

Looking Beyond Lithium-Ion -- How Soon?

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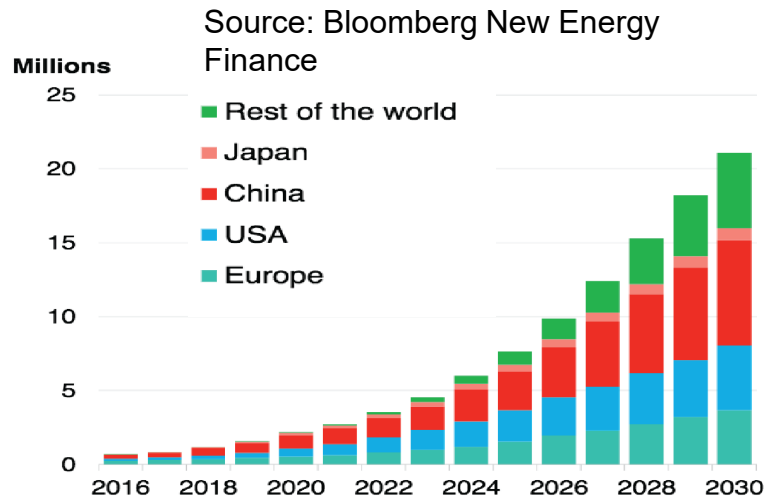
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Projected Growth of Light Duty Passenger Vehicle & Potential Concerns

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?

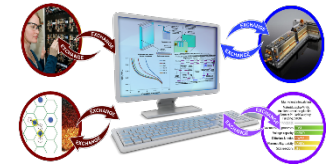
■ Future Concern

■ Sustainability

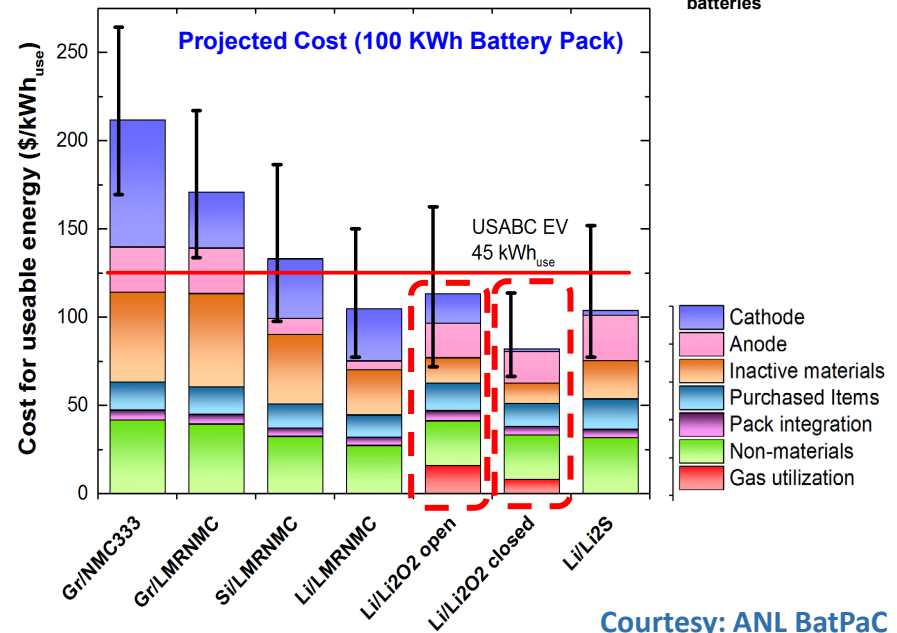
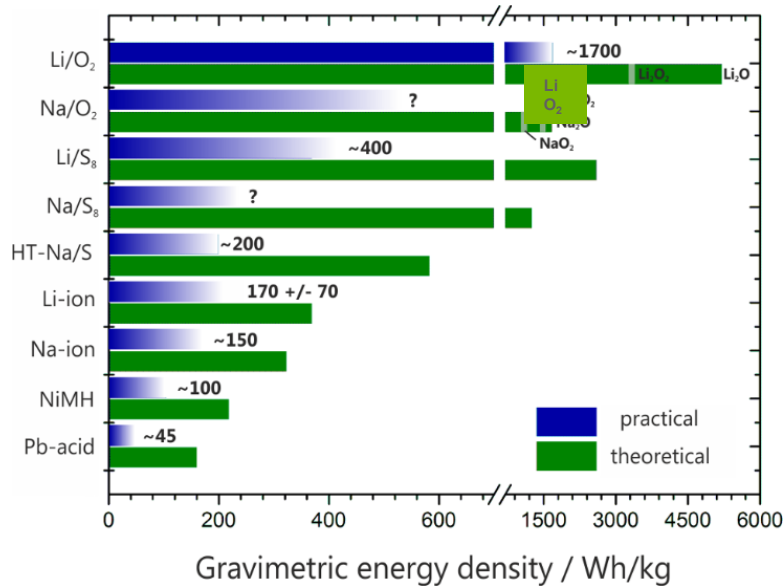
(need to move away from Co, Ni and even Li)

Na ion battery?

