

Electrochemical Systems for Large-Scale Energy Storage

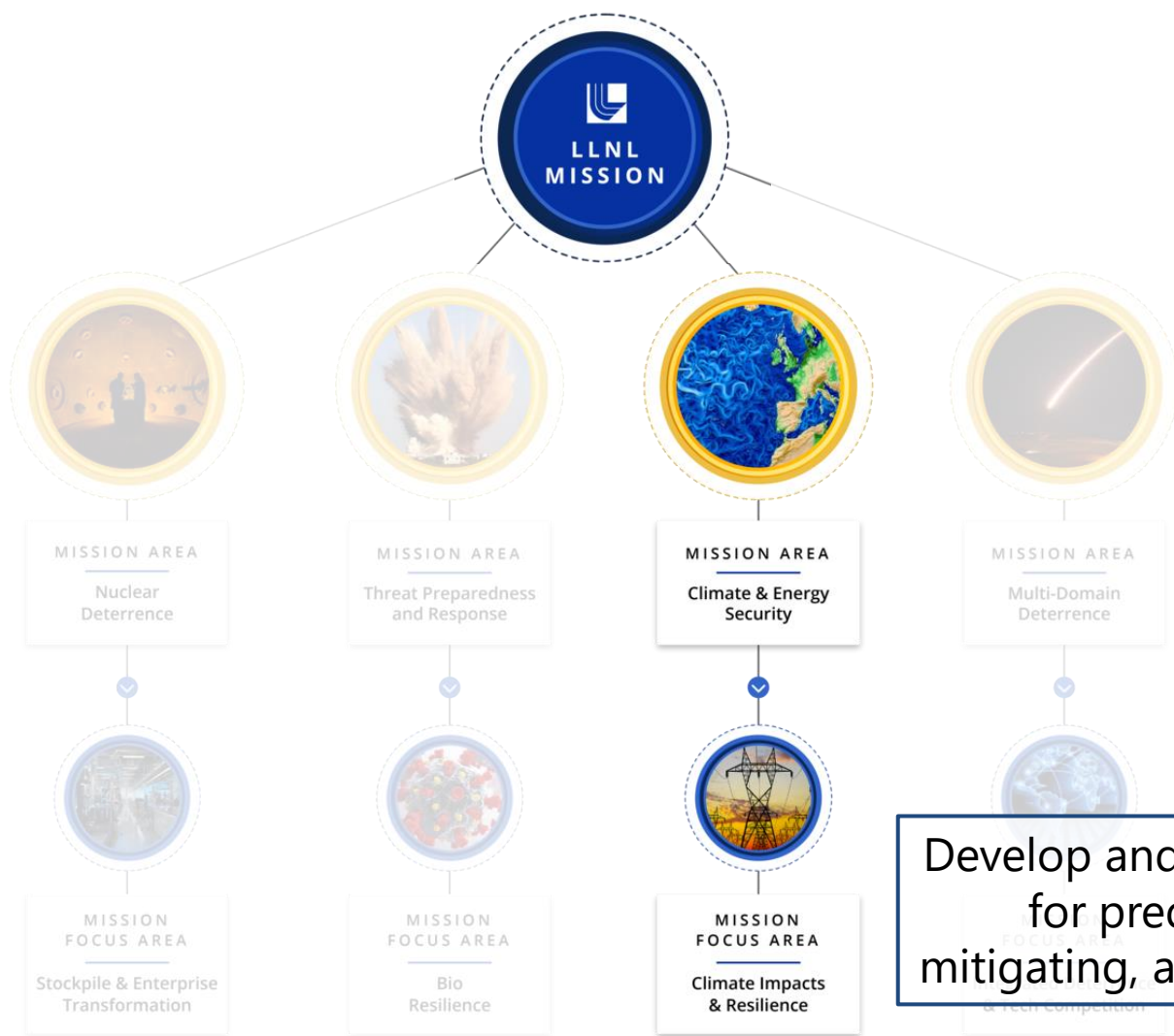
Nicholas Cross

Cal ACS Science Café

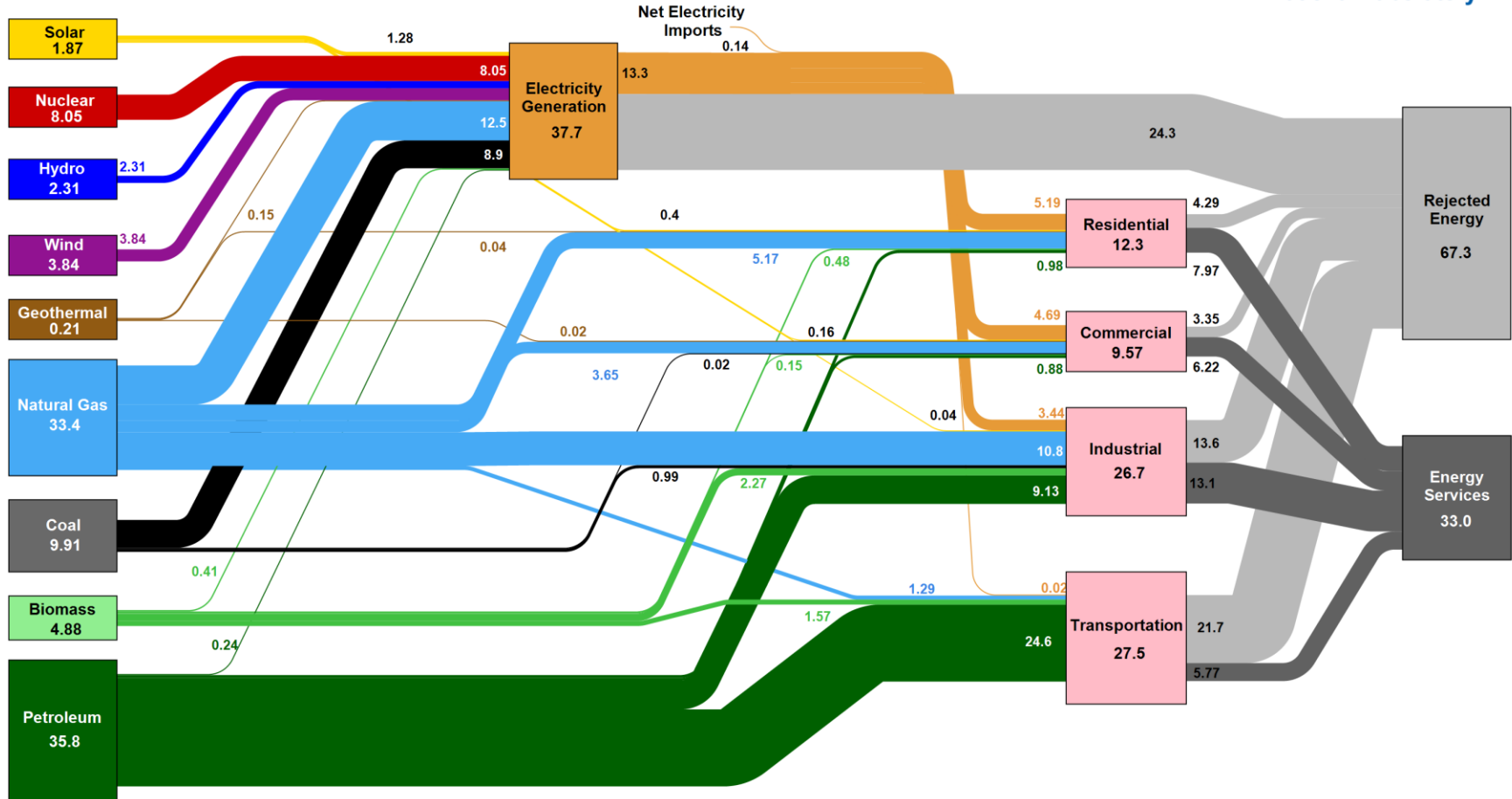
September 28th, 2024







Estimated U.S. Energy Consumption in 2022: 100.3 Quads



Source: LLNL July, 2023. Data is based on DOE/EIA SEDS (2021). If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports consumption of renewable resources (i.e., hydro, wind, geothermal and solar) for electricity in BTU-equivalent values by assuming a typical fossil fuel plant heat rate. The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 0.65% for the residential sector, 0.65% for the commercial sector, 0.49% for the industrial sector, and 0.21% for the transportation sector. Totals may not equal sum of components due to independent Rounding. LLNL-MI-410527

Renewables are a sizeable and growing part of the US energy mix

41% of electricity generation is currently produced by non-fossil sources

Need to decarbonize 22 quadrillion BTUs of energy production by 2035!

Solar
1.28

Nuclear
8.05

Hydro
2.31

Wind
3.84

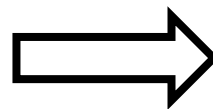
Geothermal
0.15

Natural Gas
12.5

Coal
8.90

Biomass
0.41

Petroleum
0.24



Electricity
Generation
37.7

Renewables are a sizeable and growing part of the US energy mix

22% of energy generation for all sectors is currently produced by non-fossil sources

Need to decarbonize 56.5 quadrillion BTUs of energy production by 2050!

Solar
1.87

Nuclear
8.05

Hydro
2.31

Wind
3.84

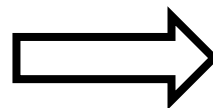
Geothermal
0.21

Natural Gas
32.1

Coal
9.91

Biomass
3.31

Petroleum
11.2



Non-Transportation Consumption
72.8

You can track grid supply and demand in real time in California



Today's Outlook

Demand

Supply

Emissions

Prices

Current

Demand trend

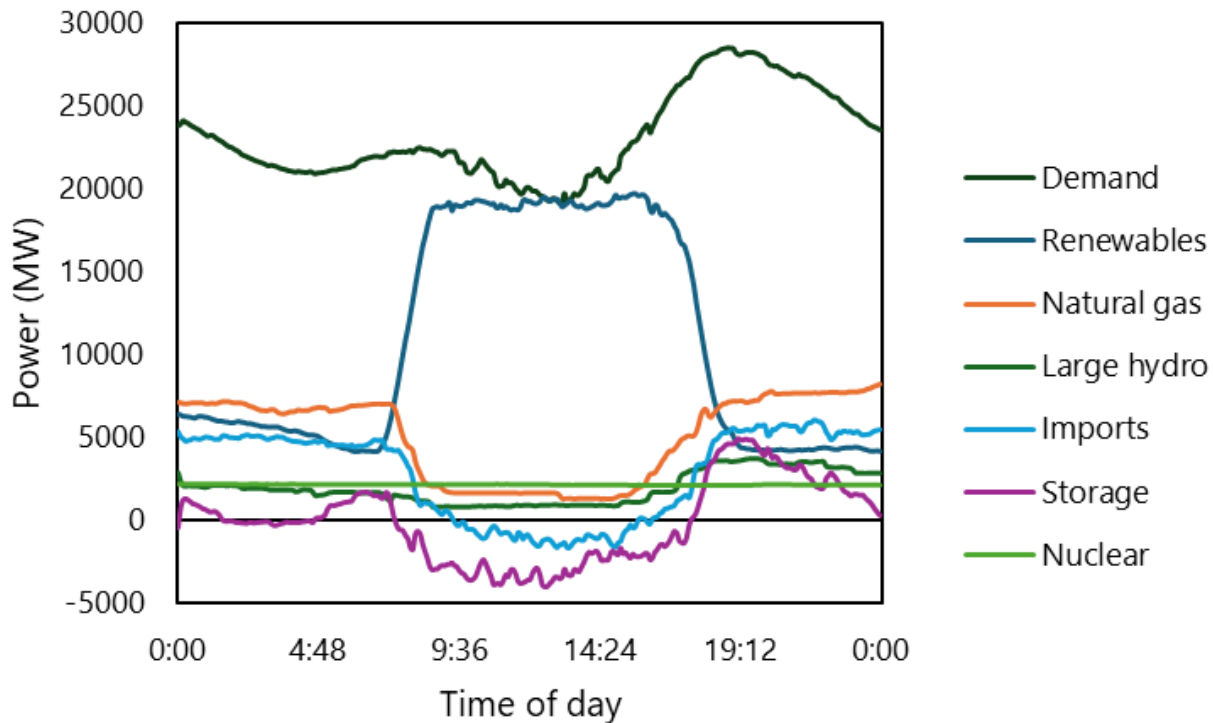
Net demand trend

Resource adequacy trend

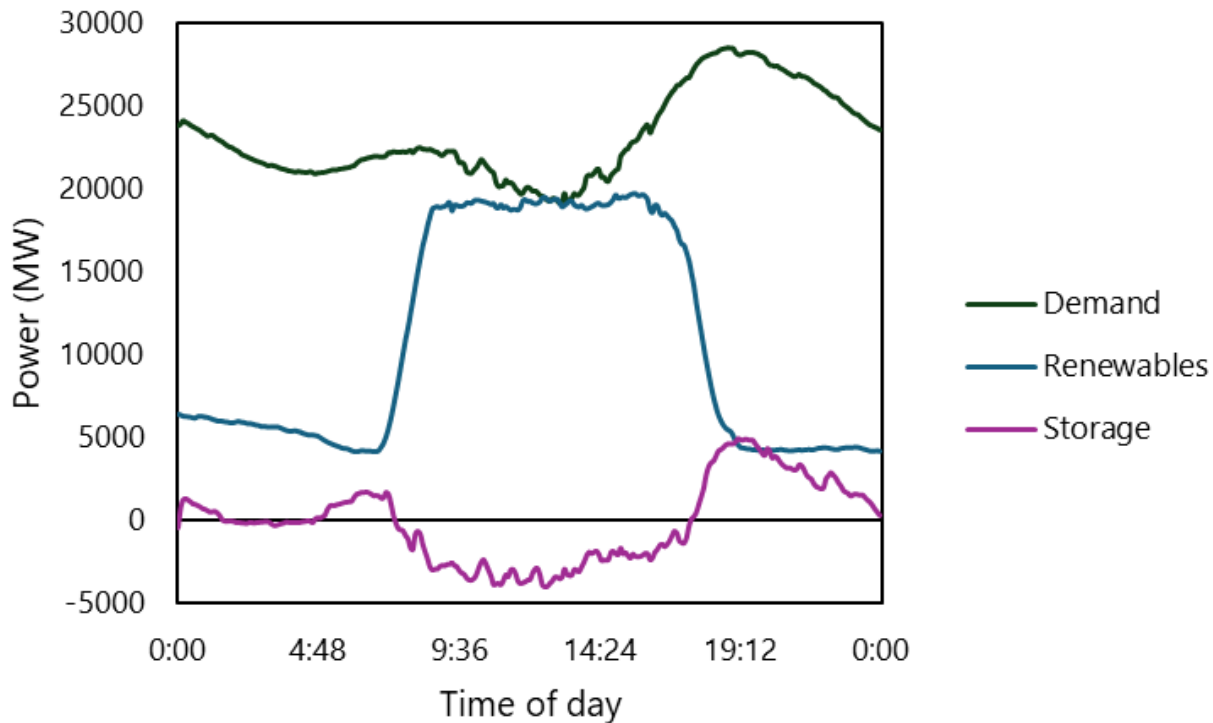
7-day resource adequacy trend

www.caiso.com/todays-outlook/

Overlaying supply and demand shows the need to time-shift the energy



Overlaying supply and demand shows the need to time-shift the energy



What are the different large-scale energy storage technologies?

