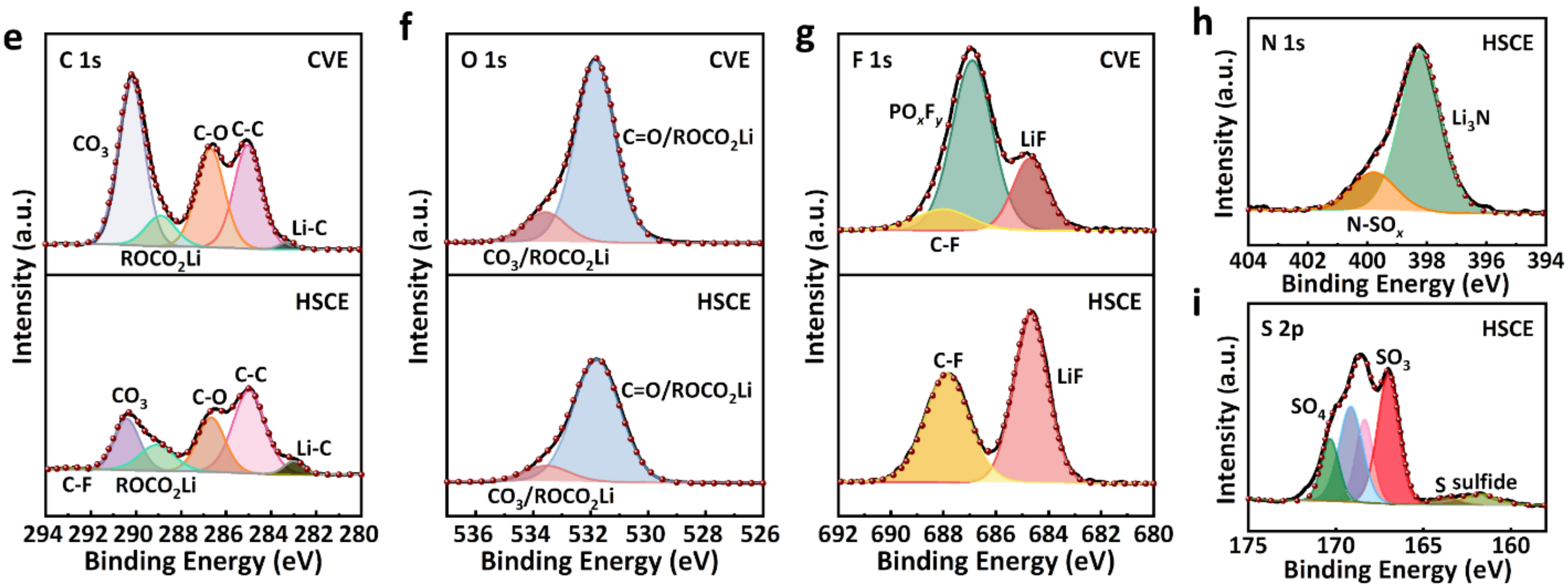
THF based SCE

* CVE: conventional electrolyte (1M $LiPF_6$ EC/DEC (1:1 v/v))
HSCE: high salt concentration electrolyte (5M LiFSI THF)



- Thinner SEI layer (3~4.5 nm)
- Lower resistance and facile Li^+ transport

Mechanism with XPS on SEI layer



- FSI^- decomposition (Anion derived SEI)

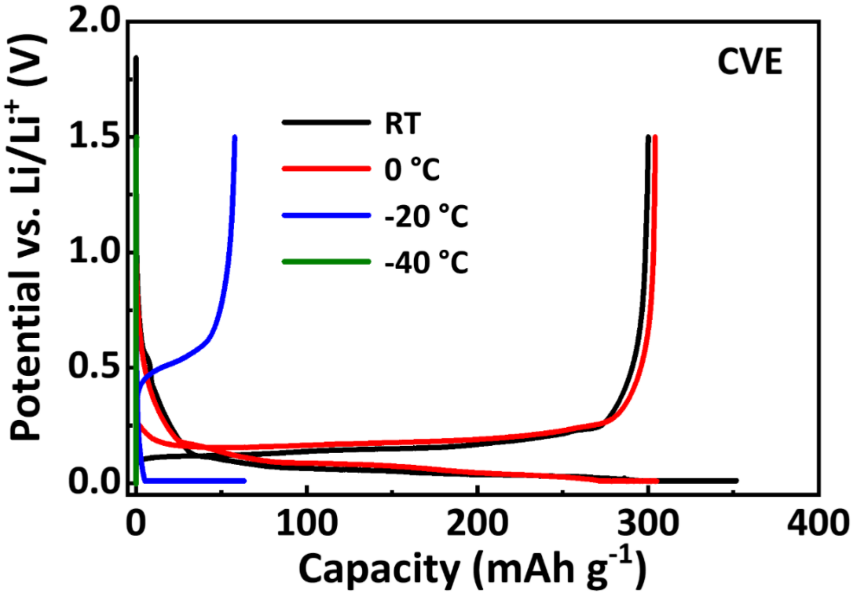
→ Organic less and inorganic rich SEI (LiF, Li_3N, and Li_2S)