Battery Architectures - Energy Densities and Project Costs

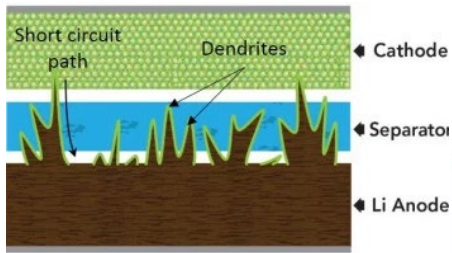


Techno-economic modeling of grid and transportation batteries

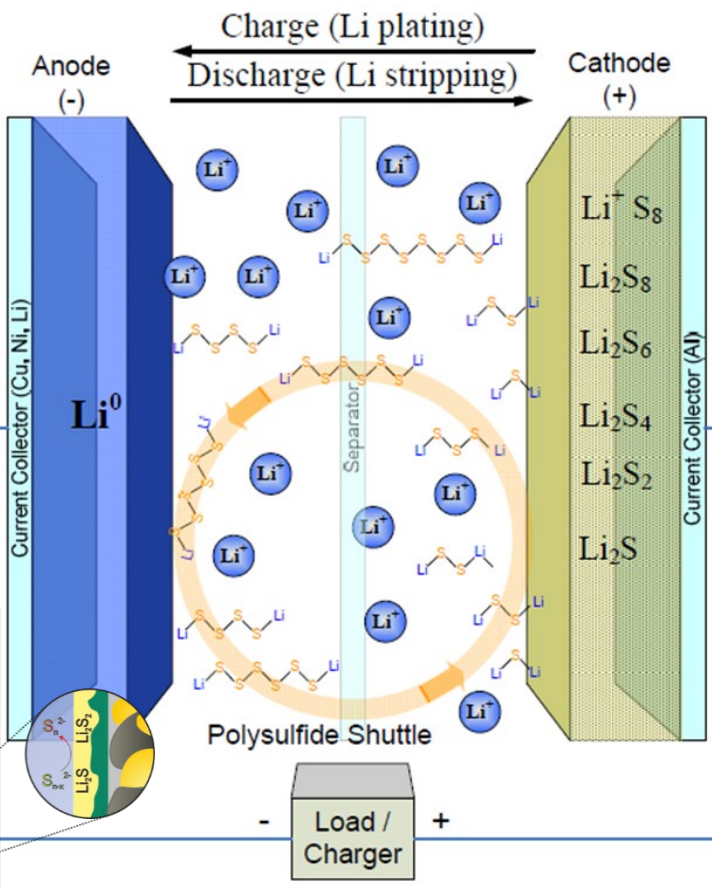


Courtesy: ANL BatPaC

Challenge of Lithium Sulfur system



Li dendrite growth



Lithium Sulfur Battery

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

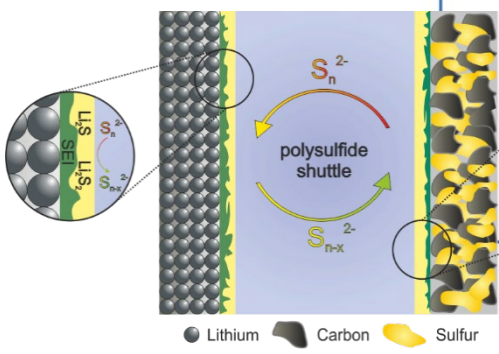
Low Conductivity of S and Li_2S

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

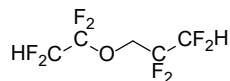


Polysulfide shuttle

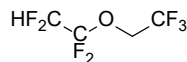


Argonne invented a class of fluorinated ether electrolytes for Li/S battery that address both the shuttle effect and Li-dendrite

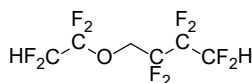
Low flammability



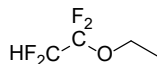
1,1,2,2-tetrafluoro-3-(1,1,2,2-tetrafluoroethoxy)propane



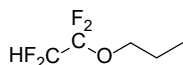
1,1,2,2-tetrafluoro-1-(2,2,2-trifluoroethoxy)ethane



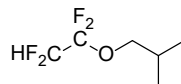
1,1,2,2,3,3-hexafluoro-4-(1,1,2,2-tetrafluoroethoxy)butane



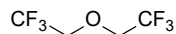
1-ethoxy-1,1,2,2-tetrafluoroethane



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



HFE-based:

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

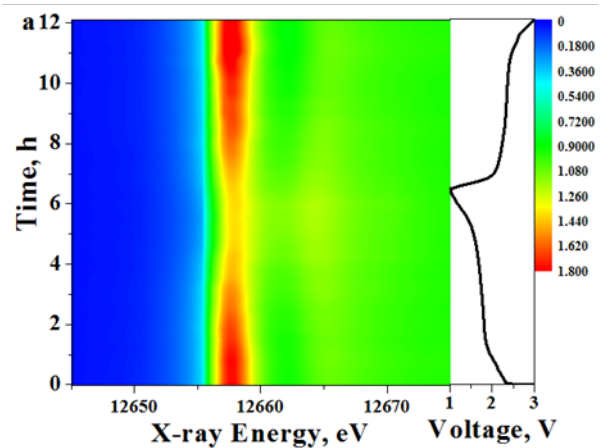
DME-based:

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

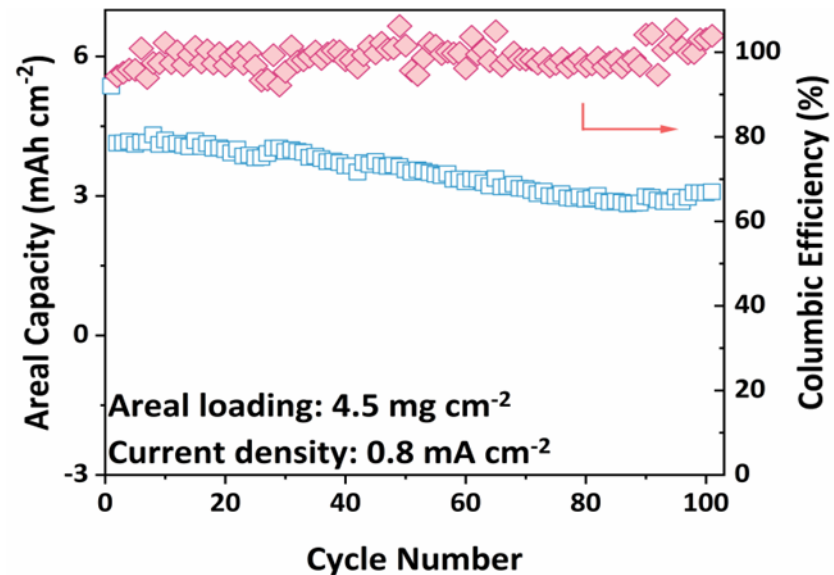
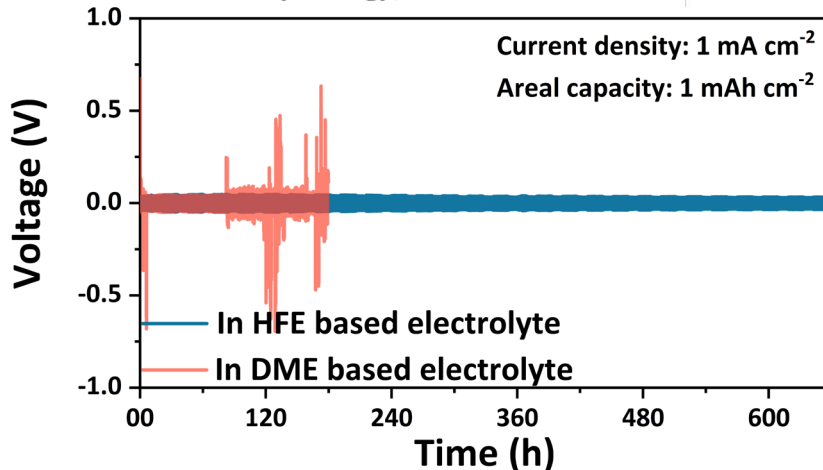
Xu, Amine, U.S. Patent granted

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

2D contour plot

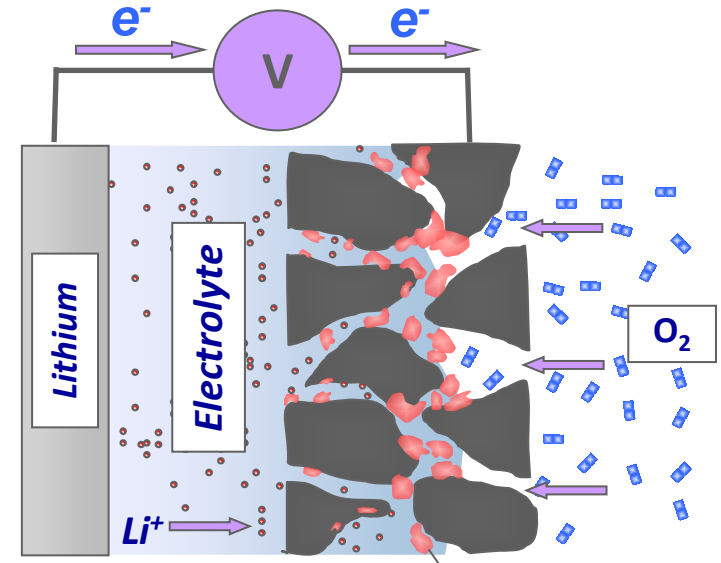
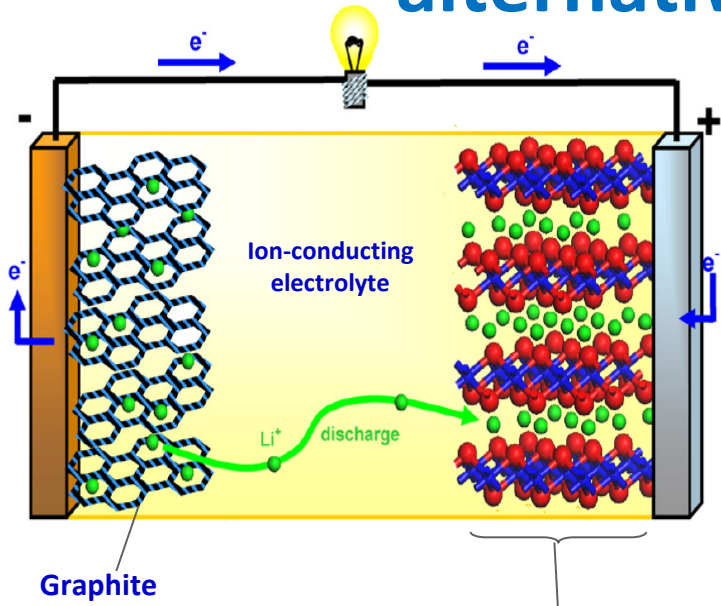


