Introduction to Long Duration Energy Storage, Part 1. Electrochemical Technologies

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Sandia National Laboratories

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Outline

Session 1:

I. Introduction — Slides 1-10
- LDES need, classifications, use cases, challenges, current state of electric power generation and energy storage in CA

II. Technology Options for LDES
1. Electrochemical — Slides 11-22
   - Few battery fundamental concepts
   - Different types: Li- ion, Na- ion, flow batteries, metal-air batteries, others.

Q & A, break

Session 2:

2. Mechanical Storage
   - PHS, variations of PHS, Gravity, Compressed air, flywheels
3. Thermal Storage
   - Molten salt, solid particle media, heater brick, molten metal, liquid air.
   - Enhanced Geo thermal
4. Chemical Energy Storage
   - Hydrogen generation, storage, transport, ammonia, hydrocarbon fuels, conversion into electric power (fuel cells and gas turbines).

III. Summary

Q & A

Long Duration Energy Storage (LDES) Need

- **Why do we need energy storage?**
  - The supply of power from renewables (solar and wind) is variable, so flexible resources such as gas powered Peaker plants and energy storage are needed to match grid supply and demand.
  - Gas powered generators are not an ideal solution because of the greenhouse gas emissions, unless we have a good method to sequester CO_2 emissions. Energy storage is the preferred solution.
  - As the percentage of renewables in the grid increases, the need for LDES increases

    (for resiliency, prepare for unpredictable weather events, reduce curtailments and grid services such as frequency response, energy shift, reactive power and voltage control, black start etc.)

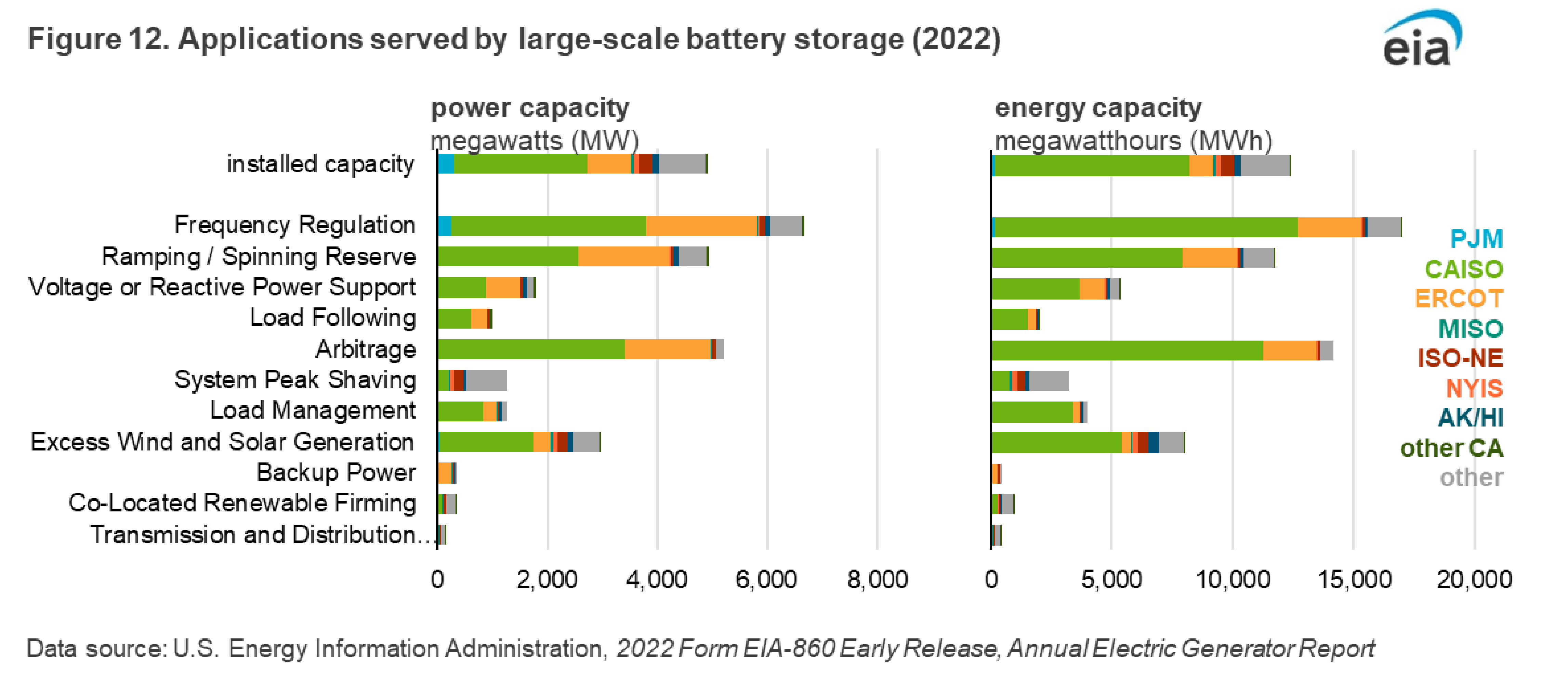
Long Duration Energy Storage (LDES) Classifications

- **Storage Classifications** (following DOE report – Pathways to commercial Liftoff: Long Duration Energy Storage, Mar 2023):
  - **Short Duration: ≤ 4hrs,** - Li ion batteries, mechanical storage technologies (fly wheels, Pumped Hydro Storage (PHS))
  - **Inter-day LDES: 10-36 hrs** (all mechanical storage, electrochemical technologies such as flow batteries, Metal-air batteries, Li-ion for 10 hrs duration and beyond is expensive)
  - **Multi-day/week LDES: 36-160+ hrs** (thermal storage, electrochemical technologies (flow batteries, metal- air)
  - **Seasonal Storage: Several months** (primarily chemical storage – hydrogen, or natural gas with carbon capture)

- **There are few other different storage classifications in use: for example;**
  - Short ≤ 4hr, Medium 4-10 hrs, and LDE 10+ hrs
  - CEC classifies over 8+ hrs as LDES

Applications Served by large-scale battery storage

EIA 2022 data

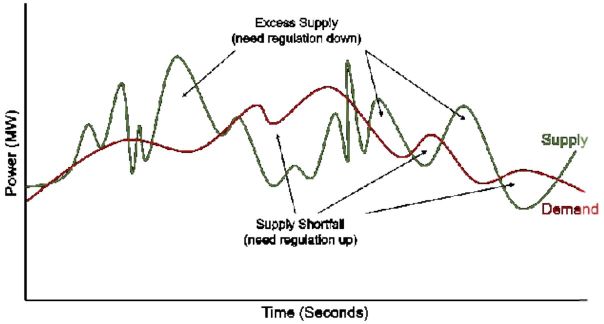


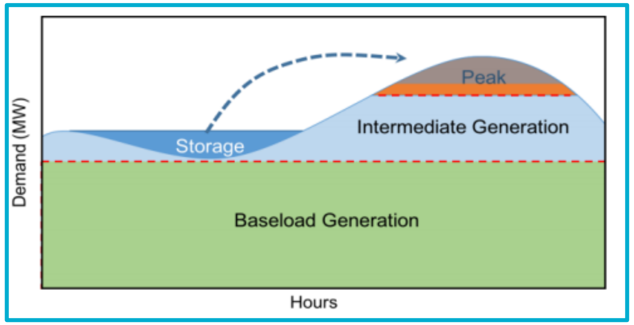
Energy Storage Market Drivers

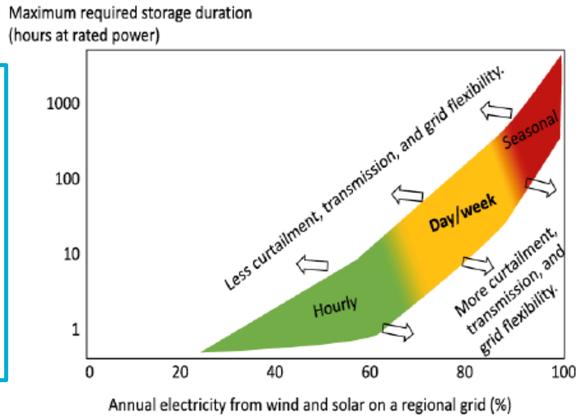
Short duration: market drivers exist | **Long duration: market drivers don't exist**

