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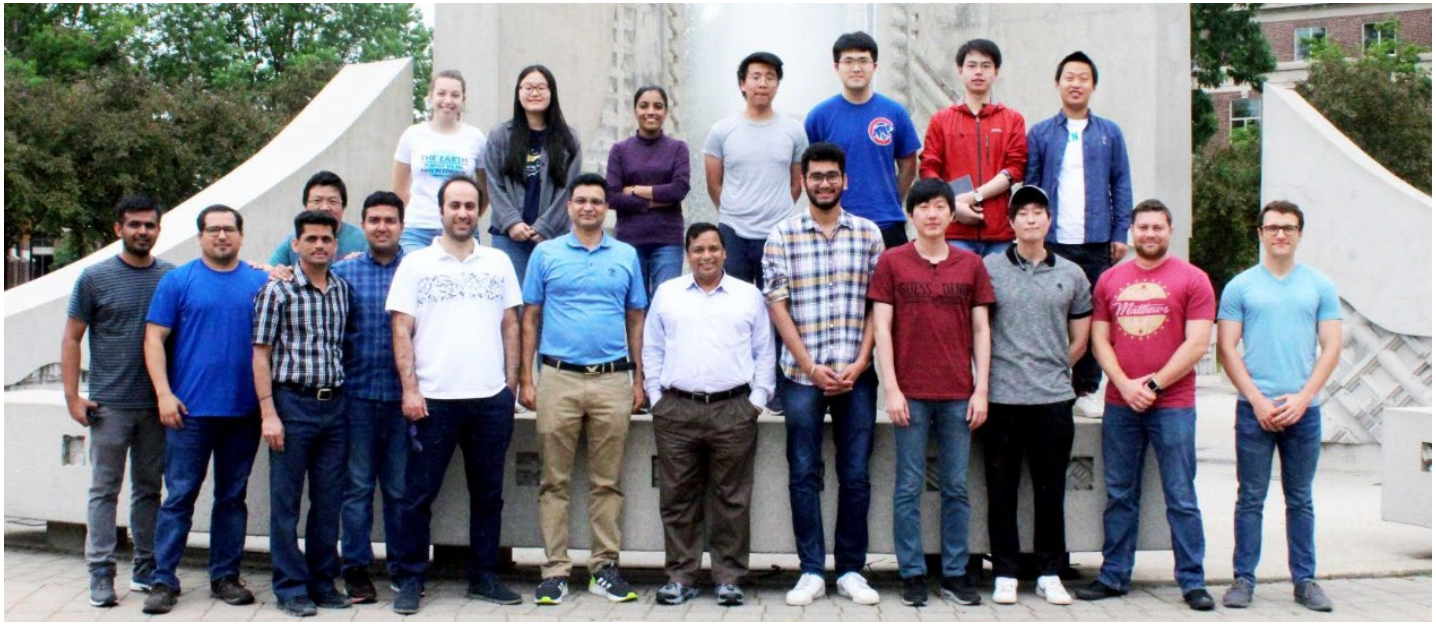
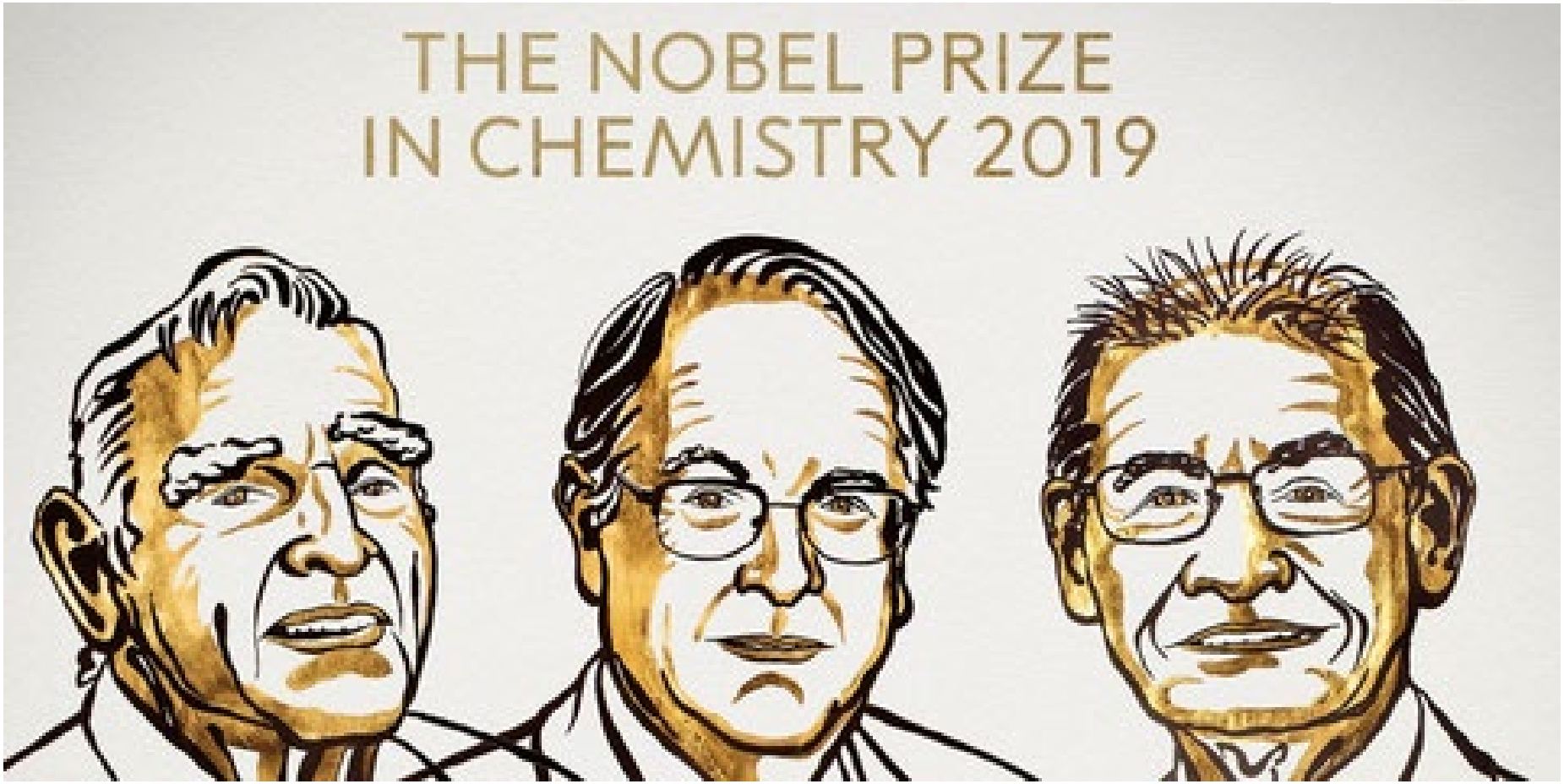
ViPER
Vilas Pol Energy Research

Li-ion Batteries: Thermally Safe and Early Sensing

Vilas G. Pol



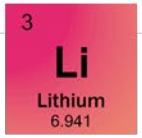
PURDUE UNIVERSITY | Purdue Process Safety and Assurance Center

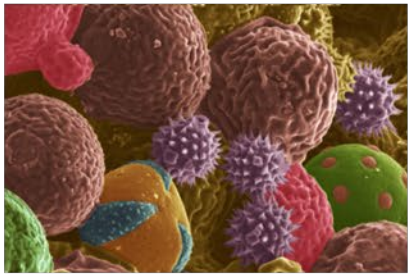


John B. Goodenough, M. Stanley Whittingham, Akira Yoshino

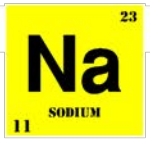
Purdue's Research on Battery Technologies

