Lecture # 11

Batteries & Energy Storage

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March 9, 2020

- Storage technologies, for mobile and stationary applications ..
- Batteries, primary and secondary, their chemistry.
- Thermodynamics and electrochemistry
- Performance, ….

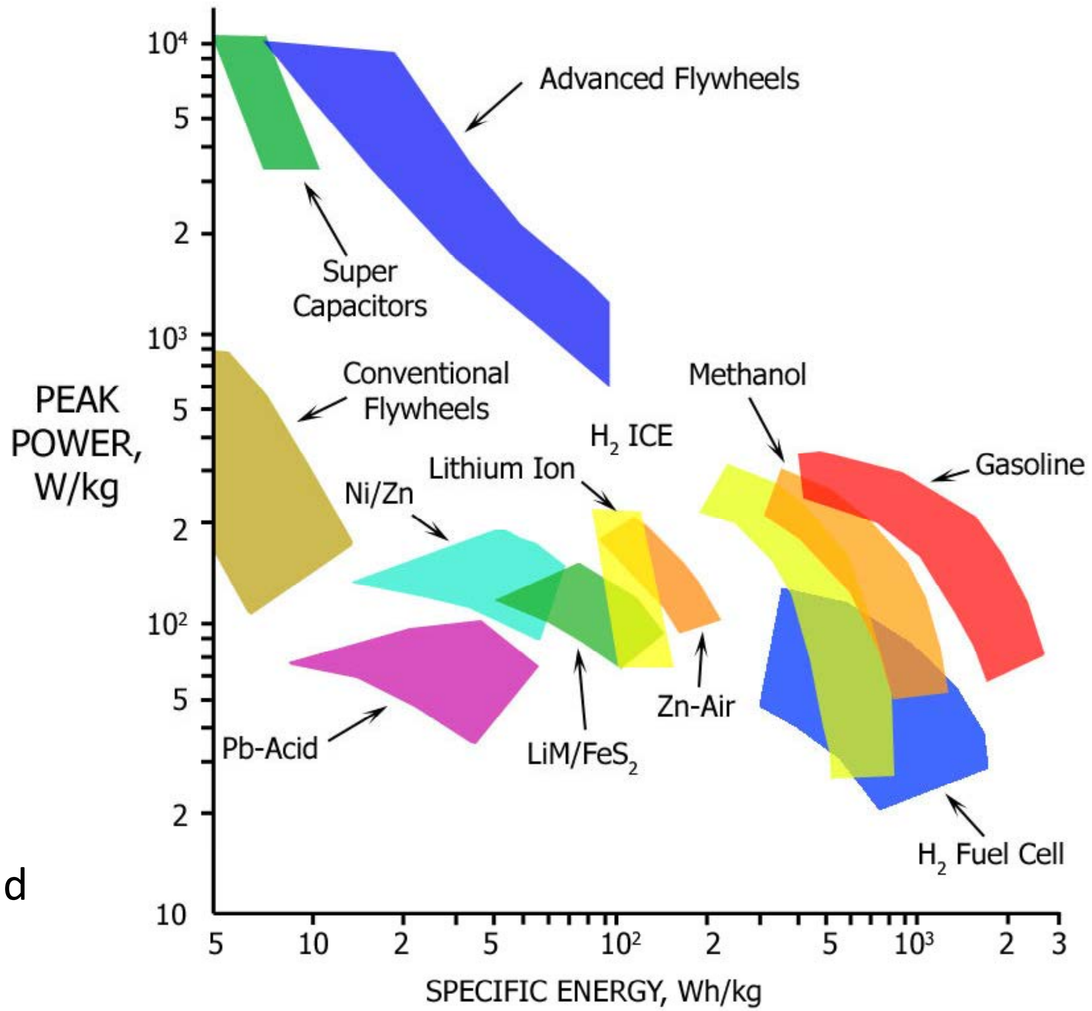
THE RAGONE DIAGRAM is more applicable to mobile applications.
Electric mobility is totally dependent on battery storage.

an important definition:

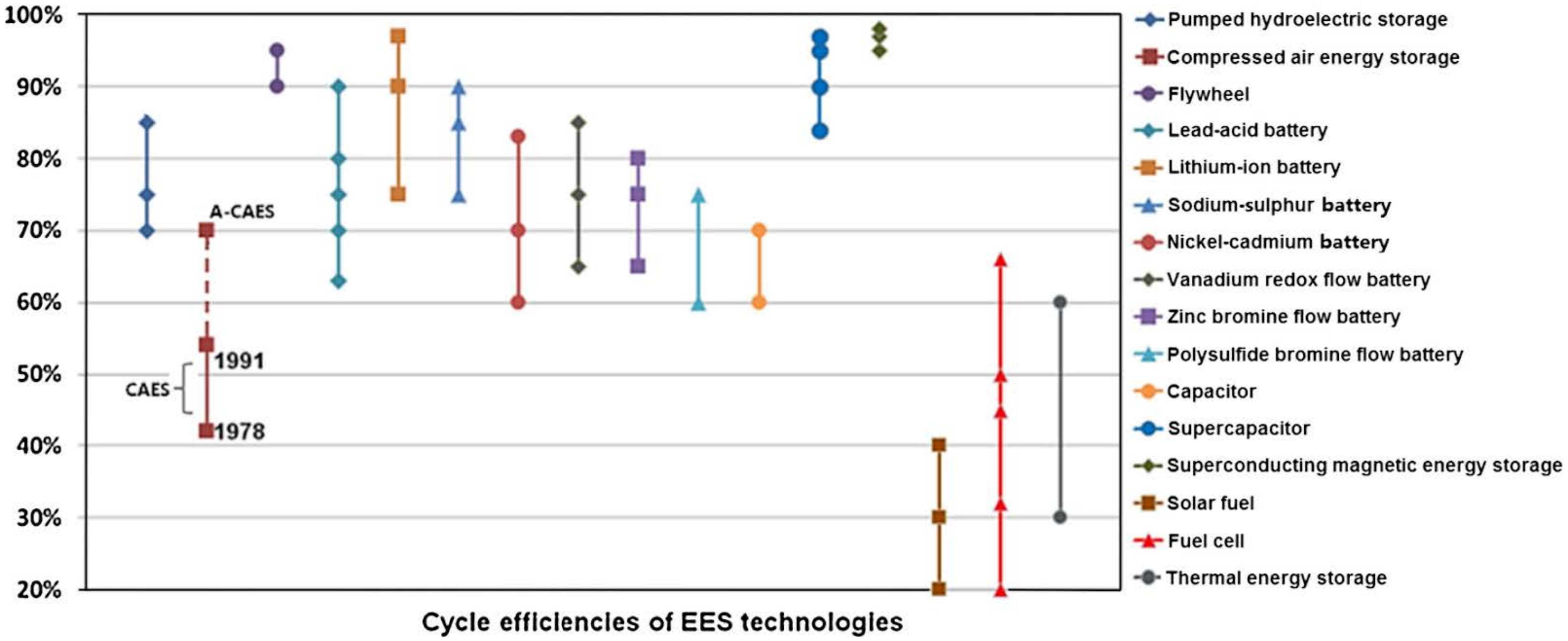
Round trip efficiency:

$$\eta_{round} = \eta_{charge}\eta_{discharge}$$

For stationary applications, criteria for selection and hence technologies can be very different.



THE RAGONE DIAGRAM. Figure shows approximate estimates for peak power density and specific energy for a number of storage technology mostly for mobile applications.



Round-trip efficiency of electrical energy storage technologies. Markers show efficiencies of plants which are currently in operation.

Courtesy Elsevier, Inc., http://www.sciencedirect.com. Used with permission.

Xing Luo, et al. Applied energy, 137:511–536, 2015.
Niklas Hartmann, et al. Applied Energy, 93:541–548, 2012.
Behnam Zakeri and Sanna Syri. 42:569–596, 2015.

Energy Storage: Overview and other options

The table shows technologies for stationary and mobile applications including mechanical and electrochemical. Capacitors are integral parts of mobile storage!

Not inclusive and other options are available and under development.

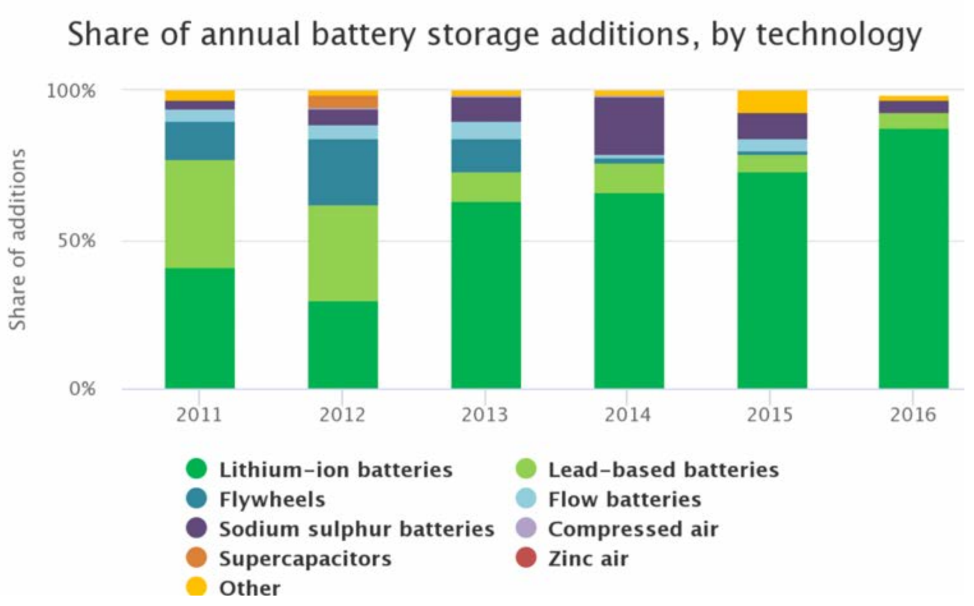
Does not show thermal (storage) and chemical (hydrogen, fuels and thermochemical) options which are very important.

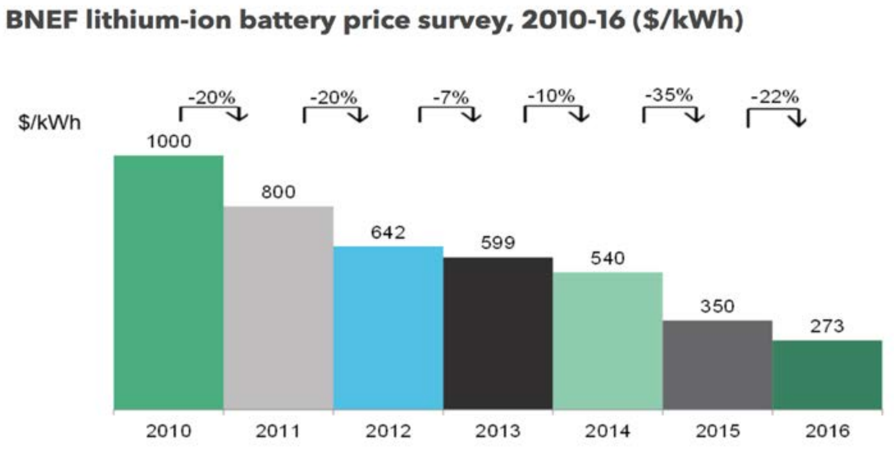
Prices change constantly but comparison is still reasonable.