Frequency regulation 0.25 — Solar shifting, Peak shaving 2-4 — Intraday renewable support 10-15 — Seasonal grid support 100+

Hours







Ref: Albertus et.al, Joule 4, 21-32, Jan15, 2020

ISO requirements for energy storage capacity resource

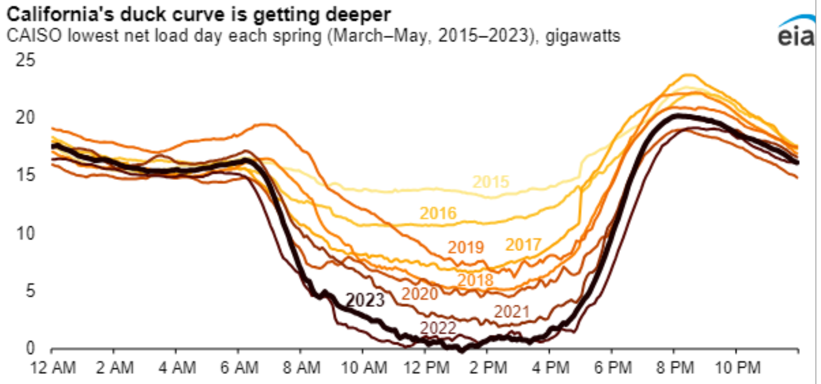
ISO	Capacity Duration (hours)
ISO-NE	2
MISO	4
CAISO	4
NYISO	4
SPP	4
PJM	10

Mainly Li ion batteries

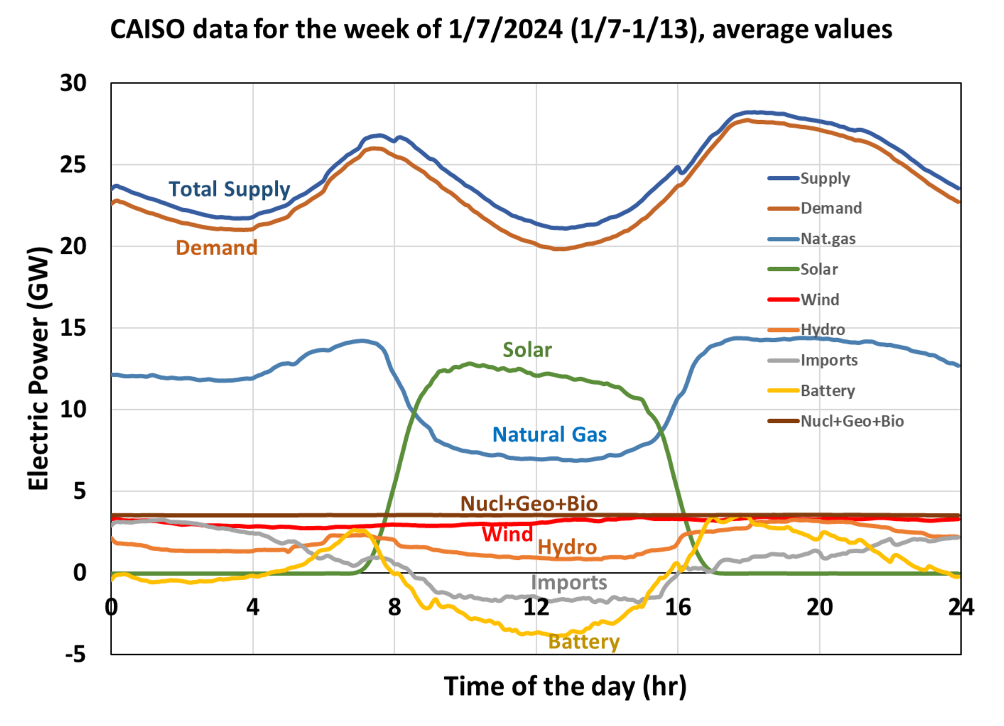
- Market drivers exist for short and medium duration energy storage.
- Today no market mechanism exist to address LDES needs.
- ISO market operations are mostly a day-ahead and intraday spot market construct.
- There is a need for market products that explicitly reflect energy storage capabilities concerning time shifting production and delivery of energy and value storage in that capacity (hedge against uncertainties).

Power Generation mix and energy storage in CA.