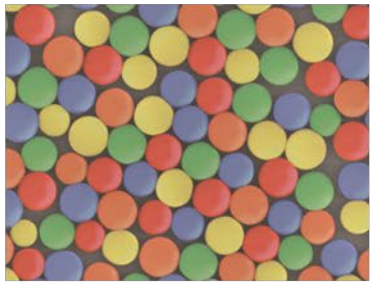
Lithium-ion





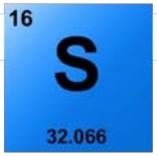
Sodium ion

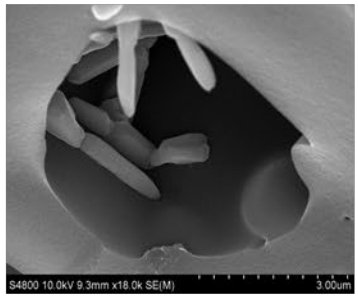


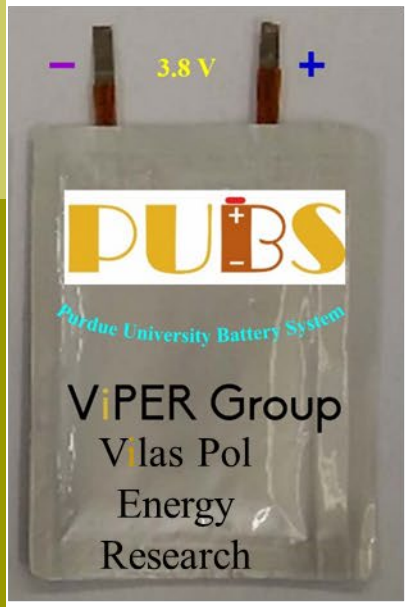


Potassium ion

Li-S/Solid state







Interest: Batteries for Renewable Energy Storage and their Safety

225 Peer-reviewed publications and 30 US Patents/applications

Battery Research Challenges

- **Cost**

  Current projected cost (25 kW battery) ~ $1000

  - Target cost (25 kW battery) ~ $500

New

- **Safety**

  Inherently safe batteries needed

  - Overcharge protection circuitry expensive

- **Life**

  Current technology ~ 5 to 10 years

  - Target ~ 15 years

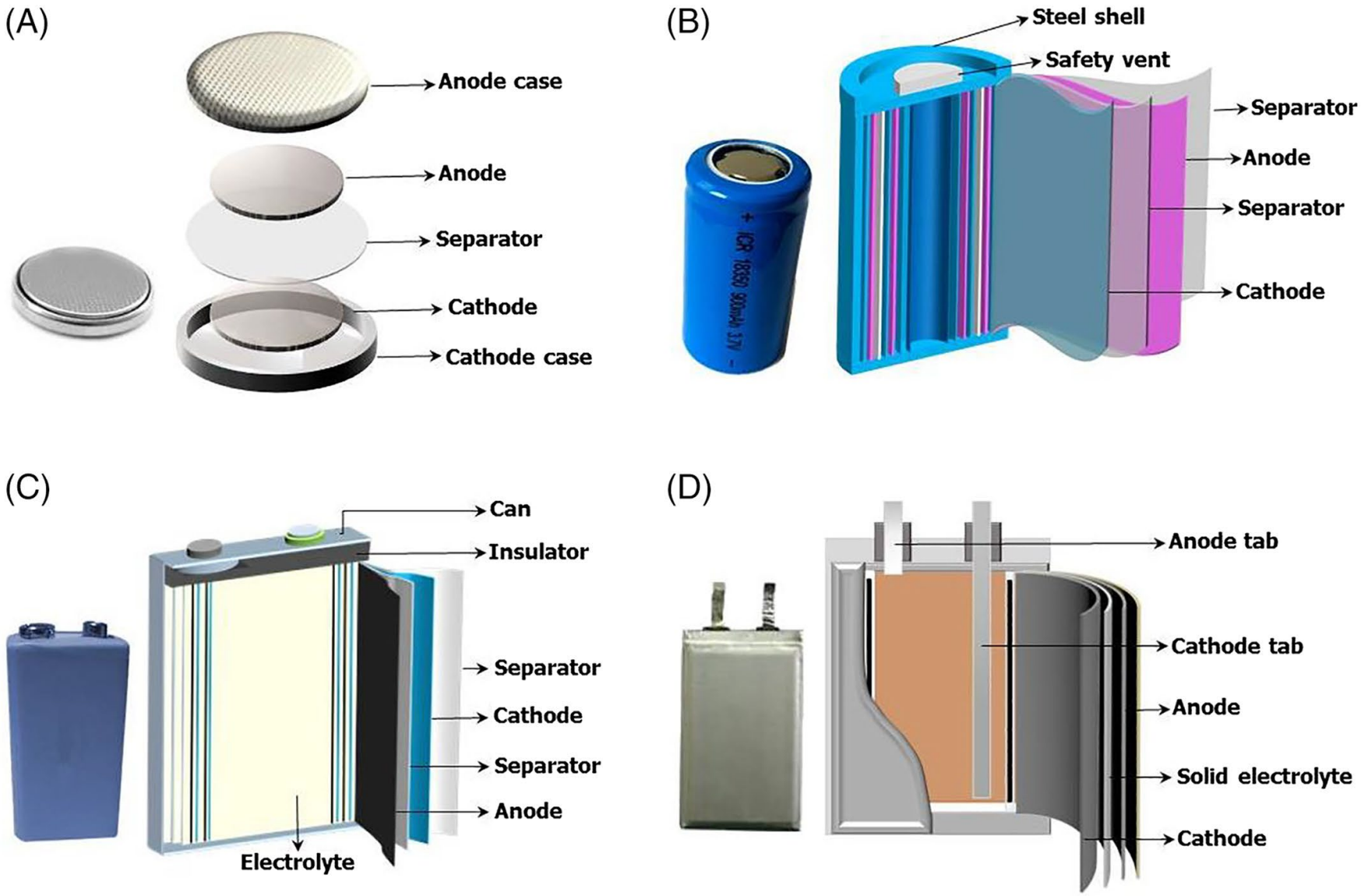
- **Low Temperature Performance**

  Current technology ~ Sluggish < 0 ºC

  - Target ~ -30 ºC (cold cranking)

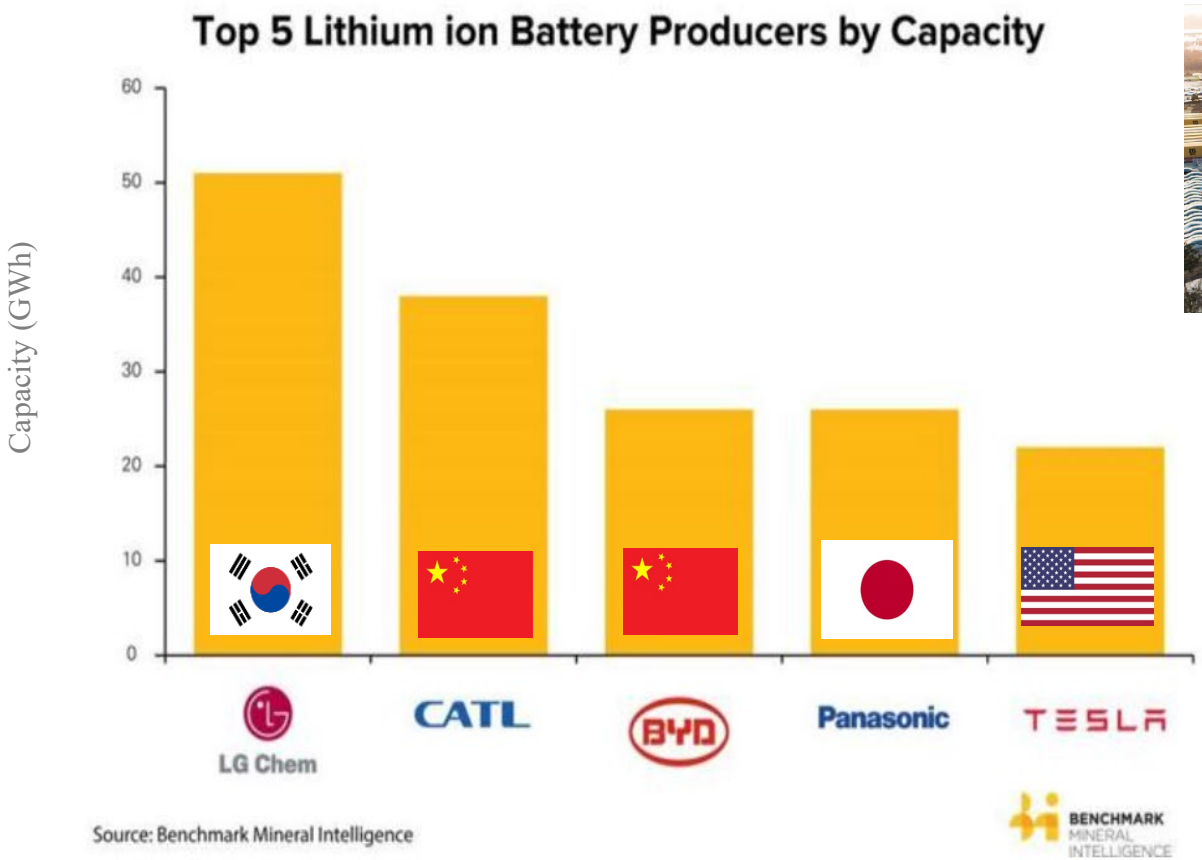
John B. Goodenough *et al.*, *Chemistry of Materials* **(2010)** *22*, 587

