Looking Beyond Lithium-Ion -- How Soon?

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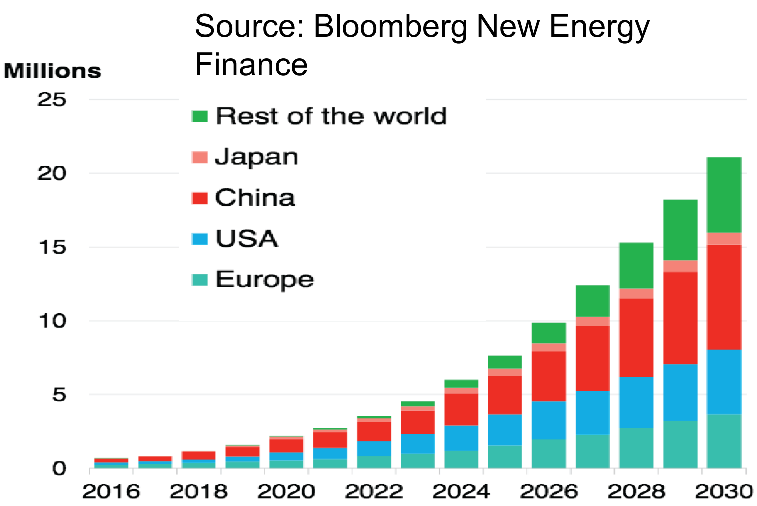
Projected Growth of Light Duty Passenger Vehicle & Potential Concerns

Global EV Forecast



- Today's concern
  - Cost
    - Current projected cost is 2 time higher
    - Near term target cost is 100$/Kwh
    - Long term target cost is 70$/kwh

(Need to increase significantly the energy density of battery to reduce cost)

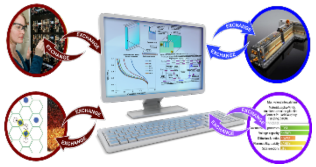
Li-S, Li-air, Li/Li2O close system?

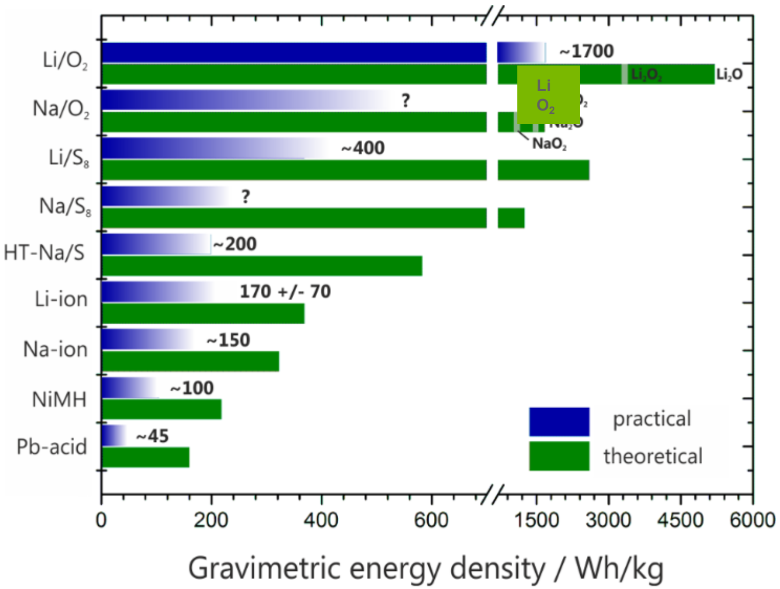
- Future Concern
  - Sustainability

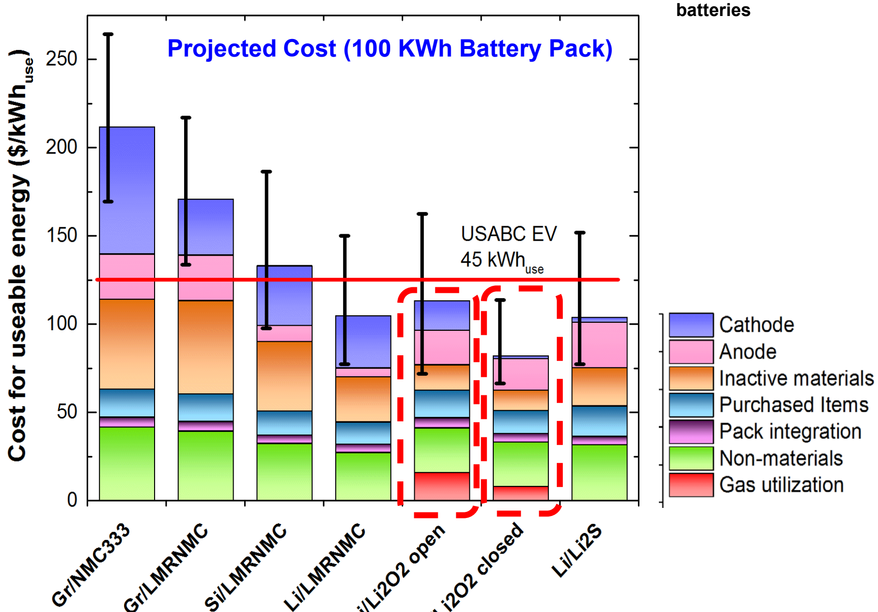
(need to move away from Co, Ni and even Li)

Na ion battery?