CAISO Data for a typical week in Jan 2024



Net load through the day

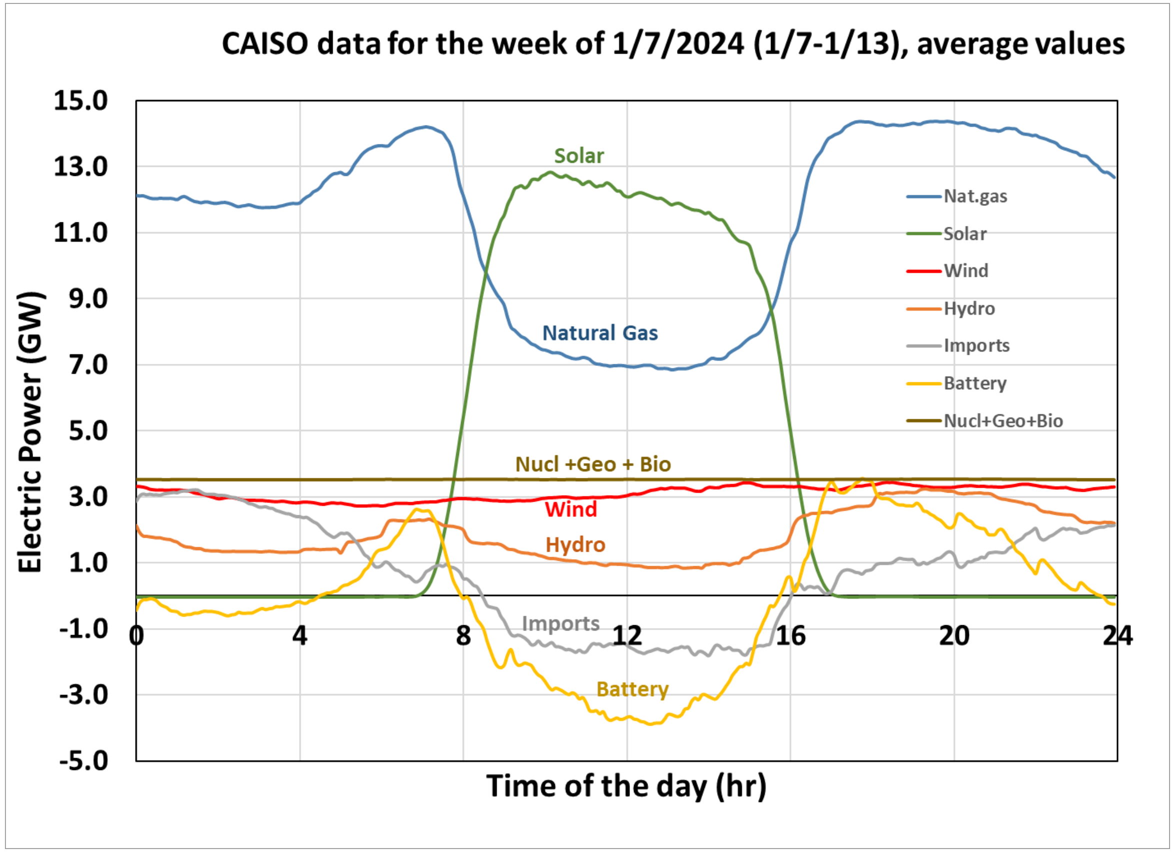


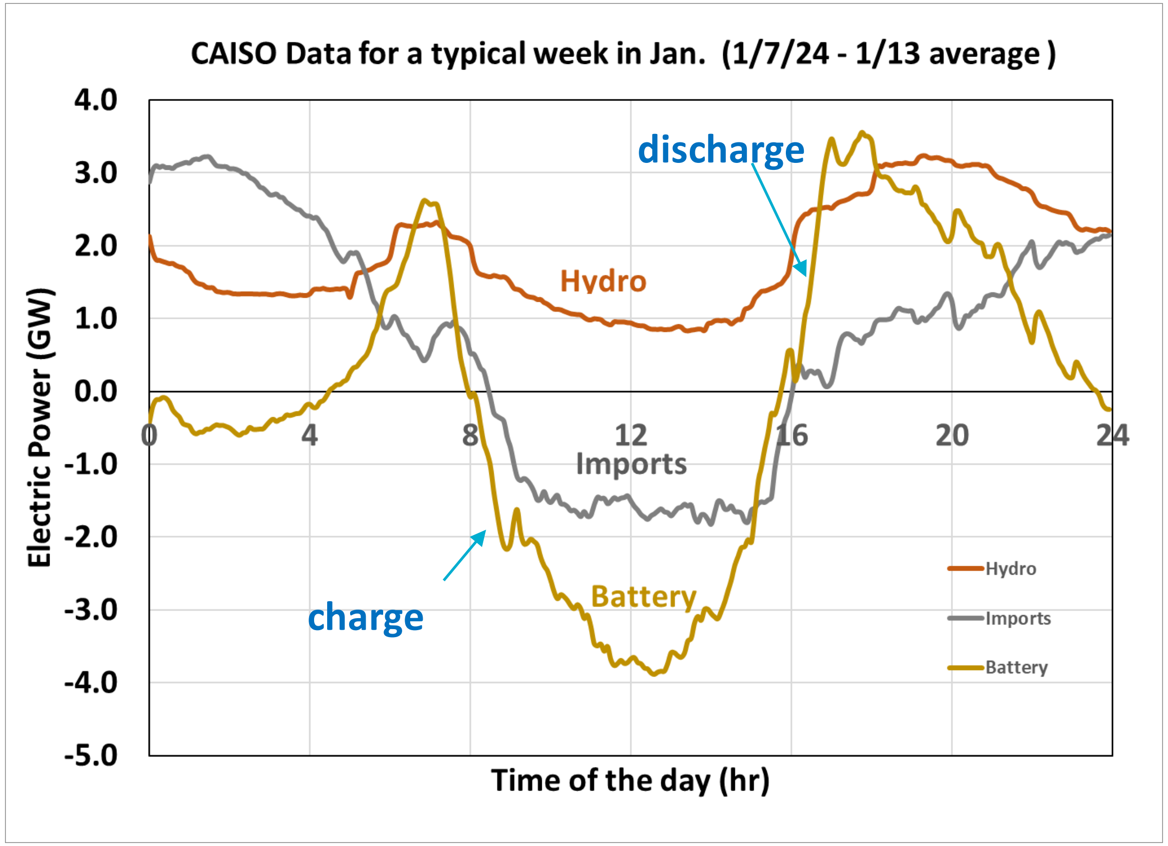
Average for the week:			
Ave. Demand:		23.47	GW
Ave. Supply:		24.34	GW
Main Supply Components:		**GW**	**%**
Natural gas:		11.41	46.9%
Solar:		3.88	15.9%
Wind:		3.10	12.7%
Nuclear, Geothermal, Bio:		3.54	14.5%
Hydroelectric:		1.86	7.6%
Imports:		0.67	2.8%
Batteries:		-0.11	-0.5%
Variable Resources Range:			
Wind:		0.99-5.07	GW
Solar		0-14.6	GW
Batteries:			
Max Charge		5 GW, ave: 1.7 GW	
Max Discharge		6 GW, ave: 1.7 GW	
Total charge and discharge energies: 21.8 and 18.9 GWh			

- Data shows a renewables penetration of ~36%.
- PV generation and drop off rates are very fast (7-9 GW/hr)
- Relatively a smaller variation with wind through the day.
- PV drop off is balanced by the fast ramp up of Nat. gas (~2.5 GW/h), battery discharge (~4 GW/h), hydroelectric (~1.2GW/h) and imports (~1GW/h).
- We need fast responding energy storage technologies with good RTE.

EIA data, Capacity factor for yr 2023 (average):
Solar: 23.3%; Wind: 33.5%; Nuclear: 93.1%; Nat. Gas: 58.8%
Hydroelectric: 34.2%.
Energy from the plot:
Nat.gas: 272 GWh, Solar: 93 GWh, Nucl, Geo, Bio: 85GWh
Lets say if we want flat 3.88 GW solar, covering the non-solar period with battery, we would need ~14hr * 3.88 GW = 54.3 GWh or 54.3 GWh/4hr = 13.6 GW battery

CAISO Data for a typical week in Jan 2024





- CAISO total battery storage: 8.2 GW. Assuming they are all 4hr duration, total energy: 32.8 GWh.
- Total charge, discharge energies are 21.8 and 18.9 GWh Battery utilization is 58-66%.
- They are doing ~ 2cycles per day. This is an aggregate of all batteries.
- CEC models show the projected energy storage need in 2035: 19.5 GW, 2045: 52 GW, driven by increased power demand and elimination of natural gas power generation plants.

LDES Key Challenges

- **Develop market mechanisms.**
  - ISO market operations are mostly a day-ahead and intraday spot market. Most energy storage is 4hr $\leq$ or less. With increasing renewables, storage requirement is slowly moving to 8-10hrs. None for multiday and seasonal storage.
  - Need market products to value LDES as hedge against uncertainties.

- **Reduction in cost.**
  - Model simulations show that for LDES, cost < $20/kWh and RTE >50% are needed.
  - LDES technologies with low cost materials and volume manufacturing is needed.

- **Develop more use cases for the adaption of LDES for a broad range of grid service applications.**
  - Because of the huge capital investment for LDES, if the LDES is used only for few very long duration cycles, the pay back period will be long. To be competitive, we need to utilize them for more applications.
  - If we have 10+ hrs storage, can we meet 1-4hr needs also? – not necessarily! (currently it is technology and application specific).

- **Energy Storage technology limitations.**
  - Technology maturity, ability to respond quickly with load changes, RTE, self discharge.
  - Difficult to meet all requirements in an optimized LDES to apply for a wide range of use cases.

Energy, Power and Applications

"Energy" applications >30 min. time scale, long duration of energy, fewer cycles

"Power" applications <15 min. time scale, fast control of the electric grid, many cycles

Energy Applications	Power Applications
Arbitrage	Frequency regulation
Renewable energy time shift	Voltage support
Demand charge reduction	Small signal stability
Time-of-use charge reduction	Frequency droop
T&D upgrade deferral	Synthetic inertia
Grid resiliency	Renewable capacity firming

- **Energy applications** involve continuous storage system discharges over periods of hours and correspondingly long charging periods. They typically involve **one or two charge-discharge cycle per day**.
- **Power applications** involve comparatively short periods of discharge (sec to minutes) and short recharging periods, often requires **many cycles per day**.
- ***Evaluate and select the energy storage system for the application requirements.***

*(for example, **Form Energy** claims it is targeting energy application. They do not want to compete with Li battery in power application. It is positioning as a supplement to it for grid reliability (under multiple day uncertainties), rather than participating in power application. Can we build all Li battery LDES? - currently it is too expensive and safety concerns.*

Few Technology Options for LDES

Electrochemical Storage (Batteries - short, medium, long duration storage)

- **Lithium-Ion Batteries,**
- Sodium-Ion Batteries, Molten Sodium Batteries
- Zn-Based Batteries, Ni-H_2 batteries
- Metal-Air Batteries
- Flow Batteries

Mechanical Storage (short, medium, long duration storage)

- **PHS (Pumped Hydro Storage)**
- Variations of PHS (Quidnet Energy, RCAM)
- Gravity (ARES, Energy Vault)
- Compressed air (CAES)
- Flywheels (short duration storage)

Thermal Storage (medium, long duration storage)

- Molten salt thermal storage, ceramic particle storage media, Fixed bed thermal storage
- Heated brick (Antora, Rondo)
- Molten metal, liquid metal battery
- Liquid air energy storage

Chemical and Hydrogen Storage (long duration and seasonal storage)

- H_2 generation (Electrolysis, SMR), H_2 storage, Electric Power generation (H_2 combustion, Fuel cells)
- Hydrocarbon or ammonia conversion

Desired ES Characteristics:

- **Ability to respond quickly for load demand**
- **High round trip efficiency**
- **Low self discharge**
- **High energy density**
- **Cost competitive**
- **Environment friendly**
- **Availability with good supply chain**
- **Safe**

1. Electrochemical Cell (or Battery) – example: Li-ion cell

Electrochemical cell:
- Consists of two electrodes, anode and cathode in an electrolyte, separated by an ion conducting separator. Electrons flow through the outer circuit.
- During discharge electrons and ions flow from anode to cathode and during charge electrons and ions are forced to move from cathode to anode with the application of applied electric field.