Typical rechargeable battery configurations: A, coin, B, cylindrical, C, prismatic, and D, pouch shapes



https://onlinelibrary.wiley.com/doi/full/10.1002/inf2.12000

Production is increasing to meet demand



- Tesla Gigafactory in Nevada
  - 20 GWh production
  - Joint project with Panasonic
- Also Gigafactories in NY and Shanghai
- More factories planned

Safety Concerns of Lithium-ion Batteries

Boeing 787, Dec. 2014 (1)

Tesla Model S, Aug. 2016 (2)

Samsung Note 7, Sept. 2016 (3)

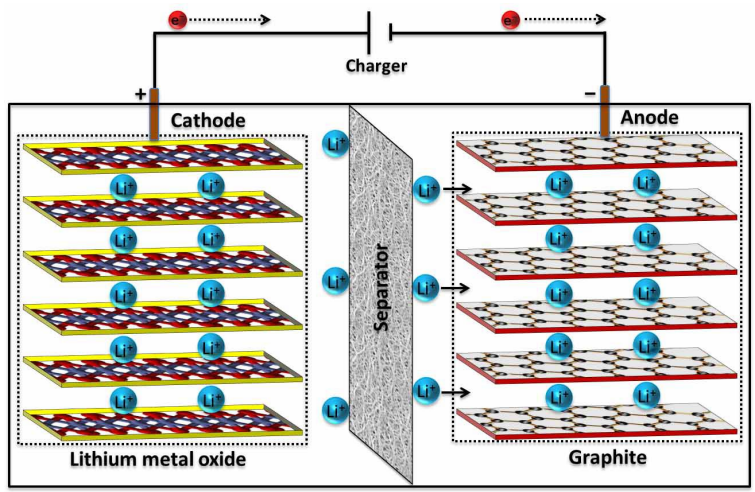
- LIBs dominate rechargeable energy storage market due to high energy density
- Safety incidents still occurring for mature Li-ion battery technology
- Susceptible to thermal runaway: can occur by overcharging, cell puncture, dendrites

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

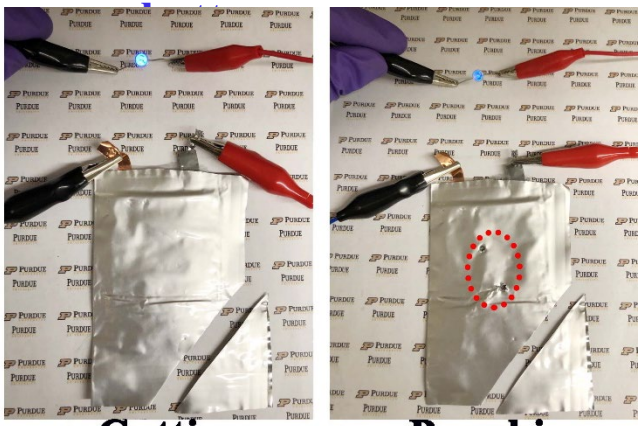


- Graphite: 372 mAh/g
- Li metal: 3840 mAh/g

Li-ion battery with liquid electrolytes

Energy density ~ 250 Wh/kg

Solid-state



Cutting **Punching**

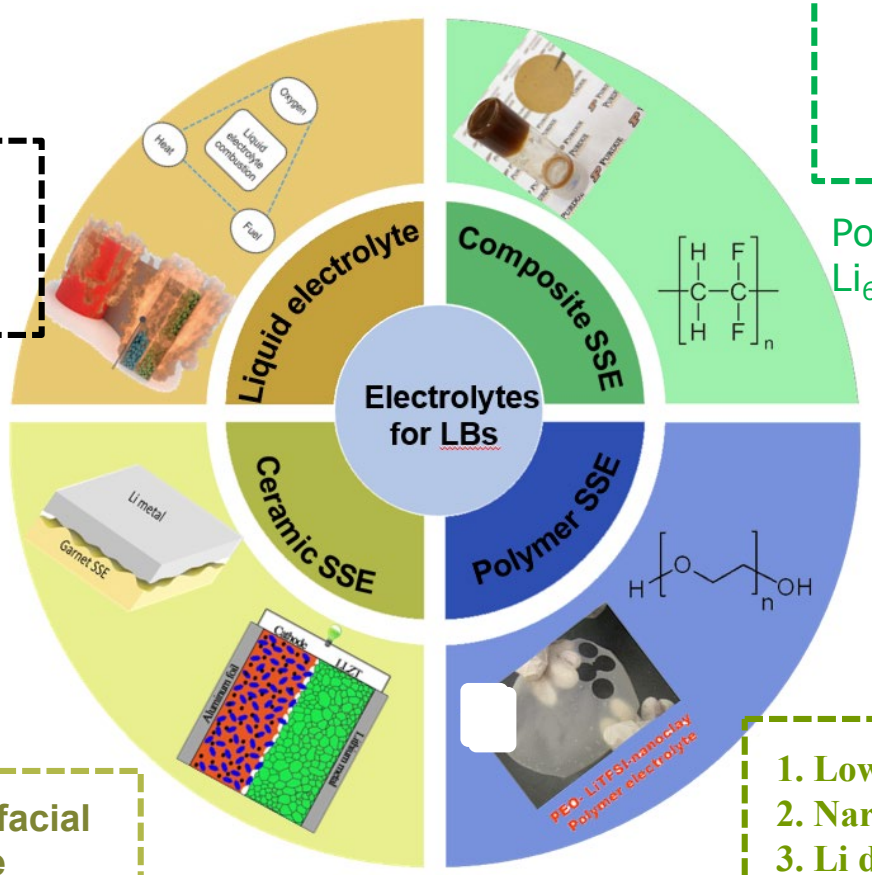
Energy density ~ 450 Wh/kg

Purdue's Advanced Technology

Our work

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

1. Flammable
2. Leak
3. Li dendrite



Polyvinylidene fluoride **(PVDF)**

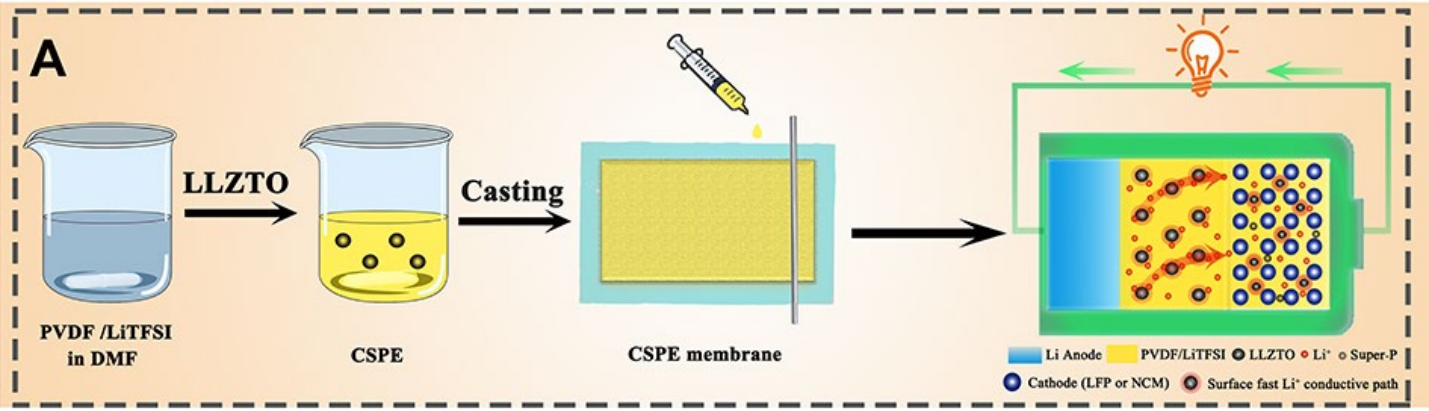
$Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ **(LLZTO)**