In-situ XANES of Li/S cell during operation shows no shift in energy during cycling. **Strong indication of no shuttle taking place (no dissolution of polysulfide)**



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

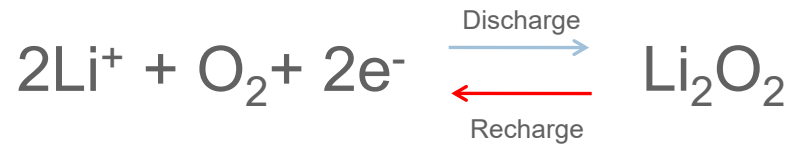
Li-air holds promise as a high energy density alternative to Li-ion



**Li-ion:
100-200
Wh/kg**

1 H 1.00794	2 He 4.003
3 Li 6.941	4 Be 9.012182
5 B 10.811	6 C 12.0107
7 N 14.00642	8 O 15.9994
9 F 18.9984032	10 Ne 20.1797
11 Na 22.98976928	12 Mg 24.304
13 Al 26.9815386	14 Si 28.0855
15 P 30.973761998	16 S 32.06
17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.078
21 Sc 44.955912	22 Ti 47.88
23 V 50.9415	24 Cr 51.9961
25 Mn 54.938045	26 Fe 55.845
27 Co 58.933195	28 Ni 58.6934
29 Cu 63.546	30 Zn 65.39
31 Ga 69.723	32 Ge 72.61
33 As 74.9216	34 Se 78.96
35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62
39 Y 88.90585	40 Zr 91.224
41 Nb 92.90638	42 Mo 95.94
43 Tc [98]	44 Ru 101.07
45 Rh 102.90550	46 Pd 106.42
47 Ag 107.8682	48 Cd 112.4118
49 In 114.818	50 Sn 117.304
51 Sb 121.757	52 Te 127.603
53 I 126.90545	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327
57 La 138.90547	58 Ce 140.12
59 Pr 140.90766	60 Nd 144.242
61 Pm [145]	62 Sm 150.36
63 Eu 151.964	64 Gd 157.25
65 Tb 158.92535	66 Dy 162.5001
67 Ho 164.93033	68 Er 167.259
69 Tm 168.93048	70 Yb 173.054
71 Lu 174.967	72 Hf 178.49
73 Ta 180.94788	74 W 183.84
75 Re 186.207	76 Os 190.23
77 Ir 192.222	78 Pt 195.075
79 Au 196.96655	80 Hg 200.59
81 Tl 204.3833	82 Pb 207.2
83 Bi 208.98038	84 Po [209]
85 At [210]	86 Rn [222]
87 Fr [223]	88 Ra [226]
89 Ac [227]	90 Th [232]
91 Pa [231]	92 U [238]
93 Np [237]	94 Pu [244]
95 Am [243]	96 Cm [247]
97 Bk [247]	98 Cf [251]
99 Es [252]	100 Fm [257]
101 Md [258]	102 No [259]
103 Nh [285]	104 Fl [285]
105 Mc [288]	106 Lv [293]
107 Ts [294]	108 Og [294]

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



Major Challenges of Li-O₂ Battery



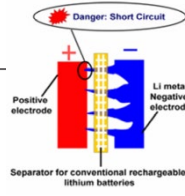
$$E_{\text{rev}} = 2.96 \text{ V}_{\text{Li}}$$



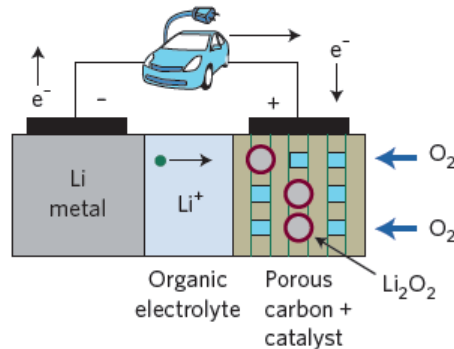
Anode

Problems of Li metal

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

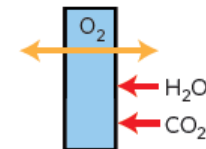


Discharge

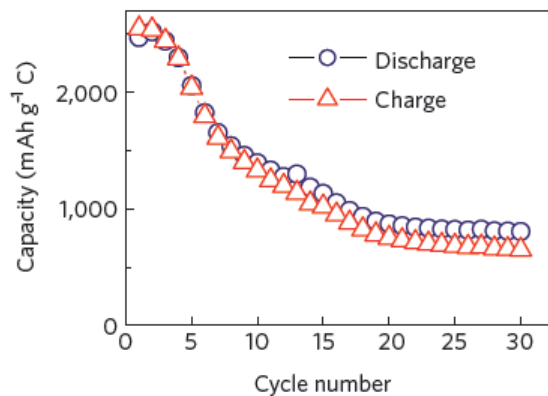


Cathode

Cathode needs a membrane to block CO₂ and H₂O, while allowing O₂ to pass.