Characteristic	PHS	CAES	Batteries	Flywheel
Energy Range (MJ)	1.8×10^6-36×10^6	180,000-18×10^6	1,800 – 180,000	1 – 18,000
Power Range (MW)	100-1000	100-1000	0.1 – 10	1-10
Overall Cycle Efficiency	64-80%	60-70%	~75%	~90%
Charge/Discharge Time	Hours	Hours	Hours	Minutes
Cycle Life	10,000	10,000	2,000	10,000
Footprint/Unit Size	Large if above ground	Moderate if under ground	Small	Small
Siting Ease	Difficult	Difficult-Moderate	N/A	N/A
Maturity	Mature	Development	Mature except for flow type	Development
Estimated Capital Costs - Power ($/kWe)	600 – 1,000	500-1,000	100-200 (LA)	200 - 500
Estimated Capital Costs - Energy ($/kWh)	10 - 15	10 - 15	150-300	100 - 800

Batteries

- Similar to fuel cells in that they convert chemical to electrical energy directly, and the secondary type can reverse the reactions
- But they store their chemicals internally in their electrodes (except for flow batteries)
- Have seen a very wide range of applications, at many scales for centuries!
- Still relatively expensive for large scales storage deployment, although convenient.
- Also heavier than ideal in mobile application.
- Must be carefully managed thermally to avoid thermal run away and fires.





Primary Batteries: the alkaline dry cell

$$\mathrm{Zn_{(s)} + 2MnO_{(s)} \rightarrow ZnO_{(s)} + Mn_2O_{3(s)}}$$

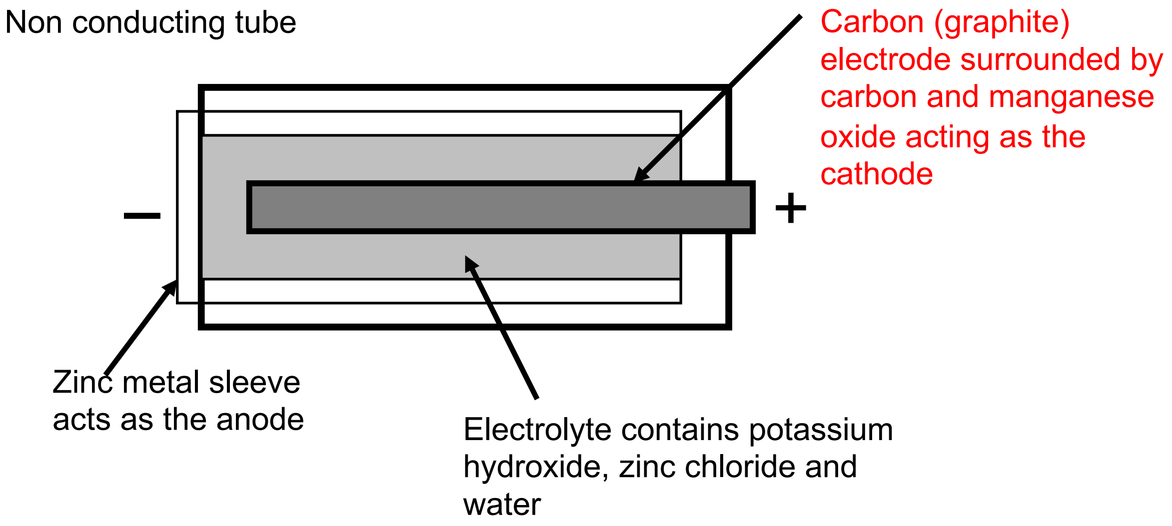
$$\text{anode: } \mathrm{Zn_{(s)} + 2OH^-_{aq} \rightarrow ZnO_{(s)}} + H_2O_{(l)} + 2e^-$$

$$\text{cathode: } \mathrm{2MnO_{2(s)} + H_2O_{(l)}} + 2e^- \rightarrow \mathrm{Mn_2O_{3(s)} + 2OH^-_{aq}}$$

$$\Delta G^o_R = -277\,kJ/mol, \quad n_e = 2$$

$$\Delta\mathcal{E}_o = \frac{277000}{96485 \times 2} = 1.44V$$

Zn: Zink
Mn: Manganese



A schematic drawing showing the internal detail of an alkaline battery

Secondary Batteries: The Lead Acid Battery

(look under the hood)

a lead electrode and a lead oxide electrode are immersed in sulfuric acid-water solutio

During discharge:

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow PbSO_{4(s)} + 2H_2O_{(aq)}$$

The Redox reactions:

$$Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^{-}$$

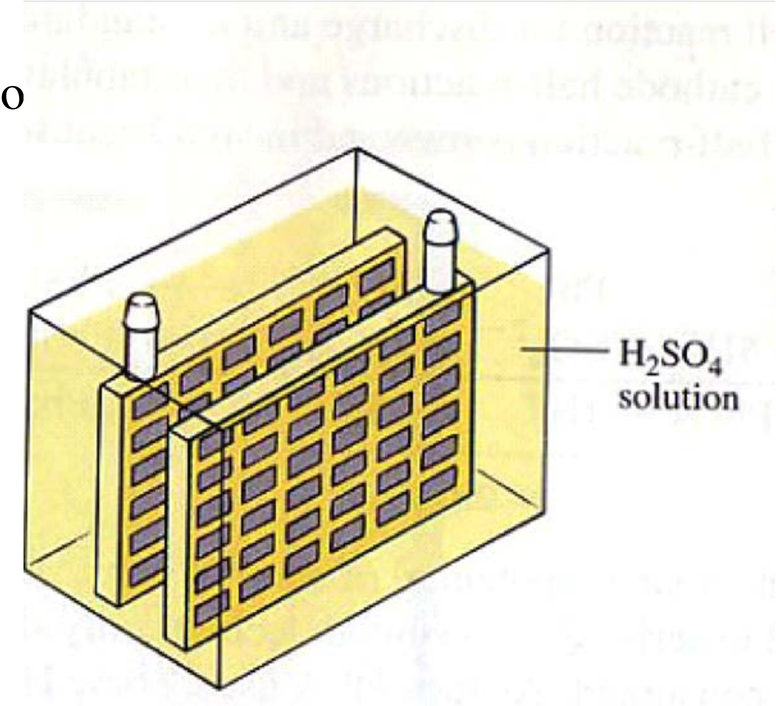
$$PbO_{2(s)} + 4H^{+} + SO_4^{2-} + 2e^{-} \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$$