1. High interfacial resistance
2. Li dendrite

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

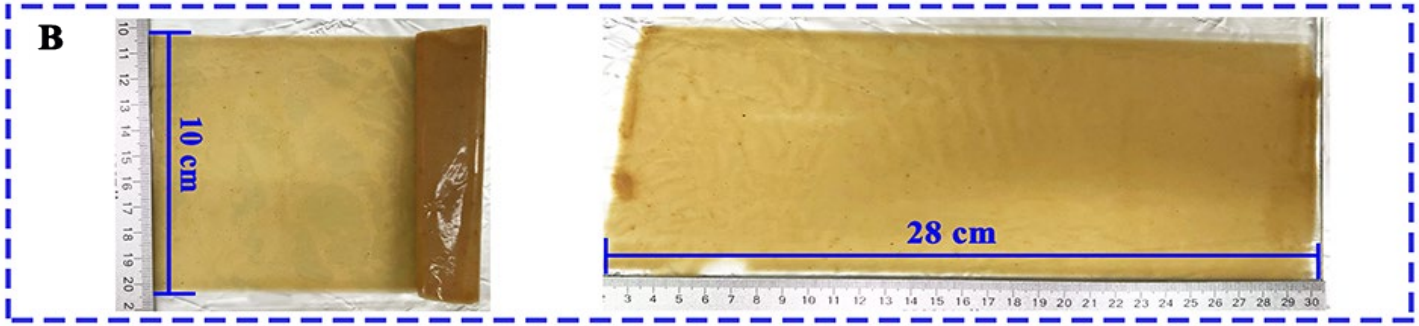
Poly(ethylene oxide) (PEO)

Scalable Fabrication of SS Composite Electrolyte



The synthesis of composite solid polymer electrolyte

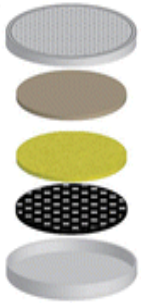
- ✓ **Facile synthesis**
- ✓ **Operation at room temperature**



Pictures of as-prepared composite solid polymer electrolyte

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

A scalable solid state battery



Anode shell

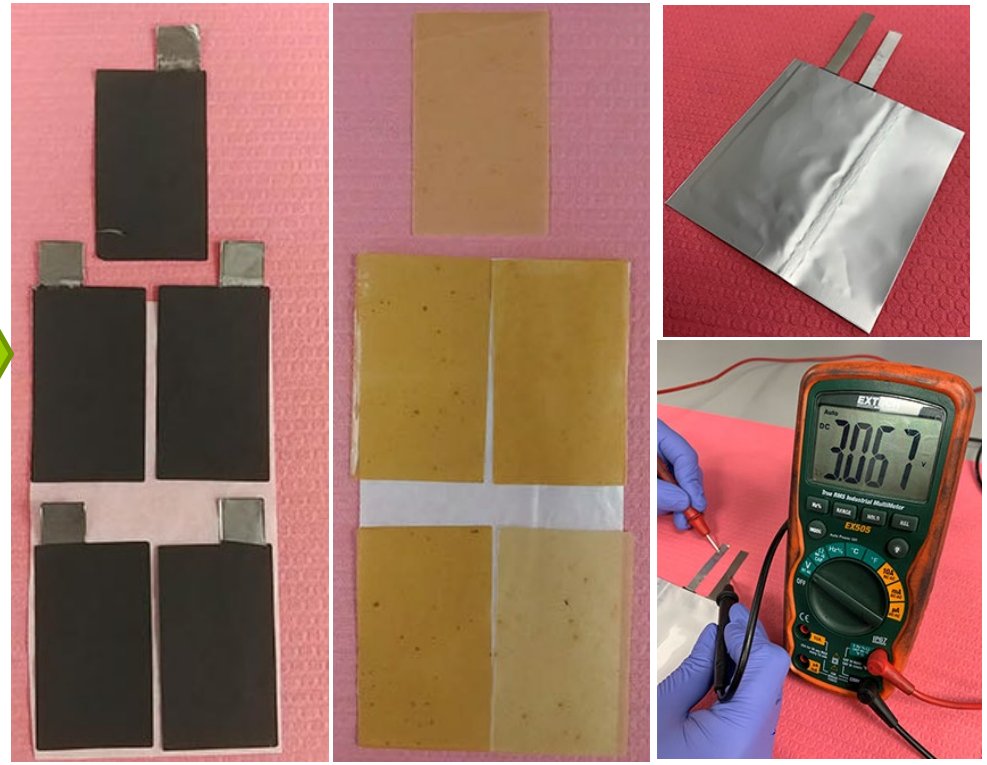
Li metal anode

Purdue's CSPE

Cathode

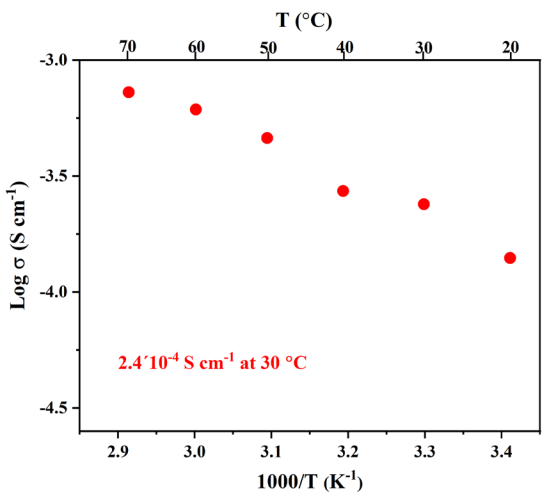
Cathode shell

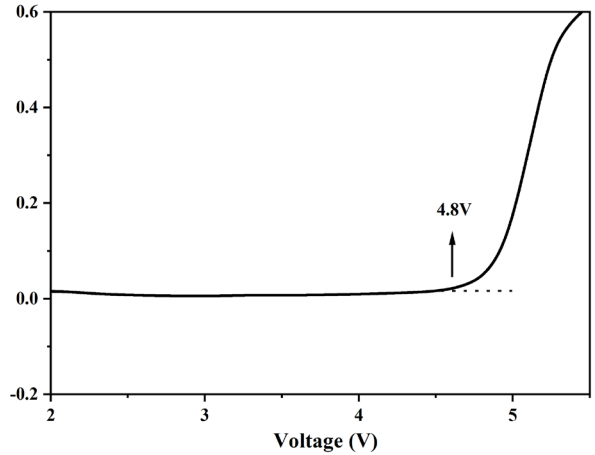
Small scale coin cell

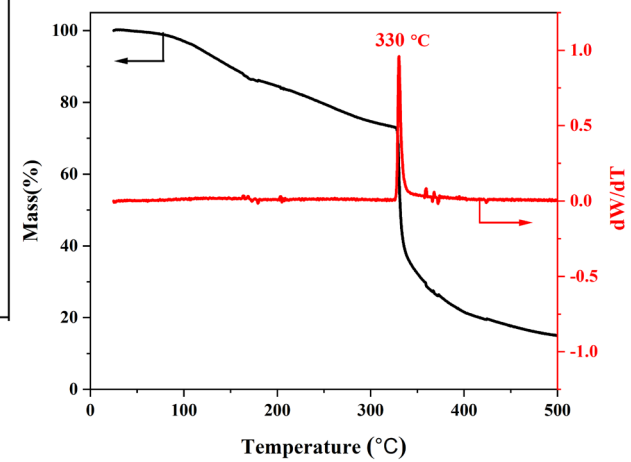


Large scale, single-layer pouch cell

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 °C)

