Electric Vehicle (EE60082)

Lecture 12: BMS part2

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Basic terminology (recap)

Cell: the most basic element of a battery;

Block: a collection of cells wired directly in parallel;

Battery: a collection of cells or blocks wired in series;

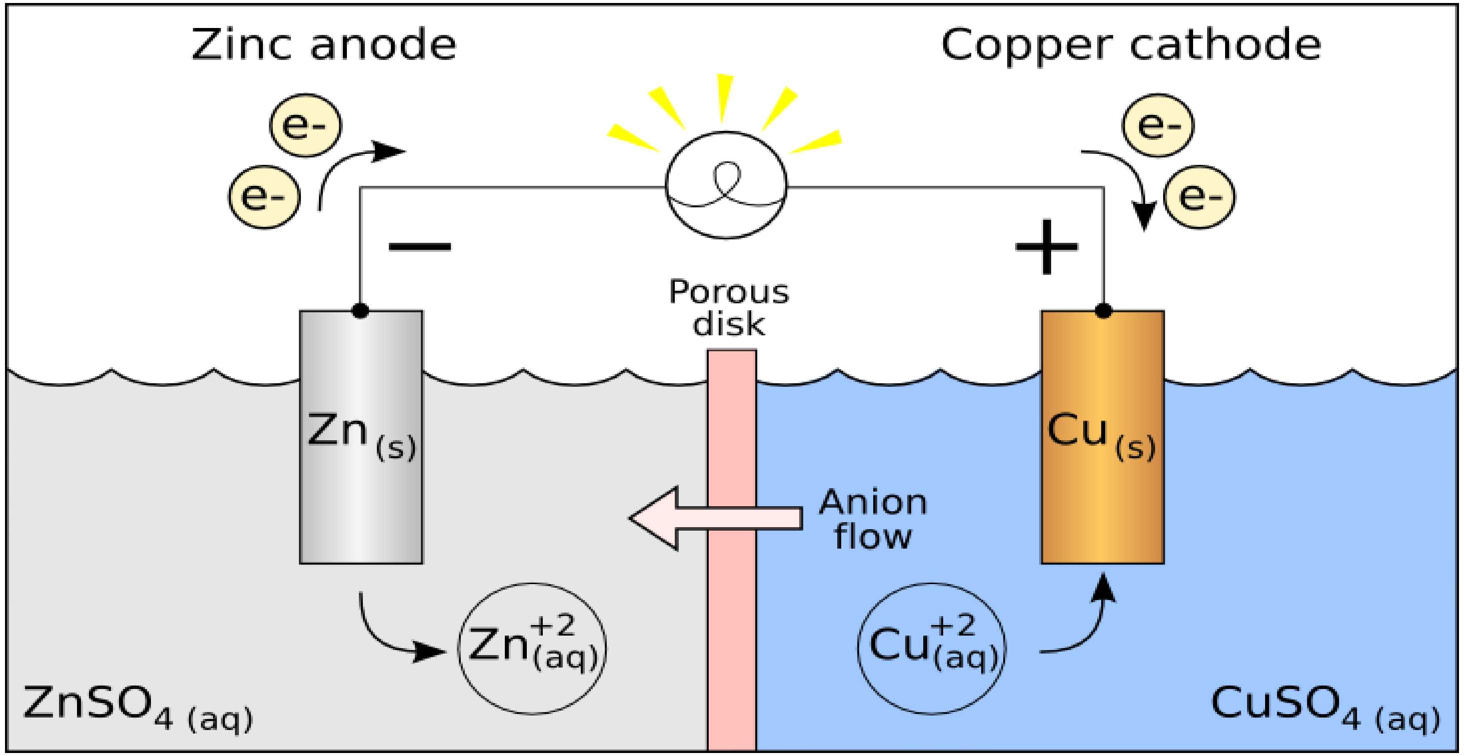
Pack: a collection of batteries.

C-rate(recap)

- C-rate is unit of current (relative to battery charge capacity)
- 1 C-rate = the current needed to discharge the battery fully in 1 hour

- Examples:
  - 40 Ah Battery, 20 A discharge.
    - Find the C-rate of discharge
  - 10 Ah, being discharged at C/2.
    - Find the time to discharge completely

Battery Chemistry (recap)



Galvanic cell

Battery Charge Density (recap)

$$\text{Li} \quad + \quad \text{MnO}_2 \quad \rightarrow \quad \text{LiMnO}_2 \quad \text{(discharge)}$$

6,94   86,9

1. Generated charge Q: one electron ($-1.602*10^{-19}$C)
2. Used mass M: $(6.94+86.9)*1.667*10^{-27}$kg
3. Charge Density: Q/M/3600=284Ah/kg
4. How to calculate energy density?

Battery OCV (recap)

Theoretical Open Circuit Voltage :

- Defined by positive and negative electrode active materials
- Calculated from standard potentials of each electrode

$$\textit{Cell Voltage} = E°_{positive} - E°_{négative}$$

Example : Li + MnO_2 → $LiMnO_2$ (discharge reaction – Li primary cell)

Negative Electrode (oxydation) : $Li \rightarrow Li^+ + 1\,e^-$ -3,04V/ENH

Positive Electrode (reduction) : $MnO_2 + Li^+ + e^- \rightarrow LiMnO_2$ 0,25V/ENH

$$V^{theo}_{cell} = 0{,}25 – (-3{,}04) = 3{,}29 \text{ V}$$

TABLE 18.1 Standard Reduction Potentials at 25°C

Stronger oxidizing agent

Weaker reducing agent

Reduction Half-Reaction			E° (V)
$F_2(g) + 2e^-$	$\longrightarrow$	$2F\,(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow$	$2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow$	$Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow$	$2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow$	$2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow$	$2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	$\longrightarrow$	$2Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow$	$Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow$	$Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow$	$H_2O_2(aq)$	0.70
$I_2(s) + 2e^-$	$\longrightarrow$	$2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow$	$4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow$	$Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow$	$Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow$	$H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow$	$Pb(s)$	−0.13
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow$	$Ni(s)$	−0.26
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow$	$Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow$	$Fe(s)$	−0.45
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow$	$Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow$	$H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^-$	$\longrightarrow$	$Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow$	$Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow$	$Na(s)$	−2.71
$Li^+(aq) + e^-$	$\longrightarrow$	$Li(s)$	−3.04

Lithium-Fluoride battery?