$$\Delta\mathcal{E} = 2.04V$$

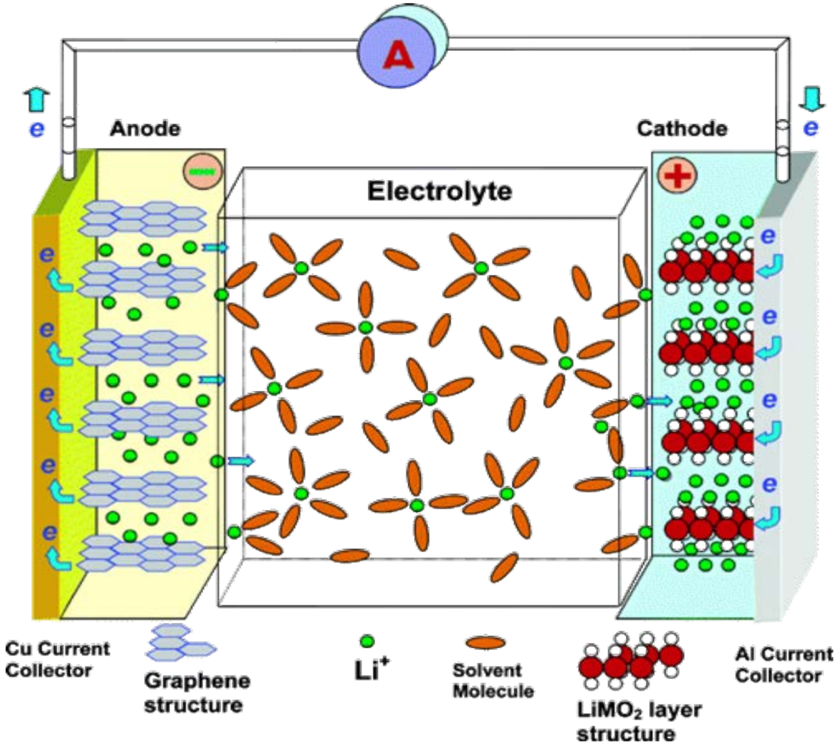
During charging, the above reactions are reversed by applying an external voltage.

Lead acid batteries charge below this value to prevent water electrolysis

can be dangerous but used extensively in cars, etc.



Lithium-ion batteries



Xu, K. Electrolytes and interphases in Li-ion batteries and beyond. *Chem. Rev.* **114**, 11503–11618 (2014).

- During operation, reversible Li^+ intercalation (insertion) into the layered electrodes' materials (leaving graphite anode during discharge).
- The overall reaction, where x is the fraction of the anode Li leaving and joining the cathode lithium cobalt oxide:

$$Li_xC_6 + Li_{1-x}CoO_2 \leftrightarrow C_6 + LiCoO_2$$

- Forward reaction: discharge ($\Delta G < 0$), Li^+ move towards cathode, as shown in figure
- Reverse reaction: charge ($\Delta G > 0$)

- Anode (-ve electrode, electrons leaving): Li metal and graphite
- Cathode (+ve electrode, electrons returning): Metal oxides (MnO_2, CoO_2, $LiFePO_4$)
- Electrolyte: Organic solvents, carbonates and lithium salts ($LiPF_6$)
- Current collectors, Cu on the anode side and Al on the cathode side.

Goodenough and Park, *JACS* 135 (2013): 1167

Lithium-ion batteries

During discharge (cobalt cathode):

Anode: $x\text{Li}_{(s)}(\text{C}) \rightarrow x\text{Li}^{+}_{(sol)} + x\text{e}^{-} + (\text{C})$

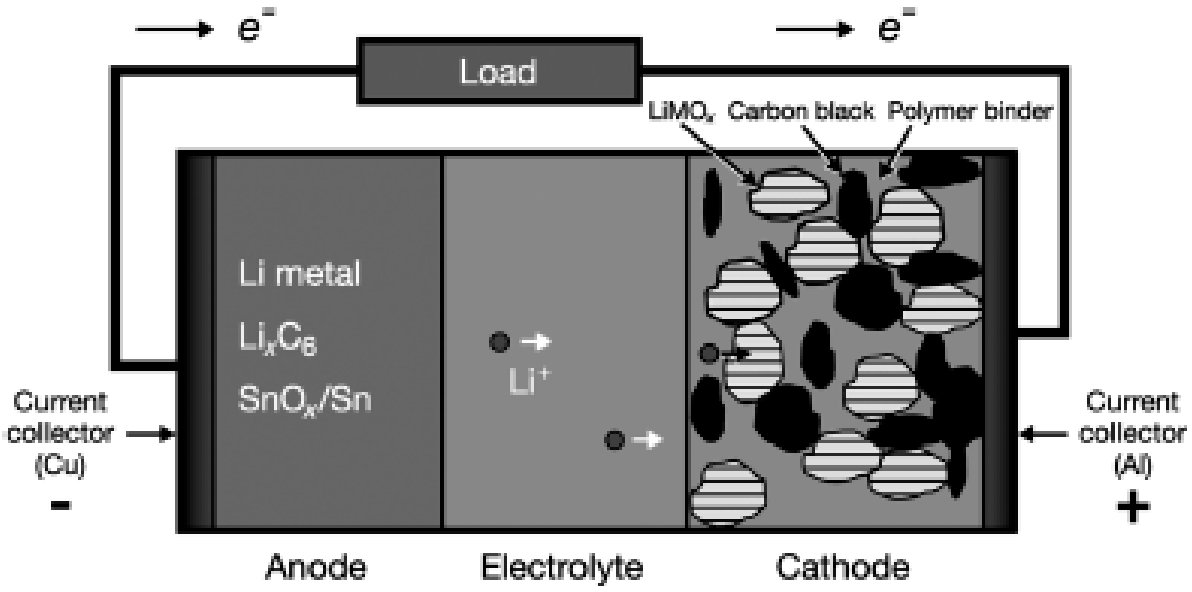
Cathode: $x\text{Li}^{+} + x\text{e}^{-} + \text{Li}_{1-x}\text{CoO}_{2(s)} \rightarrow \text{LiCoO}_{2(s)}$

Overall: $\text{Li}_{(s)} + \text{CoO}_{2(s)} \rightarrow \text{LiCoO}_{2(s)}$

The backward reactions occur during charging.