Mechanical/Thermal

Pumped hydropower

Compressed air

Flywheels

Molten salt

Electrochemical

Lithium-ion batteries

Sodium-ion batteries

Flow batteries

Supercapacitors

Hydrogen

What are the different large-scale energy storage technologies?

Mechanical/Thermal

Pumped hydropower

Compressed air

Flywheels

Molten salt

Electrochemical

Lithium-ion batteries

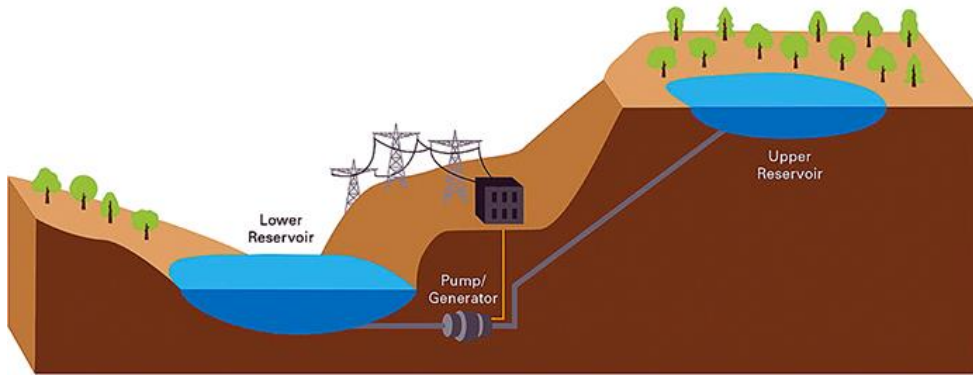
Sodium-ion batteries

Flow batteries

Supercapacitors

Hydrogen

The oldie but goodie: pumped hydropower

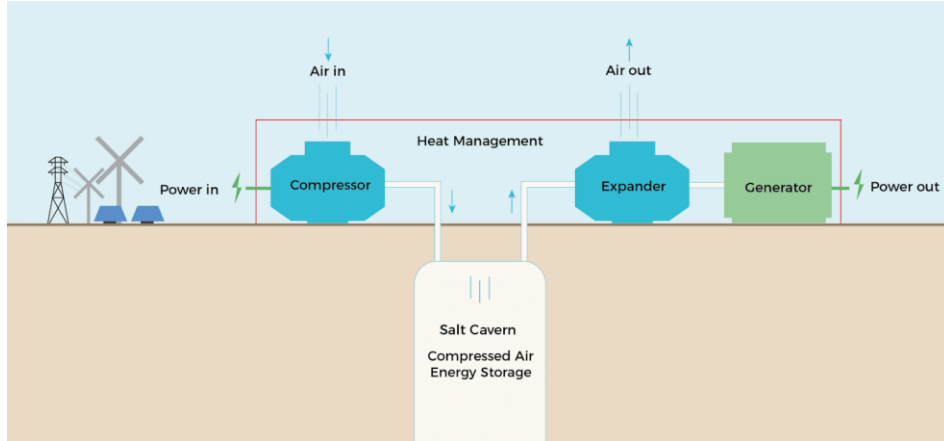


Mature

Cheap

Geographically Limited

Compressed air is also a cheap, but limited method for storing energy

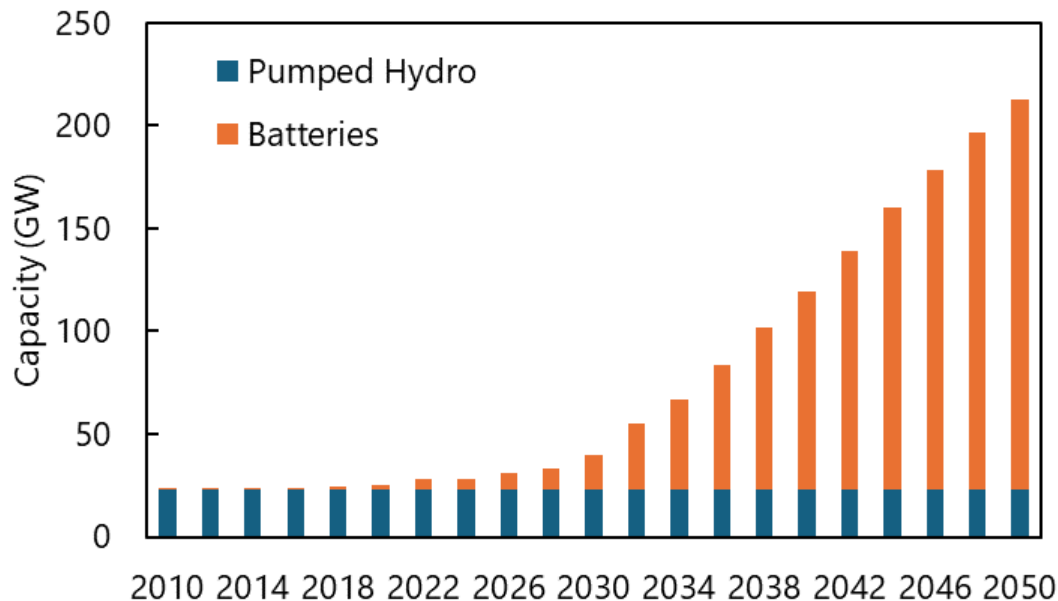


Mature

Cheap

Geographically Limited

Battery energy storage is projected to grow from 20 to 200 GW of capacity by 2050



Electrochemical systems: a “battery” of choices

Mechanical/Thermal

Pumped hydropower

Compressed air

Flywheels

Molten salt

Electrochemical

Lithium-ion batteries

Sodium-ion batteries

Flow batteries

Supercapacitors

Hydrogen

Electrochemical systems: a “battery” of choices

Science

Current Issue First release papers Archive About ▾ (

HOME > SCIENCE > VOL. 334, NO. 6058 > ELECTRICAL ENERGY STORAGE FOR THE GRID: A BATTERY OF CHOICES

🔒 | SPECIAL ISSUE REVIEW



Electrical Energy Storage for the Grid: A Battery of Choices

BRUCE DUNN, HARESH KAMATH, AND JEAN-MARIE TARASCON [Authors Info & Affiliations](#)

SCIENCE • 18 Nov 2011 • Vol 334, Issue 6058 • pp. 928-935 • DOI: 10.1126/science.1212741