Weaker oxidizing agent

Stronger reducing agent

Power density (recap)

- Battery power = battery terminal voltage x discharge current
- Power density = Maximum power per unit volume or weight
- Unit of power density = W/kg or W/l
- Power density depends on
  - loss inside the battery
  - Maximum permissible temperature in battery
  - Thermal management of battery pack

Battery Evolution (recap)

	Lead-Acid		Nickel-Metal Hydride		Lithium-Ion	
	SLI	Advanced	HEV	BEV	HEV	PHEV-BEV
V	2.0	2.0	1.2	1.2	3.3-3.8	3.3-3.8
Wh/l	60	75	100	250	150	200-400
Wh/kg	25	40	50	100	90	120-200
W/l	1200	600	2000 - 2500	500-800	3500-9000	800-2200
W/kg	500	250	1000-1300	200-400	2000-4000	500-1200

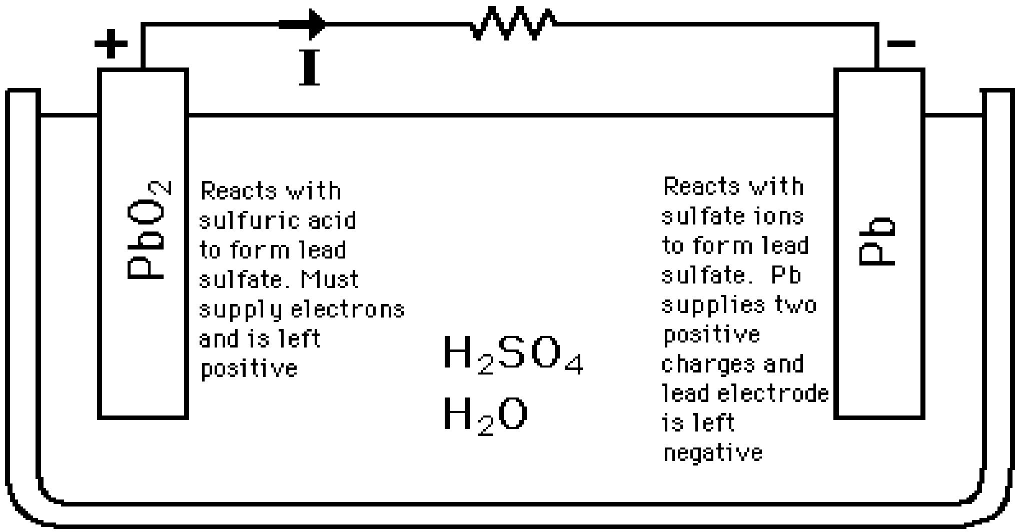
Lead-Acid Battery (recap)

Discharging

Negative Plate: $Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e-$

Positive Plate: $PbO_2 + HSO_4^- + 3H^+ + 2e- \rightarrow PbSO_4 + 2H_2O$

Overall: $PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$



Lead-Acid Battery (recap)

Question 1: What's the theoretical gravimetric charge density (Ah/kg)

Overall:	$\mathbf{PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O}$
Charge	2e-
Mass	239 207 196

Relative mass:
Pb: 207
O:16
S: 32

Other info:

1. One electron: $-1.602*10^{-19}$C
2. One hydrogen atom: $1.667*10^{-27}$kg

To transfer $Q=2*1.602*10^{-19}$C charge, we need the mass $M=(239+207+196)*1.667*10^{-27}$kg, yielding $Q/M/3600=83$Ah/kg

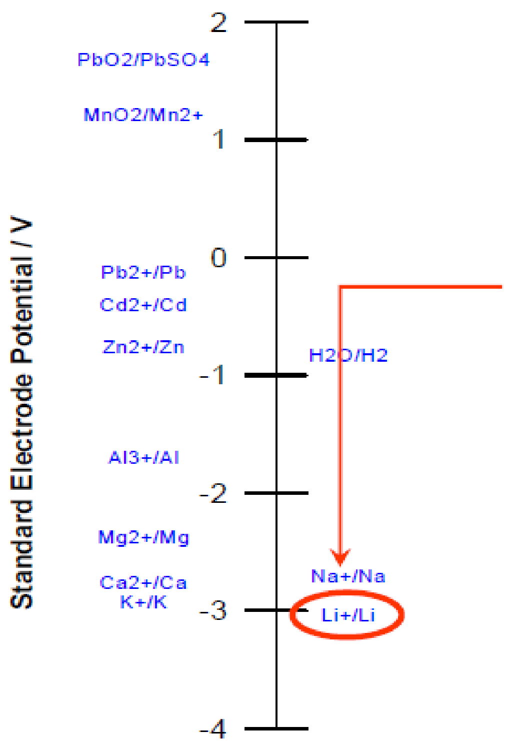
Lead-Acid Battery (recap)

Question 2: What's the theoretical gravimetric energy density (Wh/kg)

Charge density of lead-acid battery is 83Ah/kg;

Energy density of lead-acid battery is 2.1V*83Ah/kg=174Wh/kg

Not competitive in terms of the terminal voltage.