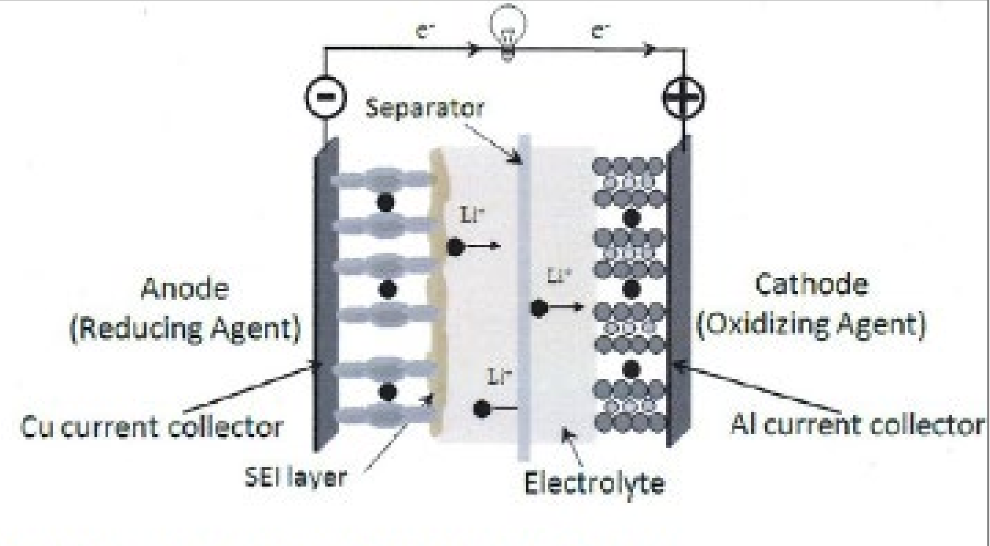


FIGURE 1. Representation of the C/$LiCoO_2$ cell.

Key Components:
- **Anode:** Graphite, Si, $LiTiO_x$, Li
- **Cathode:** layered metal oxides, phosphates ($LiNiCoAlO_2$, $LiNiMnCoO_2$, $LiFePO_4$)
- **Separator:** polyethylene (PE) or polypropylene(PP) or a combination.
- **Electrolyte:** Li salt such as $LiPF_6$ dissolved in organic solvents (EC, DMC and DEC)
- **Current collectors:** Cu and Al

Key Characteristics:
- **Voltage** (V, volts) – determined by the reaction between the electrodes and the electrolyte
- **Current** (I, amps) – reaction rate (Amp = Coulombs/sec)
- **Power** (W, watts): V x I
- **Capacity** (Ah or Wh): power as a function of time
- **RTE** (%): energy out during discharge/ energy in during charge
- **Self discharge**: typically expressed as % degradation/yr under open circuit conditions
- **Degradation**: cycle life (# charge/discharge cycles), calendar life (yrs)

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1. Electrochemical Cell or Battery – few fundamentals

- What determines the cell voltage?
  - Here we are referring to single cell voltage.
  - Battery packs are prepared by combining several single cells in series (to boost voltage) and in parallel (for current). It also includes BMS and few safety components.

- What is the electrolyte stability window?
  - Differences in aqueous electrolytes and organic electrolytes.
  - Why the current collectors are Cu at anodes and Al at cathodes in Li ion batteries?

- What is the role of SEI (secondary electrolyte interface) layer in Li ion batteries?
  - Why can't we ship Li ion batteries at zero charge? Or fully discharge the Li ion battery?

- What is voltage versus current behavior for the electrochemical cells?
  - Open circuit voltage, load voltage, voltaic efficiency
  - What is the operating window? What limits the current output?

1. Electrochemical Cell - Voltage, Current

Cell Voltage, V stability window

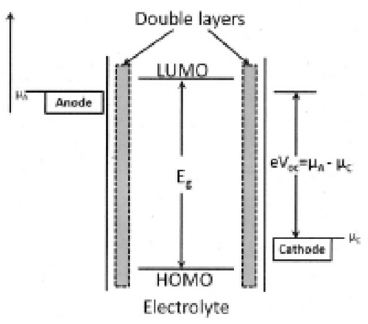
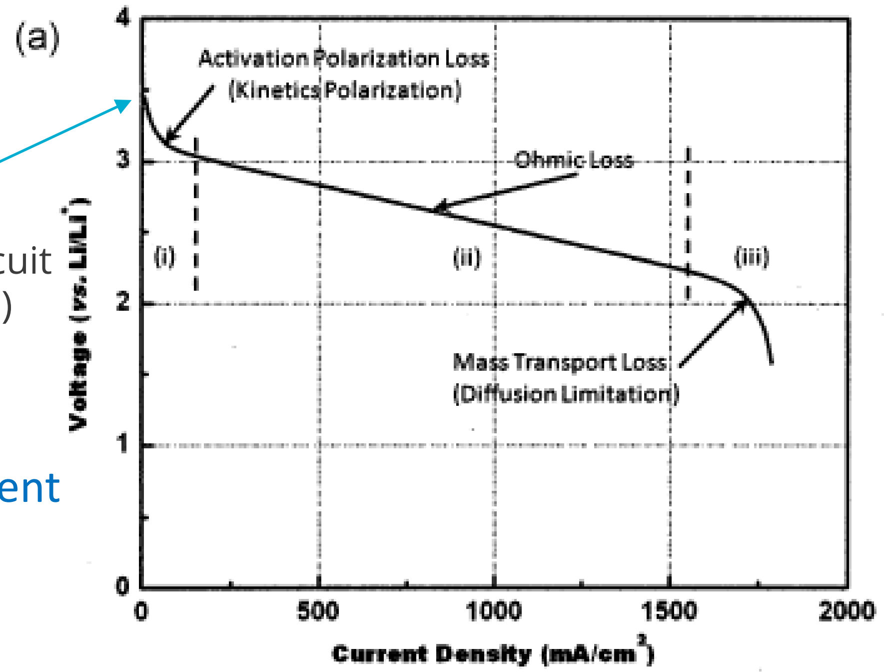