Electrochemical

Lithium-ion batteries

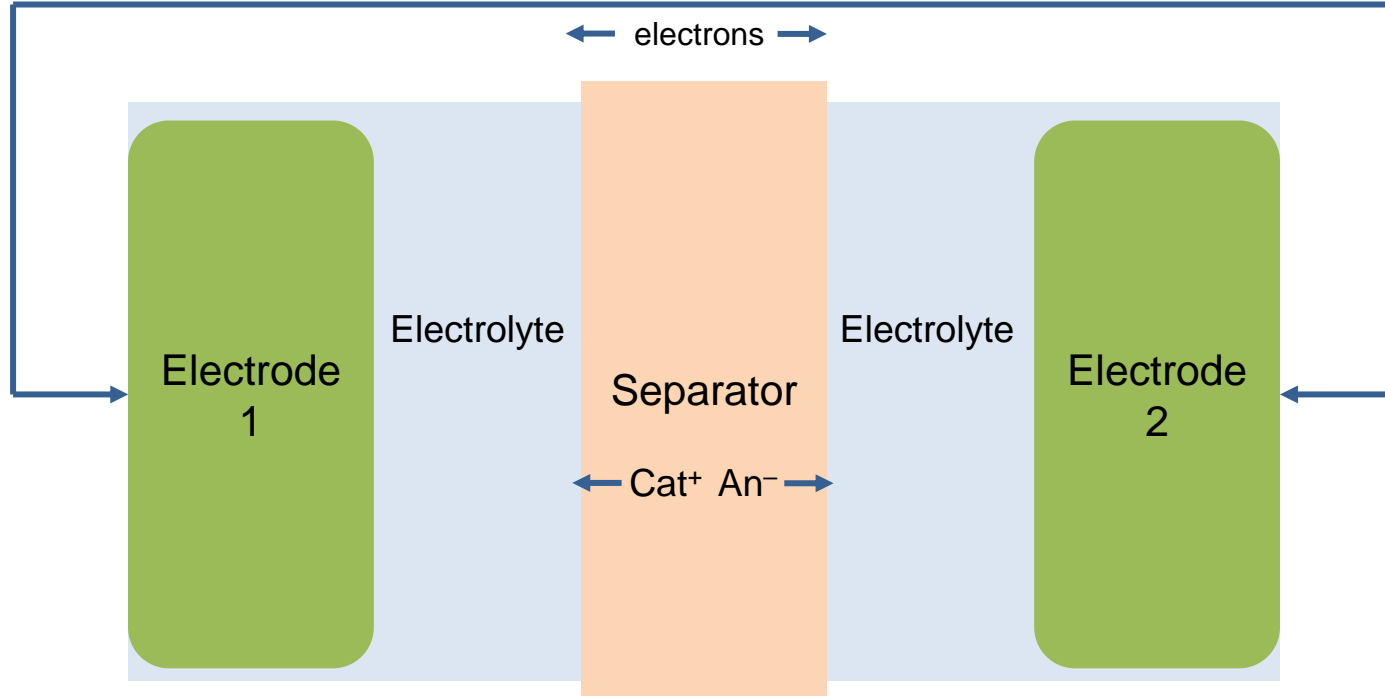
Sodium-ion batteries

Flow batteries

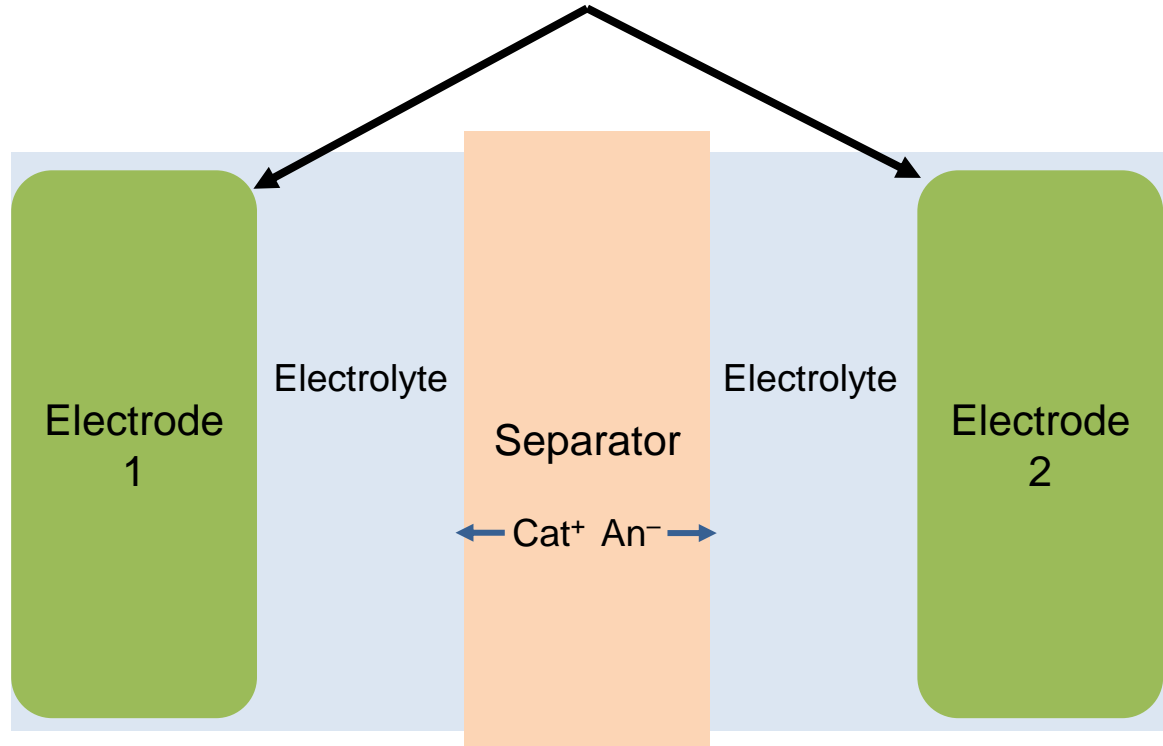
Supercapacitors

Hydrogen

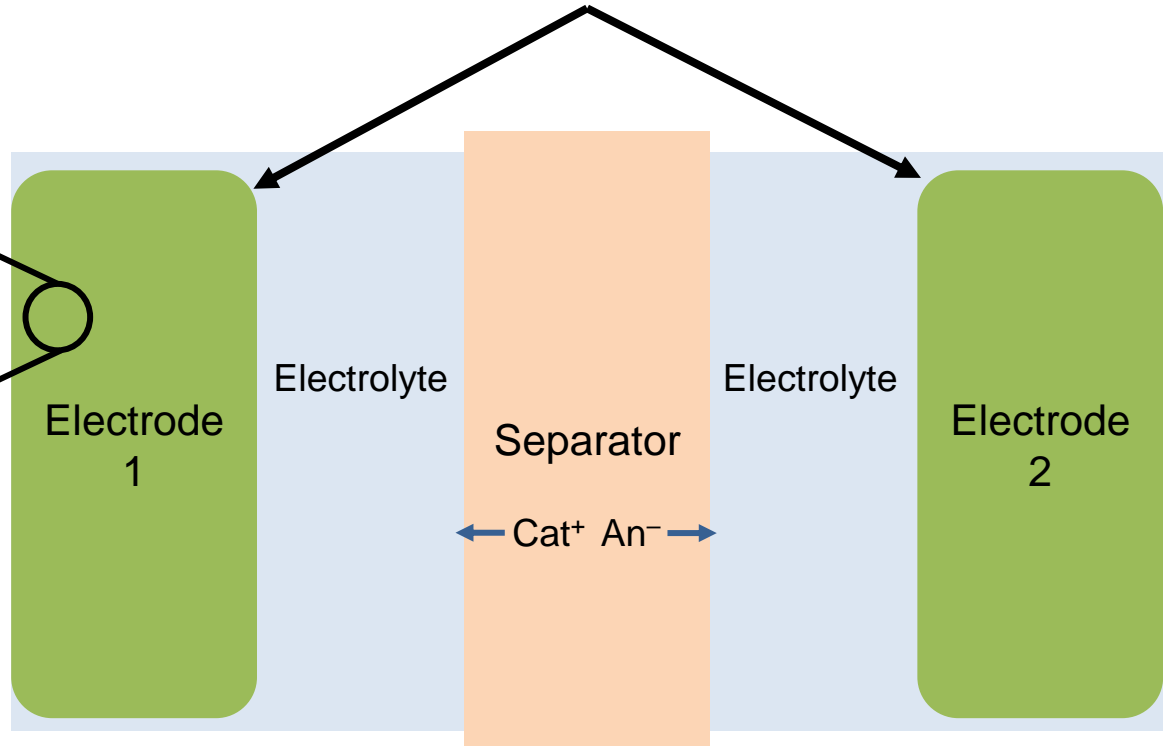
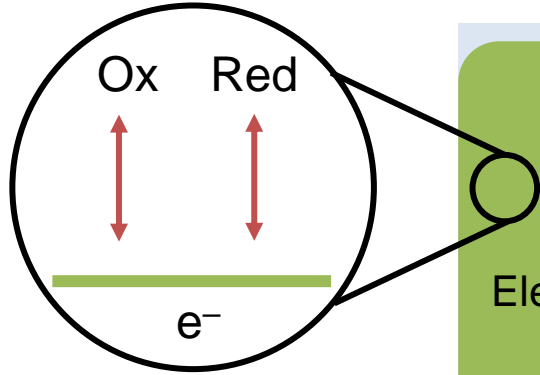
Electrochemical systems are comprised of two electrodes, an electrolyte, and (sometimes) a separator



Need unique reactions at each electrode to create a **thermodynamic** difference

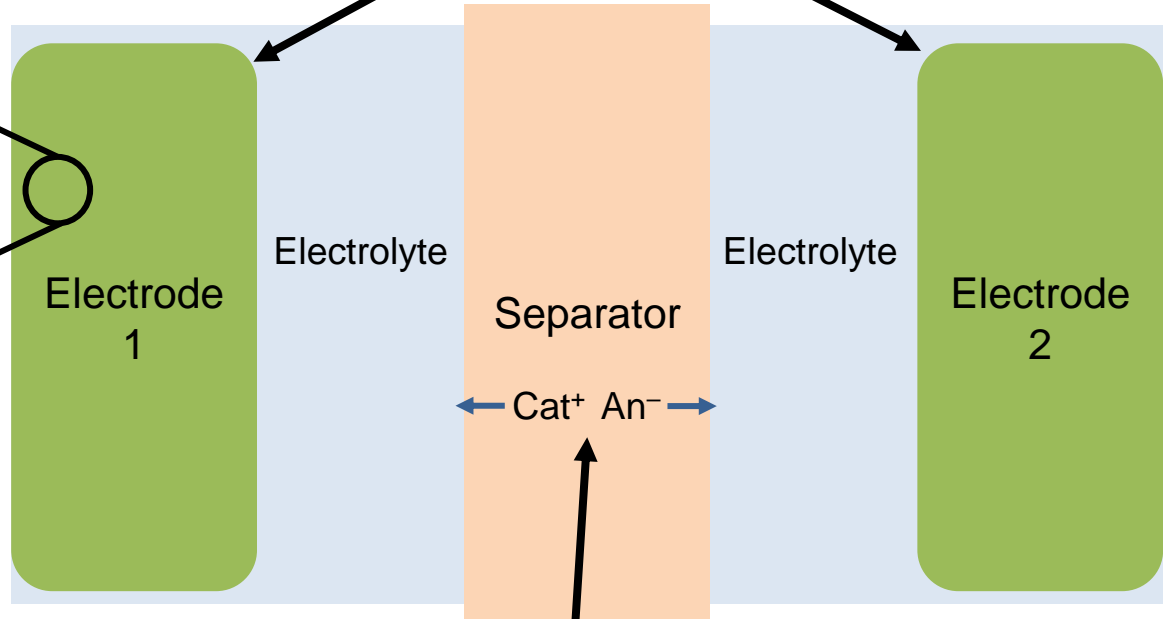
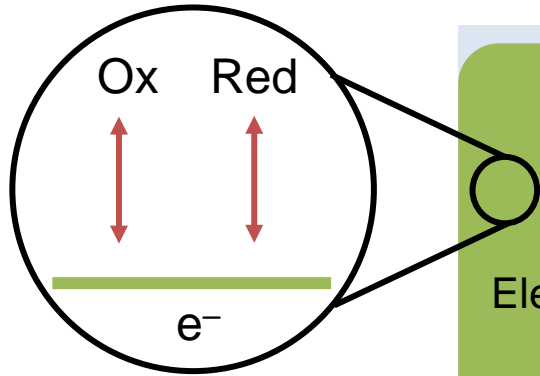


Need unique reactions at each electrode to create a **thermodynamic** difference



Need fast transport to and from the surface to reduce **mass transport** losses

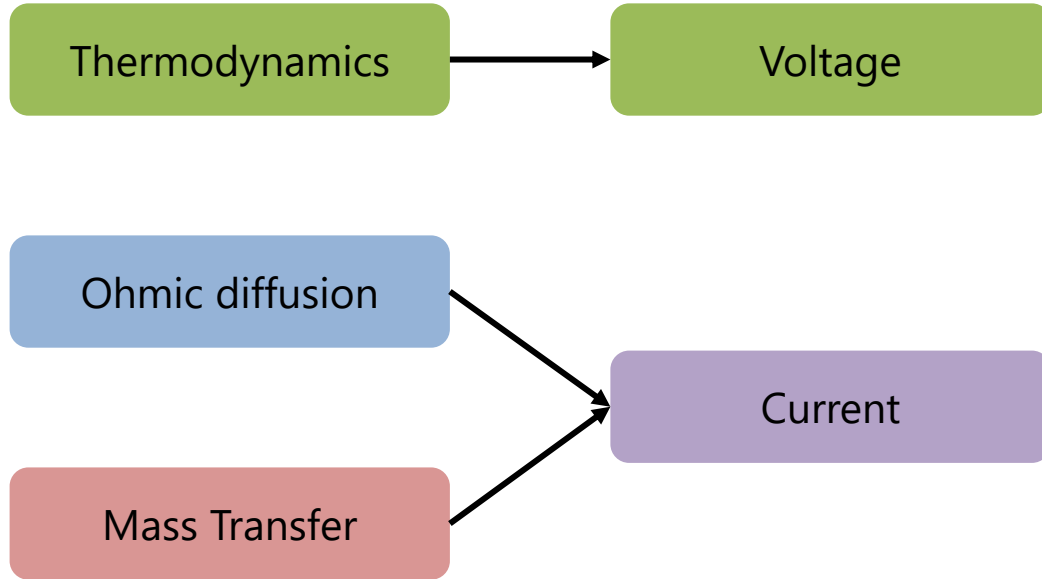
Need unique reactions at each electrode to create a **thermodynamic** difference



Need fast transport to and from the surface to reduce **mass transport** losses

Need fast diffusion through the electrolyte and separator to reduce **ohmic** losses

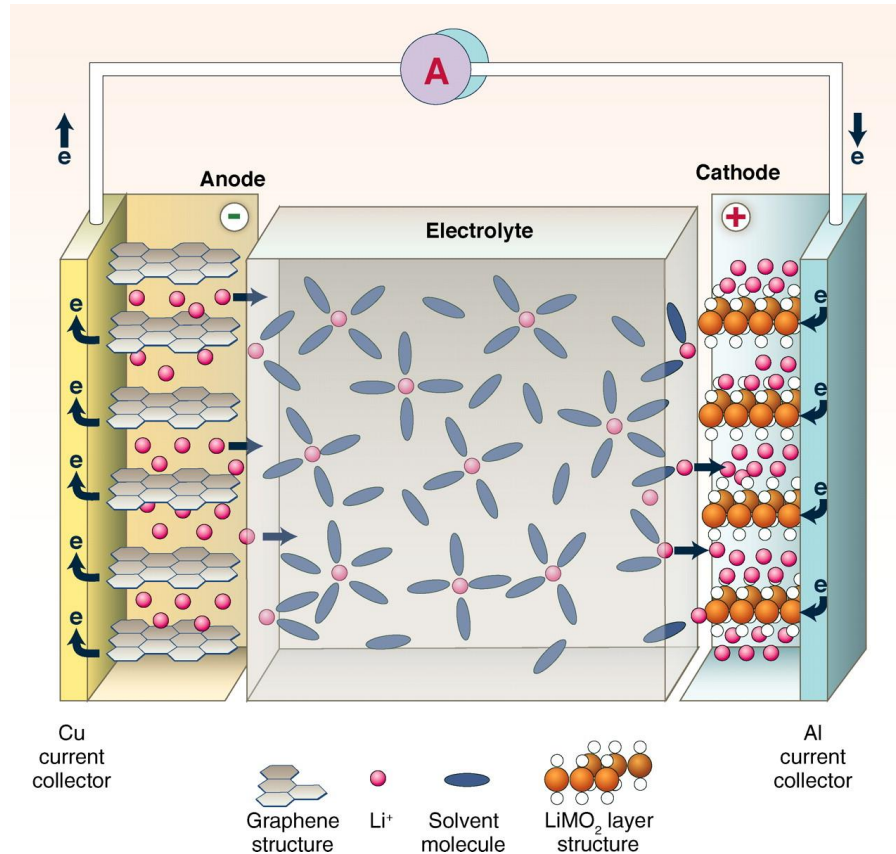
These three fundamental properties control battery performance



$$Power = Current * Voltage$$

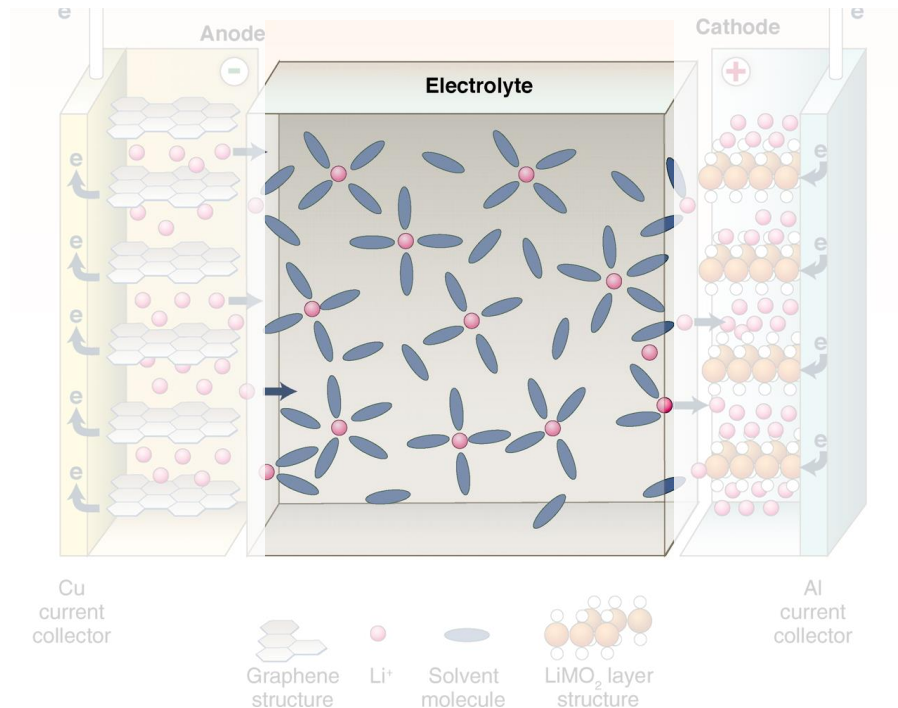
$$Energy = \int Power * Time$$

The battery you have probably heard of: the lithium-ion battery



“Generation 2” electrolyte:
 LiPF_6 with a mixture of ethylene carbonate / ethylmethyl carbonate