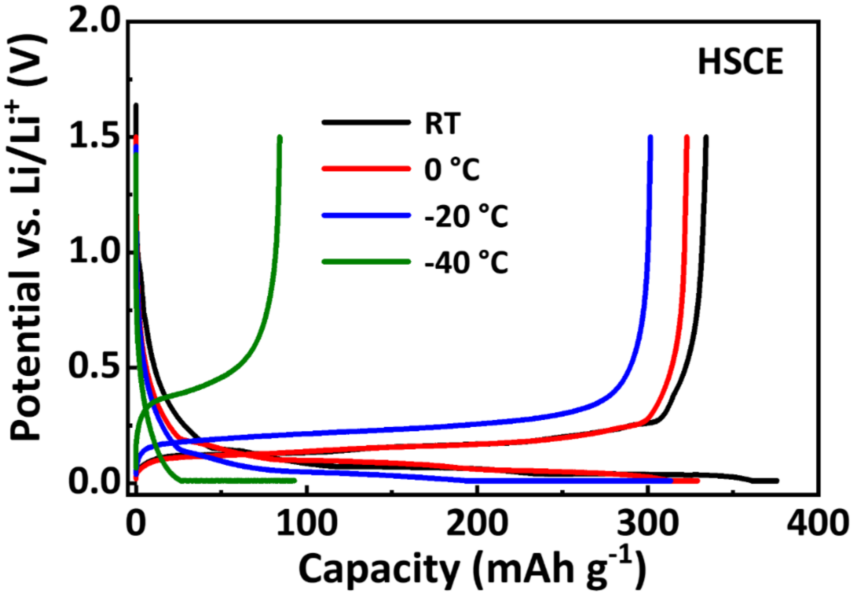
→ Stability improvement and rapid reaction kinetics at the electrolyte-electrode interfacial region

Pol et al. *ACS Appl. Mater.*, 2022, *14* (37), 41934.

Low Temperature Electrochemical Performance

Graphite||Li

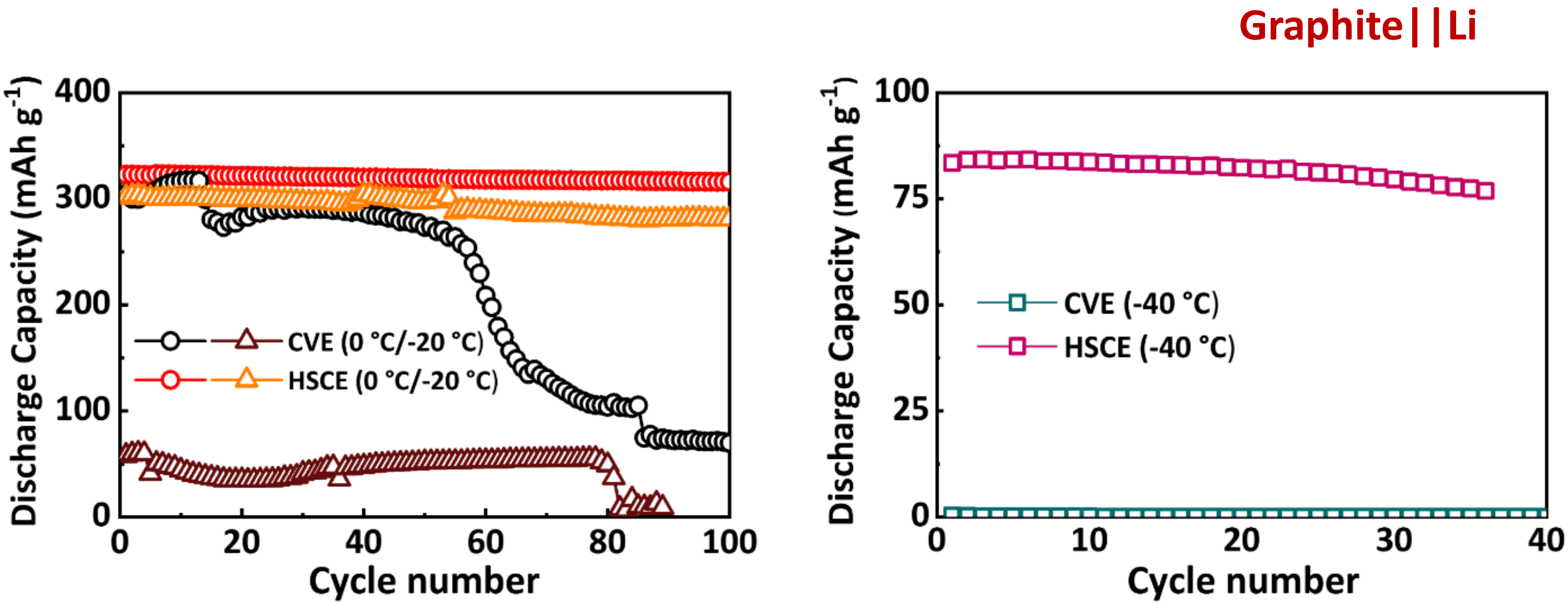




- Enhanced subzero temperature (0 to -40 °C) performance
- 330 mAh g^{-1} (RT), 300 mAh g^{-1} (-20 °C), 84 mAh g^{-1} (-40 °C)

Pol et al. *ACS Appl. Mater.,* 2022, *14* (37), 41934.

Enhanced Low Temperature Performance



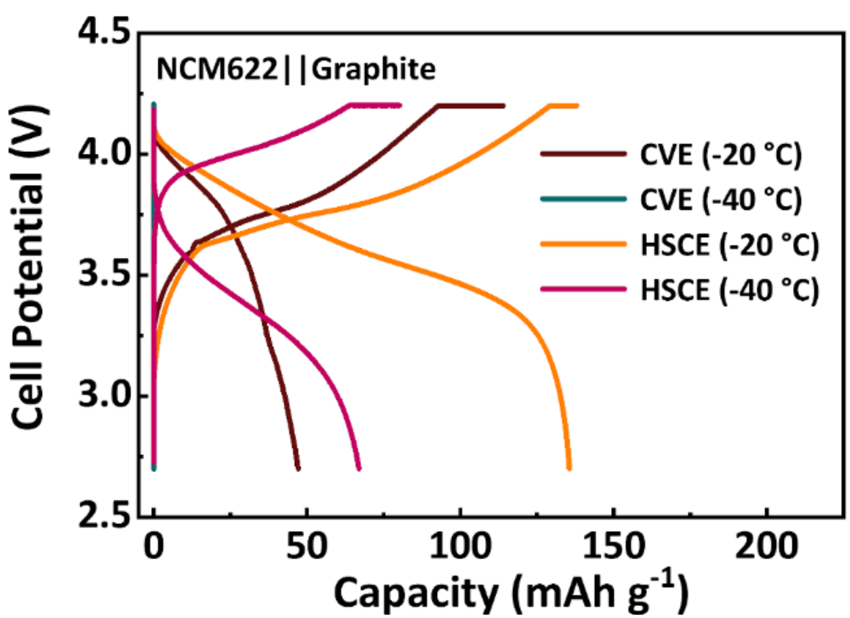
- Enhanced subzero temperature (-40 °C) performance
- Graphite||Li half-cell with THF based SCE- promising long-term cycling