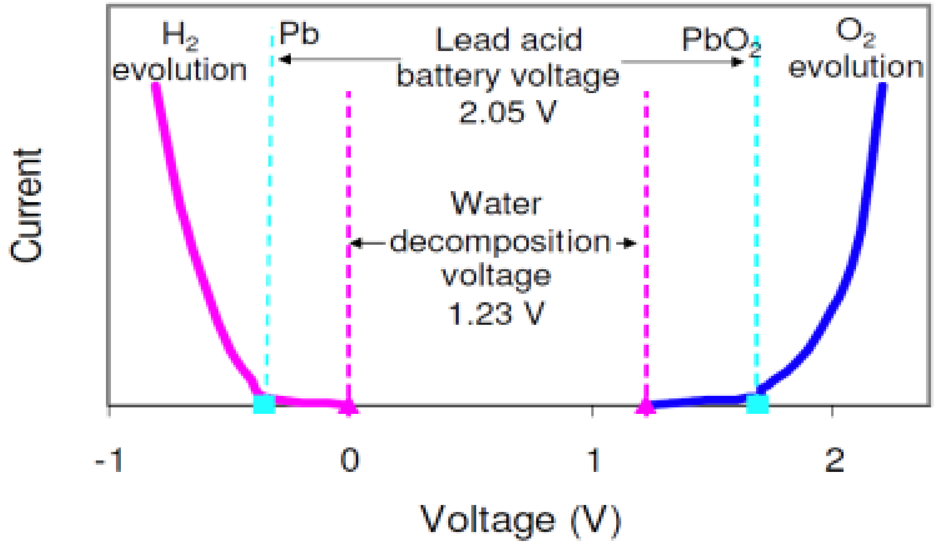
Water hydrolysis during charging (recap)