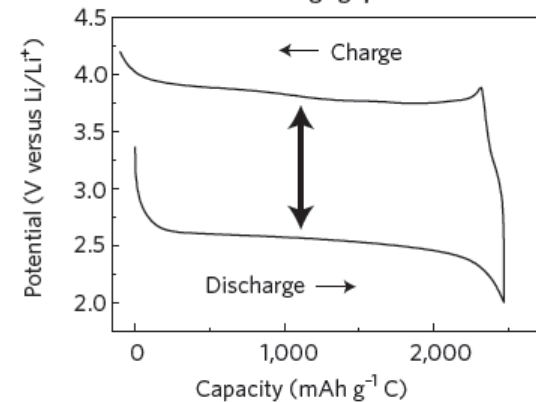
Capacity fading



Electrolyte

- Stability
- Conductivity
- Volatility
- O₂ solubility, diffusivity

Voltage gap



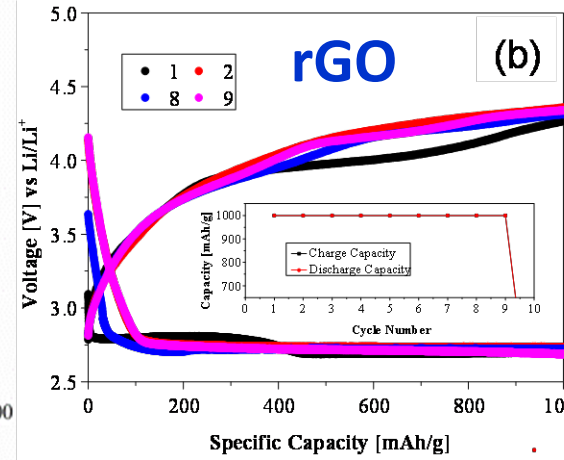
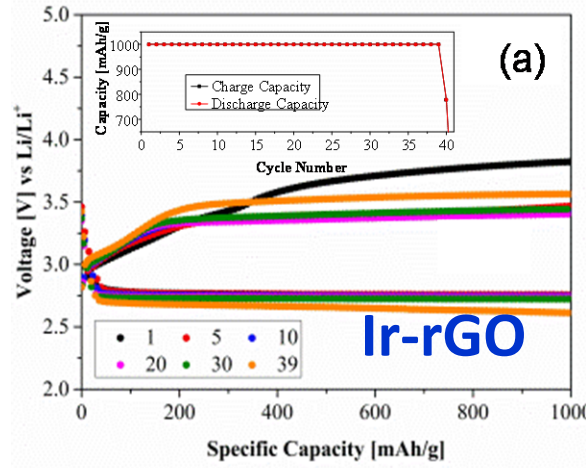
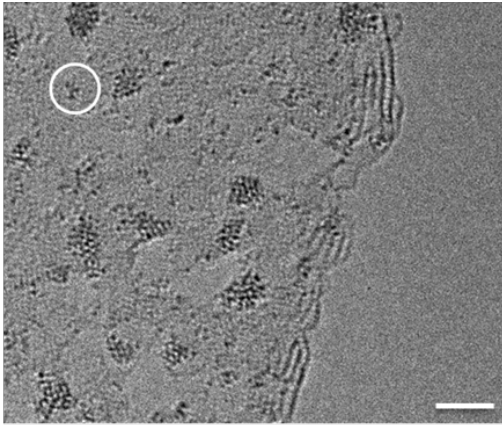
$$\text{Round-trip Efficiency} = \frac{\text{Discharge Voltage (V)}}{\text{Charge Voltage (V)}} \times 100\%$$

Porous cathode design

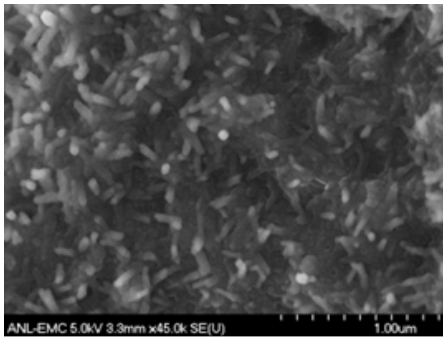
- Pore size, distribution
- Catalyst — type, distribution, loading



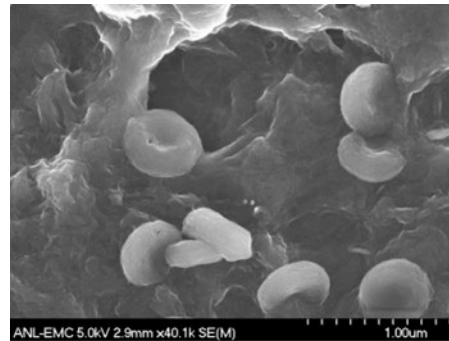
New Ir catalyst has led to stabilization of lithium superoxide (LiO₂) and enabled a new Li/LiO₂ close system