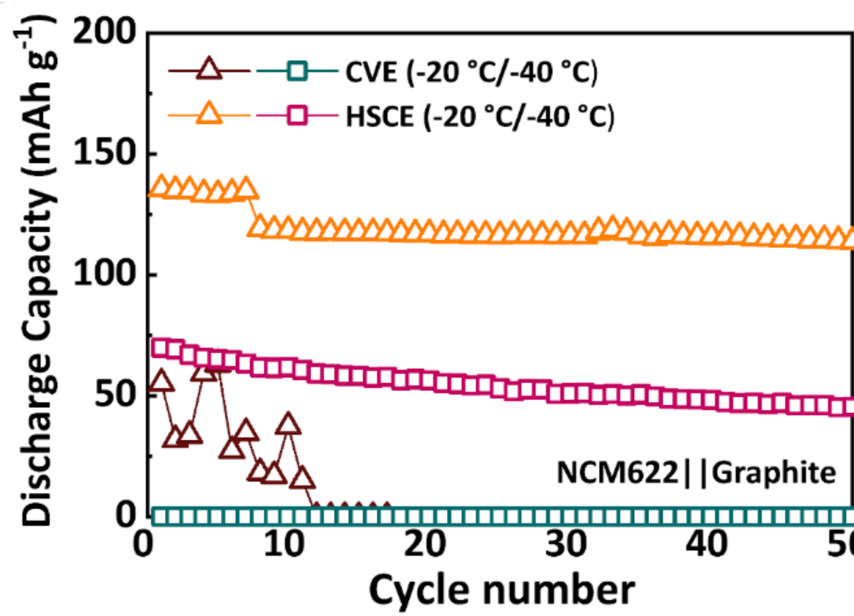
Pol et al. *ACS Appl. Mater.*, 2022, *14* (37), 41934.

Full Cell: Enhanced Low Temperature Performance

- CVE: conventional electrolyte (1M $LiPF_6$ EC/DEC (1:1 v/v))
- HSCE: high salt concentration electrolyte (5M LiFSI THF)

NCM622||Graphite





- NCM622||Graphite full-cell with THF based SCE (2.8-4.2 V)

→ 161 mAh g^{-1} (RT), 130 mAh g^{-1} (-20 °C), 70 mAh g^{-1} (-40 °C)

Pol et al. *ACS Appl. Mater.*, 2022, *14* (37), 41934.

Necessity of Reliable Battery Testing System

Extreme cold temperature environment

- Lunar surface (-173 to 127 °C) / International Space Station (-157 to 121 °C) / Polar regions of Earth (-60 to 0 °C)

Difficulty to simulate extreme cold climate for battery development

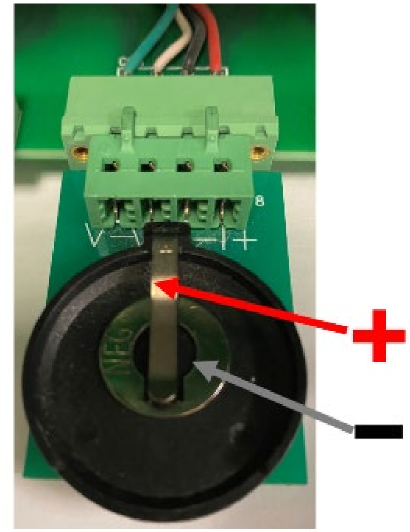
- It inhibits the ability to research, develop, and demonstrate potential battery technologies.

Current Standard Setup for Low Temperature Test

Environmental and battery chambers and coolers

Brand	Name	Lowest temperature [°C]	Technology	Cost [$]	LN_2 usage [L hr^{-1}]	Volume [L]
ESPEC	MC-812R	-85	Refrigeration	15 K	X	64
AES	SD-502	-70	Refrigeration	18 K	X	60
AES	ZBD-108	-190	LN_2	25 K	30	226
Thermotron	SM-8-8200	-68	Refrigeration	25 K	X	226
LNEYA	GX-A028N	-100	Refrigeration	15 K	X	280
TestEquity	3007-LN2	-150	LN_2	34 K	6.2	200
Purdue University system	-	-190	LN_2	24 K	0.63	N/A

Limitations for Low Temperature Battery Testing



Expensive infrastructure is required

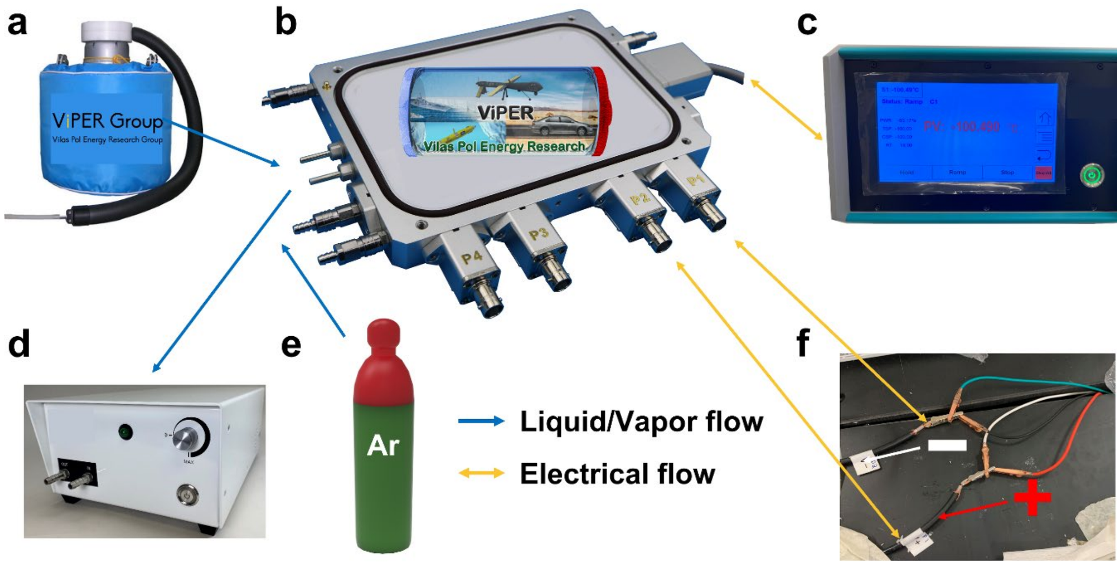
It is difficult to create a cooling system capable of -100 °C or below without LN_2.