Material	Theoretical Voltage V	Theoretical specific energy Wh/kg
Li/CoO_2	3.6	570
Li/Mn_2O_4		

Lithium is single valent, giving up a single electron during discharging (more advanced batteries would use multi valent metal such as magnesium).



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Li-Mn battery during discharge:
Li ions move from –ve electrode (anode) to +ve electrode (cathode) through solid or liquid electrolyte

“Batteries, Overview” by E Cairns, Encyclopedia of Energy, V 1, 2004, Elsevier.

Specific Energy

The <u>theoretical specific energy</u> is $-\Delta G_R / \sum M_i$ where the sum is taken over all the reactants (and products) in the redox reaction.

This expression ignores the mass of the battery housing, inert electrode material and electrolytes.

<u>Actual specific energy</u> is 20-35% of this value because of the weight of these components and the energy losses

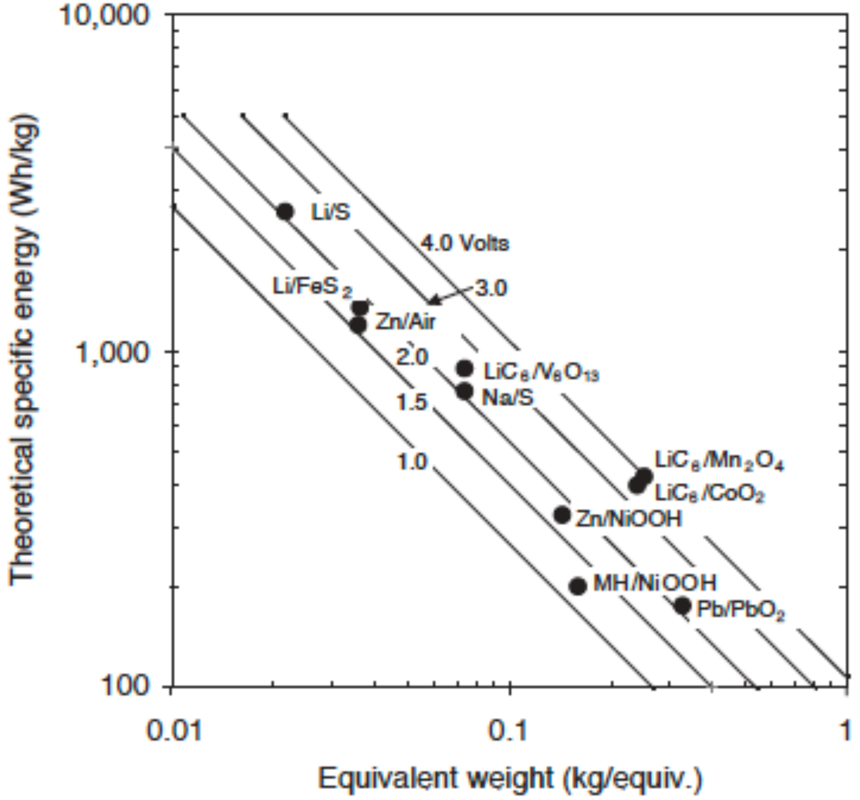

FIGURE 1 Theoretical specific energy for various cells as a function of the equivalent weights of the reactants and the cell voltage.

(Elton j Cairns, "Batteries, Overview, Encyclopedia of Energy, Vol 1, 2004 , Elsevier Inc)