Battery Architectures – Energy Densities and Project Costs

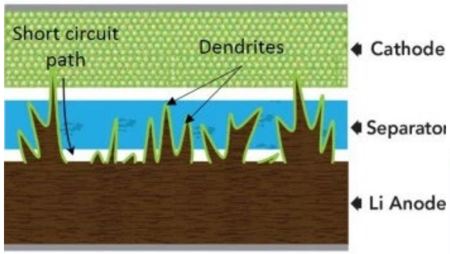




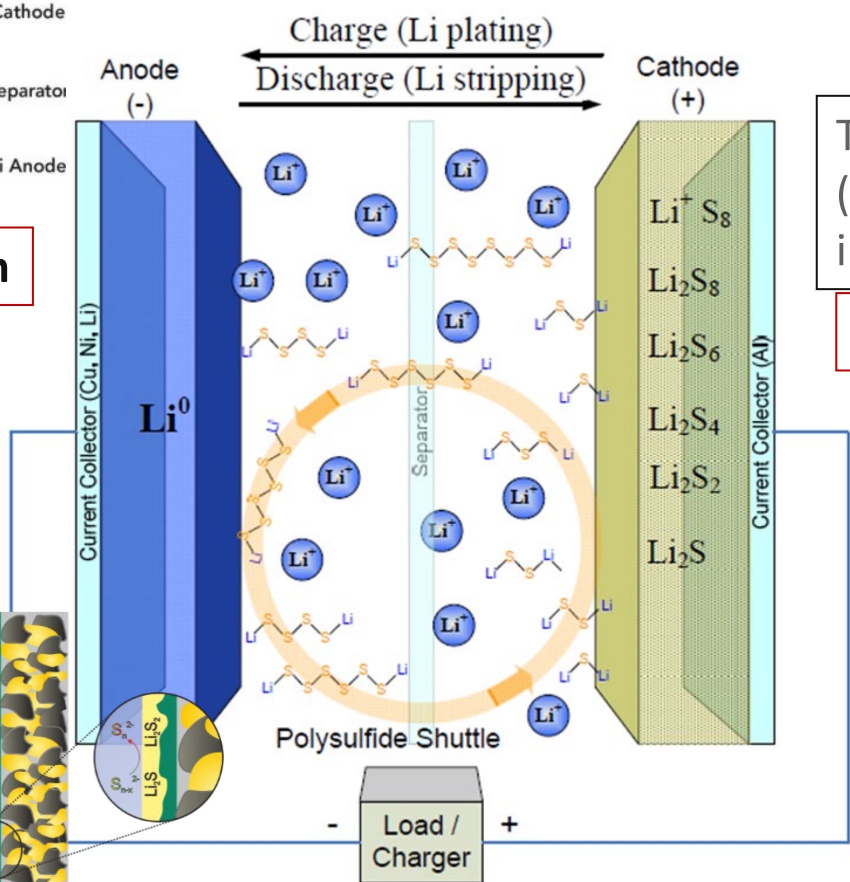


Courtesy: ANL BatPaC

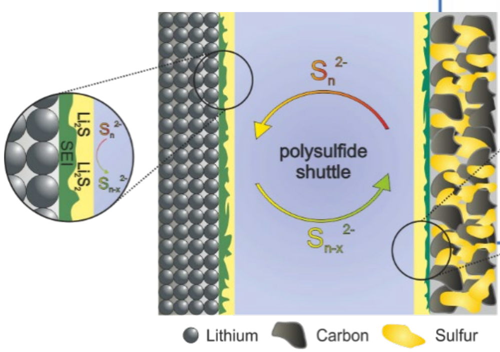
Challenge of Lithium Sulfur system



Li dendrite growth



Lithium Sulfur Battery



Polysulfide shuttle

The high resistance of sulfur (~10^{-30} S cm^{-1}) and the intermediate products.

Low Conductivity of S and Li_2S

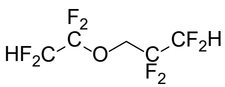
Low mass-loading of sulfur

Self-Discharge

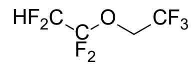
The volume expansion when sulfur is fully converted to Li_2S is as large as 80%.

Cathode Volume Change

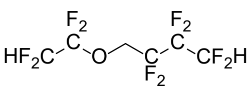
Argonne invented a class of fluorinated ether electrolytes for Li/S battery that address both the shuttle effect and Li-dendrite



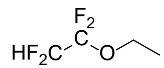
1,1,2,2-tetrafluoro-3-(1,1,2,2-tetrafluoroethoxy)propane



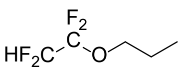
1,1,2,2-tetrafluoro-1-(2,2,2-trifluoroethoxy)ethane



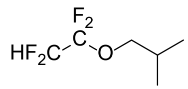
1,1,2,2,3,3-hexafluoro-4-(1,1,2,2-tetrafluoroethoxy)butane