Electrolyte needs: high lithium diffusivity, good temperature stability, high voltage window

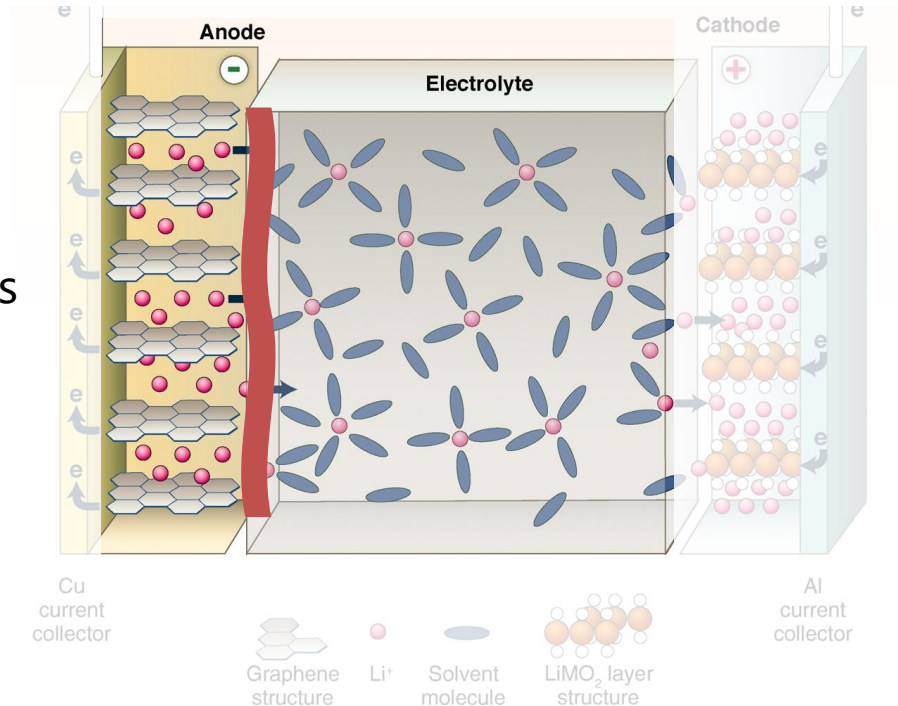


“Generation 2” electrolyte:

LiPF_6 with a mixture of ethylene carbonate / ethylmethyl carbonate

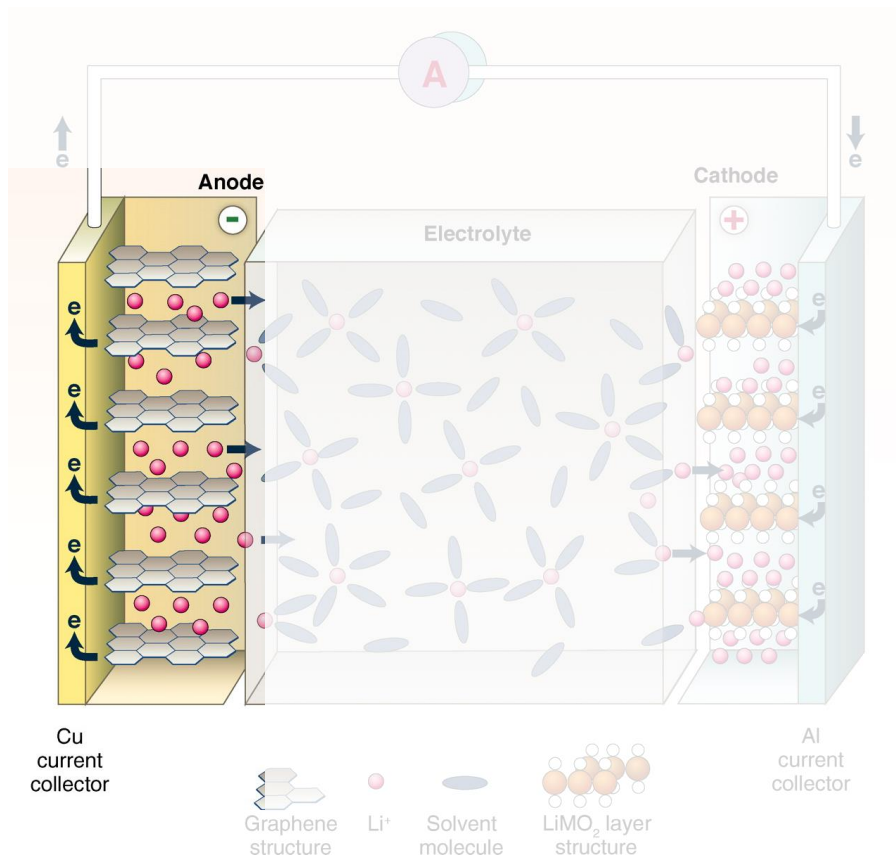
Electrolyte needs: high lithium diffusivity, good temperature stability, high voltage window

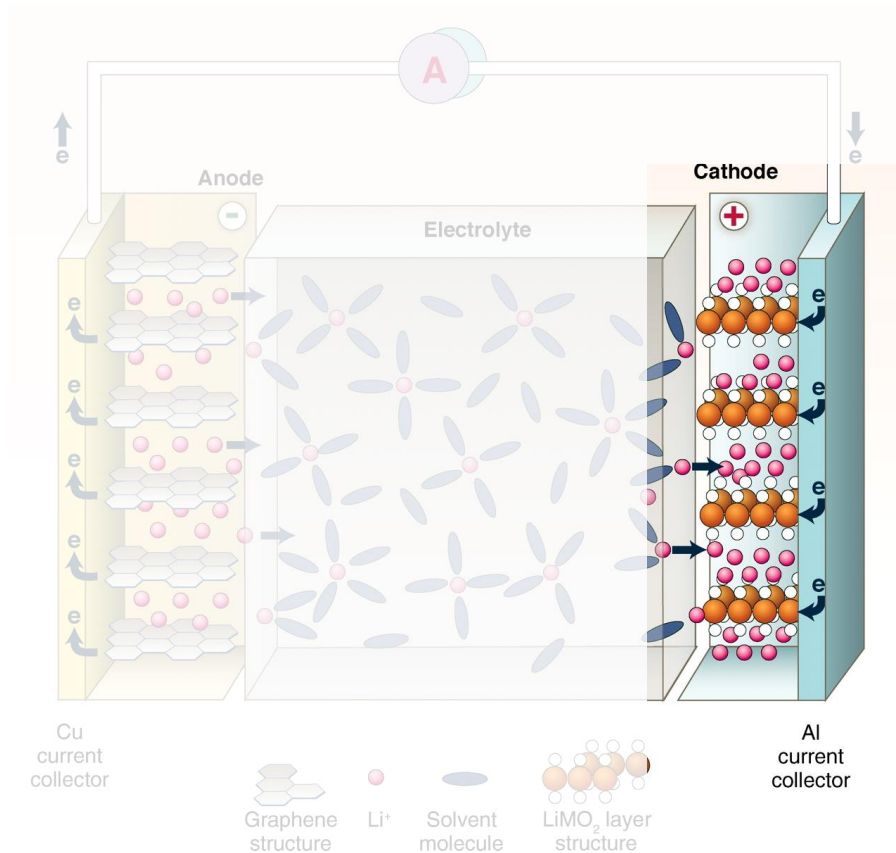
Electrolyte can breakdown to form a resistive film known as the “solid electrolyte interphase” (SEI)



Graphitic carbon
 $\text{LiC}_6 \leftrightarrow \text{C}_6 + \text{Li}$

Most of the mass
is graphite!





Two most common:

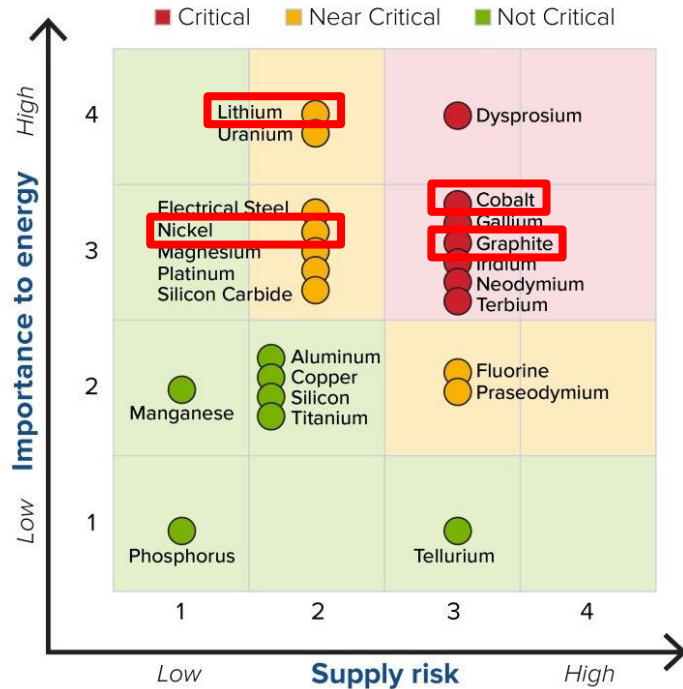
- L Lithium
- F Fe (iron)
- P Phosphate

- N Nickel
- M Manganese
- C Cobalt oxide

Not very conductive!
Add: carbon, PVDF, etc.

Materials for lithium-ion batteries have high supply risk

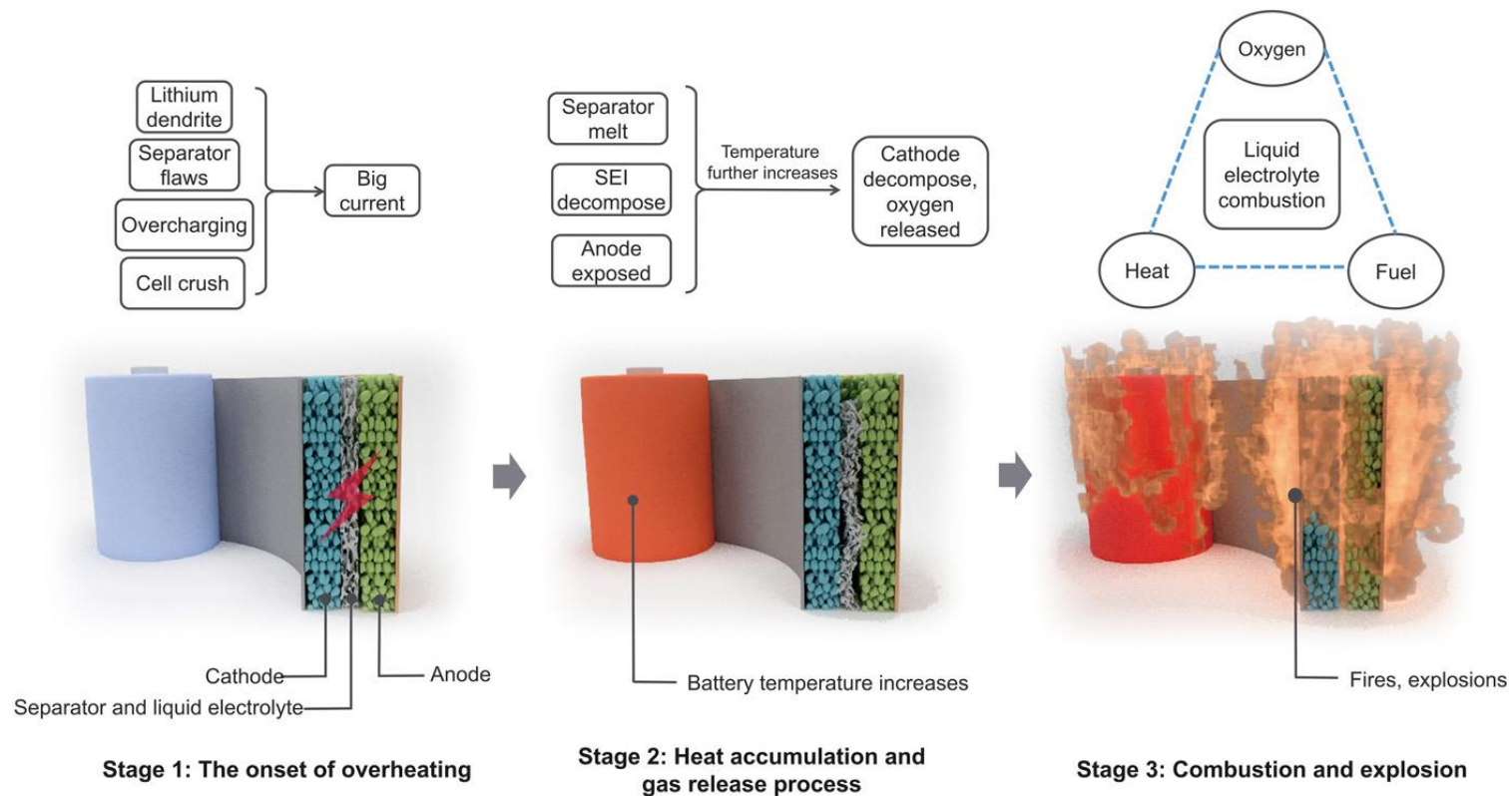
SHORT TERM 2020-2025



MEDIUM TERM 2025-2035



Thermal runaway can cause them to catch fire



**While these events are somewhat infrequent,
they can still cause concern**

Lithium Battery Fire Continues to Burn as County Considers Moratorium

TIMES
of SAN DIEGO

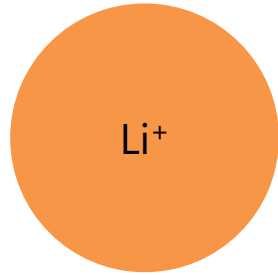
Sept. 7th, 2024

What is very similar to lithium, but not quite lithium?