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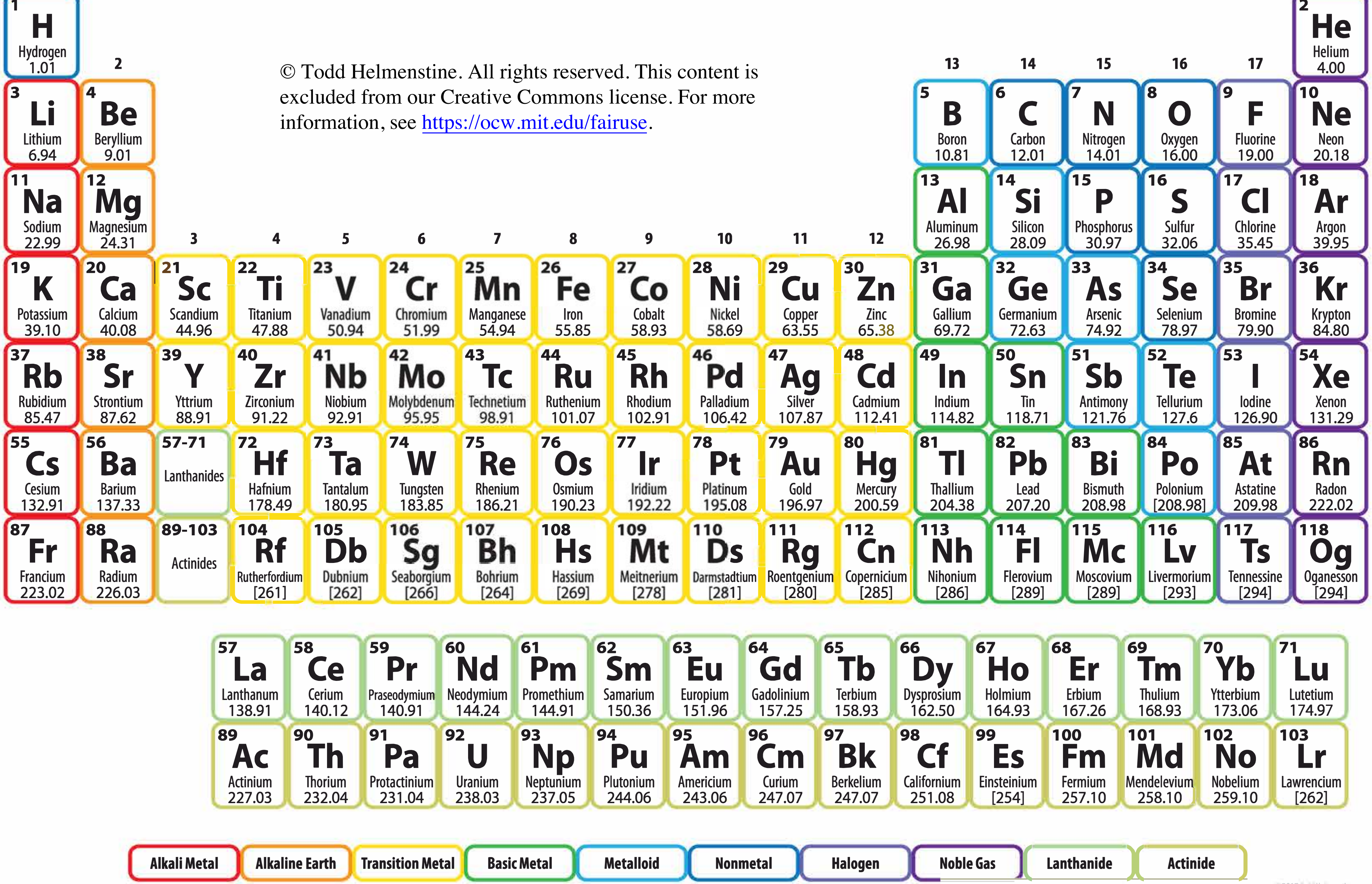
Battery Materials

Electrode materials are selected to maximize the theoretical specific energy of the battery, using reactants/reactions with a large (-ve) ΔG and light weight (small ΣM).

- Negative electrode (anode) reactants that can give up electrons easily have large (-ve) ΔG. These elements are located on the LHS of the periodic table.
- Elements with a low MW are located toward the top of the periodic table.
- Positive electrode (cathode) reactants (oxides) should readily accept electrons. These elements are located on the RHS of the periodic table.

(Elton j Cairns, “Batteries, Overview, Encyclopedia of Energy, Vol 1, 2004 , Elsevier Inc)

Periodic Table of the Elements



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.01																	2 He Helium 4.00
3 Li Lithium 6.94	4 Be Beryllium 9.01											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.88	23 V Vanadium 50.94	24 Cr Chromium 51.99	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.38	31 Ga Gallium 69.72	32 Ge Germanium 72.63	33 As Arsenic 74.92	34 Se Selenium 78.97	35 Br Bromine 79.90	36 Kr Krypton 84.80
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.95	43 Tc Technetium 98.91	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.6	53 I Iodine 126.90	54 Xe Xenon 131.29
55 Cs Cesium 132.91	56 Ba Barium 137.33	57-71 Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.85	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.20	83 Bi Bismuth 208.98	84 Po Polonium [208.98]	85 At Astatine 209.98	86 Rn Radon 222.02
87 Fr Francium 223.02	88 Ra Radium 226.03	89-103 Actinides	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]

57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium 144.91	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.06	71 Lu Lutetium 174.97
89 Ac Actinium 227.03	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium 237.05	94 Pu Plutonium 244.06	95 Am Americium 243.06	96 Cm Curium 247.07	97 Bk Berkelium 247.07	98 Cf Californium 251.08	99 Es Einsteinium [254]	100 Fm Fermium 257.10	101 Md Mendelevium 258.10	102 No Nobelium 259.10	103 Lr Lawrencium [262]

Alkali Metal | Alkaline Earth | Transition Metal | Basic Metal | Metalloid | Nonmetal | Halogen | Noble Gas | Lanthanide | Actinide

Lead-acid, nickel-metal (Cd/Fe/Mn) hydrite and Zinc batteries.

- Th round-trip efficiency of batteries ranges between 70% for nickel/metal hydride and more than 90% for lithium-ion batteries.
- This is the ratio between electric energy out during discharging to the electric energy in during charging.
- The battery efficiency can change on the charging and discharging rates because of the dependency of losses on the current.

Some rechargeable aqueous batteries

System	Cell voltage [V]	Theoretical specific energy [Wh/kg])	Actual specific energy [Wh/kg]	Specific power [W/kg]	Cycle life
Pb/PbO_2	2.1	175	30-45	50-100	>700
Cd/NiOOH	1.2	209	35-55	400	2000
Fe/NiOOH	1.3	267	40-62	70-150	500-2000
H2/NiOOH	1.3	380	60	160	1000-2000
Zn/NiOOH	1.74	326	55-80	200-300	500
Zn/Air	1.6	1200	65-120	<100	300