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

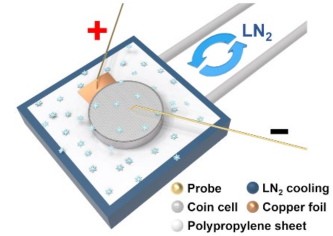
Resistance issue on commercial cell holder at low temperature

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



200 L liquid N_2 tank



Coin cell

3 cm x 3 cm Pouch cell

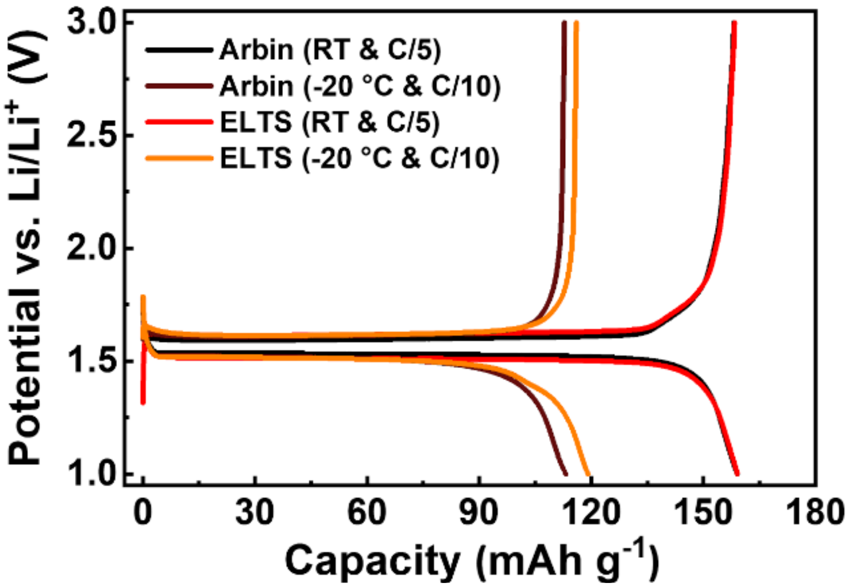
Affordable cost and accurate/reliable electrical measurement

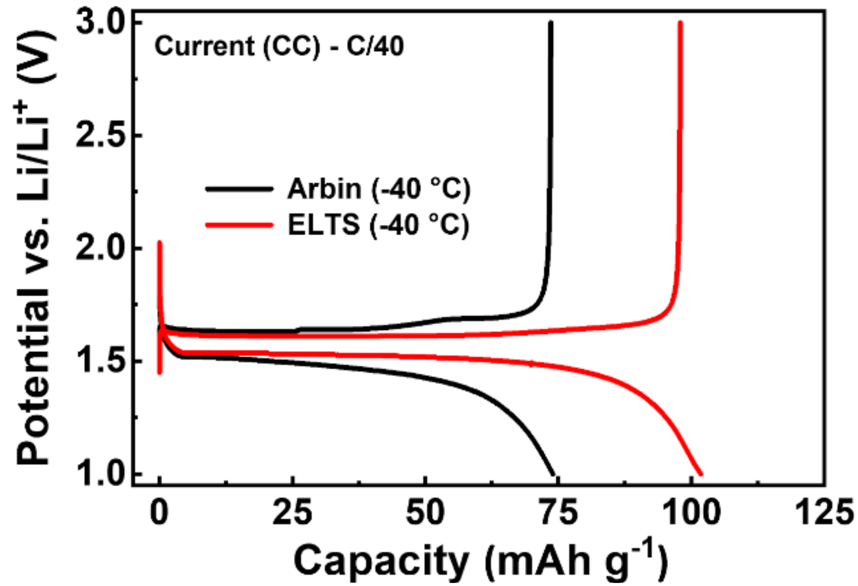
- Available temperature → Up to -175 °C, Simulating extremely cold temperature environment (Lunar, Space, High Altitude, and Polar regions)
- Efficient LN_2 flow to minimize LN_2 usage (0.63 L hr^{-1}),
- Suppressed frost buildup by Ar purging