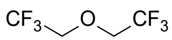
1-ethoxy-1,1,2,2-tetrafluoroethane



1-(1,1,2,2-tetrafluoroethoxy)propane

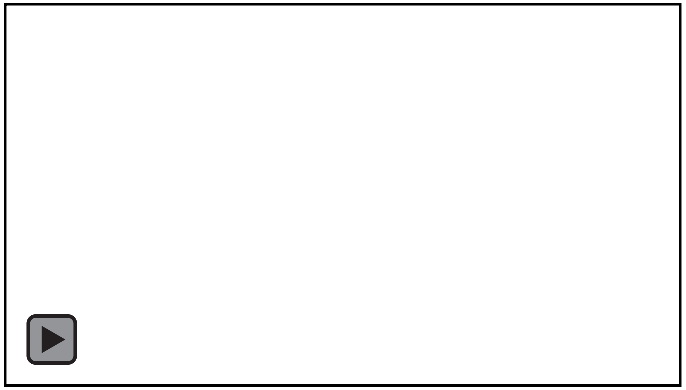


2-methyl-1-(1,1,2,2-tetrafluoroethoxy)propane



1,1,1-trifluoro-2-(2,2,2-trifluoroethoxy)ethane

Low flammability

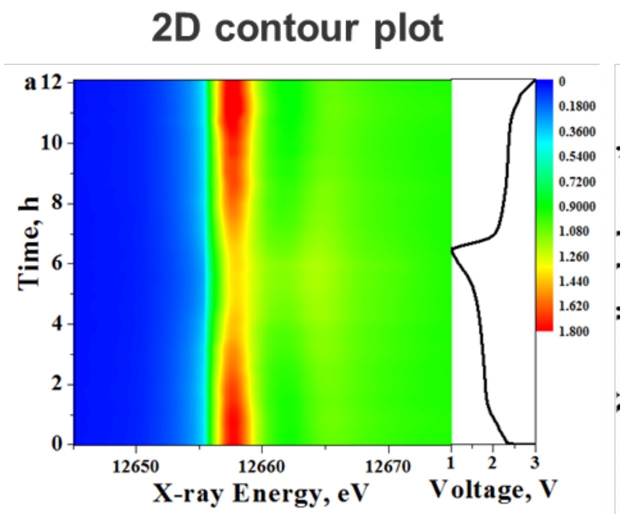


HFE-based:
1M LiTFSI + HFE/DOL (1/1 v/v) + 0.1M LiNO3

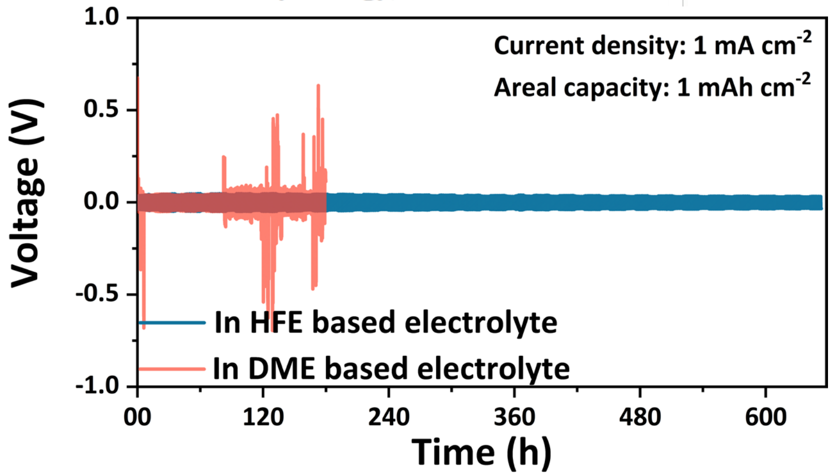
DME-based:
1M LiTFSI + DOL/DME (1/1, v/v) + 0.1M LiNO3

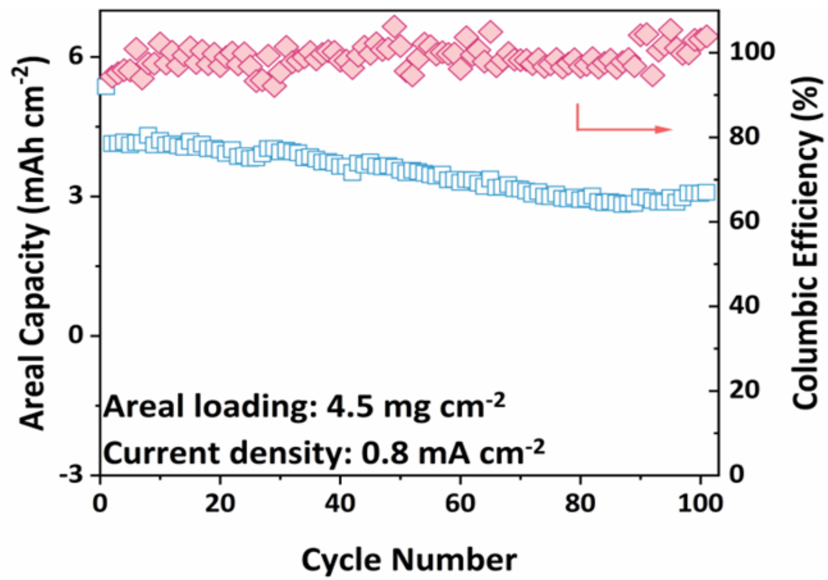
Xu, Amine, U.S. Patent granted

No shuttle effect and better Li plating/stripping stability was observed when using fluorinated ether electrolytes



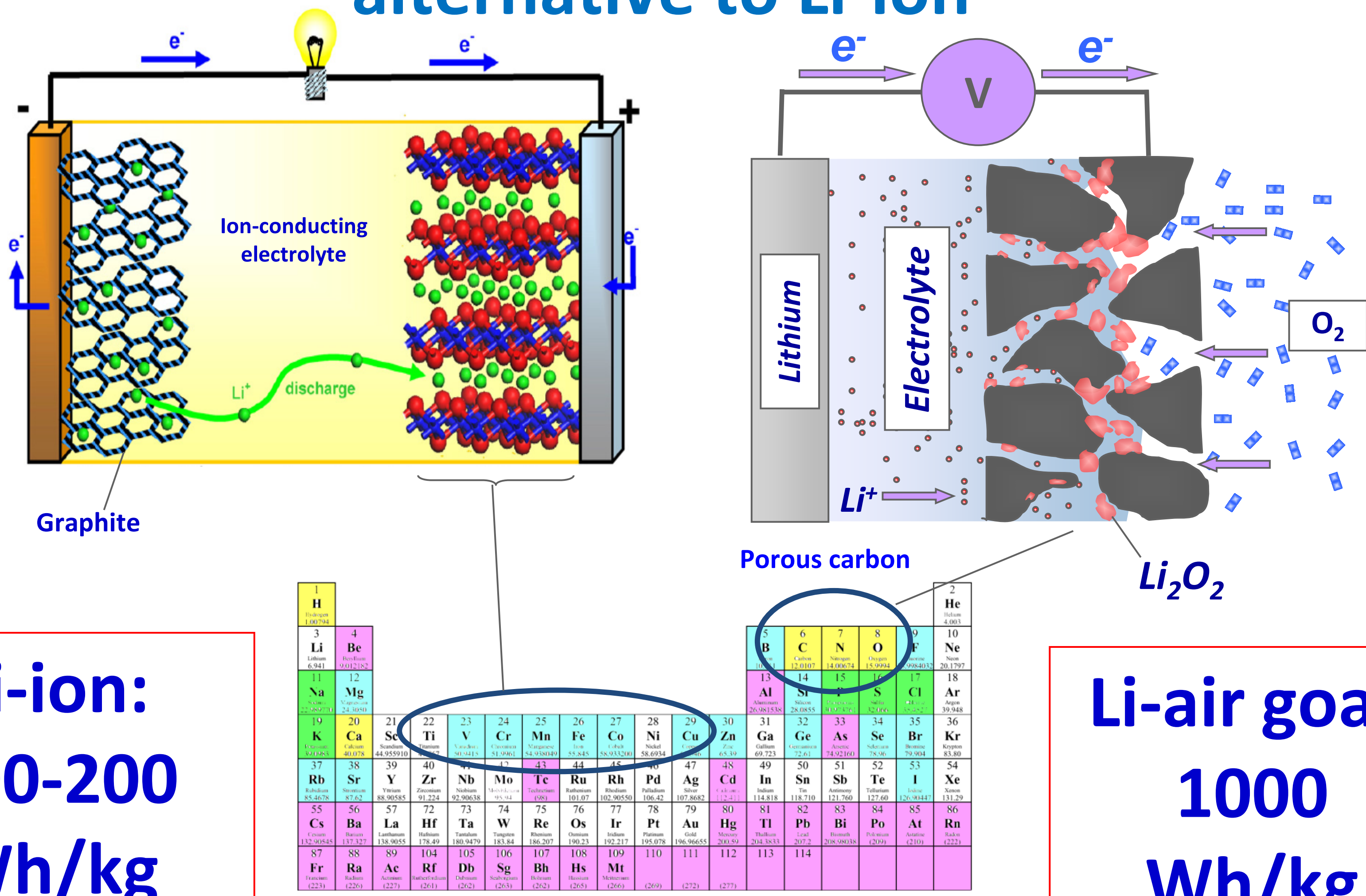
In-situ XANES of Li/S cell during operation shows no shift in energy during cycling. Strong indication of no shuttle taking place (no dissolution of polysulfide)