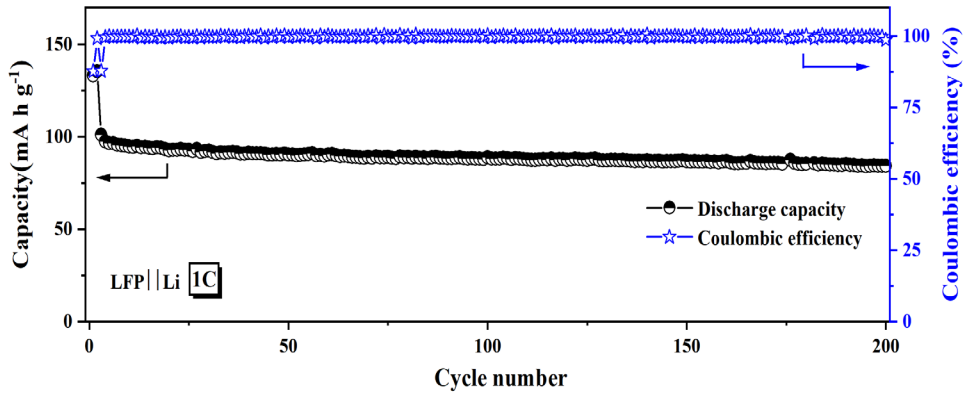
Purdue's Composite solid polymer electrolyte

VS

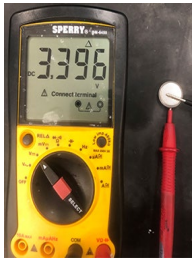
- × Low room-temperature ionic conductivity (10^{-7} -10^{-5} S cm^{-1})
- × Narrow voltage window (~ 3.8 V)
- × Inferior thermal stability (~ 230 °C)

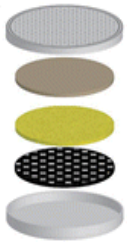
Typical PEO-based polymer electrolyte

Electrochemical Performance of Solid-state Full Cell



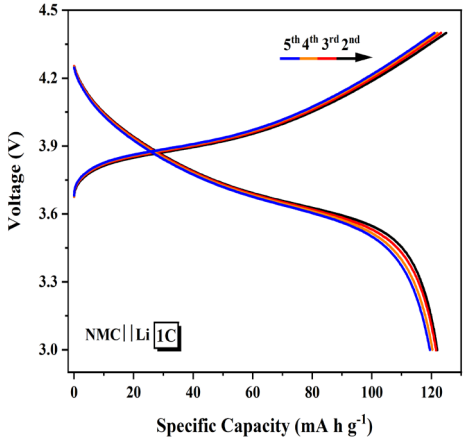
$LiFePO_4$
2.8 ~ 3.8 V

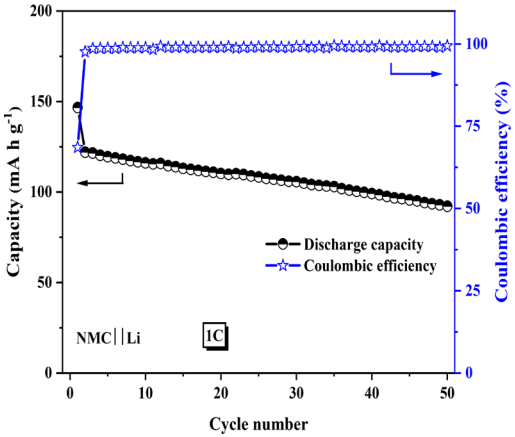




Anode shell
Li metal anode
Purdue's CSPE
Cathode
Cathode shell

Room Temperature



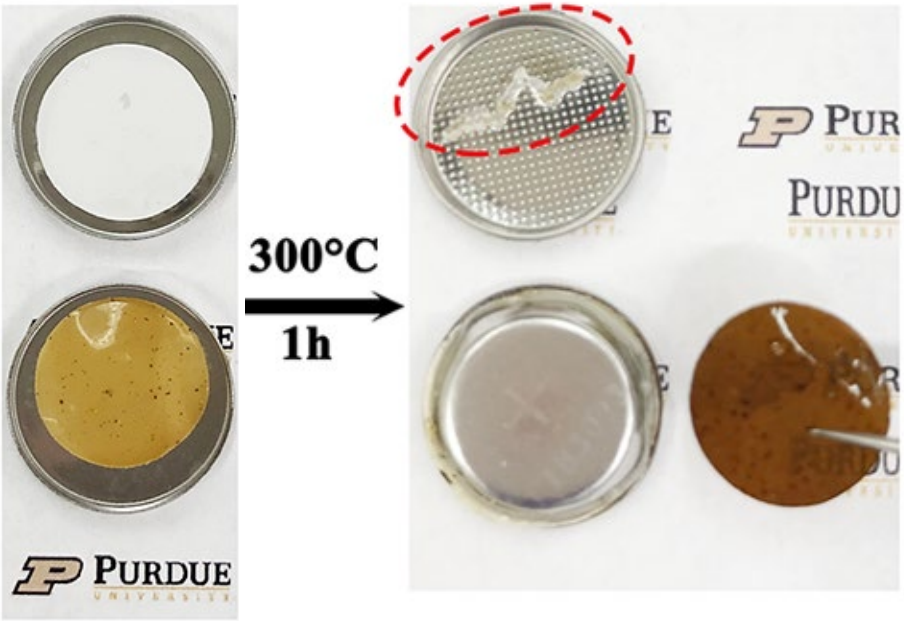


$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
3 ~ 4.4 V

Thermal Stability

Commercial PP separator

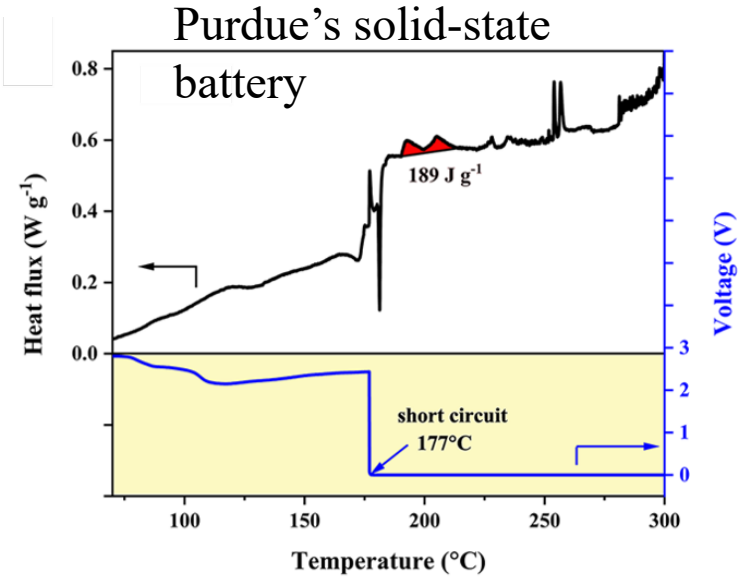
Purdue's CSPE

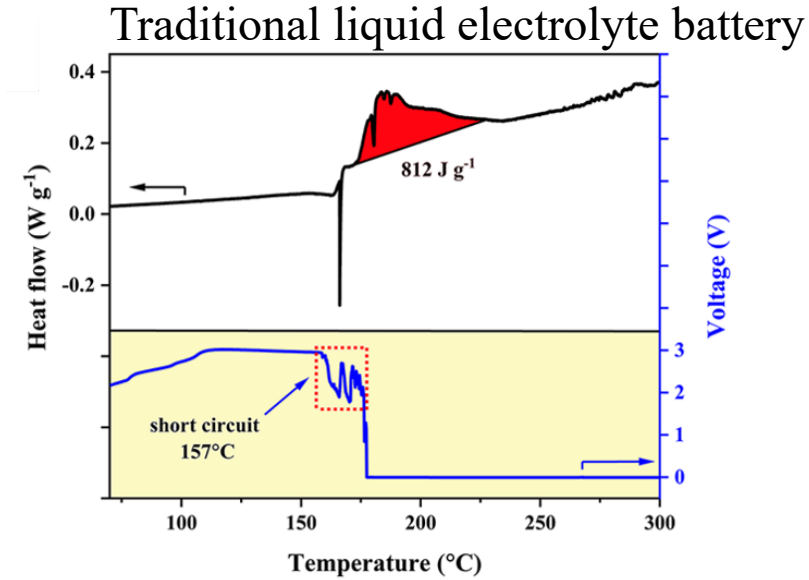


× Melt and shrink

✓ Maintain its structure

Thermal Safety Performance





Thermal stable window:

Heat generation:

✓ up to 177 °C

✓ 189 J g^{-1}

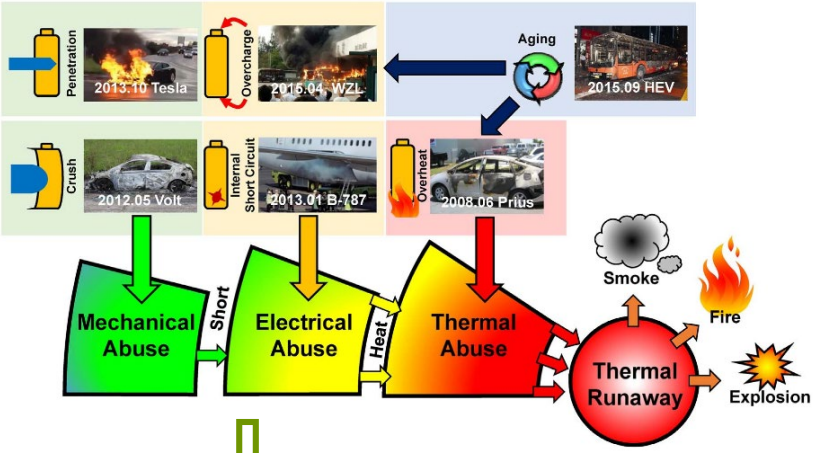
VS

× up to 157 °C

× 812 J g^{-1}

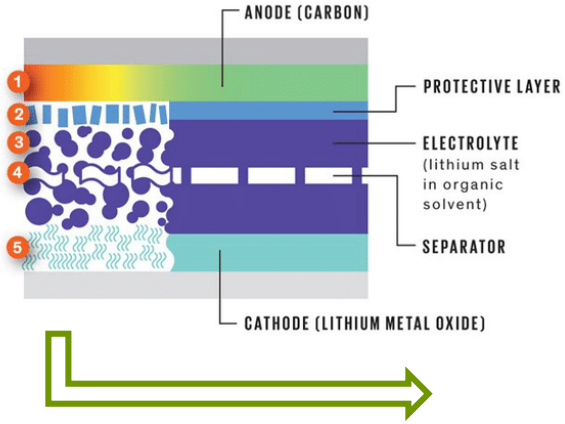
Conventional Li-ion- Can we Sense the VOCs and Gases Early?

Causes of Thermal Runaway

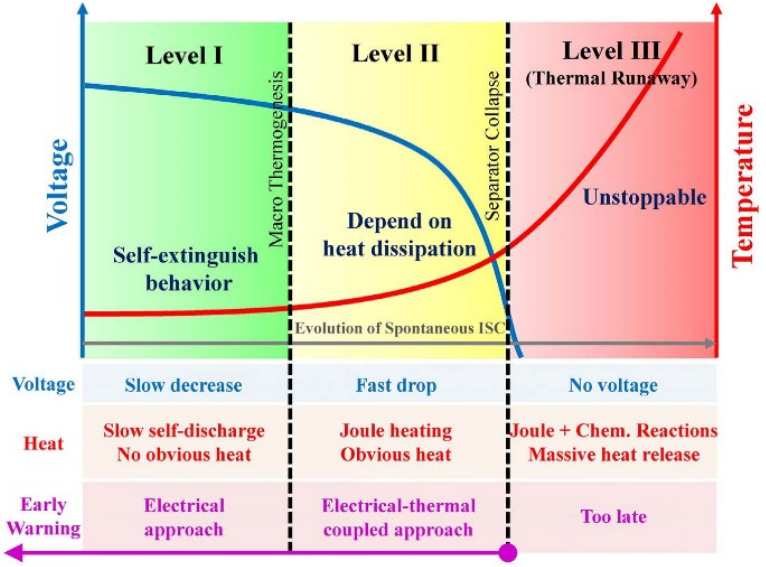


Stages of Thermal Runaway

1. Heating starts.
2. Protective layer breaks down.
3. Electrolyte breaks down into flammable gases.
4. Separator melts, possibly causing a short circuit.
5. Cathode breaks down, generating oxygen.

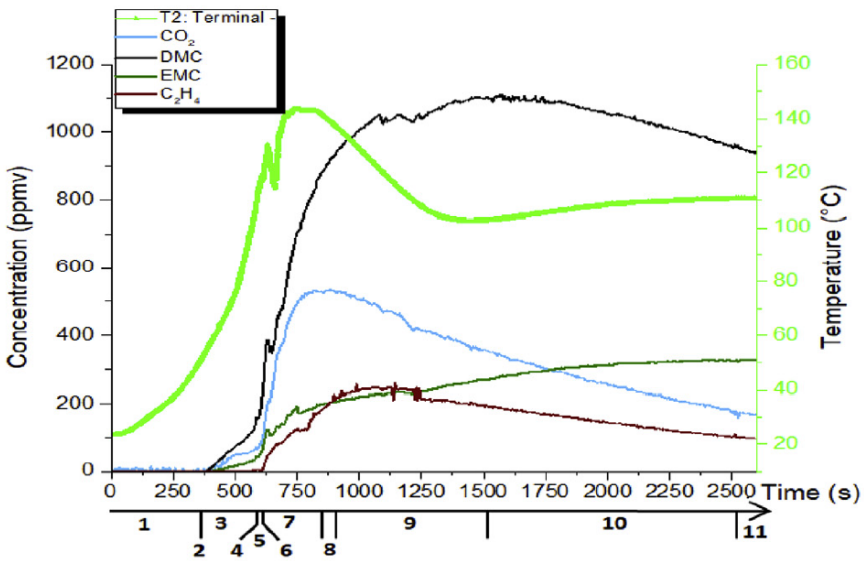


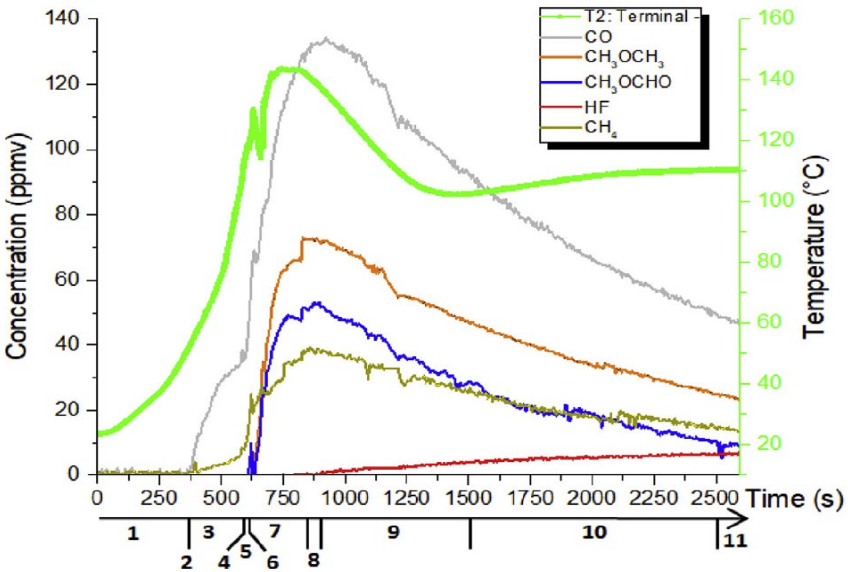
Level of Internal Short Circuit (ISC)



Arora, Shashank. (2018). Selection of thermal management system for modular battery packs of electric vehicles: A review of existing and emerging technologies. Journal of Power Sources. 400. 621-640. 10.1016/j.jpowsour.2018.08.020.