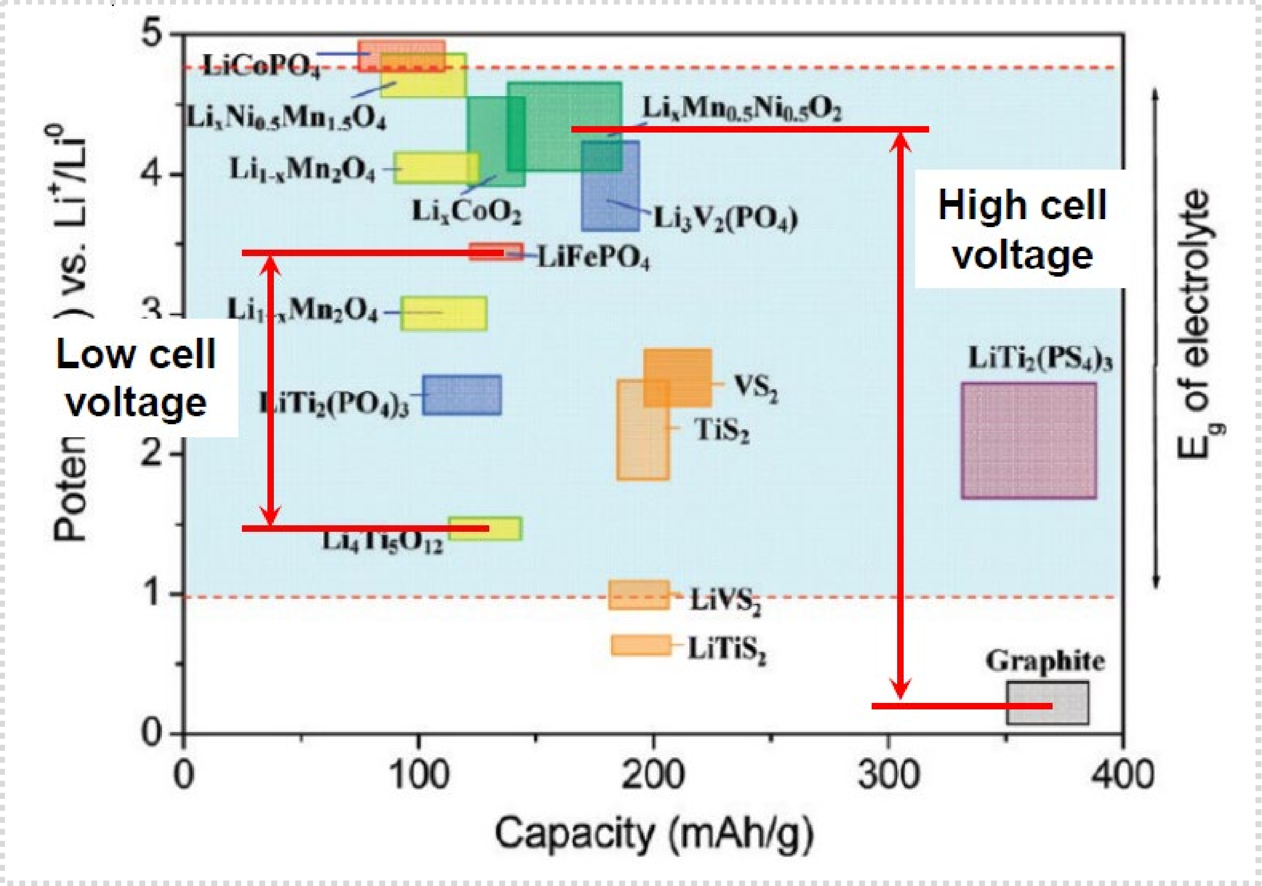
FIGURE 3. Relative energies of μ_A and μ_C versus the LUMO–HOMO window of the electrolyte; $V_{OC} = (\mu_A - \mu_C)/e$, where e is the magnitude of the electron charge.

Voc (open circuit voltage)



V Vs current

Li-ion technology choices



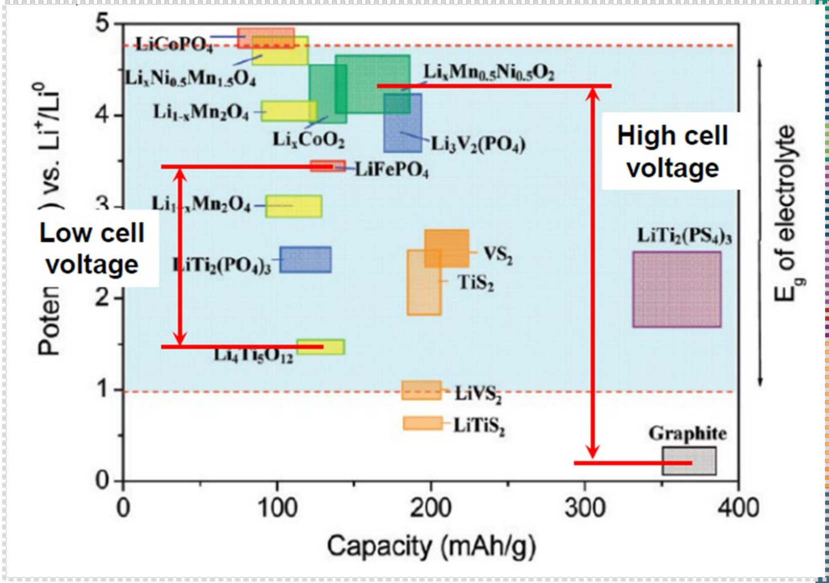
Different chemistries, cell V output, electrolyte stability window

- LFP is more stable, but low voltage (thus low ED), lower cost.

1. Electrochemical – Li and solid state batteries

- **Li-ion batteries**
  - The most dominant technology up to 4hr, as the costs are going down they are becoming competitive at 8-10hrs also.
  - They support a wide range of duty cycles with good RTE.
  - Cost and safety are major concerns for LDES.
  - **Different flavors of Li-ion batteries: LFP** (Lithium Iron Phosphate), **NMC** (Lithium Nickel Manganese Cobalt), **NCA** (Lithium Nickel Cobalt Aluminum Oxide), **LMO** (Lithium ion Manganese Oxide), **LCO** (Lithium ion Cobalt Oxide), **LTO** (Lithium Titanate Oxide)
  - LFP is most preferred for grid scale applications. Slightly lower energy density compared to others, but less prone to thermal runaway and uses low cost raw materials.
- **Solid State Batteries**
  - Uses thin film ceramic solid electrolyte separator replacing the liquid electrolyte and the polymer membrane.
  - Promises higher energy density, better safety. Issues are degradation due to interfacial separation between the electrolyte and the electrode, fragility of the ceramic membranes. Thermal runaway issues are not fully mitigated. Still in R&D stage.