- Fluorinated ether electrolytes exhibited better Li plating/stripping stability than conventional DME electrolytes

Li-air holds promise as a high energy density alternative to Li-ion



Li-ion: 100-200 Wh/kg

Li-air goal: 1000 Wh/kg (cell)

$$2Li^+ + O_2 + 2e^- \underset{\text{Recharge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Li_2O_2$$

Major Challenges of $Li\text{-}O_2$ Battery

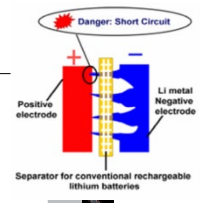
$$2Li^+ + 2e^- + O_2 \leftrightarrow Li_2O_2 \text{ (solid)}$$

$E_{rev} = 2.96\ V_{Li}$

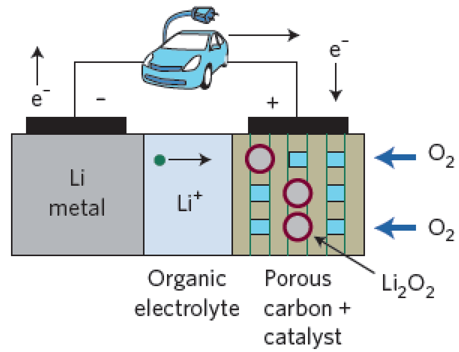
Anode

Problems of Li metal

- Dendrite formation
- Cycling efficiency
- Requires stable solid-electrolyte interphase
- Safety issues

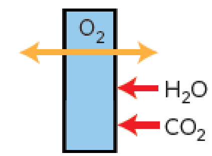


Discharge

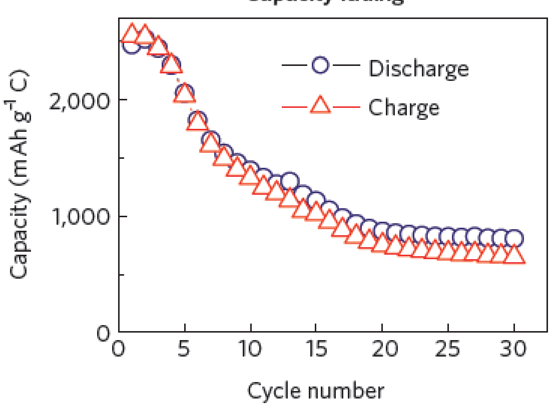


Cathode

Cathode needs a membrane to block CO_2 and H_2O, while allowing O_2 to pass.