Gases Released from Li-ion Batteries During Thermal Runaway





Gases Released from Batteries:

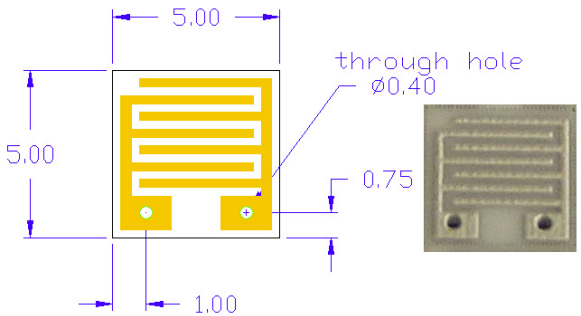
- Carbon Dioxide
- Carbon Monoxide
- Hydro-fluoride

VOCs Released from Batteries:

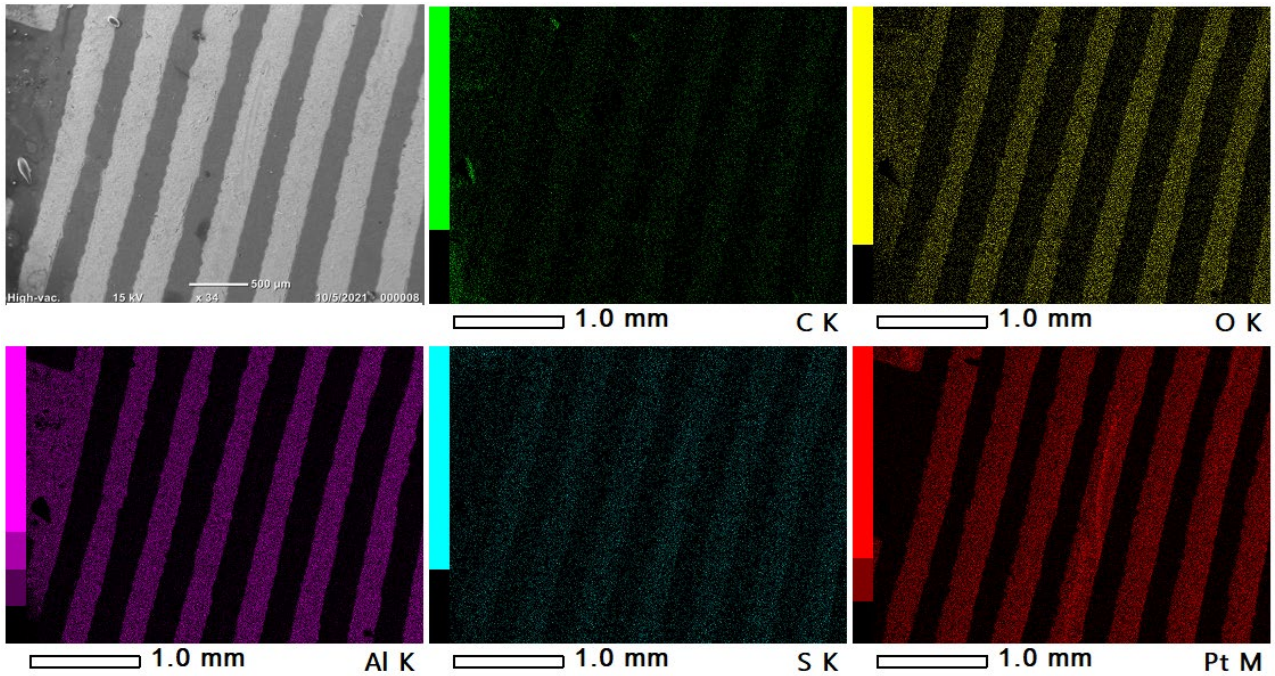
- Di-methyl Carbonate
- **Ethyl methyl carbonate**
- Ethylene
- Dimethyl ether
- **Methyl formate**

Y. Fernandes, A. Bry, S. de Persis, Identification and quantification of gases emitted during abuse tests by overcharge of a commercial Li-ion battery, Journal of Power Sources, Volume 389, 2018, Pages 106-119, ISSN 0378-7753

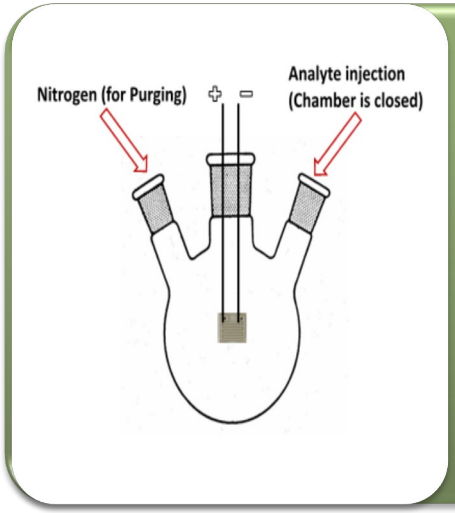
PEDOT:PSS (poly(3,4-ethylenedioxythiophene polystyrene sulfonate) Sensor



- Interdigitated-Platinum Electrode
- Spin Coated
- Energy dispersive X-ray spectroscopy (EDS)
- Uniform coating of C, S and O indicate presence of PEDOT:PSS

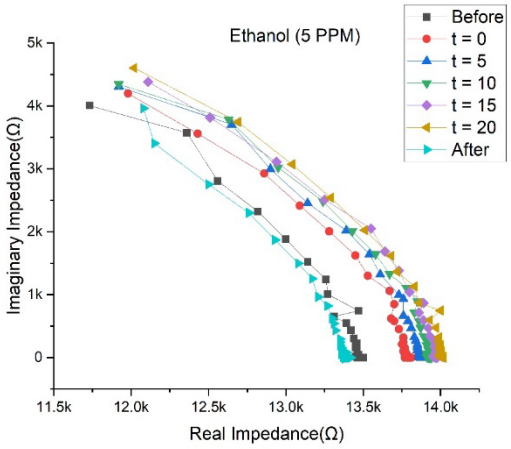


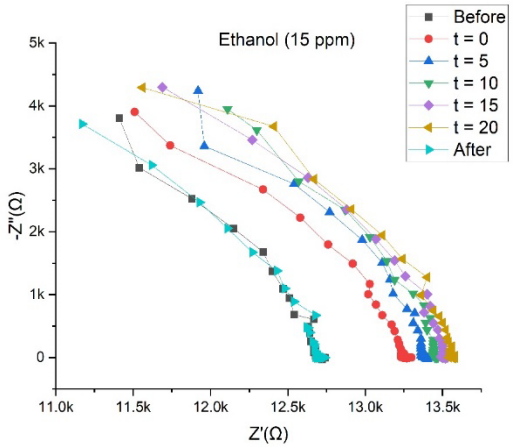
Impedance Response of Sensor

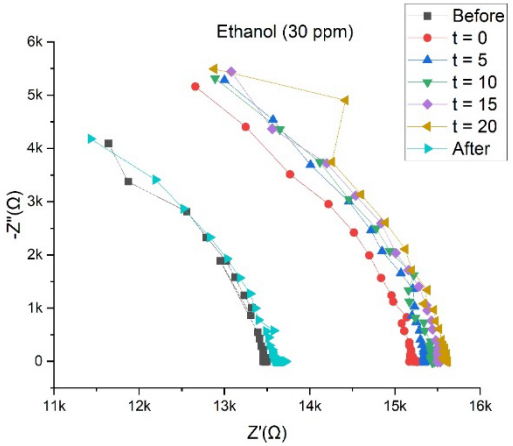


Parameters & Observations:

Instrument: Gamry 600+
Frequency: 1 Hz- 1MHz
Samples: 5 samples/Analytes
Room Temperature
Mechanism: Adsorption/Desorption
Fast Recovery