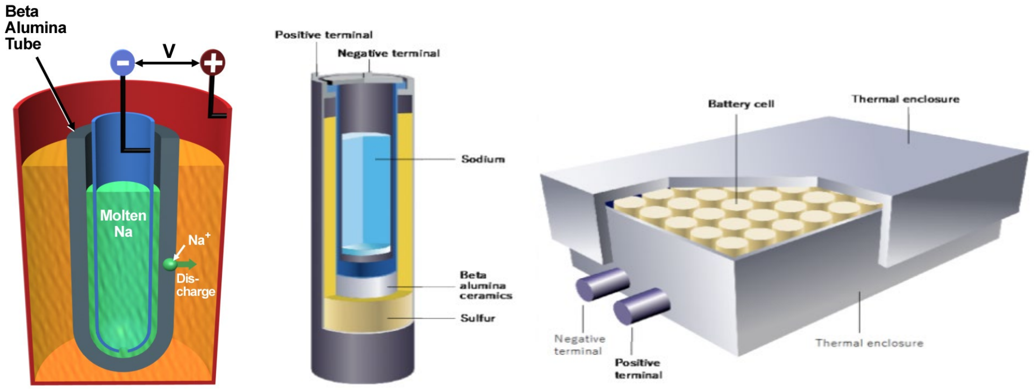
Li-ion technology choices



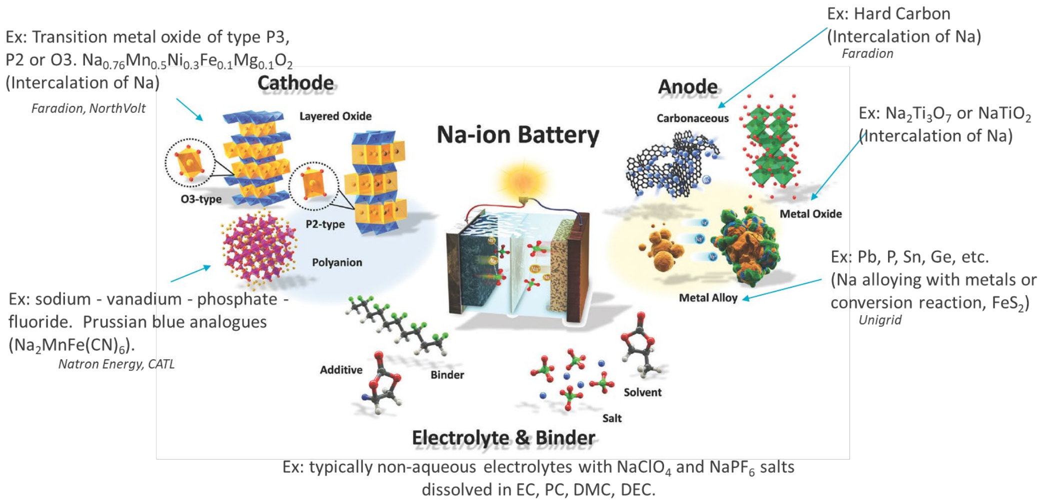
Tesla Megapacks, Moss Landing

1. Electrochemical – Na batteries

- **Sodium ion batteries**
  - There is a lot of excitement about Na-ion batteries. They use earth abundant materials that are lower in cost and safe (?). They are not yet in commercial high volume manufacturing.
  - **Different types of Na ion batteries:**
    - **High temperature** (molten Na-S batteries – **NGK, BASF**), Zebra batteries (Na-metal chloride).
    - **Low temperature** (Li ion battery analogues). Several different different chemistries are in development. Anodes: Hard carbon, Ti based intercalation oxides, conversion and alloying, Cathodes: layered oxides, polyanionic, Prussian blue. **Companies**: Faradion, Natron, HiNa, CATL, Farasis, Tiamet, NorthVolt.
    - Less thermal runaway problems. They can be **shipped in zero charge state** (much safer during shipping).
    - Uses **Al current collectors** on both sides.



Commercial. RTE ~70%, thermal management, losses



Na - ion Battery Types Schematic

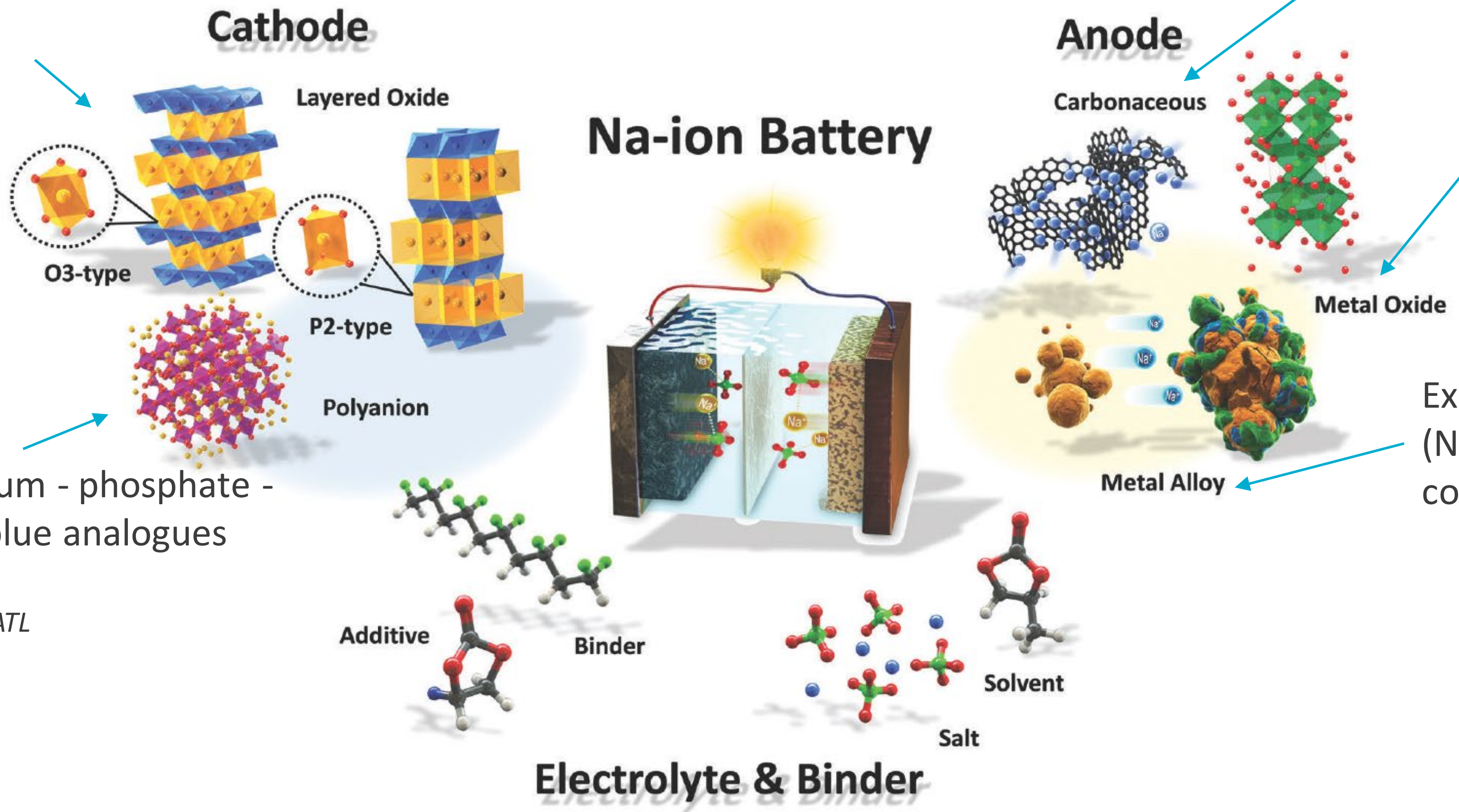
Ex: Transition metal oxide of type P3, P2 or O3. $Na_{0.76}Mn_{0.5}Ni_{0.3}Fe_{0.1}Mg_{0.1}O_2$ (Intercalation of Na)

Faradion, NorthVolt

Ex: Hard Carbon (Intercalation of Na)

Faradion

Ex: $Na_2Ti_3O_7$ or $NaTiO_2$ (Intercalation of Na)



Ex: sodium - vanadium - phosphate - fluoride. Prussian blue analogues ($Na_2MnFe(CN)_6$).

Natron Energy, CATL

Ex: Pb, P, Sn, Ge, etc. (Na alloying with metals or conversion reaction, FeS_2)

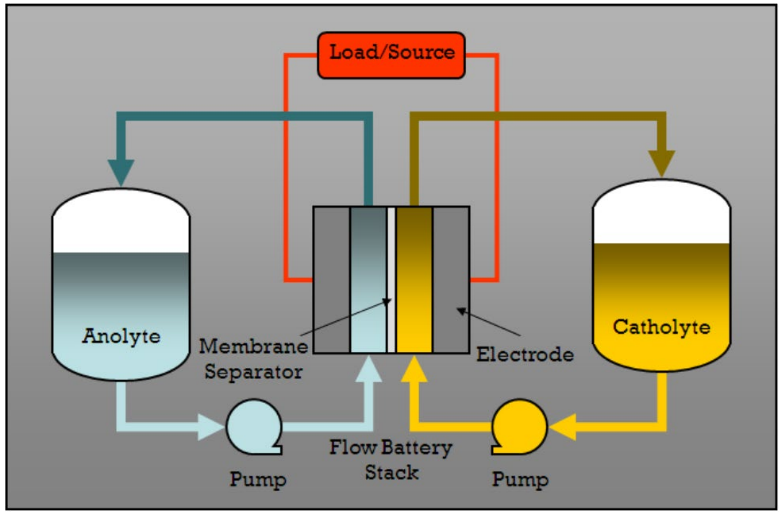
Unigrid

Ex: typically non-aqueous electrolytes with $NaClO_4$ and $NaPF_6$ salts dissolved in EC, PC, DMC, DEC.