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

Ultra Low Temperature Battery Testing

LTO||Li cell with CPME based WSE

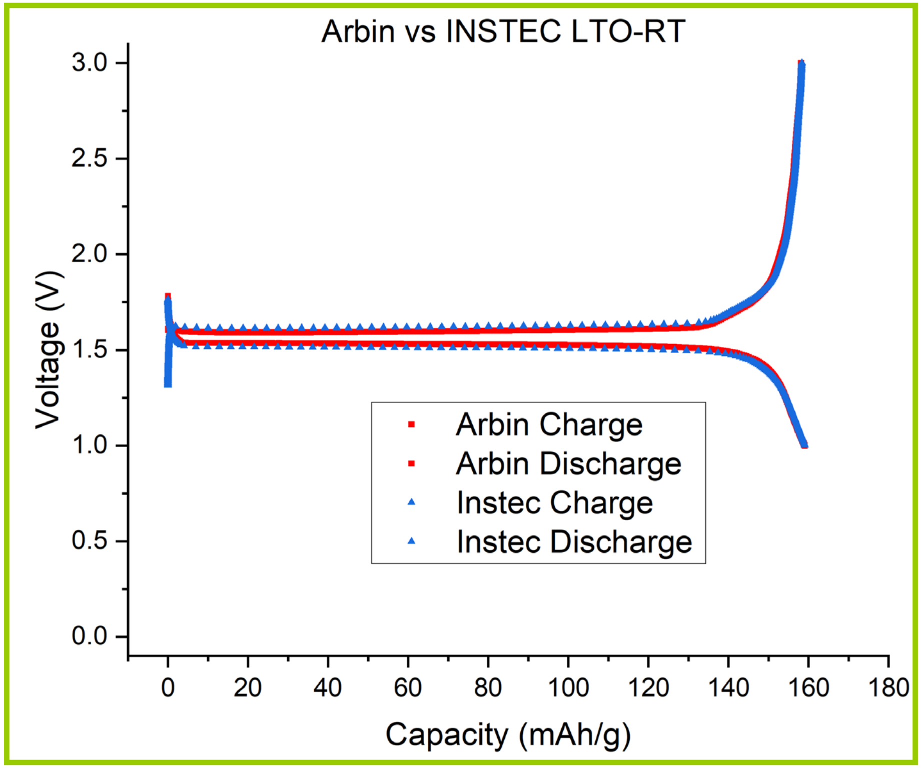


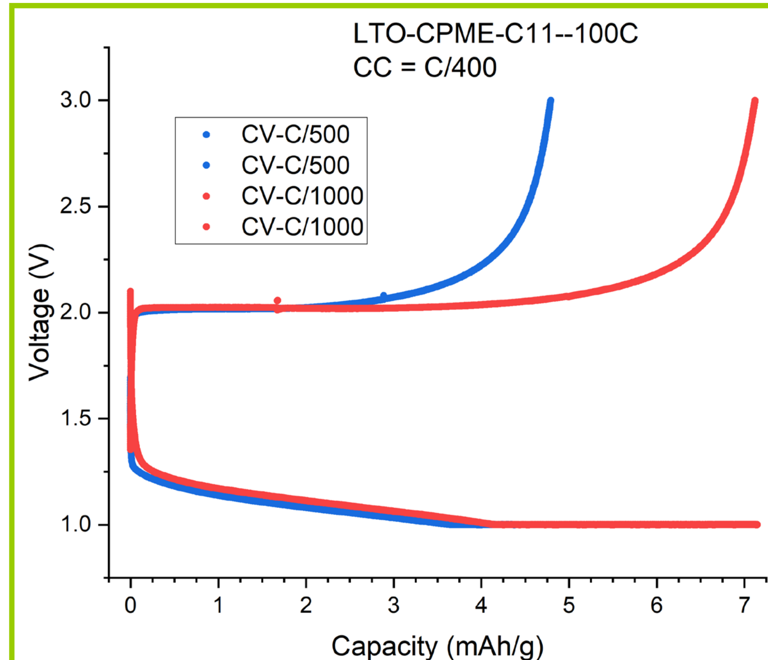


- Coin cell test in Arbin-ESPEC chamber (commercial) and our system
- Limitations in commercial cell holders (resistance issue at low temperatures)
  → Large deviation in voltage profiles below -40 °C