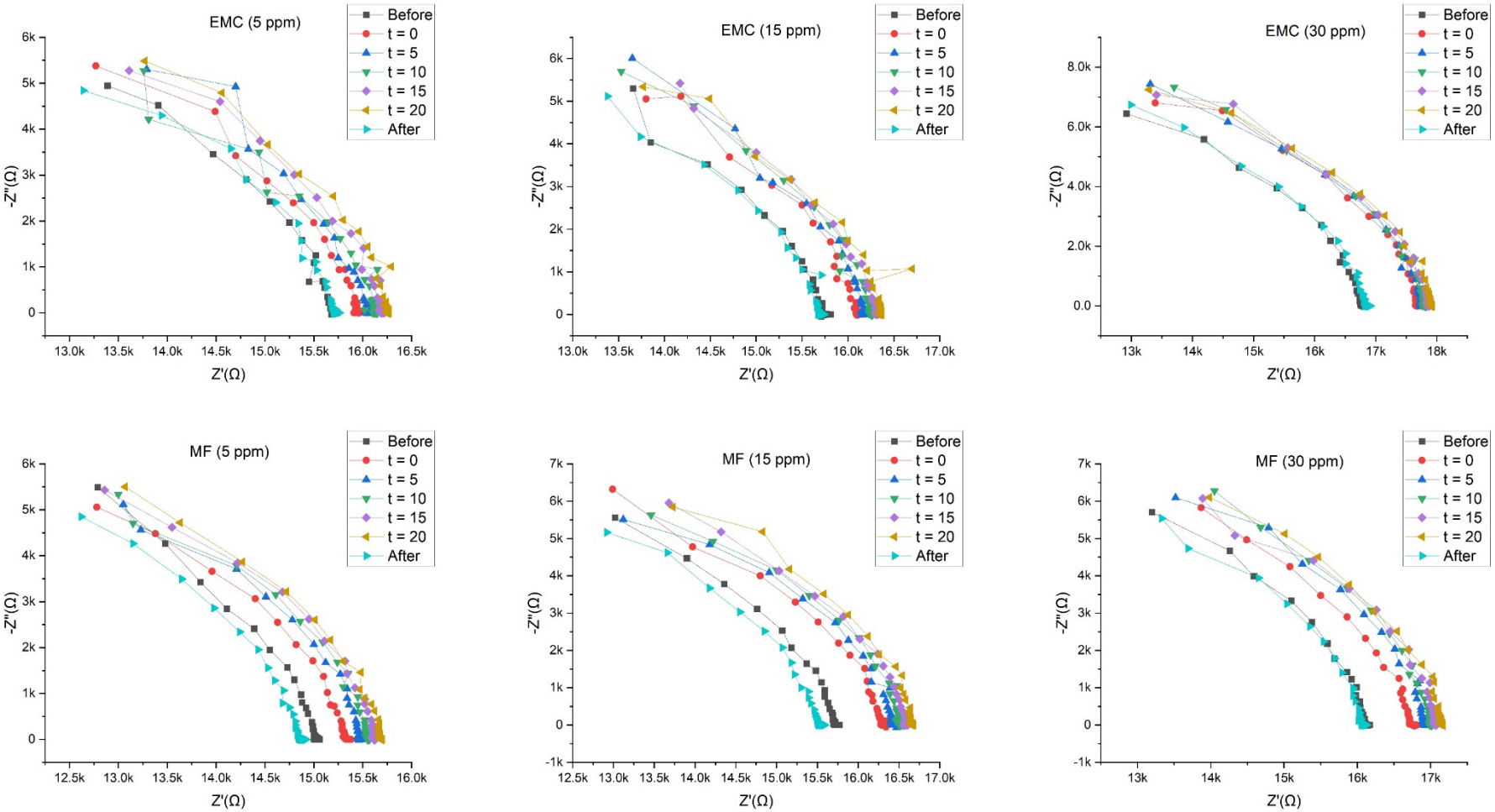




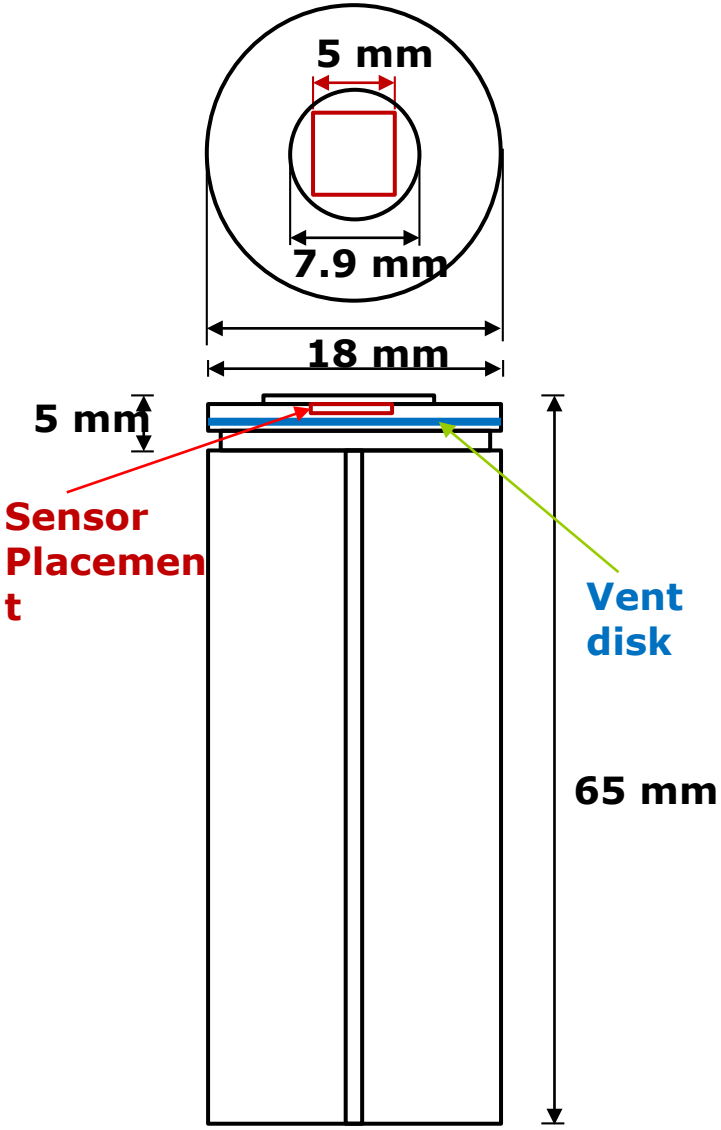


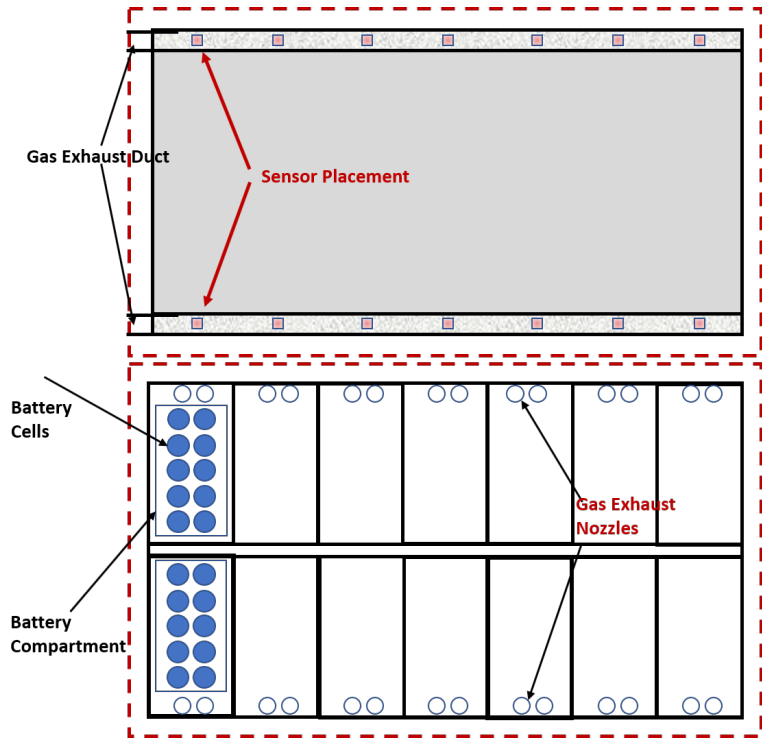
Impedance Response to VOCs

(EMC and MF released as the byproduct of decomposition of Electrolytes)



Applications of developed Chemosensor





- ✓ EV charging station,
- ✓ Private parking area,
- ✓ Battery storage rooms,
- ✓ Military applications

Summary

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

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

3. Early chemosensing could stop the catastrophic runaway of Li-ion batteries

4. Chemosensors can be applied to various places including parking garages, battery storage area, charging stations etc.