Oxidation reaction at the positive electrode

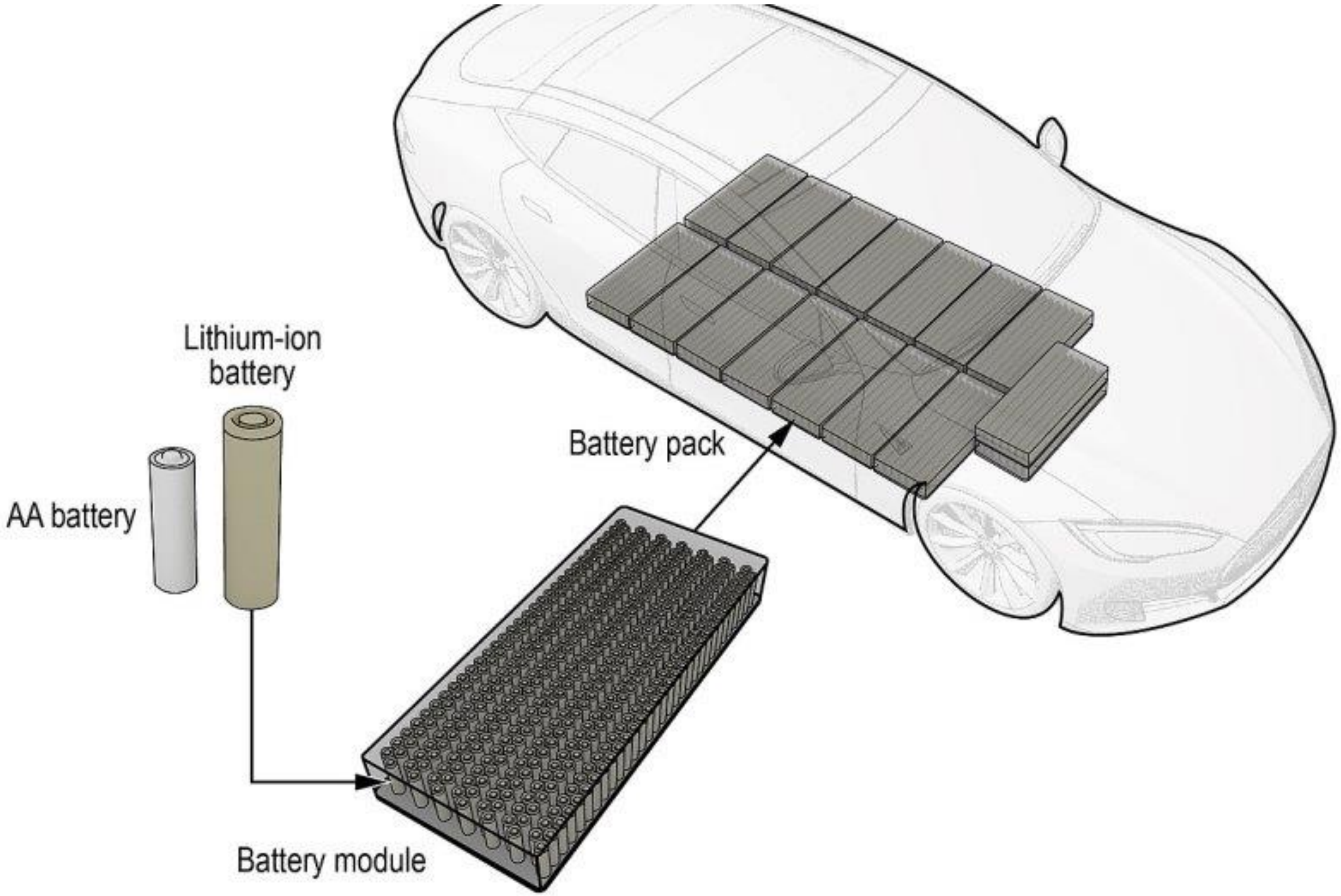
$2H_2O <=> O_2 + 4H^+ + 4e^-$

Reduction reaction at negative electrode

$H^+ + e^- <=> \frac{1}{2} H_2$



Li-ion cells

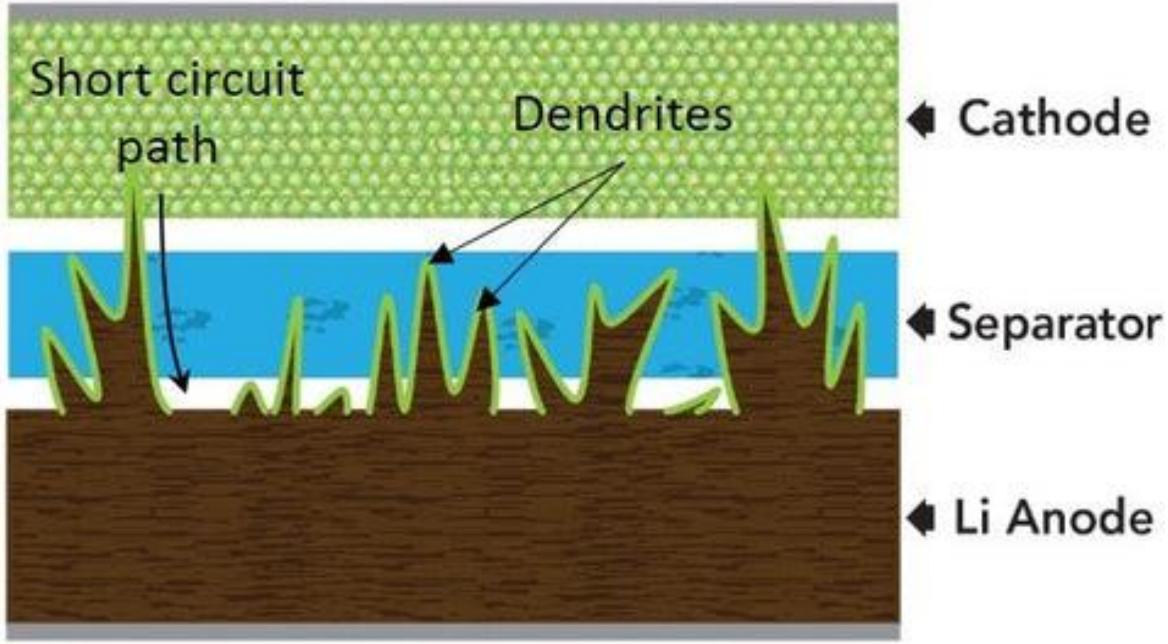


Lithium-ion battery
AA battery
Battery pack
Battery module

Li-metal battery

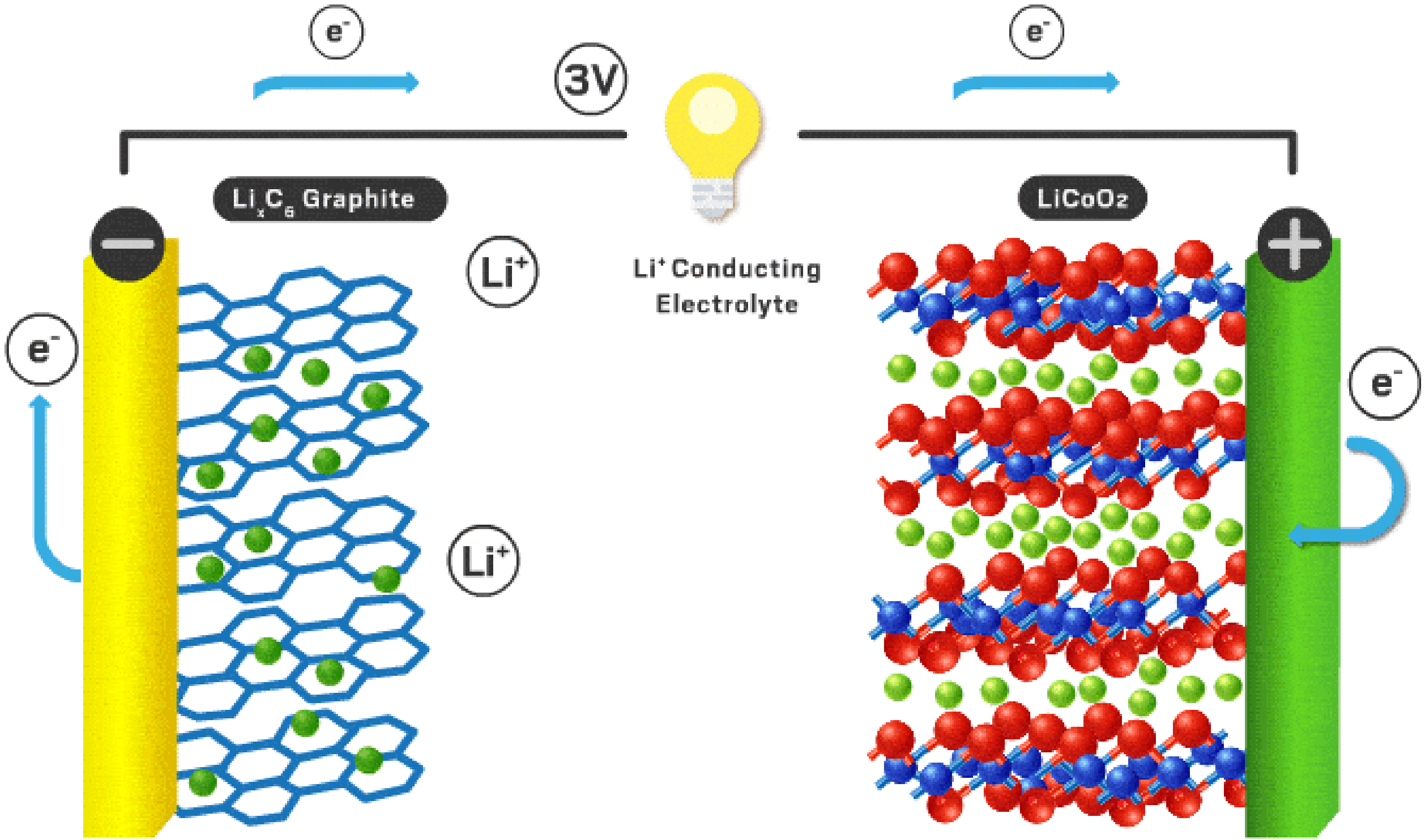
Ex: Li-Sulfur battery $$2Li + S \rightarrow Li_2S$$