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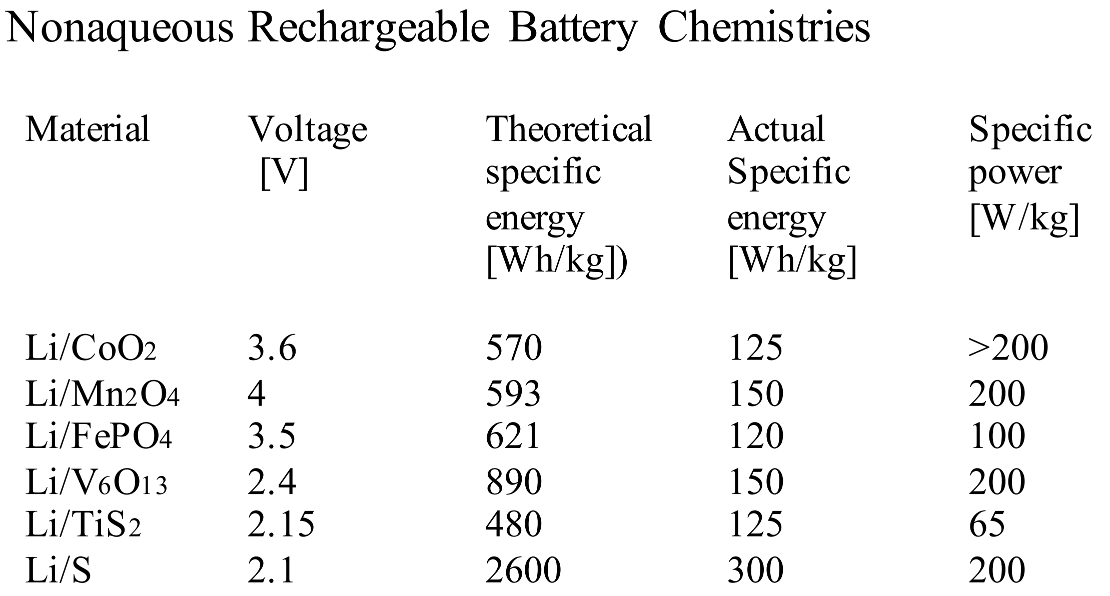
Elton j Cairns, "Batteries, Overview, Encyclopedia of Energy, Vol 1, 2004 , Elsevier Inc

The power density is ~ O(20 kW/100kg), need ~ 500 kg to power a 100 kW motor.

Lithium Ion batteries

The open circuit potential of a $LiCoO_2$ battery is ~ 4.2 V. Specific energy is ~3-5X, specific power is 2X higher than lead-acid. **Table** shows the characteristics of lithium ion batteries with different positive electrode (cathode) materials: Co (cobalt), Mn (manganese), Fe (iron), Ti (titanium), or S (sulfur), etc., for improved stability, specific energy and power.



Nonaqueous Rechargeable Battery Chemistries

Material	Voltage [V]	Theoretical specific energy [Wh/kg])	Actual Specific energy [Wh/kg]	Specific power [W/kg]
Li/CoO_2	3.6	570	125	>200
Li/Mn_2O_4	4	593	150	200
$Li/FePO_4$	3.5	621	120	100
Li/V_6O_{13}	2.4	890	150	200
Li/TiS_2	2.15	480	125	65
Li/S	2.1	2600	300	200

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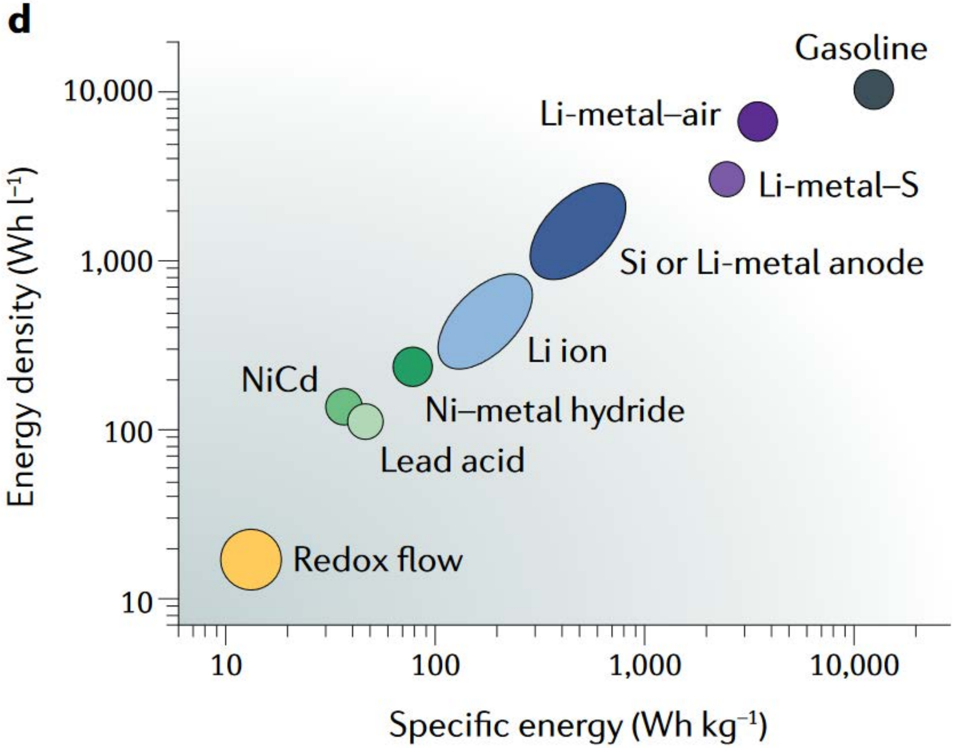
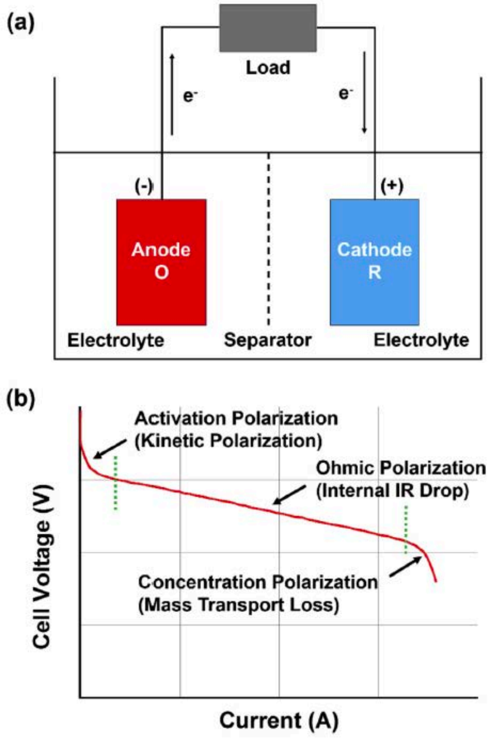
“Batteries, Overview” by E Cairns, Encyclopedia of Energy, V 1, 2004, Elsevier.