Sodium!

What is different about lithium and sodium?

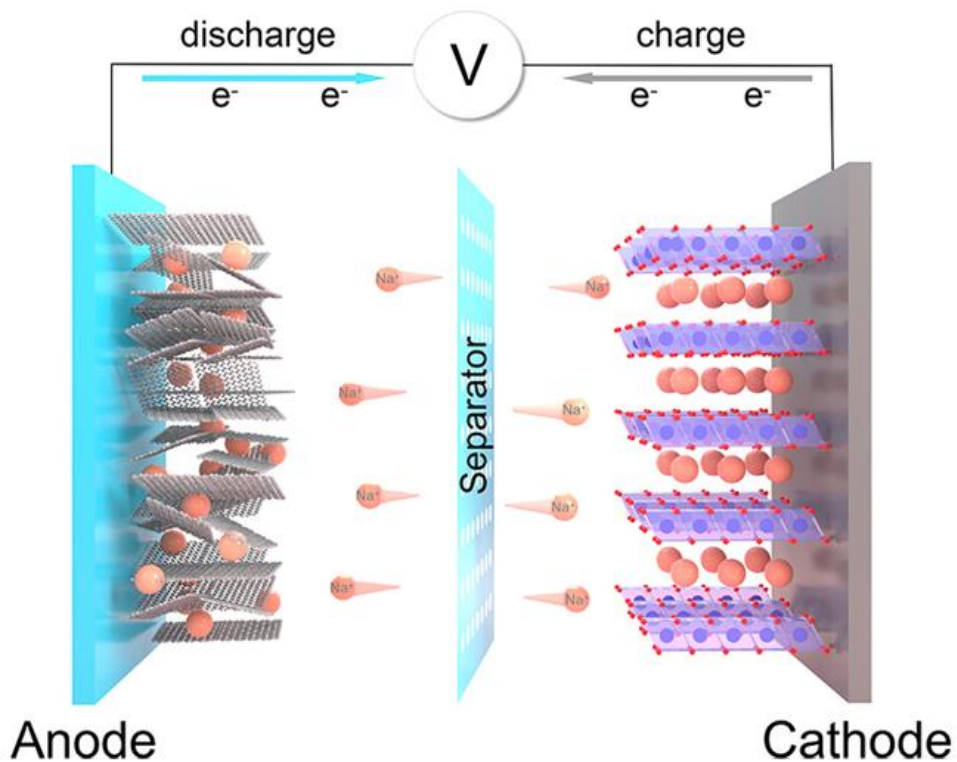
Molecular size!



This impacts

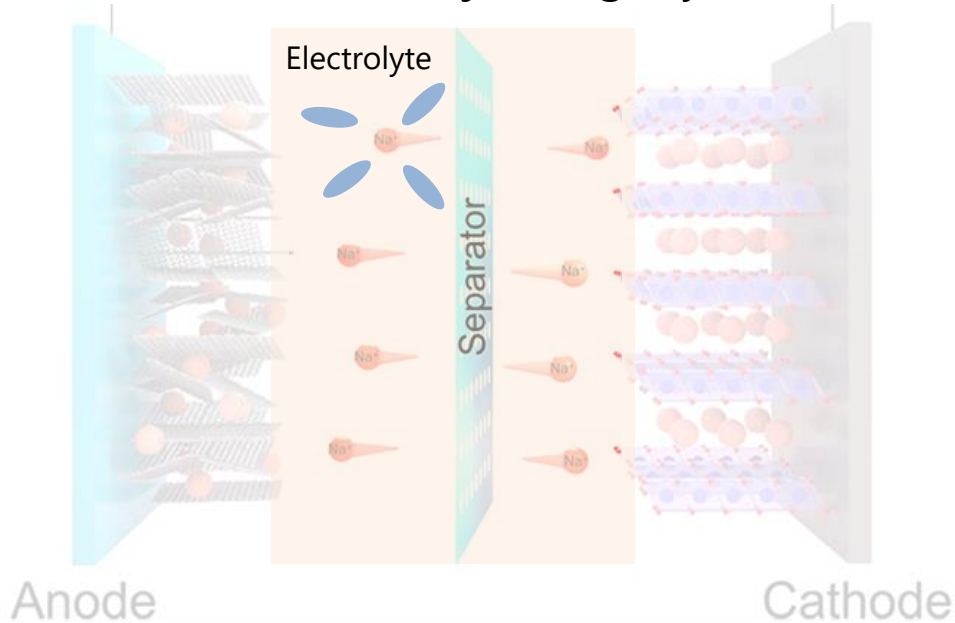
- solvent-ion relationship changing diffusivity
- ion intercalation into electrode materials
- weight of the battery

How does that change the materials needed?



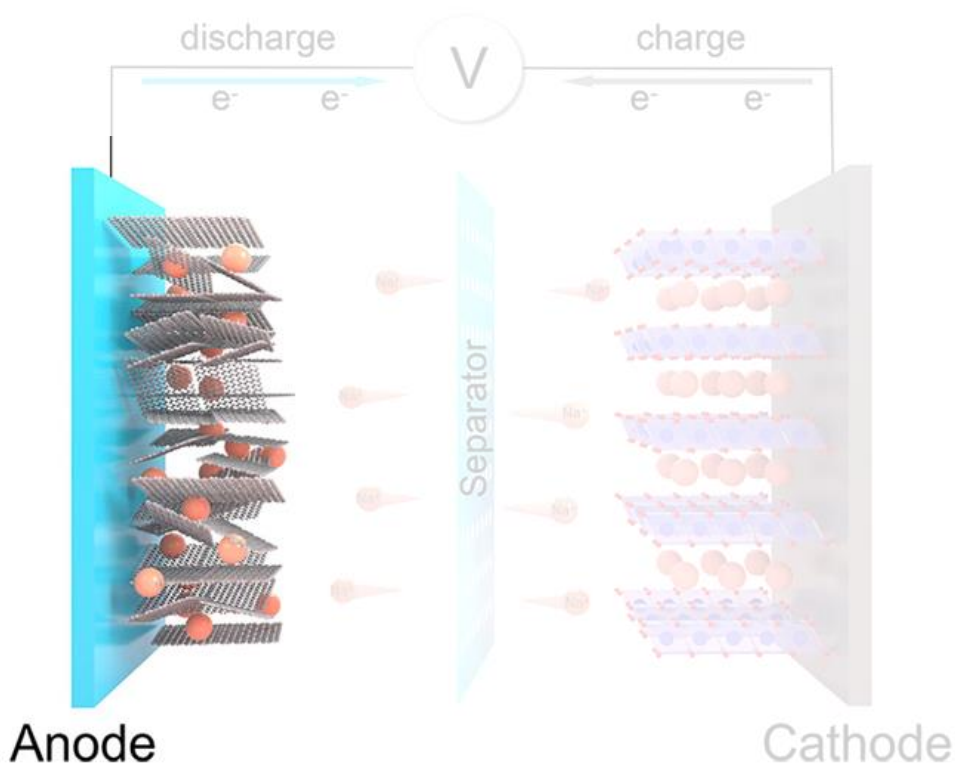
Electrolyte can vary, but is quite similar to lithium
 NaPF_6 or NaClO_4 with a mixture of
ethylene carbonate / diethyl carbonate or propylene carbonate

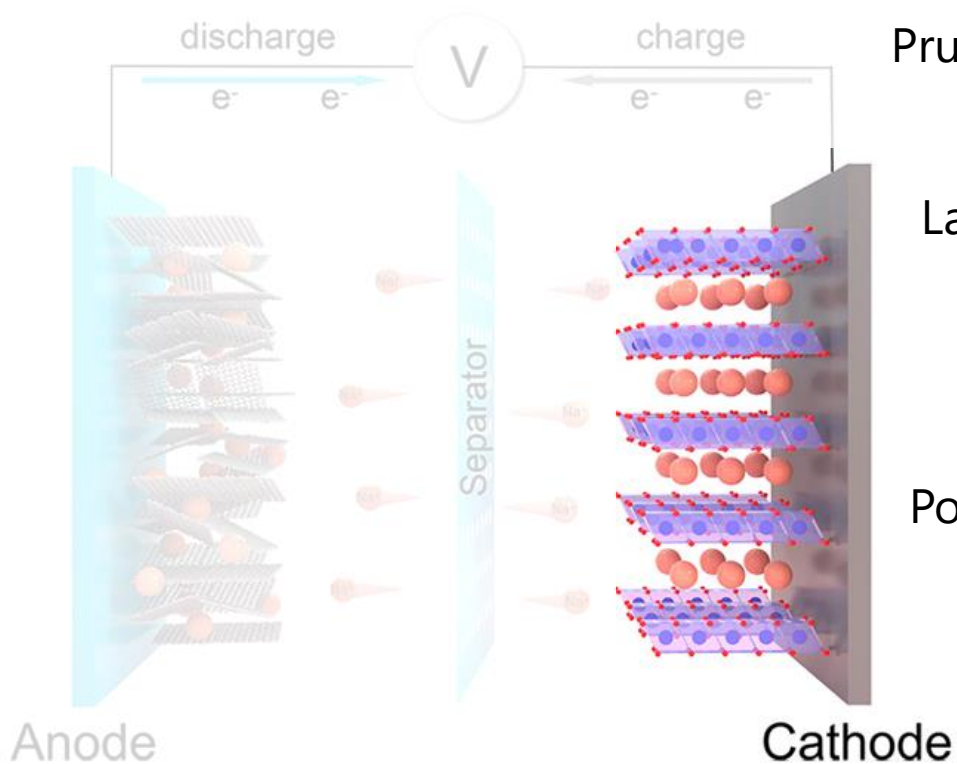
Conductivities are just slightly lower



Sodium insertion
into graphitic
carbon is poor!

“Hard” Carbon
(similar to charcoal)
or graphene are
more often used





Prussian Blue Analogues
 $Mn[Fe(CN)_6]_3$

Layered Metal Oxides

MnO_2

VO_2

FeO_2

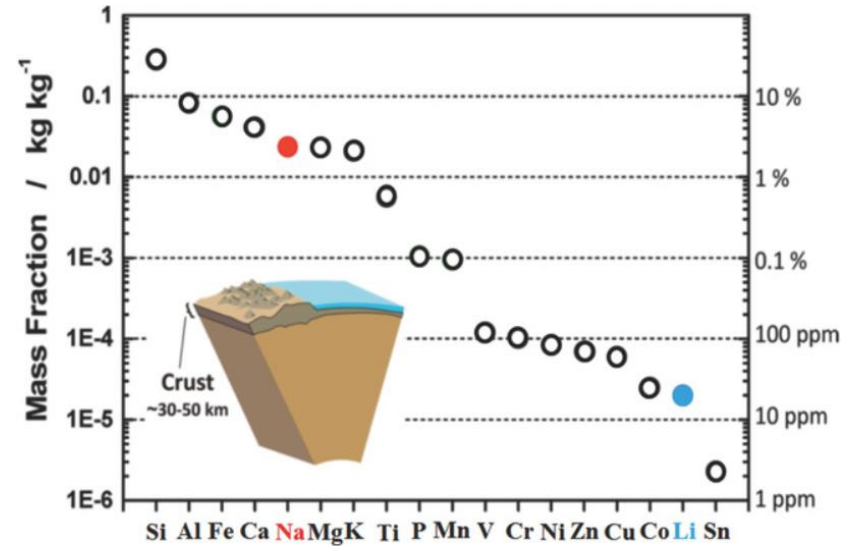
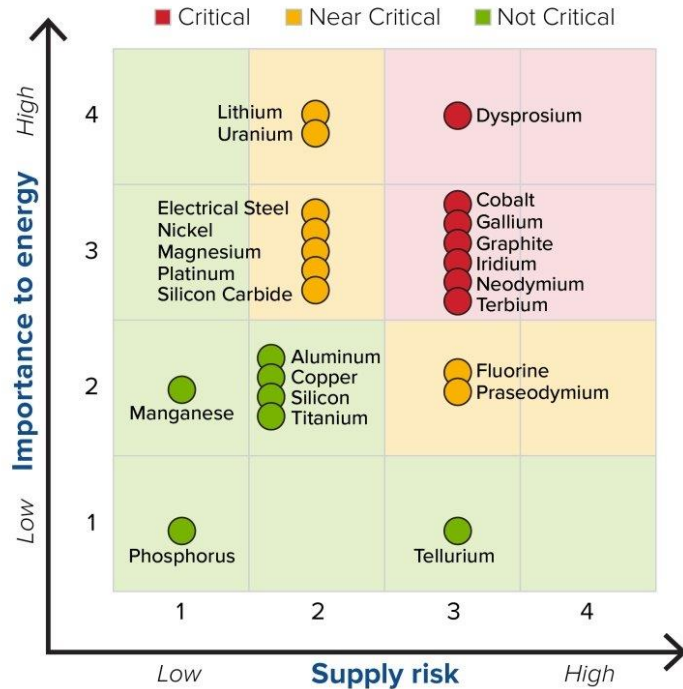
Polyanion Compounds