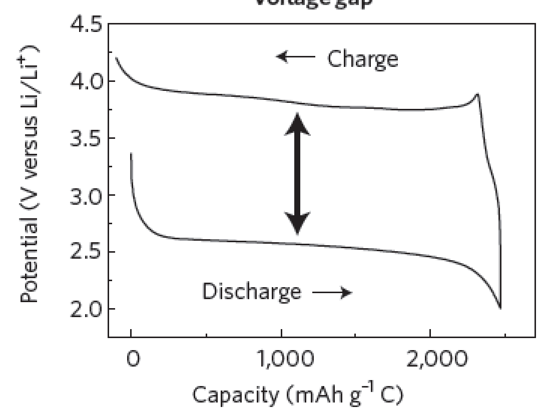
Capacity fading



Electrolyte

- Stability
- Conductivity
- Volatility
- O_2 solubility, diffusivity

Voltage gap

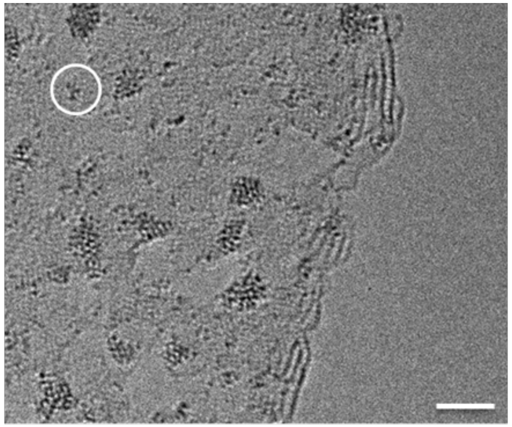


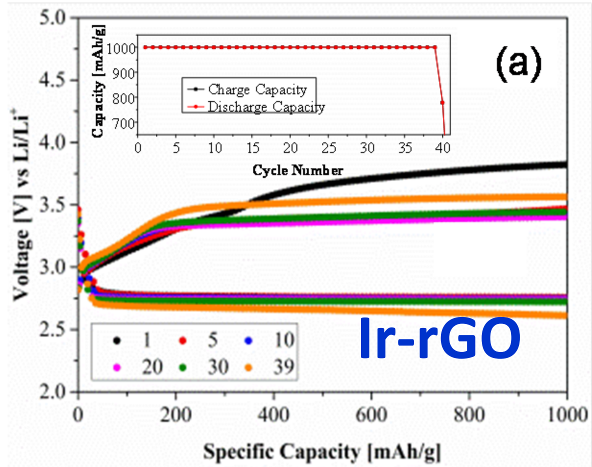
$$\text{Round-trip Efficiency} = \frac{\text{Discharge Voltage (V)}}{\text{Charge Voltage (V)}} \times 100\%$$

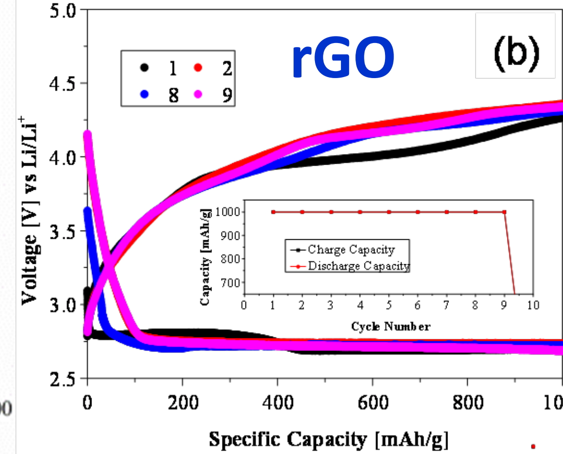
Porous cathode design

- Pore size, distribution
- Catalyst — type, distribution, loading

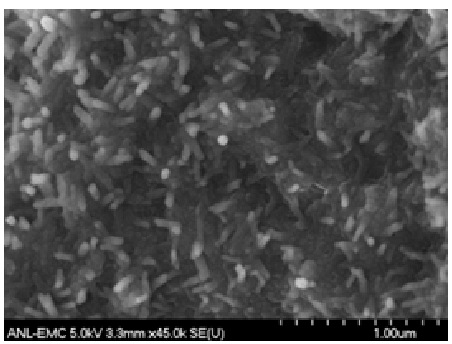
New Ir catalyst has led to stabilization of lithium superoxide (LiO2) and enabled a new Li/LiO2 close system



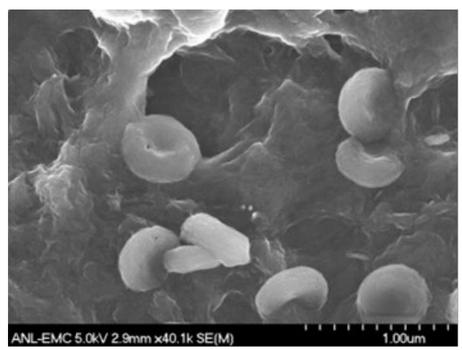




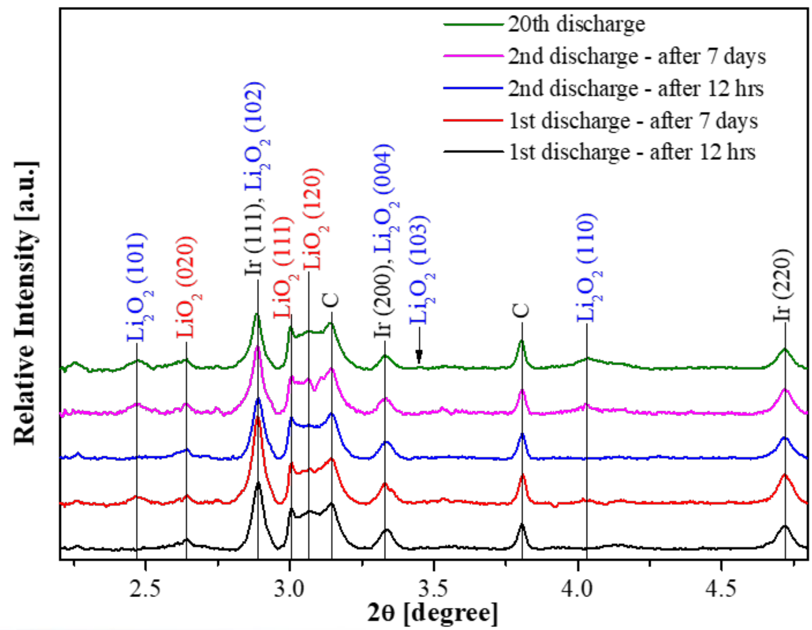
Cathode: Ir nanoparticles (<2 nm) on rGO