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

LTO anode INSTEC (-100 ºC) Cycling



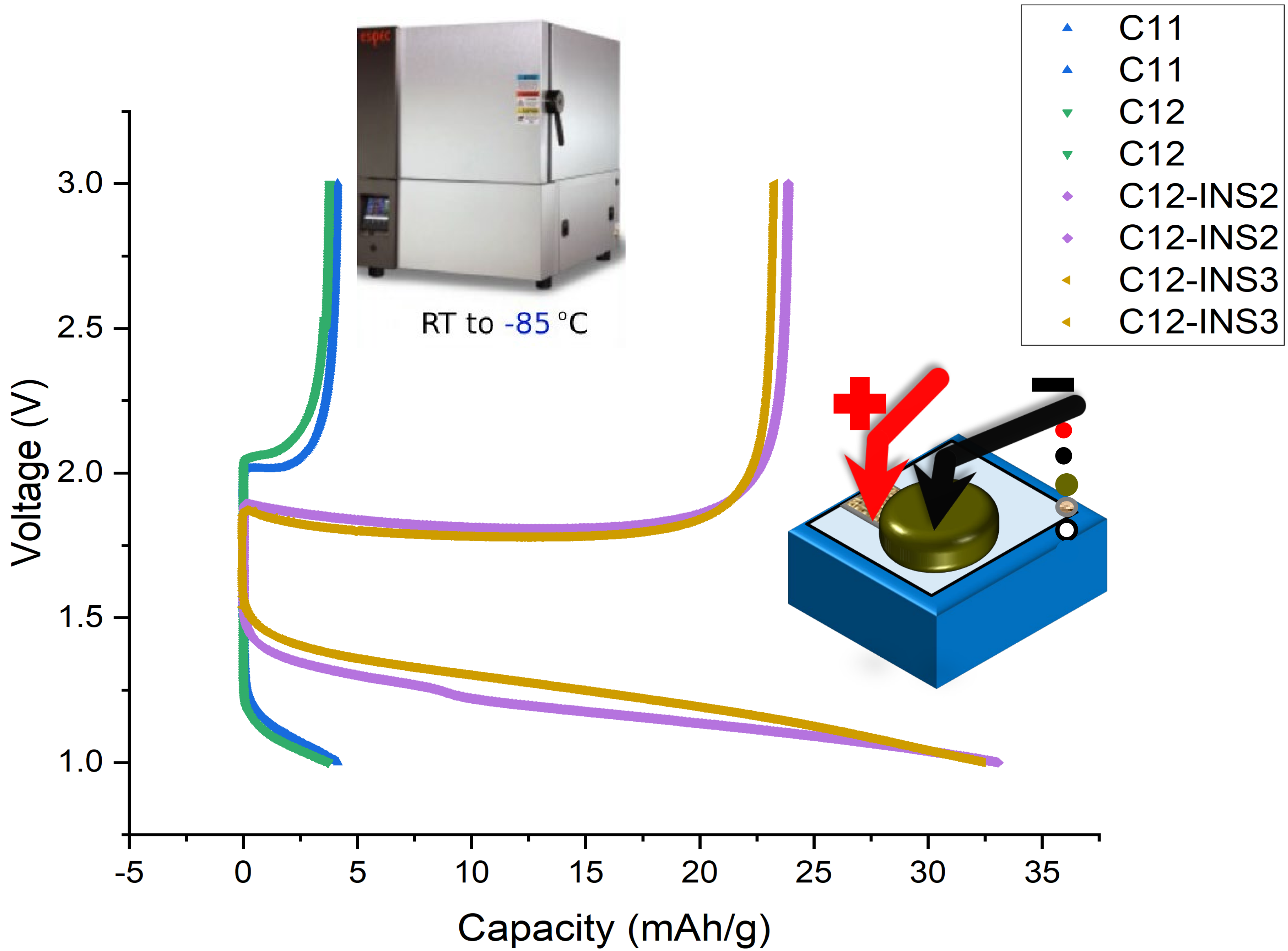


- $Li_4Ti_5O_{12}$ Spinel produces 160 mAh/g capacity at room temperature that is significantly reduced at -100 ºC.

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

Ultra-low Temperature Battery Cycling (-60 ºC)

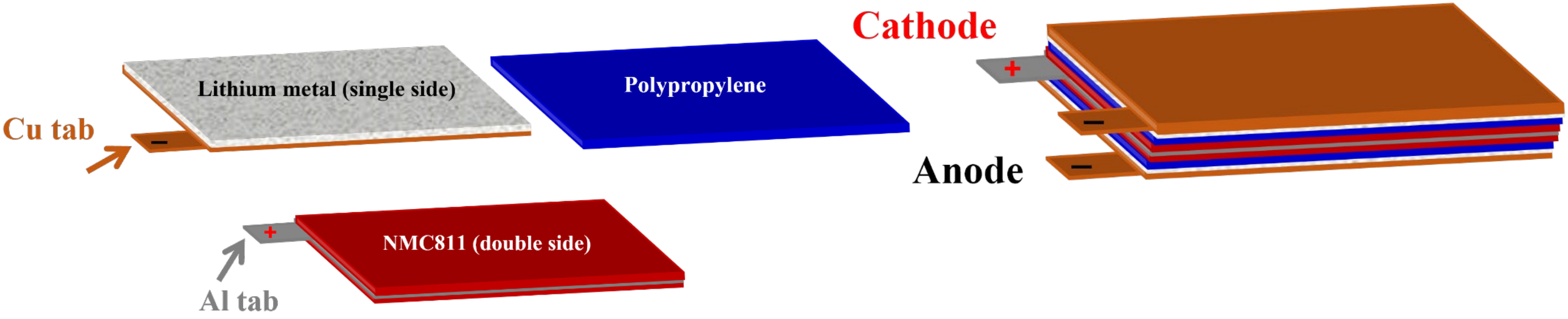
-



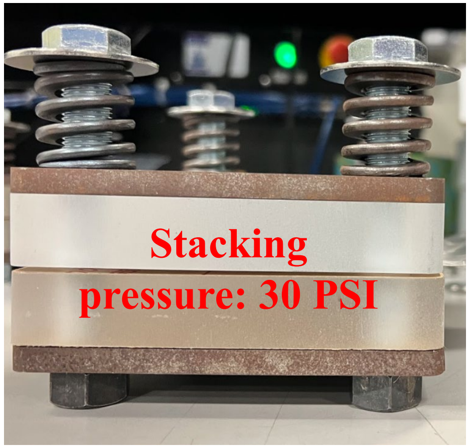
Pouch Cell Preparation

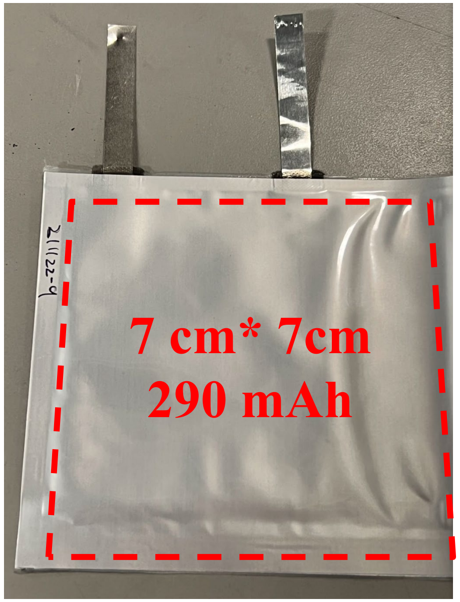
Lithium Metal Battery Pouch Cell's Specification and Schematics