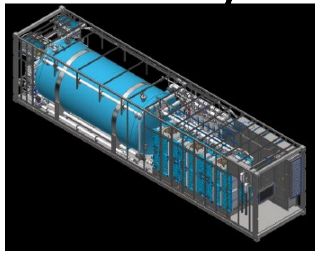
https://en.wikipedia.org/wiki/Sodium-ion_battery

1. Electrochemical – Flow batteries

- **Flow Batteries**
  - Reactants are dissolved in a dilute electrolyte solution and circulated over anode and cathode. It allows the separation of power (battery stack) and energy (storage tank). Easy to scale up for larger system.
  - **Drawbacks:** Uses dilute solutions, so energy density is low. System complexity is high, requires more ancillaries such as pumps, sensors and control circuits. Needs bipolar stacks, uniform flow fields, ion conducting separator. Some flow batteries requires catalyst. Cross-over of species and higher self discharge. RTE ~65-75% Not competitive with Li- ion batteries for short duration storage.
  - **Different types of flow batteries:**
  - V redox flow battery (Invinity), Fe-Cl flow battery (ESS), Zn-Br flow battery (RedFlow), Zn-Br hybrid battery (EOS). CMBlu –organic flow battery, uses a solid mediator to increase the energy density.



Invinity, V redox flow battery



ESS, Iron Flow Battery

CMBlu organic flow battery

EOS, Zn-Br Hybrid battery

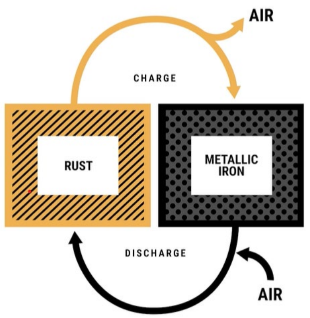
Red Flow, Zn-Br flow

1. Electrochemical – Metal air batteries

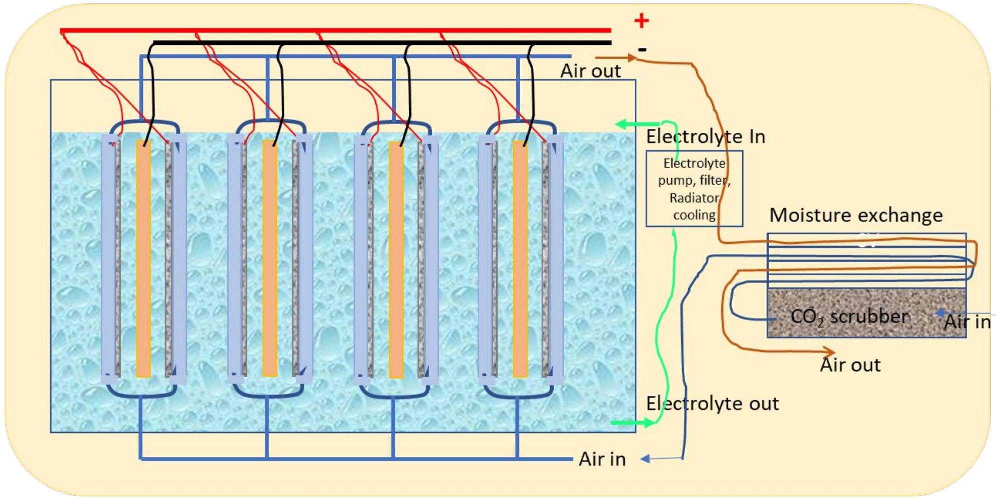
- **Metal-air Batteries (Fe-air, Zn-air**)
  - Uses metal anode and air cathode. Since air is supplied by the atmosphere, only one reactant is carried in the cell, thus these batteries can have a higher energy density.
  - During discharge the metal is oxidized forming an oxide or hydroxide. It is reduced back to metal during charge
  - Zn-air primary batteries are commercialized for few specific applications, such as hearing aid batteries. Rechargeable Zn-air batteries are being developed for Grid scale energy storage application. **Issues: Zn dendrite growth, balance of plant, high self discharge, air cathode limitations, RTE ~60%.**
  - Form energy is developing Fe-Air batteries for 160+hr storage application. DOE funded development work on Fe-air batteries at Westinghouse in 1970s. **Issues: low RTE (~40%), balance of plant, air cathode limitations**.

Form energy

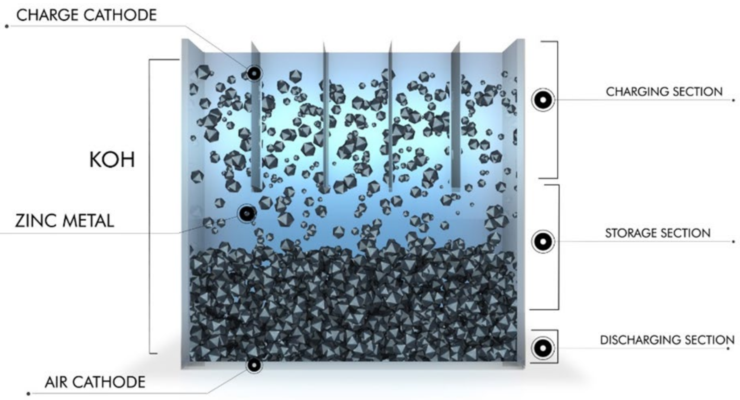
Energy Storage for a Better World



Fe-air battery system schematic



E-Zinc, Zn-air



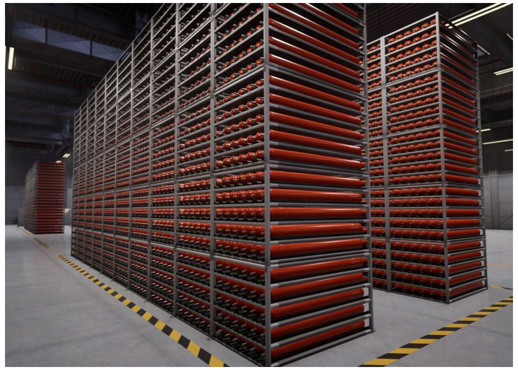
1. Electrochemical – other types

- **Other electrochemical batteries:**
  - **Ni-H_2 Batteries**
  - **Zn-Mn rechargeable alkaline batteries**
  - **Ni-Zn**

- **Ni-H_2:** Cathode is Ni hydroxide, anode is H_2 gas. During charging H_2 is generated and during discharge H_2 is oxidized producing water. Proven technology for space application. Long cycle life and operating life. Wide operating temperature range. High self discharge rate. Low volumetric energy density (60-100 Wh/L). Uses Ni metal and Pt catalyst. EnerVenue start up out of Sanford, developed a low cost non-precious metal catalyst. Despite the use of H_2 and pressure vessel, the cells are proven safe.
- Good for short duration storage, cost may be concern for LDES.

- **Zn-Mn:** These are very similar to the widely used alkaline primary batteries, but rechargeable. UEP innovation is the development of rechargeable chemistry with high energy density. – Development stage.

- **Ni-Zn:** ZincFive, AEsir technologies – targeting data center applications replacing Pb-Acid batteries.