- High energy density
- Dendrite formation



- Dendrite formation, leading to short-circuit and thermal runaway
- Shorter life-span

Intercalation electrode



Li-Ion Battery

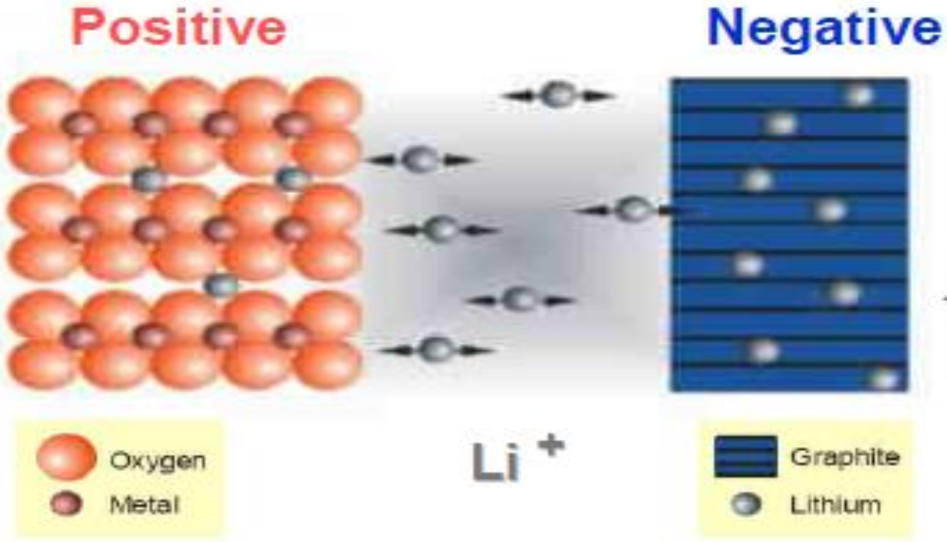
Many Li-Ion chemistries are available. They are usually named according to the composition of the *cathode (positive electrode).*

- $LiCoO_2$: Standard lithium-cobalt-oxide;
- LiMnNiCo: Lithium-manganese-nickel-cobalt;
- $LiFePO_4$: lithium-iron-phosphate;
- $LiMnO_2$: Lithium-manganese-oxide;
- $Li_4Ti_5O_{12}$: Lithium-titanate;
- $LiMn_2O_4$: Lithium-manganese-oxide;
- $LiNiO_2$: Lithium-nickel-oxide.

Li-Ion Battery

Lithiated Metal Oxide :

- Cobalt ($LiCoO_2$)
- NCA ($LiNiCoAlO_2$)
- Manganese ($LiMn_2O_4$)
- NMC ($LiNiMnCoO_2$)
- Iron Phosphate ($LiFePO_4$)



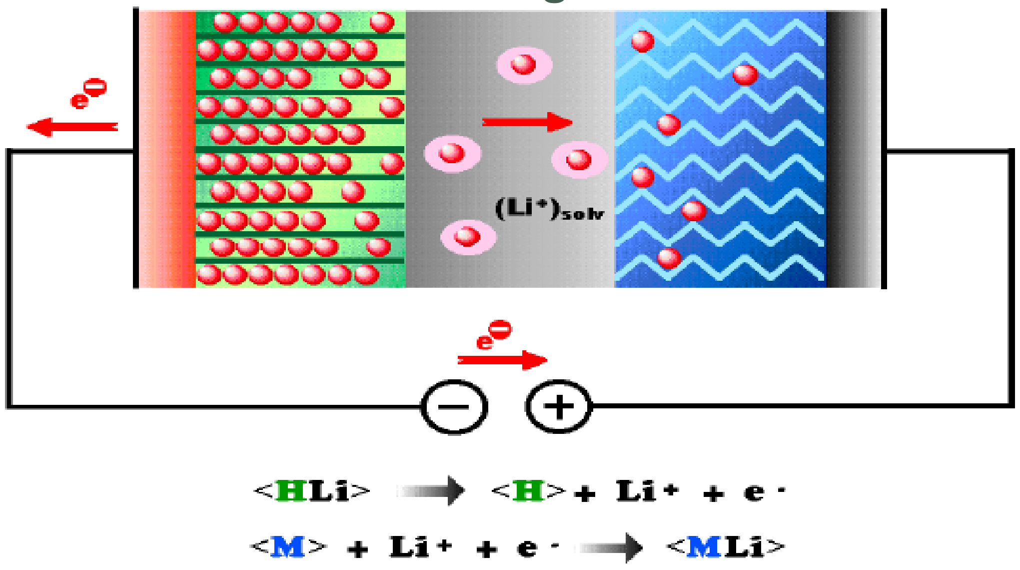
- Graphite
- *Hard Carbone*
- *Titanate*
- *Li-Alloy (Si, Sn...)*