$V_2(PO_4)_3F$

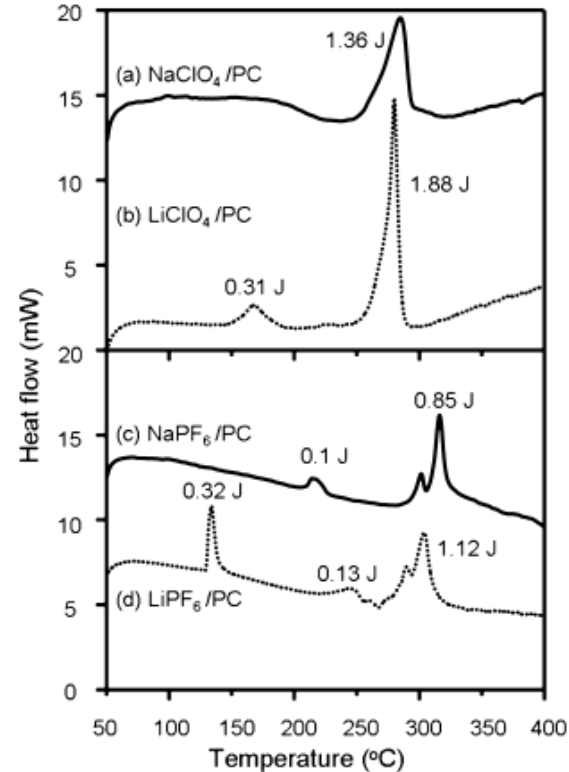
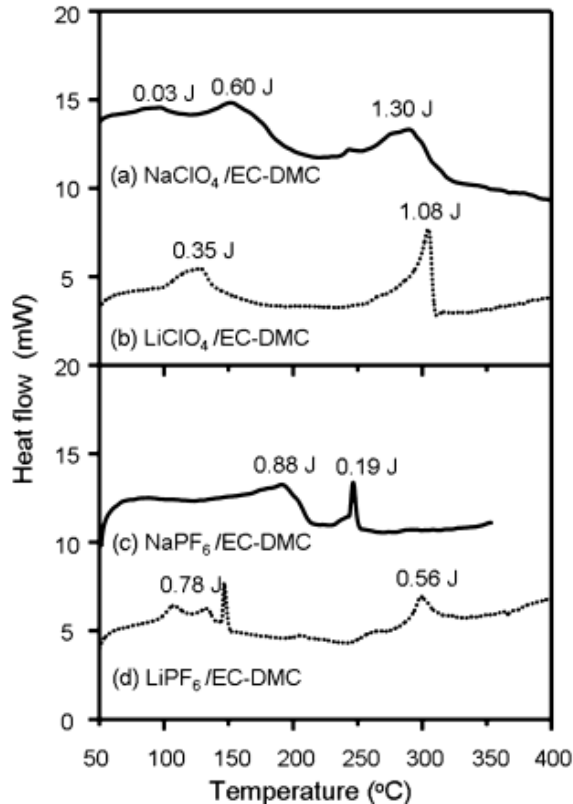
$Fe_2(SO_4)_3$

Materials for sodium ion batteries have low supply risk and are abundant

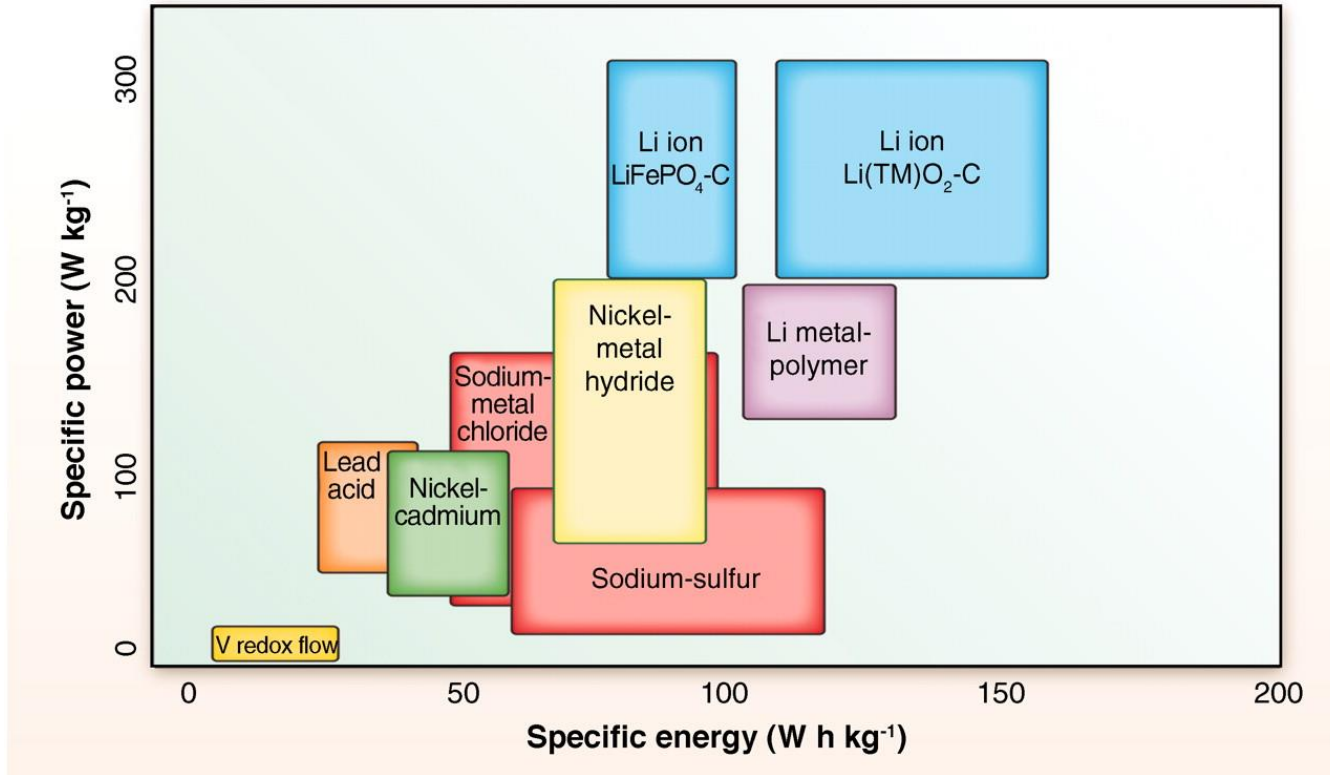
SHORT TERM 2020-2025



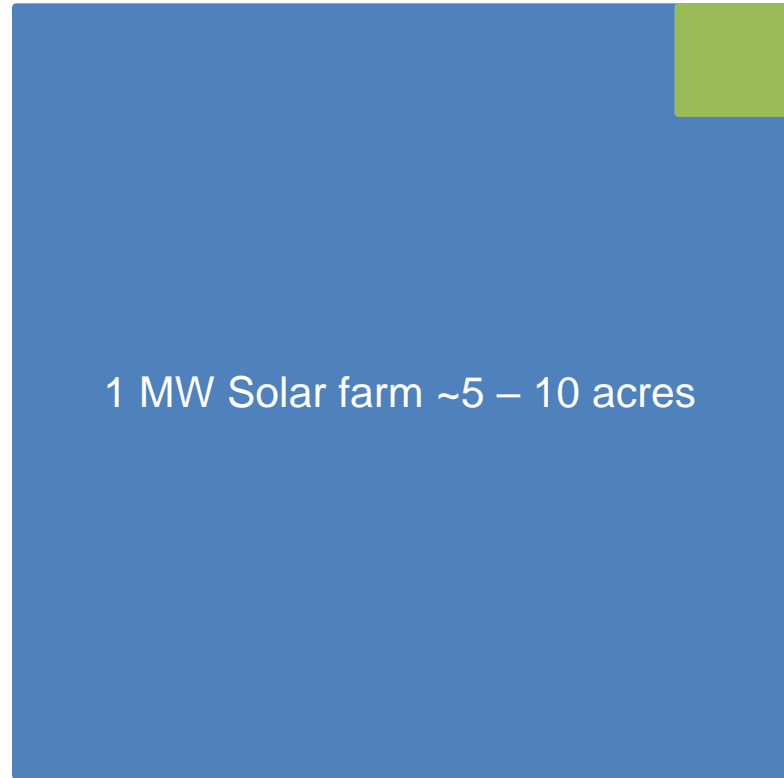
Sodium ion materials have been shown to be less prone to thermal runaway



Non-flow batteries are very power and energy dense



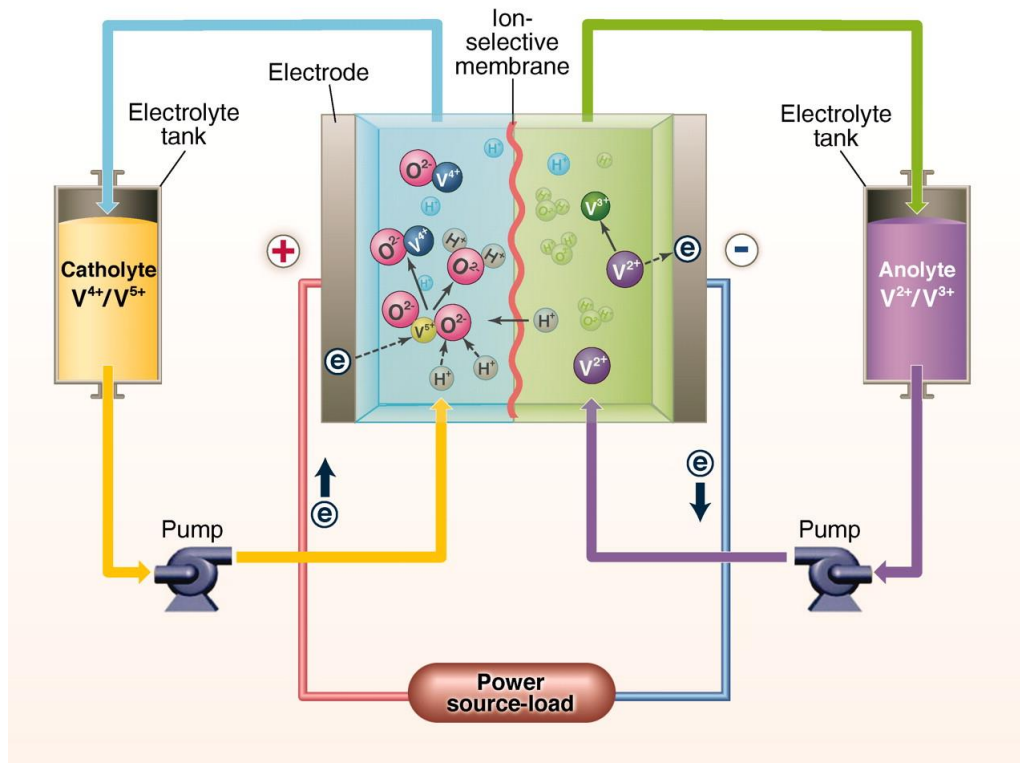
For grid scale storage, energy density is not a huge deal for system footprint