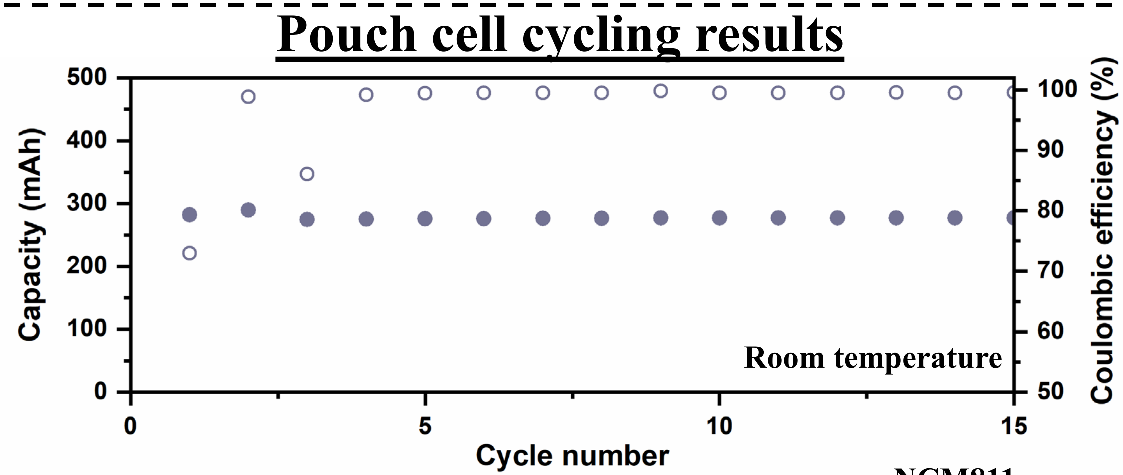
Anode	: Lithium Metal Foil (2S)
Cathode	: NMC811 (1D)
Thickness	: 65 μm (LM)/ 140 μm (NMC811)
Separator	: Polypropylene
Electrode Area	: 7 X 7 cm^2
Cell capacity	: ~300 mAh
Cell voltage	: 3.8 V



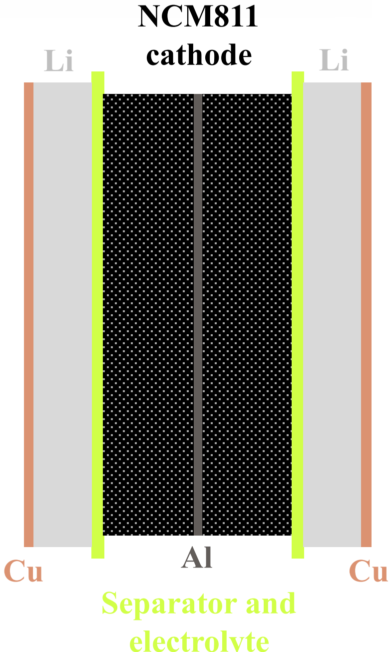
Pouch Cell Electrochemical Performance





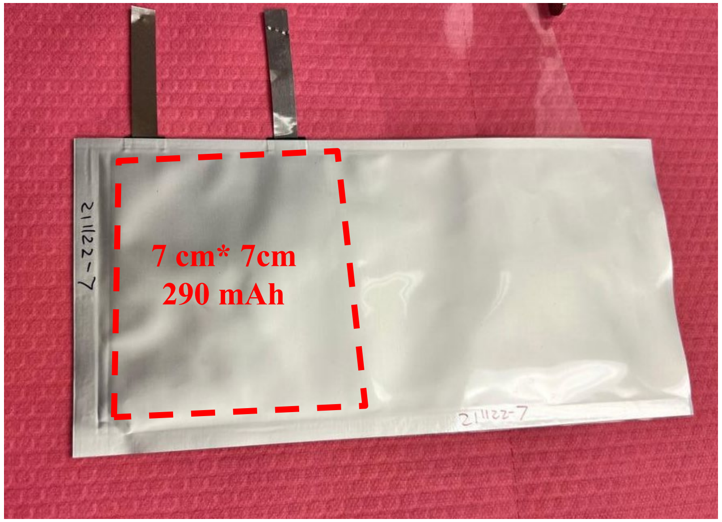


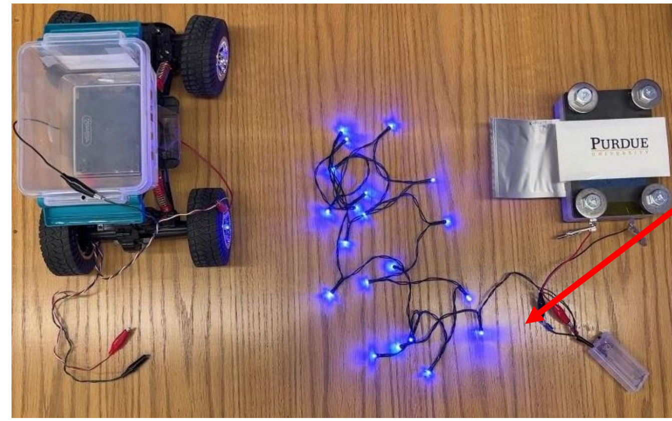
Larger-scale pouch cells (290 mAh) were prepared to demonstrate the cyclability of LMB with designed ether-based electrolyte



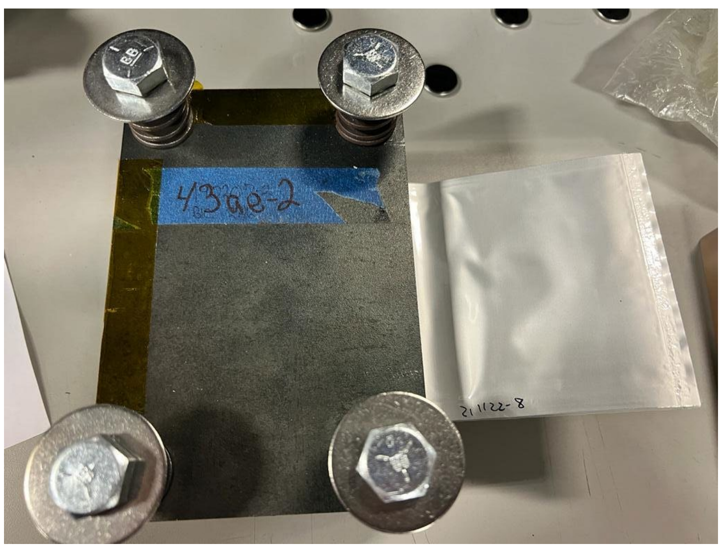
65 um Li; 3 mAh/cm^2 cathode, E/C ratio = 5 g/Ah