Li-Ion cell reaction

Positive Electrode: <M>

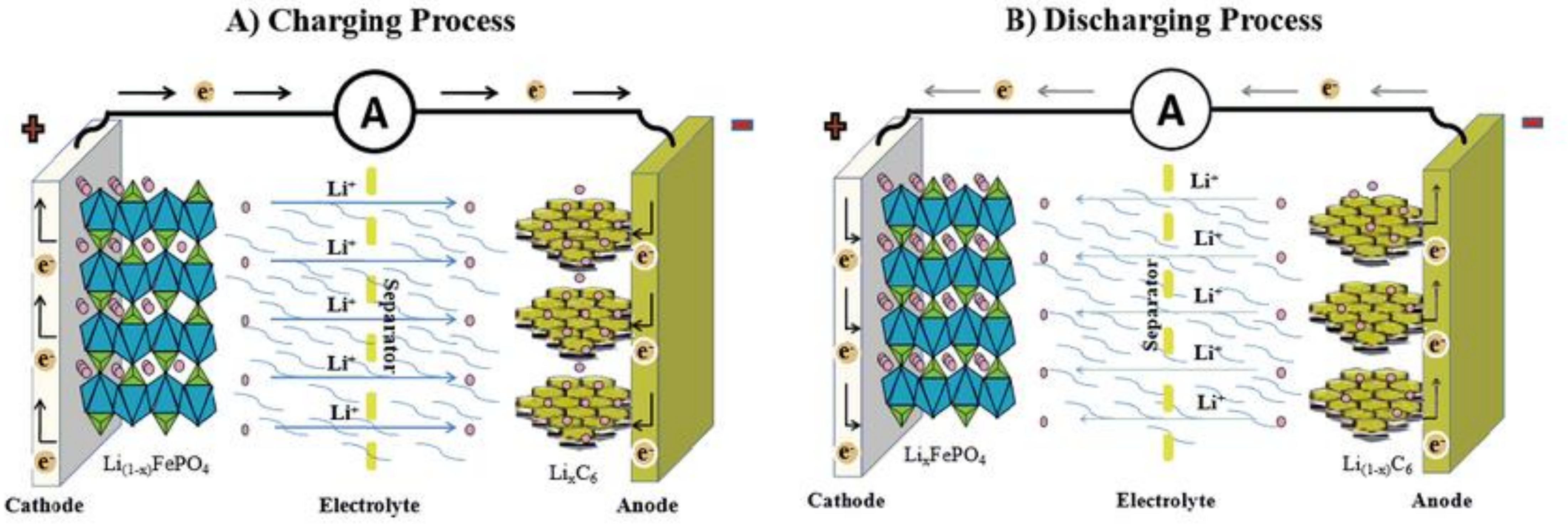
Negative Electrode: <HLi>

Discharge



<M> + <HLi> → <MLi> + <H>

$LiFePO_4$ cell reactions



Example – LiCoO2 cells

A fully charged Li-ion battery has positive electrode as CoO_2 and negative electrode as LiC_6

$$\langle M\rangle + \langle HLi\rangle \rightarrow \langle MLi\rangle + \langle H\rangle$$

Here M= CoO_2, <HLi>=LiC_6

Therefore the overall chemical reaction when discharging is

$$CoO_2 \quad + \quad LiC_6 \quad \rightarrow LiCoO_2 \quad + \quad 6C$$

Relative mass:

Li: 6.9

Co:59

O: 16

C: 12

Other info:

1. One electron: $-1.602*10^{-19}$C
2. One hydrogen atom: $1.667*10^{-27}$kg
3. Cell OCV 3.4V

Example – LiCoO2 cells

CoO_2 + LiC_6 → $LiCoO_2$ + 6C

Relative mass 59+16*2 6.9+12*6

To generate $Q=1.602*10^{-19}C$, we need $M=169.9*1.667*10^{-27}kg$. Therefore the gravimetric charge density is Q/M/3600=157Ah/kg.

The energy density is 3.4V*151Ah/kg=534Wh/kg

What are those parameters of the Pb-Acid Battery?

83Ah/kg
174Wh/kg

Battery chemistry	Energy density (Wh/kg)	
	Theoretical	Practical
Pb-acid	174	60-75
Li-ion	534	120-200

Example – $LiFePO_4$ cells

A fully charged Li-ion battery has positive electrode as $FePO_4$ and negative electrode as LiC_6

Relative mass:

Li: 6.9

Fe: 55.9

O: 16

P: 31

Other info:

1. One electron: $-1.602*10^{-19}$C
2. One hydrogen atom: $1.667*10^{-27}$kg
3. Cell OCV is 3.2V

Find out the charge density and energy density of the cells.

Example – $LiFePO_4$ cells

$$FePO_4 \quad + \quad LiC_6 \quad \rightarrow \quad LiFePO_4 \quad + \quad 6C$$

Relative mass $\quad 55.9+31+16*4 \quad\quad 6.9+12*6$

To generate $Q=1.602*10^{-19}C$, we need $M=229.8*1.667*10^{-27}kg$. Therefore the gravimetric charge density is $Q/M/3600=116Ah/kg$.

The energy density is $3.2V*116Ah/kg=372Wh/kg$

How do those parameters compare with LiCoO2 chemistry?

Battery chemistry	Charge density (Ah/kg)	Energy density (Wh/kg)
LiCoO2	157	534
LiFePO4	116	372

Use of $LiFePO_4$ cells

Advantages of $LiFePO_4$ cells

- Longer life (3000-5000 cycles vs. 500-1500 cycles in case of other Li-ion chemistries)
- Thermally stable: do not catch fire like other Li-ion cells
- Wider temperature range (-20^0C to 60^0C)
- Lower self-discharge rate
- Eco-friendly and non-toxic