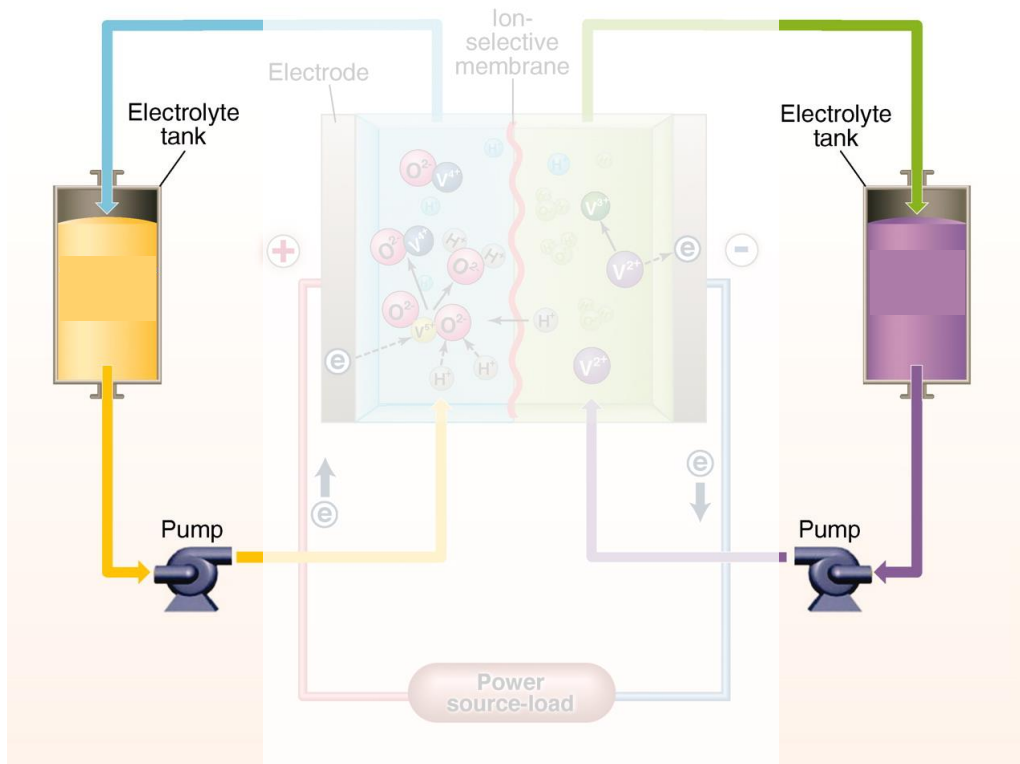
1 MW Solar farm ~5 – 10 acres

1 MW battery ~0.1 acres

Flow batteries store the electrolytes in external tanks and pump them through the electrodes



Positive electrolyte
"Posolyte"
Metal Salt 1
Supporting Salt
Water



Negative electrolyte
"Negolyte"
Metal Salt 2
Supporting Salt
Water

There is a myriad of metal combinations for aqueous flow batteries

Aqueous Chemistries

Posolyte

Negolyte

Vanadium FB



Supporting electrolyte: H_2SO_4 , HNO_3

Iron-Chromium FB



Supporting electrolyte: HCl

"Hybrid" Chemistries

Posolyte

Negolyte

All-Iron FB



Supporting electrolyte: HAc , KCl

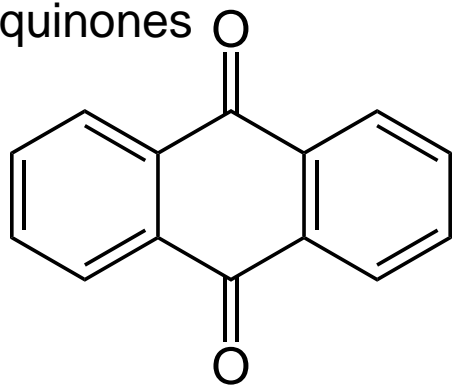
Zinc-Bromide FB



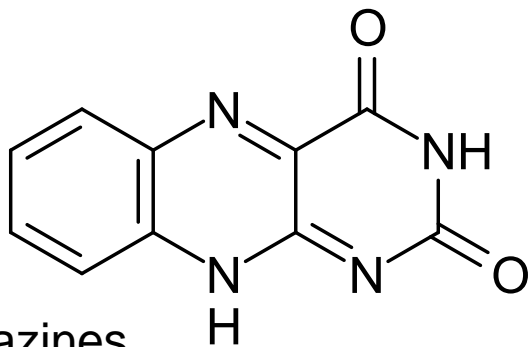
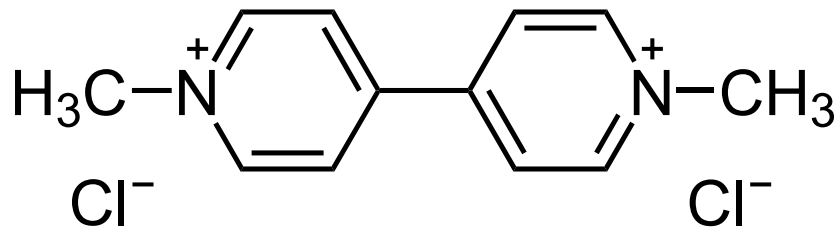
Supporting electrolyte: HBr

Organic chemists can have fun too!

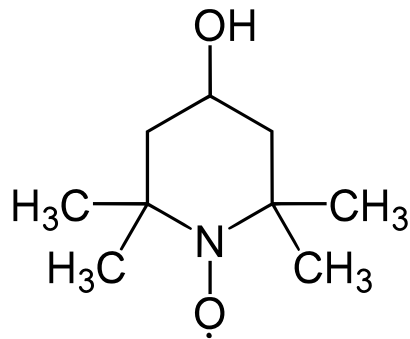
(Anthra)quinones



Viologens

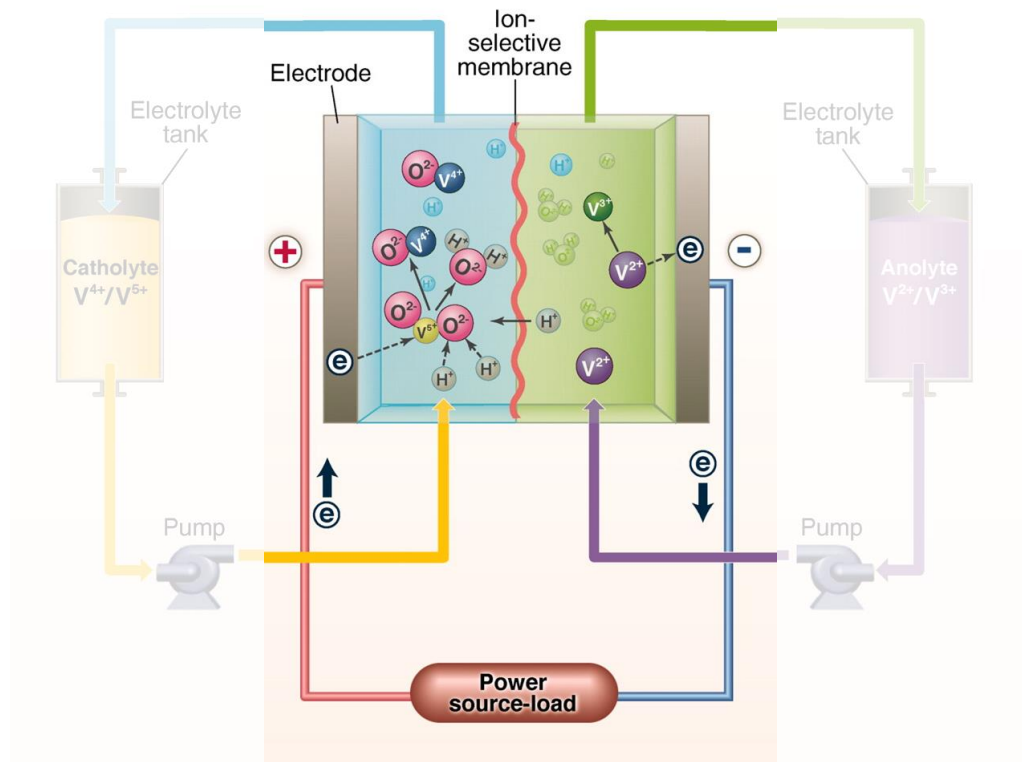


Alloxazines



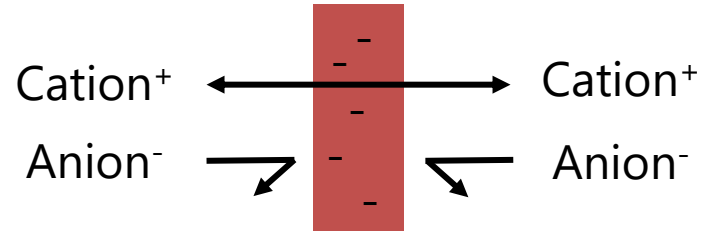
TEMPO

Charged polymeric membrane

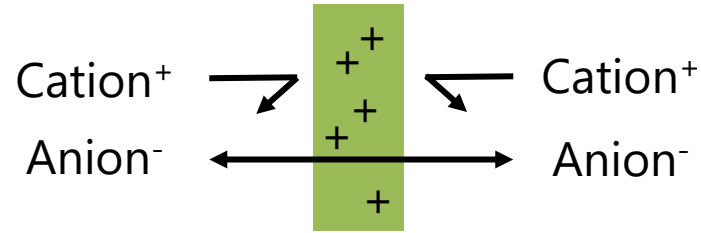


Charged polymeric membrane

Cation Exchange

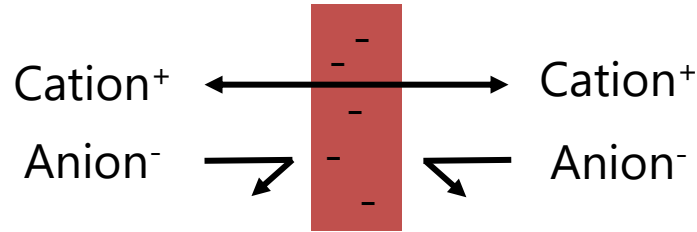


Anion Exchange



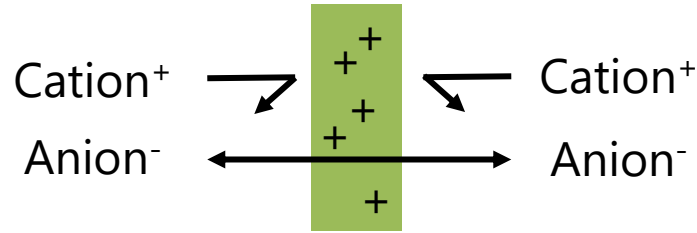
Charged
polymeric
membrane

Cation Exchange



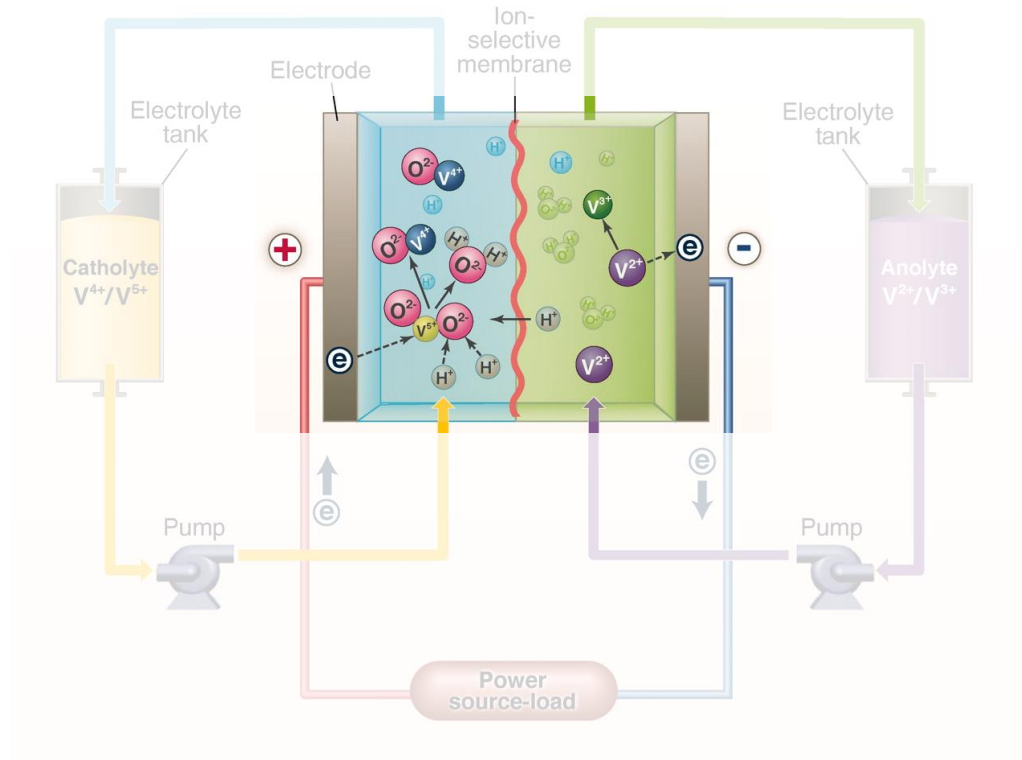
Most conductive cation: H^+

Anion Exchange

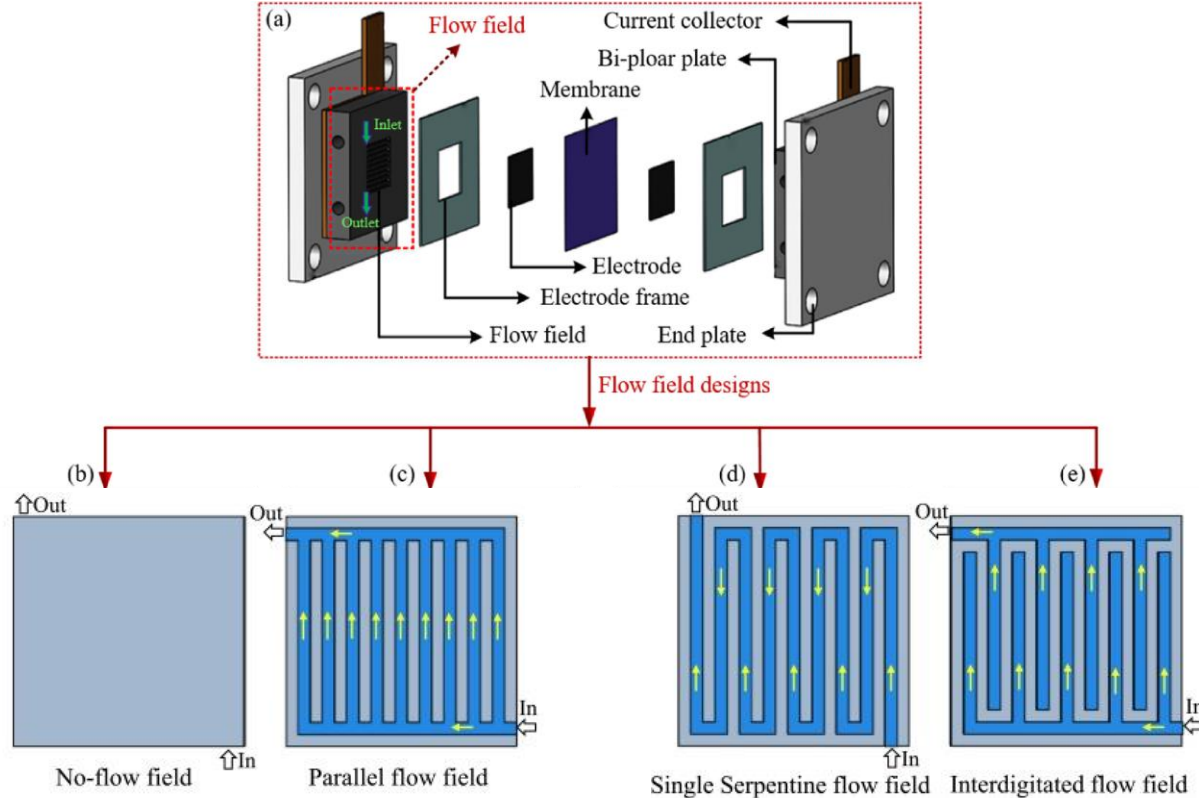


Most conductive anion: OH^-

How do we move the electrolyte through the electrodes?