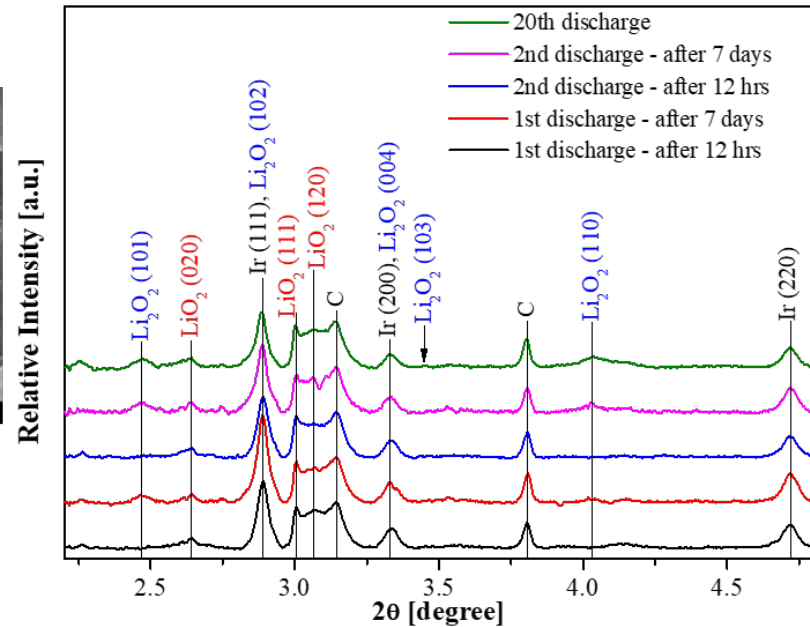
Cathode: Ir nanoparticles (<2 nm) on rGO



Ir-rGO



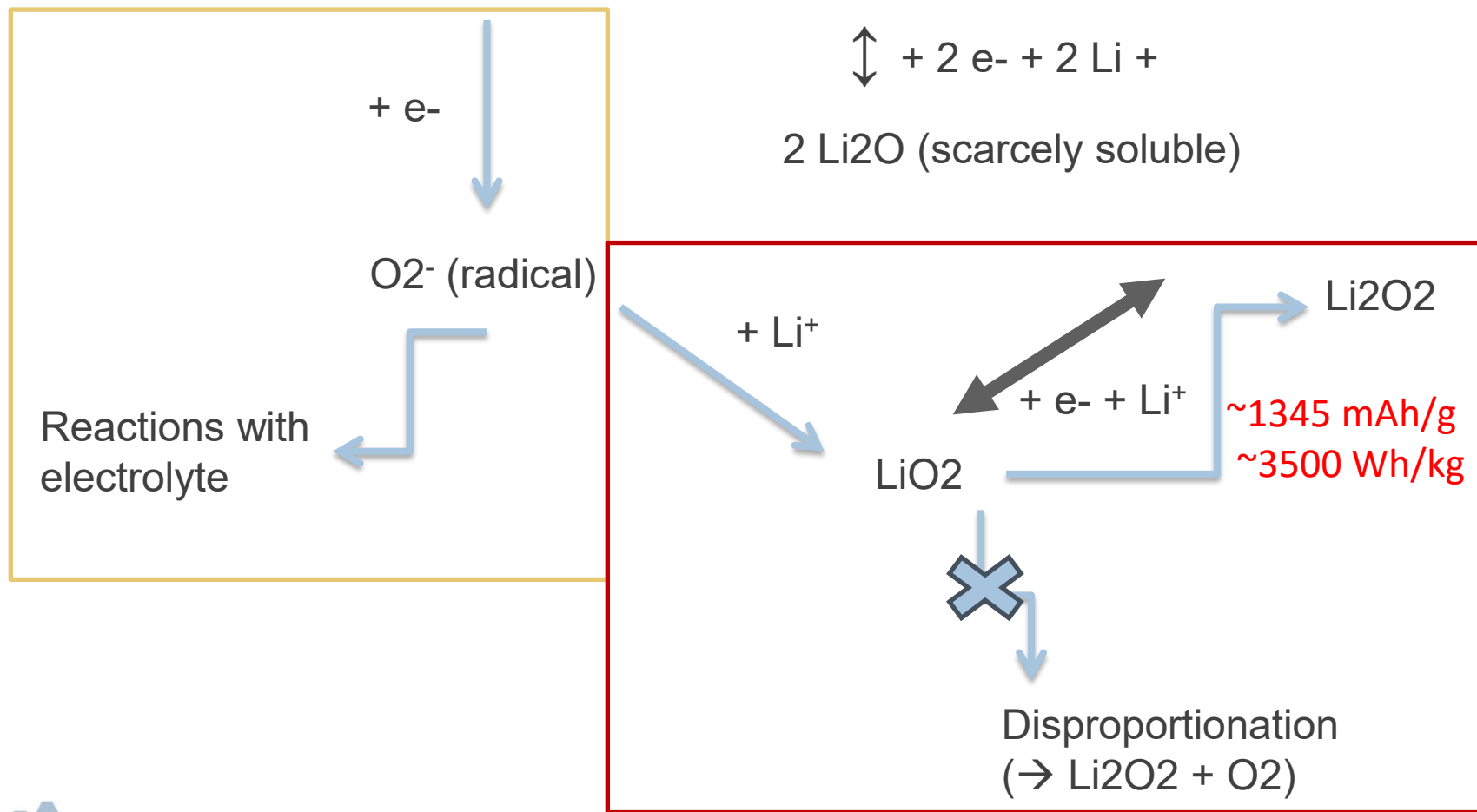
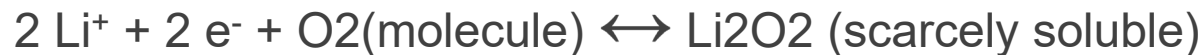
rGO