Tesla Model 3 Standard Range LFP battery pack

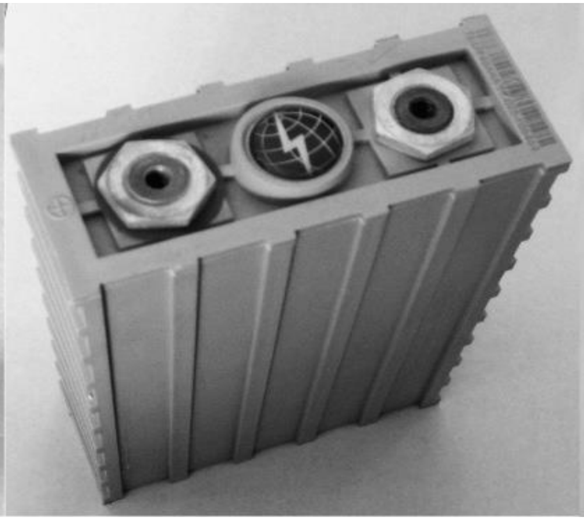
Comparison of Li-ion chemistries

Key Active Material	Lithium-Iron Phosphate	Lithium Nickel Manganese Cobalt Oxide	Lithium Manganese Oxide	Lithium Nickel Cobalt Aluminum	Lithium Titanate
Technology Short Name	LFP	NMC	LMO	NCA	LTO
Cathode	$LiFePO_4$	$LiNi_xMn_yCo_{1-x-y}O_2$	$LiMn_2O_4$ (spinel)	$LiNiCoAlO_2$	variable
Anode	C (graphite)	C (graphite)	C (graphite)	C (graphite)	$Li_4Ti_5O_{12}$
Safety					
Power Density					
Energy Density					
Cell Costs Advantage					
Lifetime					
BESS Performance					