There are multiple common flow field designs



Why are aqueous flow batteries safe? They extinguish fire



Current flow battery limitations

Expensive materials
(metals and membrane)

Strong acid electrolytes

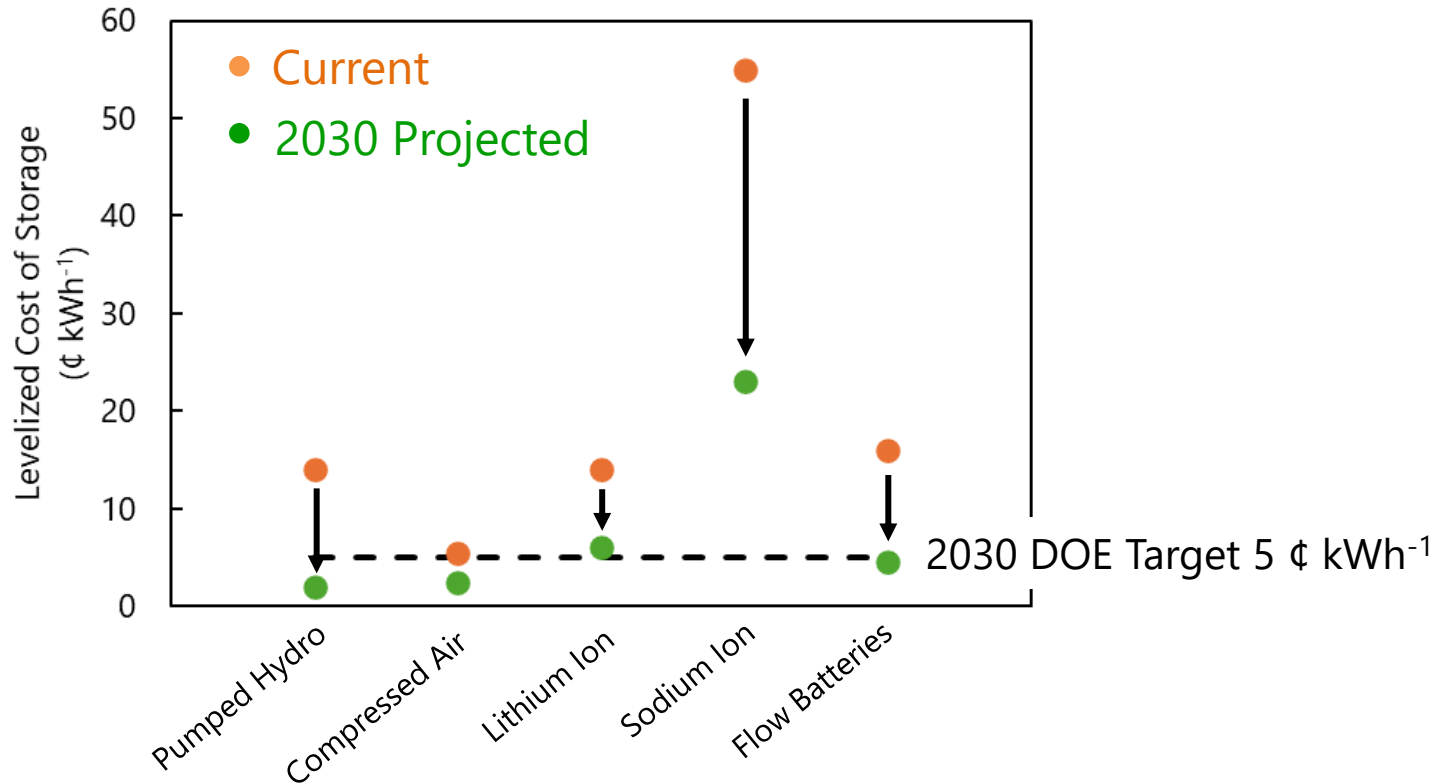
Low voltages to avoid
water splitting

Low round-trip
efficiency (~70%)

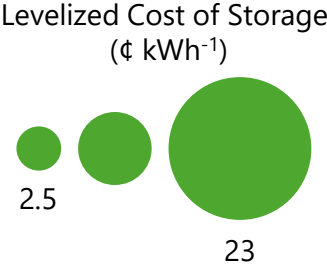
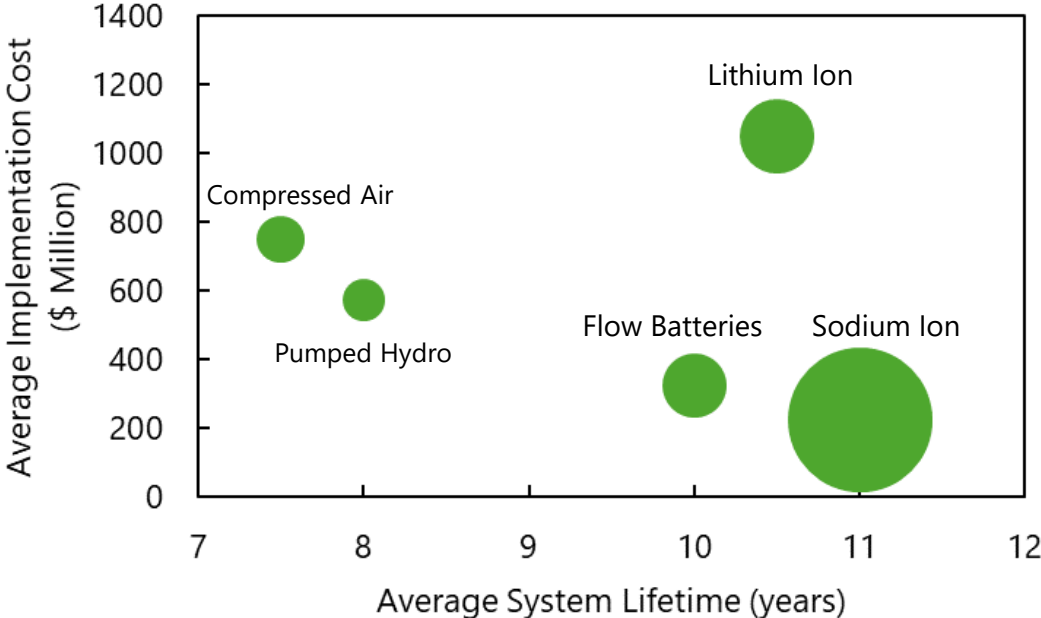
Now that we know the main technologies, we can compare them all with the universal metric:

Money

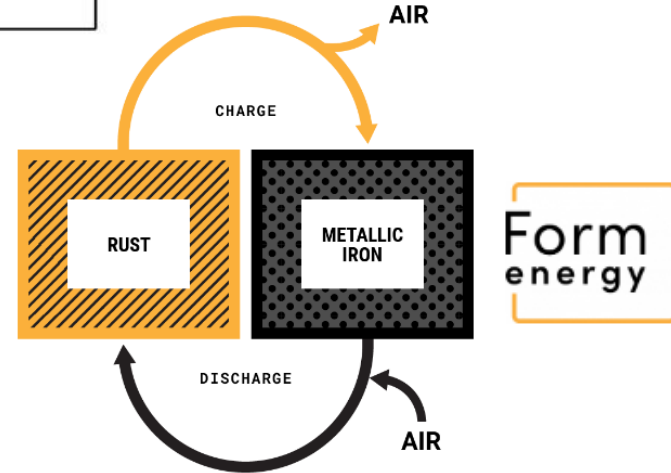
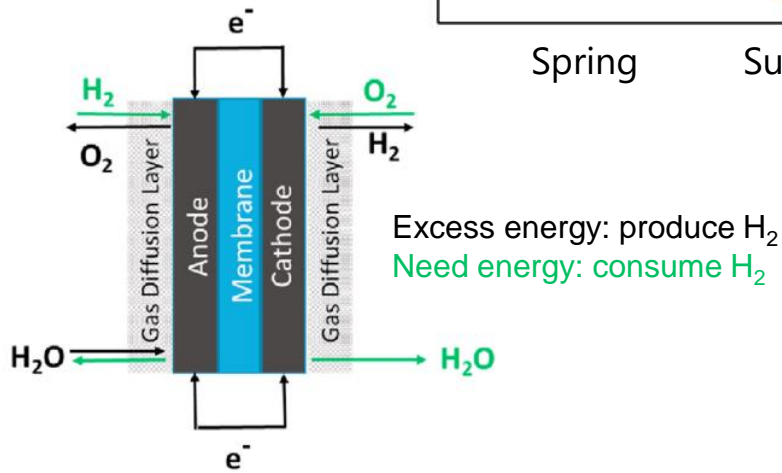
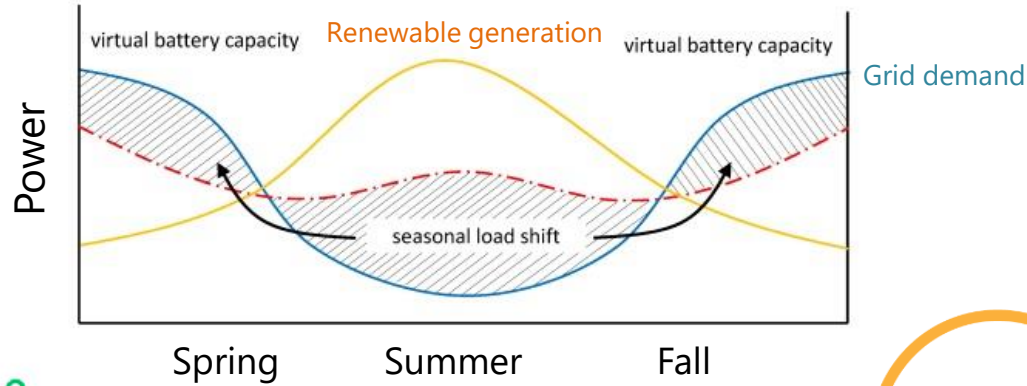
Future cost of most technologies is below the US Department of Energy target



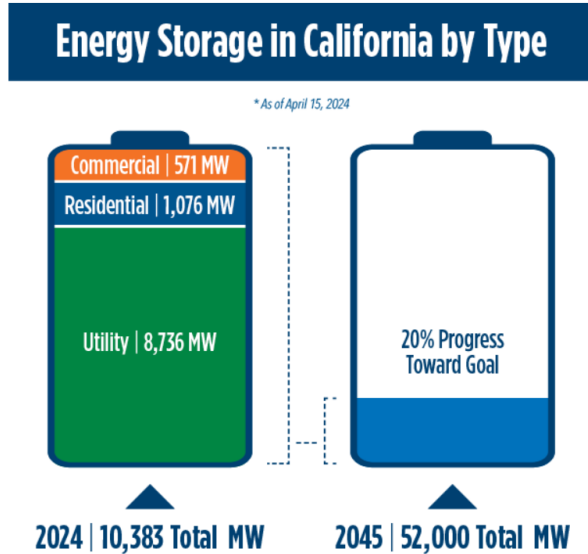
Capital cost and lifetime vary significantly



Other technologies that I didn't have time for: hydrogen and ultra-long duration storage



Progress in California: 10 GW of storage added has already helped prevent blackouts during heatwaves



Los Angeles Times

CALIFORNIA

California has new weapons to battle summer blackouts: Battery storage, power from record rain

The Mercury News

Environment | 'A game changer': How giant batteries are...



NEWS > ENVIRONMENT • News

'A game changer': How giant batteries are making California's power grid stronger, and reducing the risk of blackouts during heat waves

Thank you!