Li-O2 Battery (Open System):

Electrochemical reaction scheme in Li-air cells

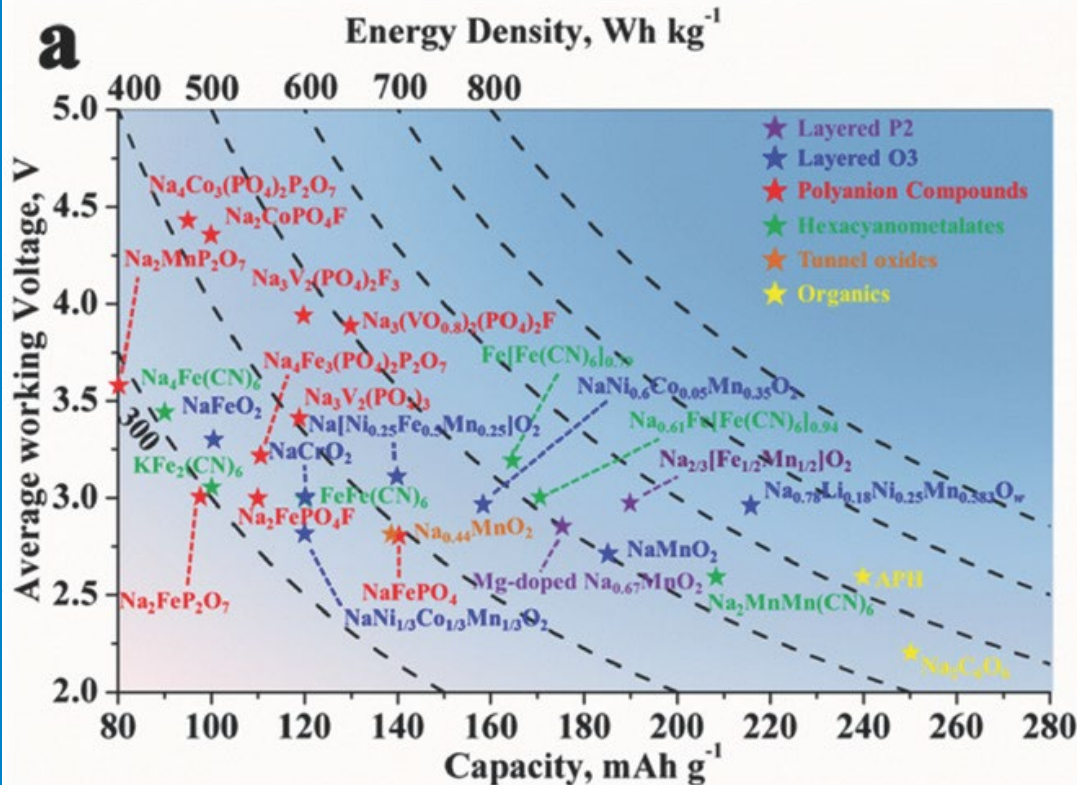
Ideal reaction scheme (on the air cathode):



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

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

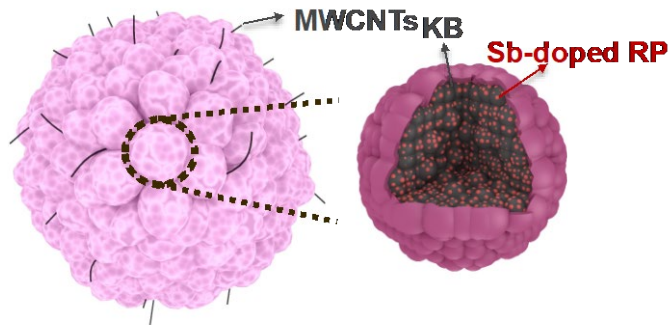
The only anode that is proven to work in the Na-ion system is hard carbon (high average voltage and low capacity)



