Batteries

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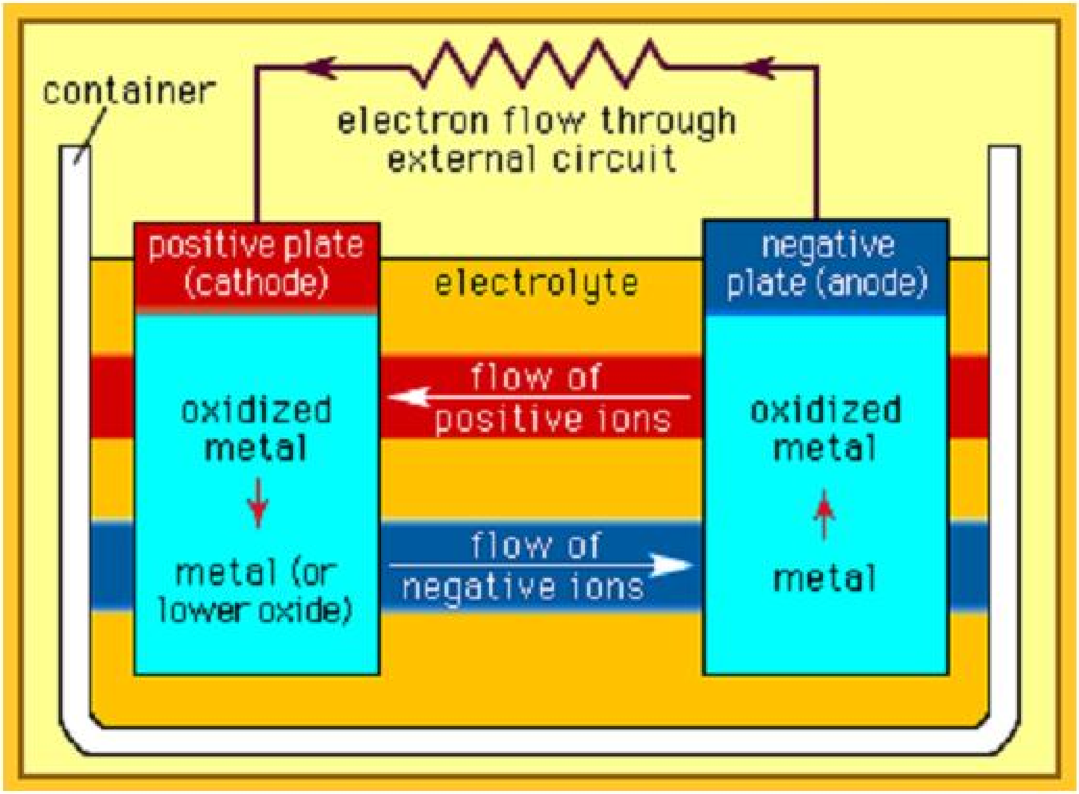
What is battery ?

Chemical energy — Charge / Discharge — **Electrical energy**



Several Kinds of Batteries

Chemical

- **Primary**
  - Mn battery (first invent, cheap, disposable, 1.2V)
  - Alkaline battery (popular, toy, remote contr.)
  - Hg battery (flat round, watch, no use)
  - Air battery (hard maintenance)
  - SOCl Li battery (high V, now using)
- **Secondary**
  - Ni-Cd (wireless phone, 1.2V, Env. Prob.)
  - Lead-acid (Power for car, 1.9V (S-L-I))
  - Ni-MH (artificial satellite, Solar cell)
  - Li (Li-Metal, Li-Ion, Li polymer, thin film battery)

→

- High performance
- Newly rising
- Mobile communication

Physical

- **Fuel Cell**
- **Capacitor**
- **Solar Cell**

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Comparison of Batteries

System	Anode	Cathode	Electrolyte	Working voltage (V)	Energy density (Wh/L)
Lead-acid	Pb	PbO_2	H_2SO_4 (aq. solution)	1.9	70
Ni-Cd	Cd	NiOOH	KOH (aq. solution)	1.2	90
Ni-MH	MH	NiOOH	KOH (aq. solution)	1.2	200
Li-ion	C	$LiMO_2$	Li salt	3.6	300

OOH: oxyhydroxide

Principles of 2nd Batteries

● Nickel-Cadmium RXN

Anode : $Cd + 2OH^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Cd(OH)_2 + 2e^-$