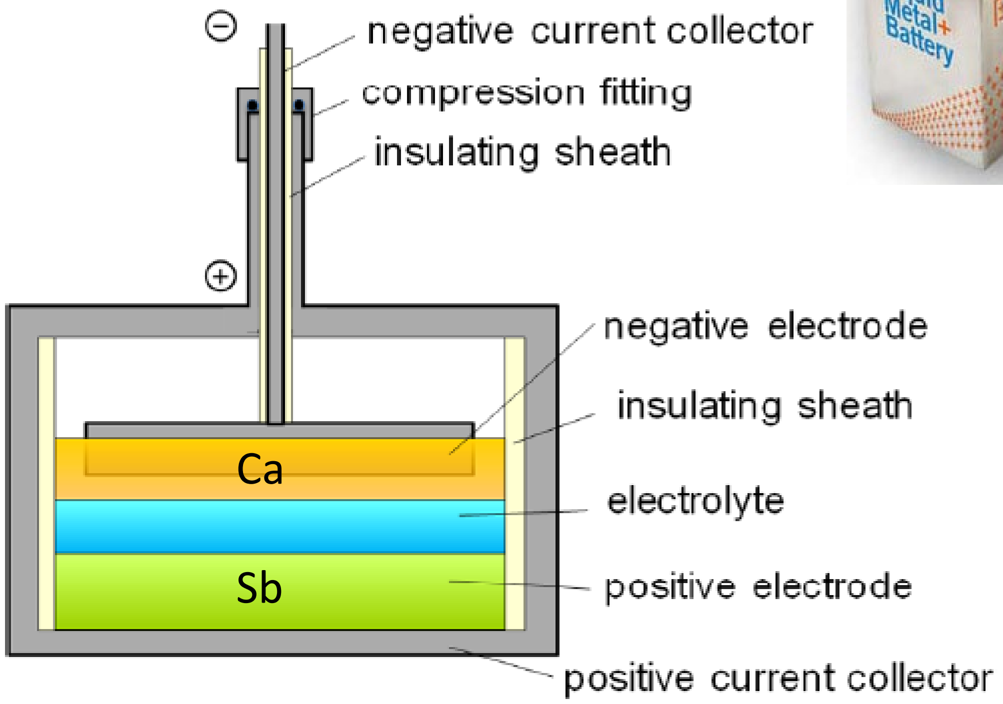
URBAN ELECTRIC POWER

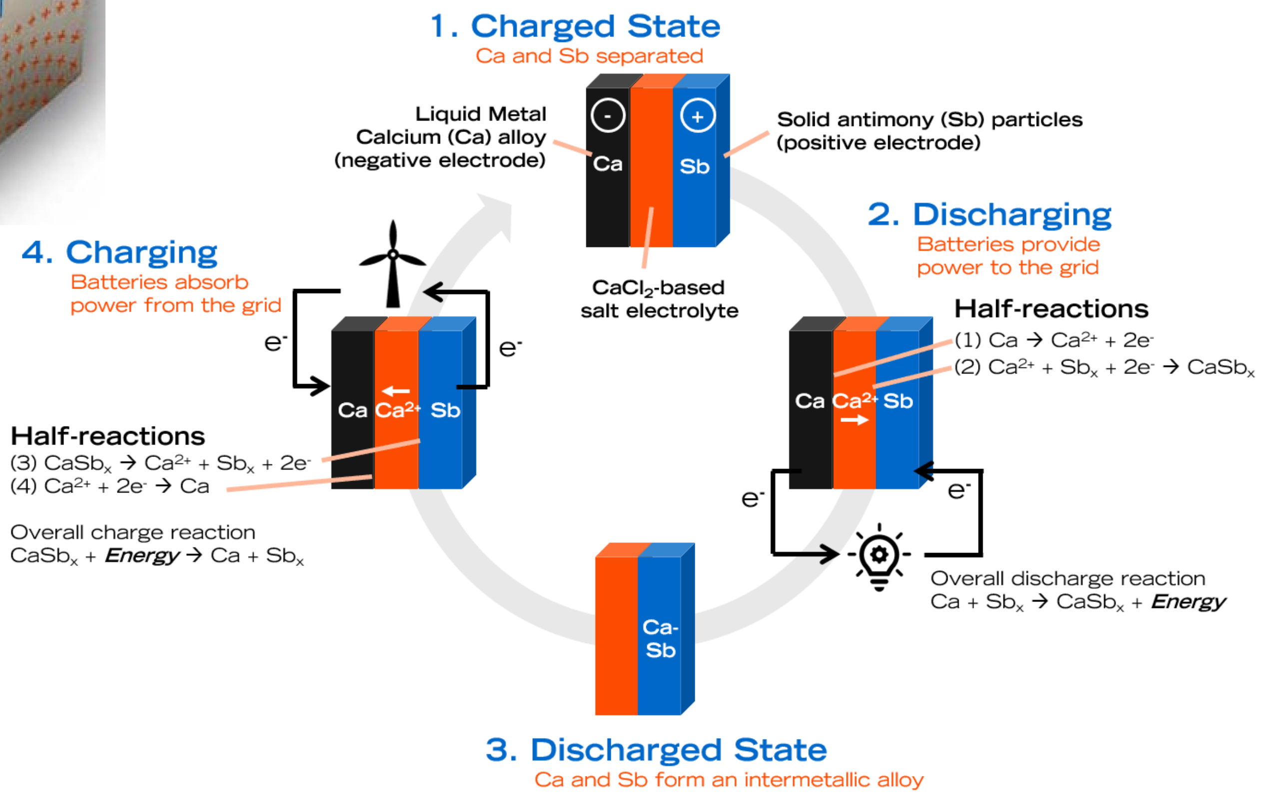
ZincFive

Æsir Technologies, Inc.

1. Electrochemical – Liquid metal battery

- Ambri is a start up out of Prof. Sadoway's group at MIT.
- Liquid metal battery consists of two liquid metal layers (anode and cathode) separated by a molten salt electrolyte that segregates into three layers based on density and immiscibility.
- Charge discharge process consists of alloying and dealloying.
- Low cost raw materials. No safety issue other than heat. System suitable for large grid scale applications. Still in R&D stage.





1. Electrochemical – Supercapacitors

- **Difference between batteries and capacitors:**
  - In batteries the energy is stored in bulk chemical reactants, where as it is stored as surface charge in capacitors.
  - The energy density of batteries is much higher than capacitors
  - In batteries the charge/discharge rates are limited by reaction kinetics and mass transport. These limitations don't apply to capacitors.
  - With supercapacitors, quick charge/discharge is possible. They offer higher power density, superior cycle life and wide operating temperature range, they also have a higher self discharge rate.
  - The output voltage of batteries is relatively constant, it changes linearly with time in supercapacitors.

- **Different types of supercapacitors**
  - EDLC (electric double layer capacitors) – Energy stores in the double layer at the electrode/electrolyte interface - *most common type and commercial.*
  - Psuedocapacitor –involves reversible surface redox reactions for higher capacitance. – *in development.*
  - Hybrid – utilizes both mechanisms for higher performance – *in development*.

- **<u>Applications:</u>**
- Good for "power applications" – frequency response, voltage support etc. Competition – Li-ion batteries.
- A prudent combination of supercapacitor and a battery can be used advantageously to reduce the battery size, extend its life and allows for quick charging.
- Similarly, a fuel cell-supercapacitor hybrid is also ideal in the fuel cell design to reduce the peak power demand and optimize the fuel cell size and increase its efficiency and life.

Summary

- Most of the energy storage in the US is currently 4hrs or less. With increased penetration of renewables more energy storge with longer duration is needed to mitigate the uncertainties with renewables for grid resiliency.

- The percentage of renewables in CA is approaching 40%. The contribution of natural gas power plants is >46%.

- The quick ramp up and ramp down capabilities of the gas plants are helpful in mitigating the daily fluctuations of the solar power. Energy storage technologies with similar capabilities are needed to replace gas plants with greenhouse gas emission problems.

- In CA, the average daily energy load demand is ~24GW and supply is ~25GW. Major supply components are: Natural gas - 11.4GW, Solar - 3.9GW (0-14.6GW), Wind - 3.1 GW , Battery storage is ~10GW. Battery storage is projected to increase to 13 GW by the end of 2024.

- On aggregate, the batteries are on the grid are doing 2cycles for day with an average utilization of ~60%.

- Li ion batteries are the most dominant energy storage technology for 4hr duration or below. With high volume manufacturing and reduction in costs they are becoming competitive for 8-10hr storage also. Due to the inherent materials cost limitations, the Li ion battery system costs may not reduce <$20/kWh needed for wider deployment of LDES on the grid. Also there are safety concerns.

- Na ion batteries are in the early stages of development. Promises to be a lower cost and safer option. High temperature molten Na batteries are commercial, uses low cost raw materials, but the battery systems costs are still expensive.

- Flow batteries may be competitive in the 6-10 hr storage duration. Low energy density and higher system costs are concerns for long duration storage.

- In metal –air batteries, Zn-air batteries suffer from zinc dendrite growth and air cathode durability issues and Fe-air batteries with low RTE, air cathode limitations and high self discharge. Form Energy is targeting their batteries for 100+ hr storage for resiliency application with fewer cycles.