Lopez, Jeffrey, et al. "Designing polymers for advanced battery chemistries." *Nature Reviews Materials* 4.5 (2019): 312-330.

finite current performance



The i-V curve of a battery resembles that of a fuel cell, with similar loss mechanisms affecting the performance at higher currents.

Cho et al., PECS 48 (2013) 84

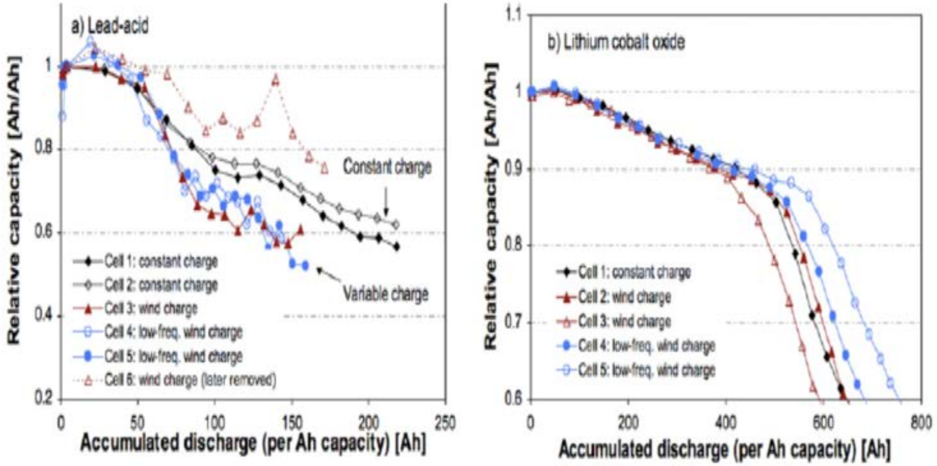


Figure 1: Capacity fade as a function of normalized discharge throughput in a lead-acid and a lithium-ion battery. Lead-acid batteries show rapid capacity fade compared to the lithium-ion batteries. [Source: Krieger et al. 2013[4]]

- Since all the reactants are stored internally, performance can change with degree of discharge.

- As more current is drawn from a battery, the reactants concentrations drop (and products concentrations increase) leading to significant increase in concentration overpotential and performance degradation under deep discharge conditions.

Redox Flow Batteries, the All-Vanadium design

Overall

$VO_2^+ + 2H^+ + V^{2+} \rightarrow VO^{2+} + H_2O + V^{3+}$

On the negarive elctrode side:

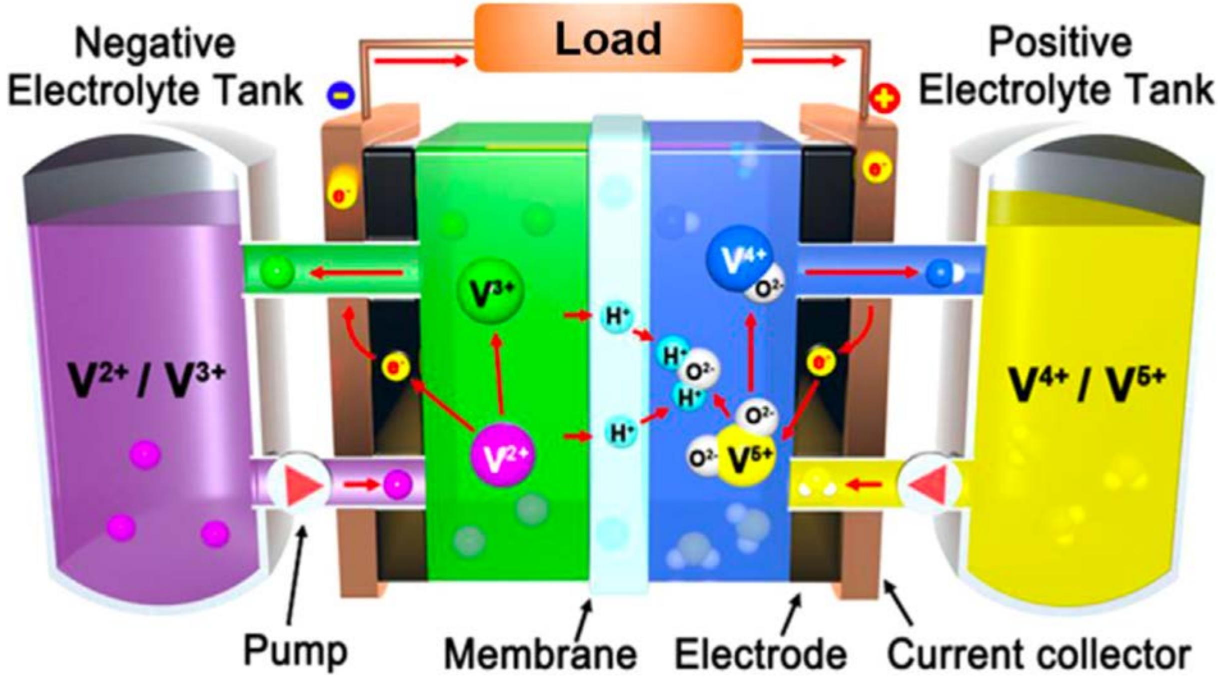
$V^{2+} \rightarrow V^{3+} + e^-$

On the positive electode side

$VO_2^+ + 2H^+ + e- \rightarrow VO^{2+} + H_2O$

Open circuit voltage is ~ 1.26V.

Observed efficiency (round trip!) ~85%.



Cho et al., PECS 48 (2013) 84

2.60J Fundamentals of Advanced Energy Conversion
Spring 2020