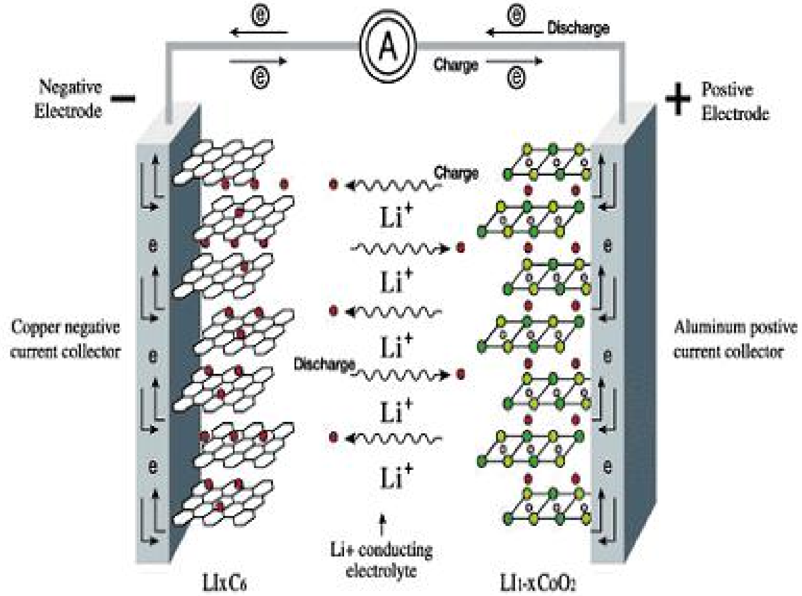
Cathode : $NiOOH + H_2O + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Ni(OH)_2 + OH^-$

● Ni-metal hydride RXN

Anode : $MH + OH^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} M + H_2O + e^-$

Cathode : $NiOOH + H_2O + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Ni(OH)_2 + OH^-$

● Lithium ion RXN



$$Li_yC_6 \rightarrow C_6 + yLi^+ + ye^-$$

$$Li_xCoO_2 + yLi^+ + ye^- \rightarrow Li_{x+y}CoO_2$$

Electrode RXN of Li 2nd Batteries

Anode

- Lithium (alloy)

$Li(Al) \leftrightarrow Li^+ + (Al) + e$

- Carbon compounds

$Li_xC_n \leftrightarrow xLi^+ + C_n + xe$

Cathode

- Oxide ($LiMn_2O_4$, V_2O_5, $LiCoO_2$, $LiNiO_2$)

$Li_{1-x}CoO_2 + xLi^+ + xe \leftrightarrow LiCoO_2$

- Chalcogenides (MoS_2, TiS_2 layered structure)

$TiS_2 + xLi^+ + xe \leftrightarrow Li_xTiS_2$

Mo: molybdenum

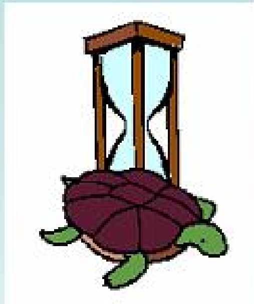
Characteristics of 2^{nd} Batteries

	Advantage	Disadvantage	Application
Ni-Cd	- High current discharge - Cheap - Long cyclability	- Memory effect - Low energy density - Toxic element (Cd)	- Power tool - Toy
Ni-MH	- Mid current discharge - High energy density - Environmental affinity - Large scale	- Low voltage (1.2 V) - Heavy - Low memory effect	- Cheap - Wireless set - Non-professional tool - Electric vehicle
Li-ion	- High energy density - High voltage (>3.6V) - Light weight - No memory effect - Various materials	- High price - Multiple protection - large scale prob.	- 3C - High voltage cell - Electric vehicle