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

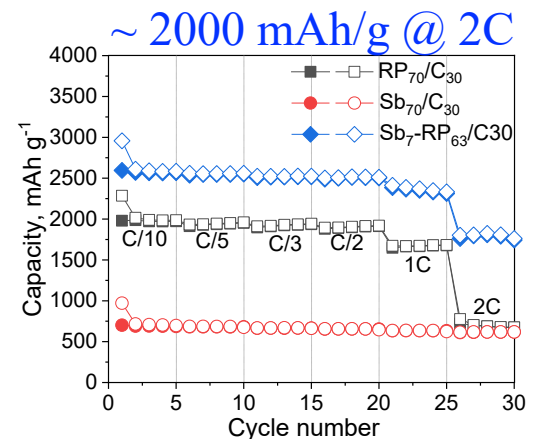
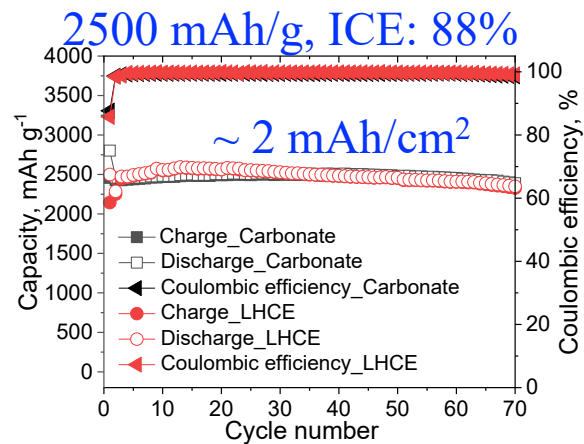
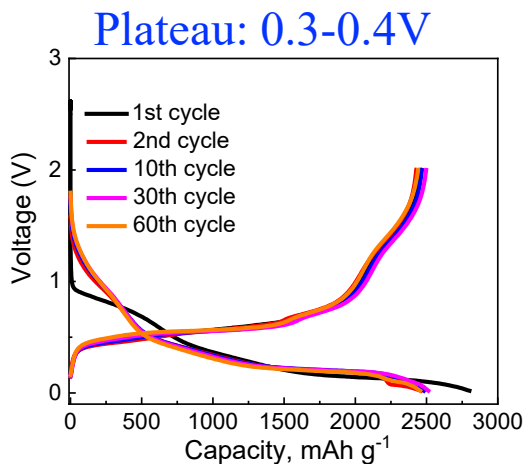
To enable Na-ion in EVs, we just need to match the energy density of LFP that is widely used in Today's EV

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



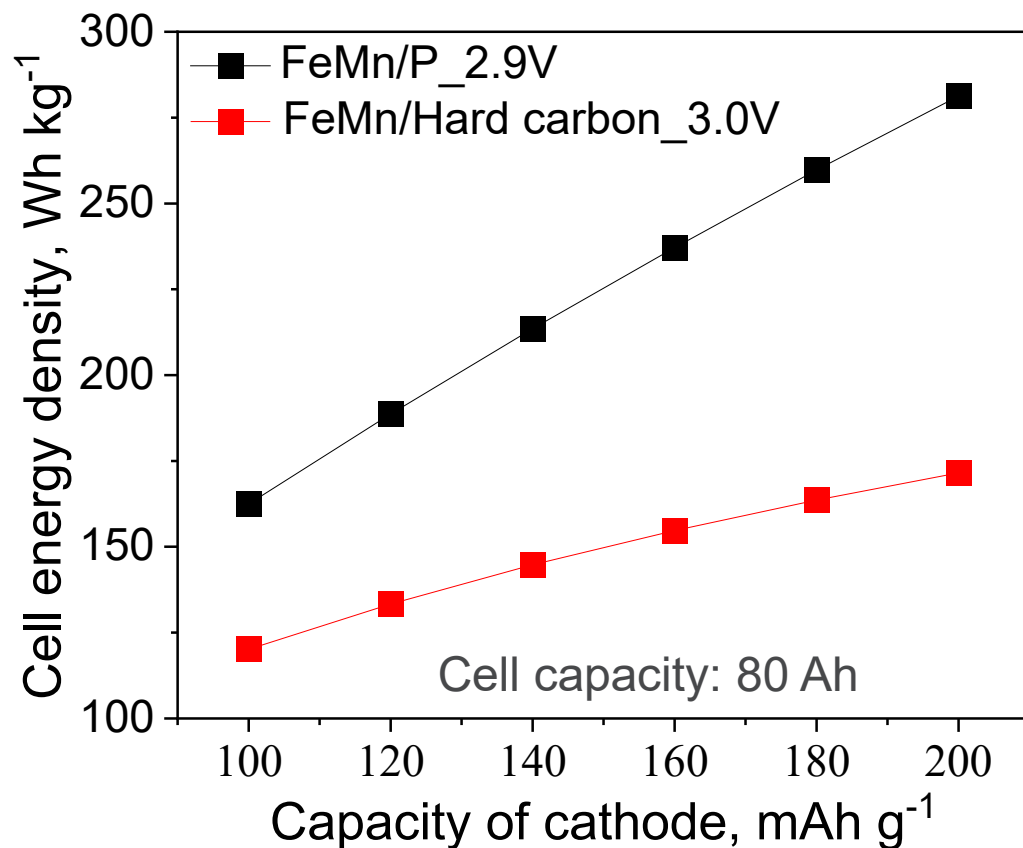
Sb_x - RP_{70-x} /KB-MWCNTs

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



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

Filters Reset Filters 281 Results Sort by Status Date

Keyword Search

enter keyword

Jurisdictions

Battery Chemistry

Topics

Federal Agencies

Status

Type

Download Results Link to Results Open All

Critical Materials Assessment **New**

Type: Policy | Status: Enacted 7/31/2023 | Jurisdictions: Federal

Electric Vehicle (EV) Battery Study **Updated 8/2/2023**

Type: Policy | Status: Enacted 7/23/2023 | Jurisdictions: Washington

Lead Acid Battery Study **Updated 8/2/2023**

Type: Policy | Status: Enacted 7/23/2023 | Jurisdictions: Washington

Battery Waste Regulations **New**

Type: Policy | Status: Amended 7/8/2023 | Jurisdictions: New York

Critical Emerging Technology Standards Development

Type: Policy | Status: Enacted 5/4/2023 | Jurisdictions: Federal

Battery Waste Regulations

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