Ir-rGO



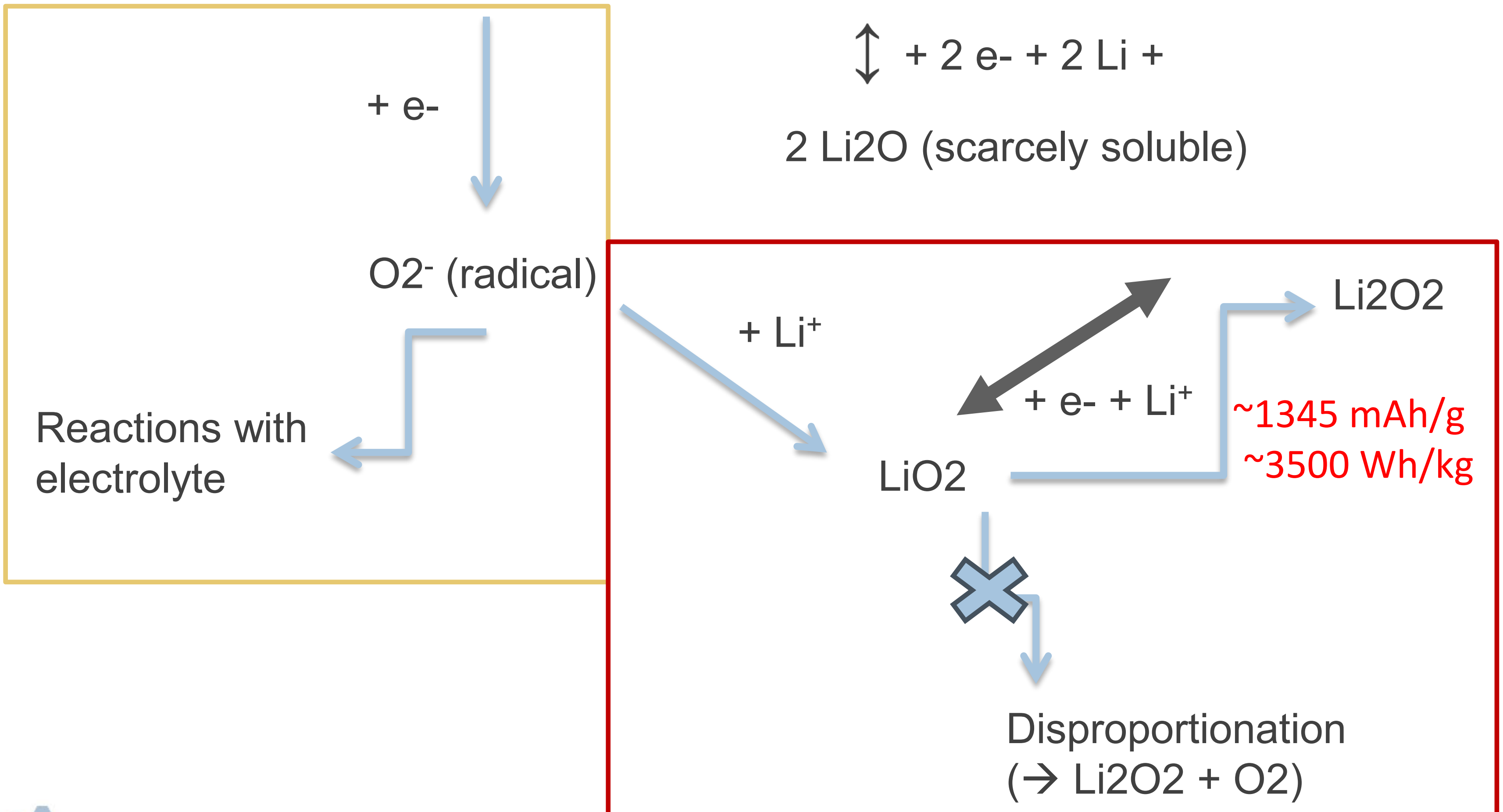
rGO



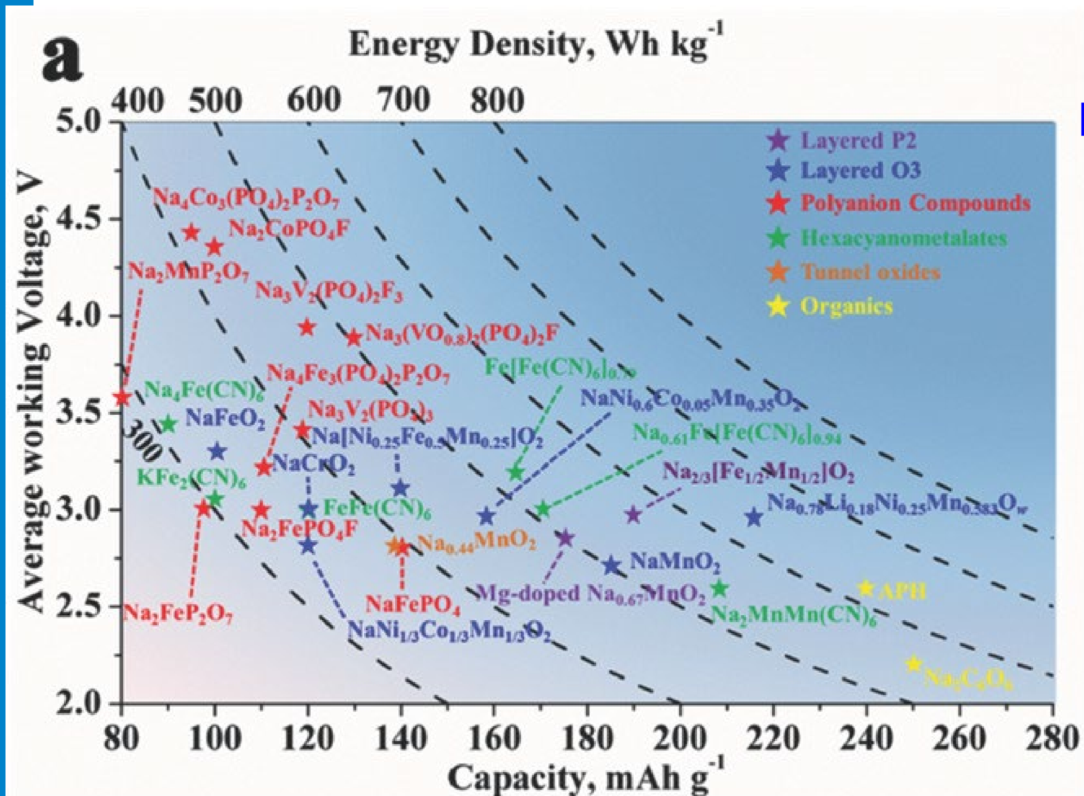
Li-O2 Battery (Open System): Electrochemical reaction scheme in Li-air cells