New energy source

Development of portable electronic products

High energy density



High stability

Lighter

Environmental

Advanced Li Polymer Battery

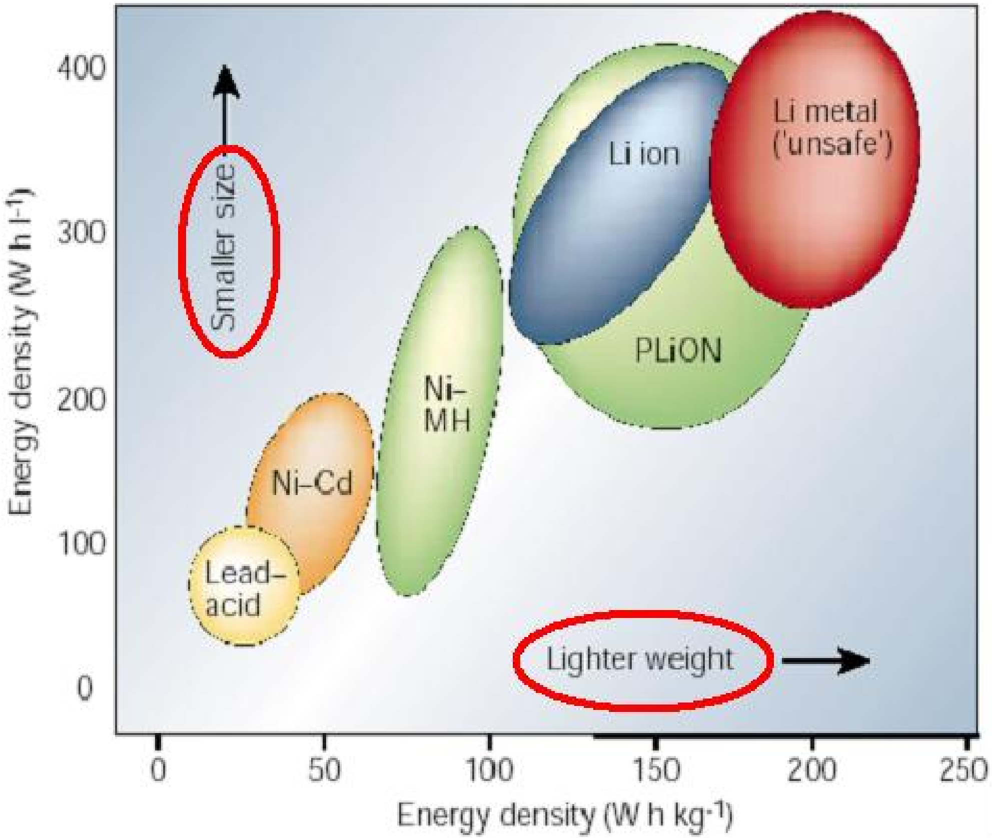
Why lithium ?

- **Lightest** metal (relative atomic mass = 6.94)
- High specific capacity (3.86 Ahg^{-1})
- **Much negative** electrochemical reduction potential (-3.04V)

Cathode (Reduction)	Half-Reaction Standard Potential E° (volts)
$Li^{+}(aq) + e^{-} \rightarrow Li(s)$	-3.04
$K^{+}(aq) + e^{-} \rightarrow K(s)$	-2.92
$Ca^{2+}(aq) + 2e^{-} \rightarrow Ca(s)$	-2.76
$Na^{+}(aq) + e^{-} \rightarrow Na(s)$	-2.71
$Mg^{2+}(aq) + 2e^{-} \rightarrow Mg(s)$	-2.38
$Al^{3+}(aq) + 3e^{-} \rightarrow Al(s)$	-1.66
$2H_2O(l) + 2e^{-} \rightarrow H_2(g) + 2OH^{-}(aq)$	-0.83
$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$	-0.76

Lowest !!

Comparison of 2^{nd} Batteries



▸ **Lithium battery**
~ promising E source!!

▸ **Portable devices demand high energy density battery.**

- **small battery weight**
- **drive more power**
- **longer battery life**

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History of Li 2nd Batteries

1972 Concept of chemical intercalation

1973 Discovery of conductivity in PEO/metal complexes (P. V. Wright)

1978 Concept of polymer based electrolyte (M. B. Armand)

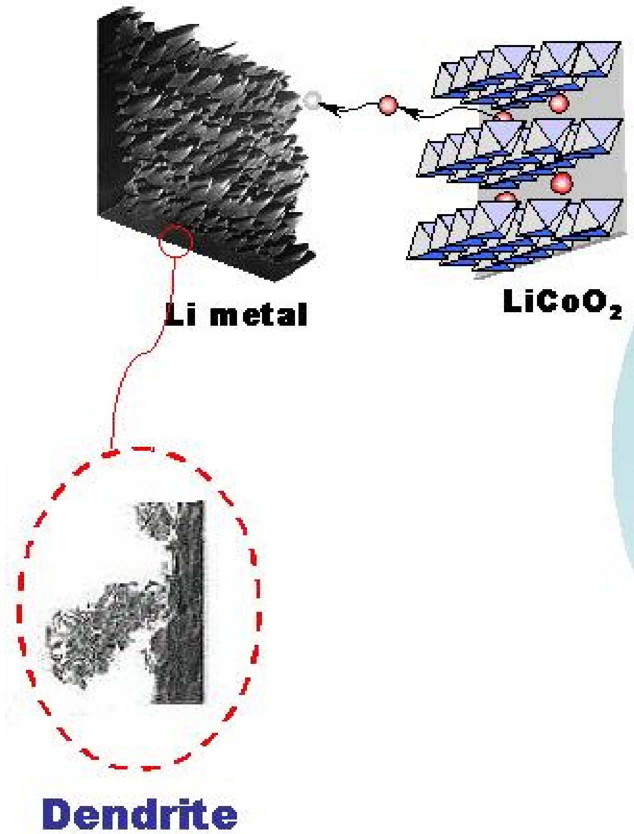
1985~1990 Li-ion battery and Li polymer battery