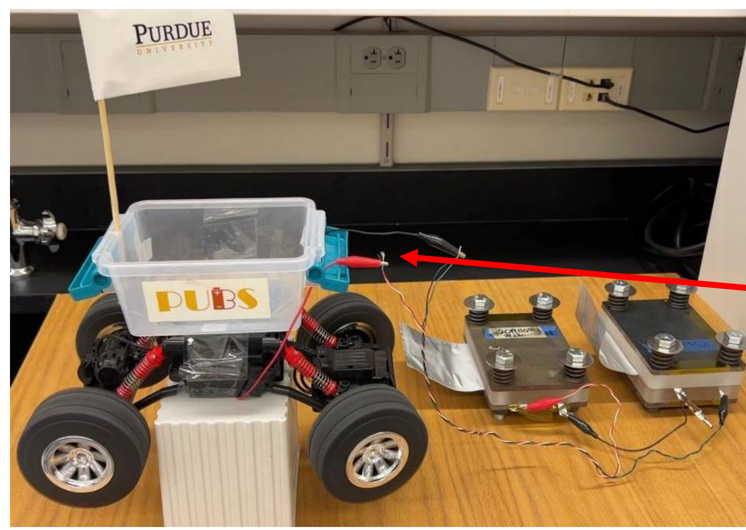
Room Temperature Prototype Demonstration





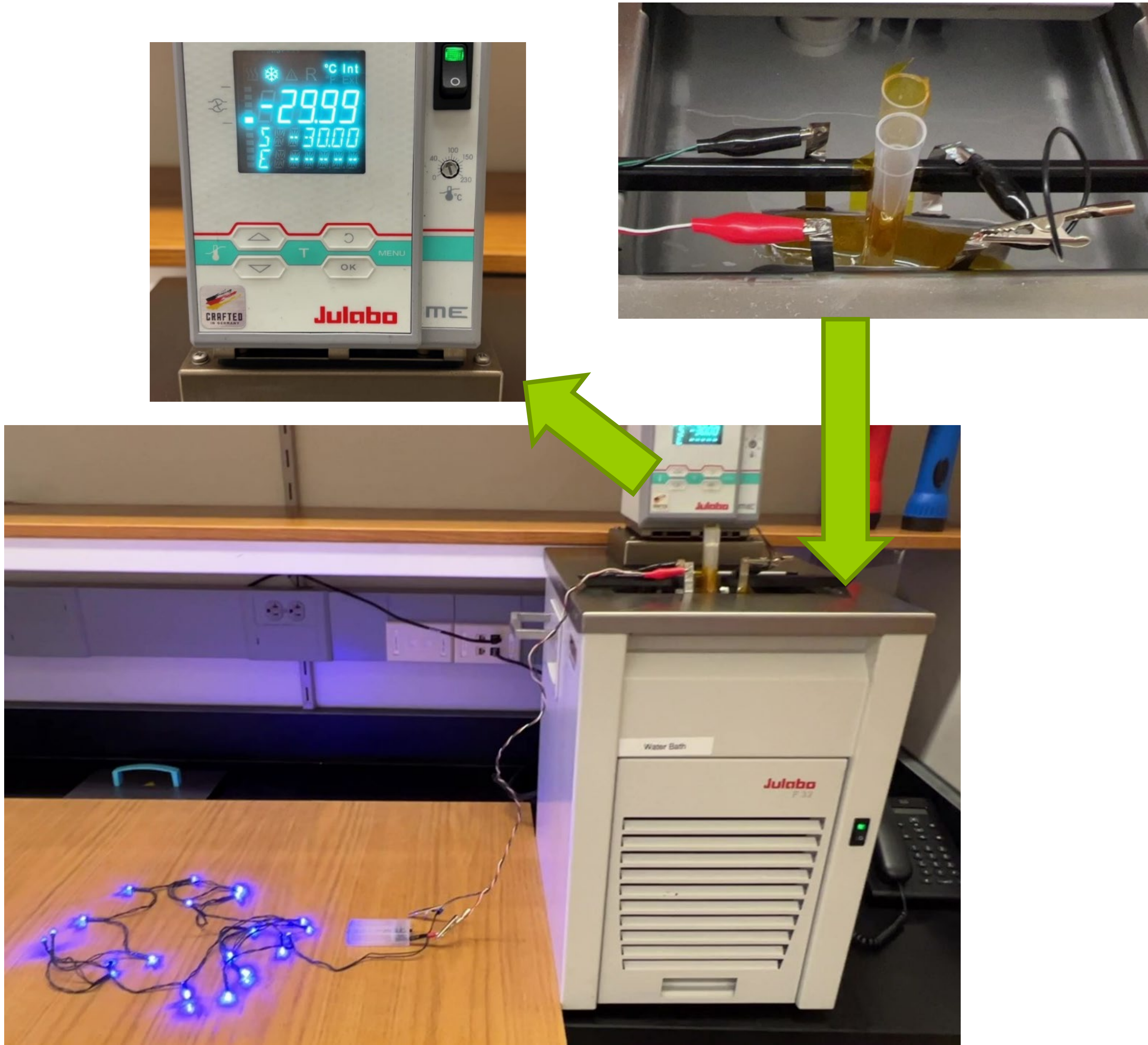
15 mA lights





300 mA toy car

Pouch Cell Operating at -30 ^{o}C



OFFICIAL ATTEMPT

Record Title: "Purdue University's Advanced Lithium-ion Battery Charging and Discharging at Lowest (-100 Degree Celsius) Temperature

Record Holder Name: Vilas Pol Energy Research (ViPER) Group, Davidson School of Chemical Engineering, Purdue University, IN 47907, USA

Date/time : Dec. 21, 2022 @ 2pm

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

Summary

- Low temperature batteries are showing huge promise via electrolyte designing and tailoring.

- Solvent, salt and concentration of electrolyte modifications could design extreme temperature batteries

- We have developed extreme low temperature (-195 ^{o}C) battery testing facility for coin and pouch cells.

- Extreme cold power generation strategies are outlined.

Acknowledgement

NAVSEA WARFARE CENTERS CRANE

DEPARTMENT OF THE NAVY
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Science & Technology

Naval Enterprise Partnership
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Teaming with Universities for National Excellence

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