Source: International Renewable Energy Agency (IRENA), 2017

Li-Ion Cell Packages

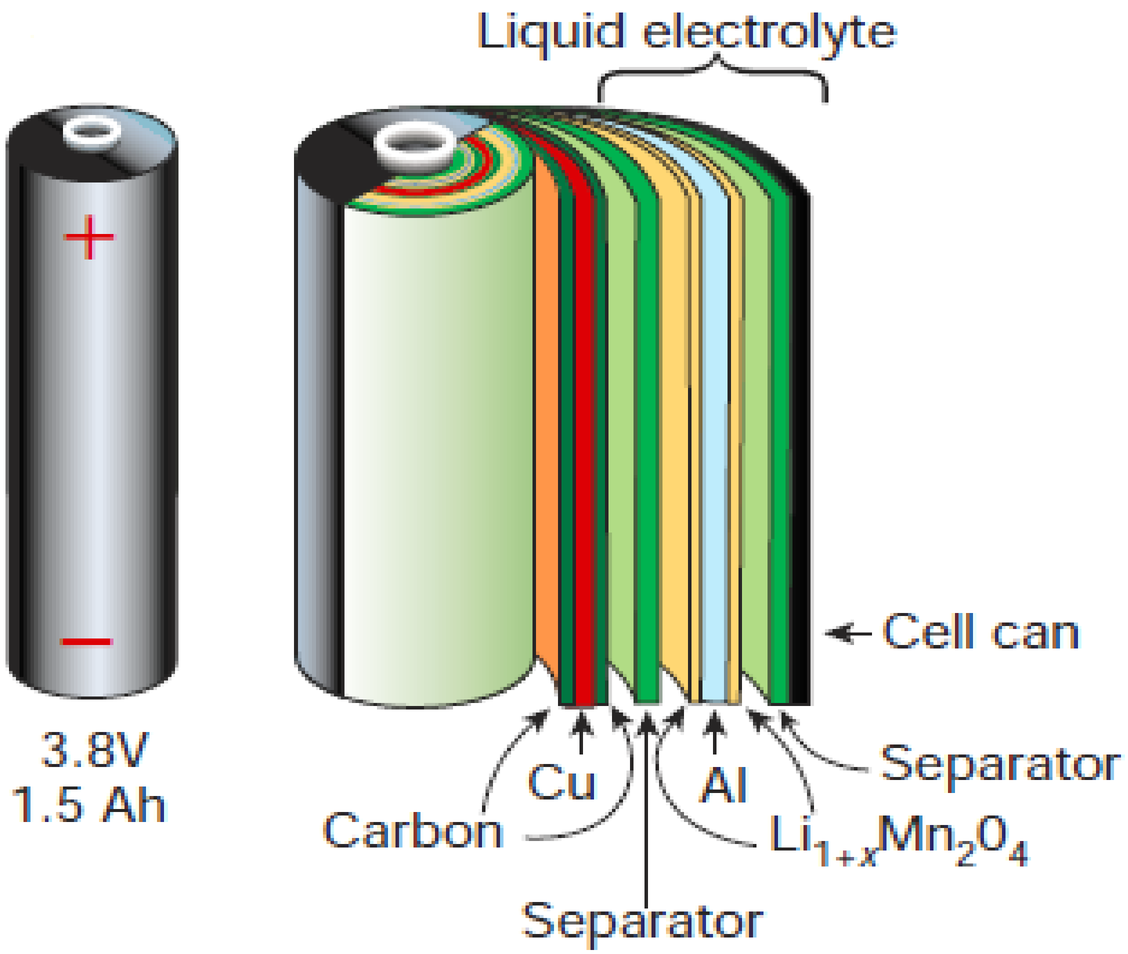
Cylindrical



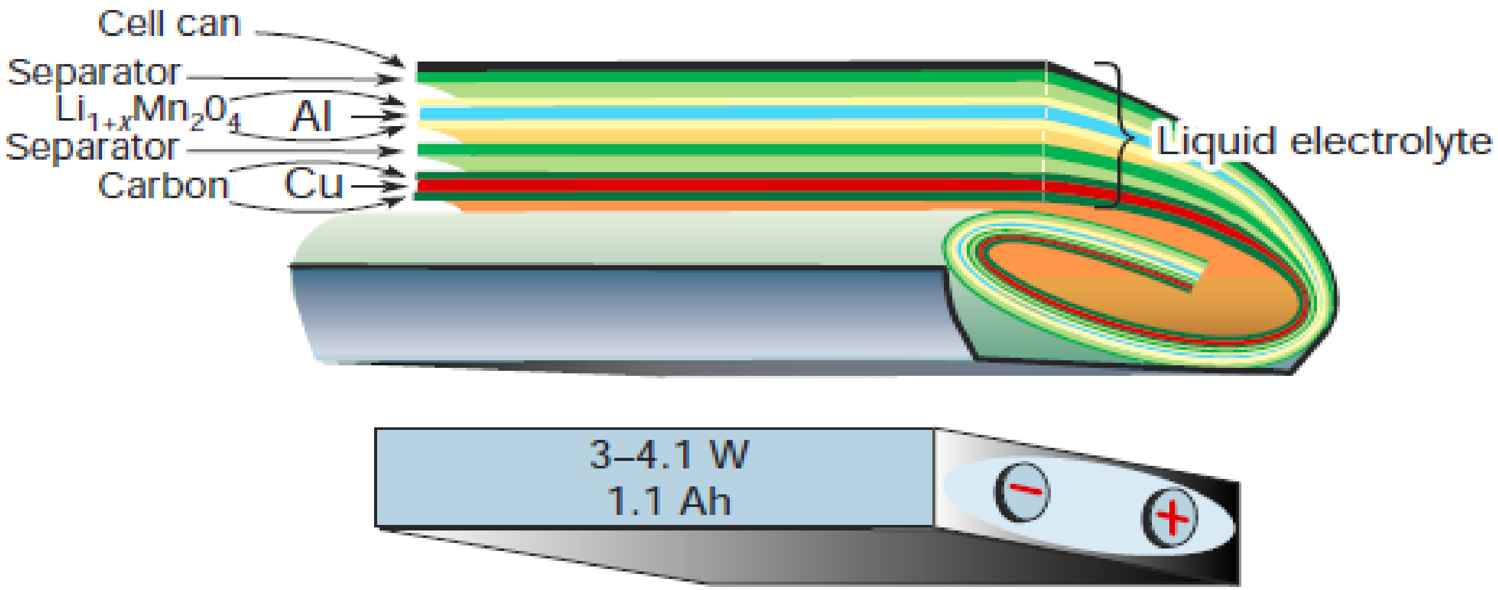
Prismatic (convenient)

Pouch

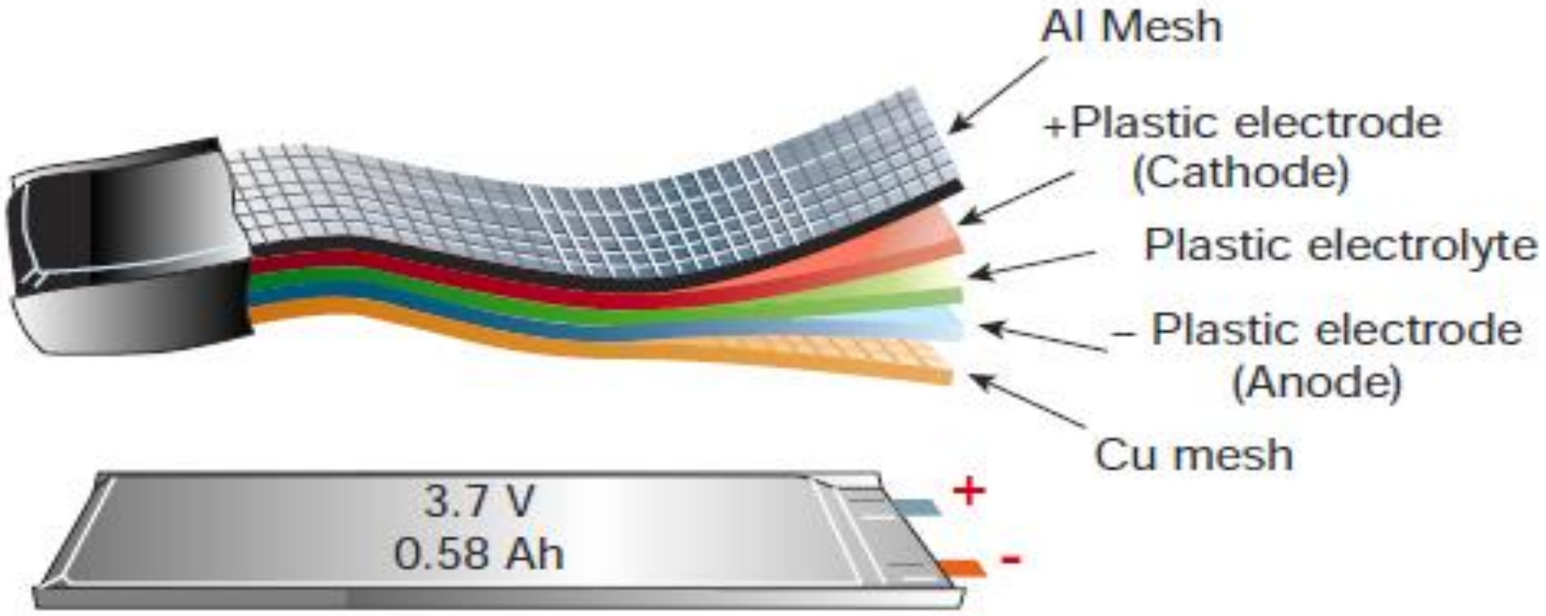
Cylindrical (Hard Can)



Prismatic (Hard Can)



Pouch



Al Mesh
+Plastic electrode
(Cathode)
Plastic electrolyte
– Plastic electrode
(Anode)
Cu mesh
3.7 V
0.58 Ah
+
-

Li-polymer cells

Li-polymer cells use gel-like or solid polymer electrolyte (in flexible pouch packaging)

- Advantages:
  - Slim & Lightweight Design
  - Better Safety & Stability
  - Customizable Shapes
  - Improved Fast Charging
- Limitations:
  - Lower Energy Density
  - Shorter Lifespan (about half)
  - Higher Cost

Thank you!