Ideal reaction scheme (on the air cathode):

$2\ Li^+ + 2\ e^- + O_2(\text{molecule}) \leftrightarrow Li_2O_2$ (scarcely soluble)



Na-ion, a Potential system to address the battery sustainability issues in EVs



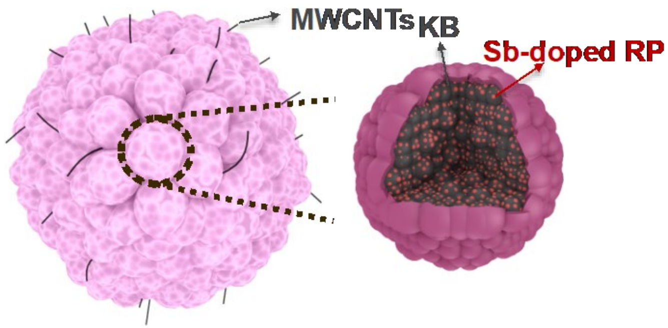
Xu et al., *Adv. Energy Mater.* 2018, 8, 1702403

Unlike Li-ion, There are more Na- cathodes that are based on sustainable Mn, Fe, Ti , P

The only anode that is proven to work in the Na-ion system is hard carbon (high average voltage and low capacity)

To enable Na-ion in EVs, we just need to match the energy density of LFP that is widely used in Today's EV

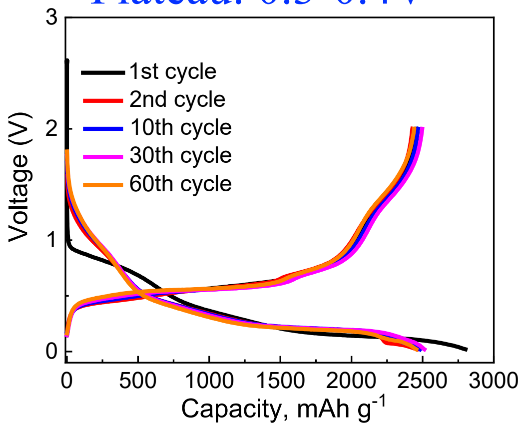
ANL has developed a low-cost and high-capacity red phosphorus-based anodes



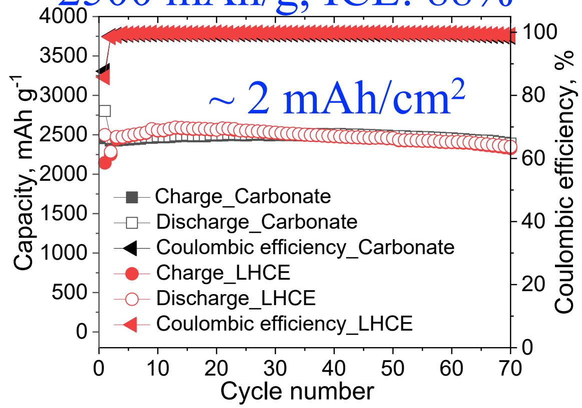
Sb_x-RP_{70-x}/KB-MWCNTs

Red P/KB: low-cost and abundant
Ball-milling: scalable
Sb-doping (Sb:RP=1:9, w/w):
significantly increase the electrical conductivity

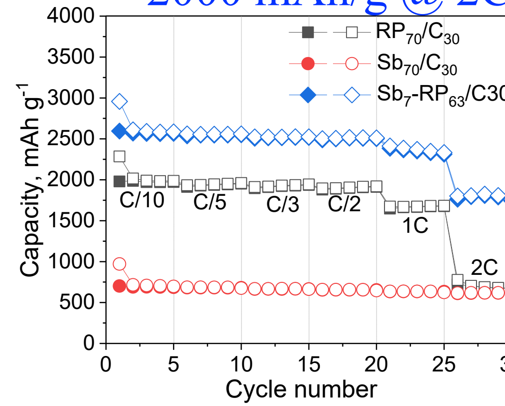
Plateau: 0.3-0.4V



2500 mAh/g, ICE: 88%

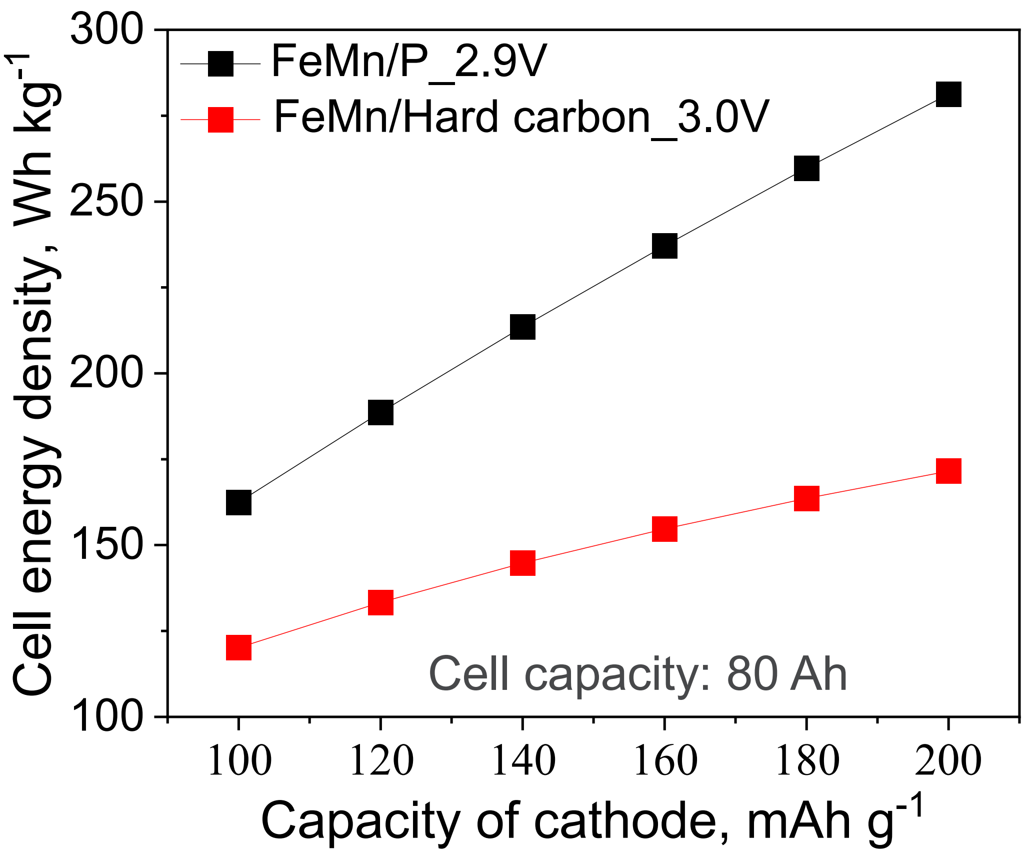


~ 2000 mAh/g @ 2C



Xu, Amine et al., Acs Energy Lett. 2021, 6, 547-556.
Xu, Amine, Liu, US Patent 11394022B2

Argonne BatPaC simulation on the cell energy density of sodium-ion battery using red phosphorous and hard carbon



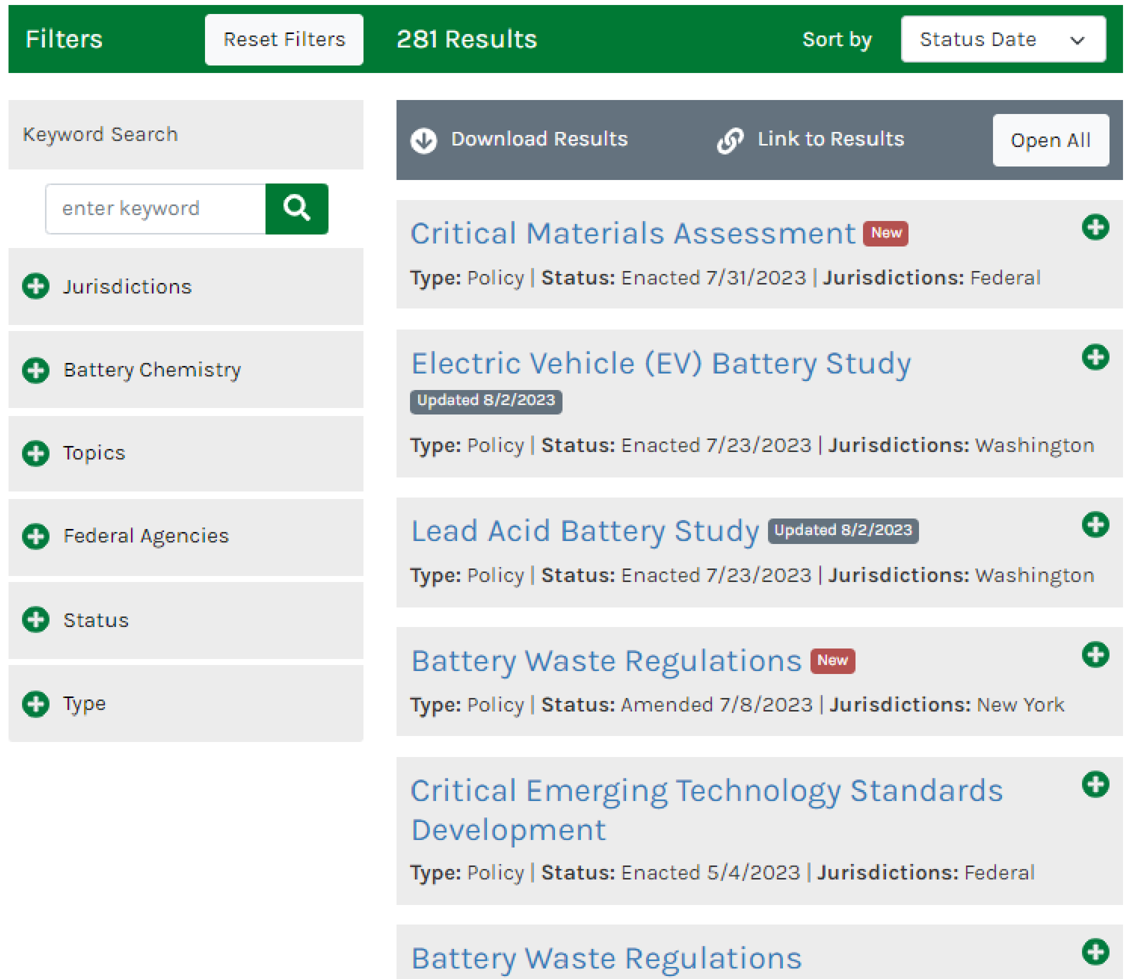
- Hard carbon anode would limit the cell energy density to < 180 Wh/kg even with high-capacity cathode

- System based on Red phosphorus anode coupled with Na-cathode that offers 180mAh/g can reach energy density of 260 Wh/kg

Battery Policies and Incentive Database: Highlights and Features

- Going back 80 years of legislative results
- Currently 282 total entries, extracted using nearly 100 key terms
- Multiple filters to sort policies and incentives by jurisdiction (federal vs individual states), battery chemistry, and industry application

The National Renewable Energy Laboratory (NREL) maintains a database for the Federal Consortium for Advanced Batteries with state and federal policies and incentives related to batteries developed for electric vehicles and stationary energy storage. Specifically, the database includes legislation related to battery manufacturing, recycling, safety and transport, environmental impacts, critical domestic material/battery supply chain, and the relevant battery implications of the Defense Production Act and the United States-Mexico-Canada Agreement



https://www.energy.gov/eere/vehicles/battery-policies-and-incentives-search#/

BatteryInfo@icf.com)