70'~1985 Li metal battery

- **Cathode: intercalation compounds**
- **Anode: Li metal or Li-Alloys**

1990 Li-ion battery (carbon anode)

Development of Li 2nd battery



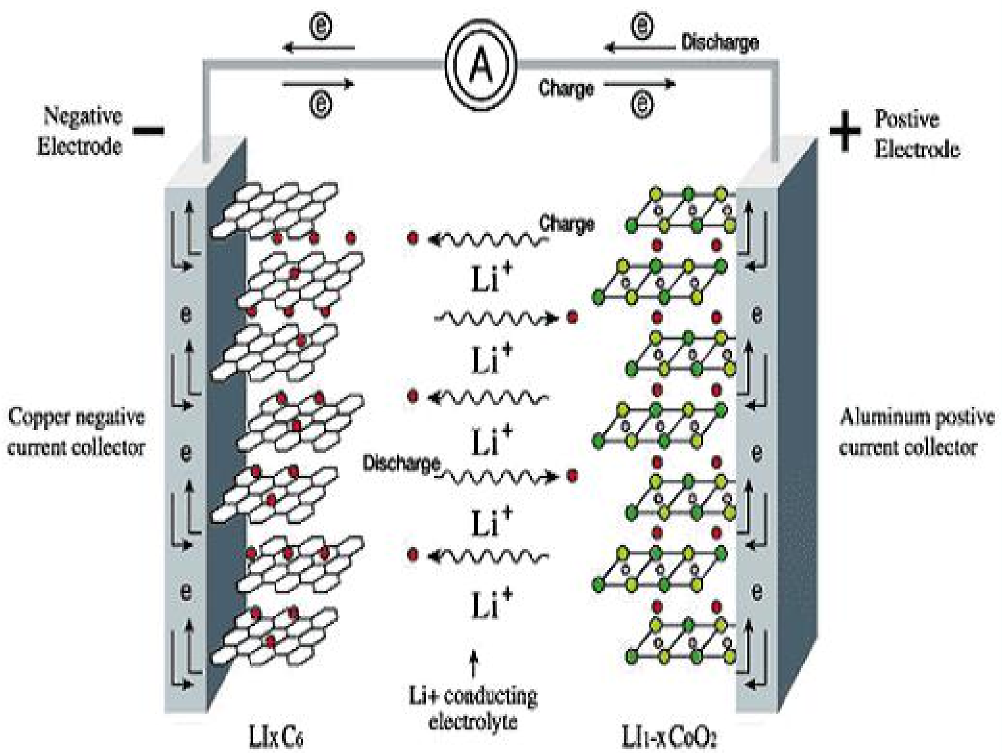
● **Li metal battery**

1. **High reactivity** of Li metal
2. **Dendritic formation** of Li during the charging process

- Poor cycle performance (~20 cycles)

  (cf. > 600 cycles for commercialization)
- Longer charging time
- Poor safety characteristics

Principle of Li 2nd battery



► ***Main components***

1. Intercalation structure (C)

2. Polymer electrolyte

► **Cathode reaction**

$$Li_xCoO_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_{1-x}CoO_2 + xLi^+ + xe^-$$

► **Anode reaction**

$$C_n + xLi^+ + xe^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} C_nLi_x$$

► **Net reaction**

$$LiCoO_2 + C_n \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_{1-x}CoO_2 + C_nLi_x$$

Comparison of Li Batteries

	Lithium Ion	Lithium Ion Polymer	Lithium Polymer
Anode	Carbon	Carbon	Carbon
Electrolyte	Organic solvent	Gel-type polymer	Solid-type polymer
Cathode	Metal oxide ($LiCoO_2$, LiN_2O_2, $LiMn_2O_4$)	Metal oxide ($LiCoO_2$, LiN_2O_2, $LiMn_2O_4$)	Metal oxide, Organic sulfur, Conducting polymer
Voltage	3.6V	3.6V	2.0~3.6V
Energy density	High	High	Very High
Cycle	Excellent	High	Poor
Low temp.	Good	Medium	Poor
Safety	Medium	Good	Good
Flexibility of cell design	Poor	Good	Good
Application / commerization	3C market / Sony (1991)	3C market / Ultralife (1997)	3C, EV(high capacity) developing

* 3C : Cellular phone, Computer, Camcoder

Advantages of Li polymer battery

High energy density

3.6V per unit cell
(~ Ni-Cd × 3, MH battery × 1.5)
→ Compact effect

Productibility

Useless hard case: slim (<1mm)
Flexibility : process simplification

Long life

500 ~ 1000 cycles

Low self-discharge

< 5% at 20 °C
(Ni-Cd or MH battery : 15%)

Safety

No leakage, low risk of exploision

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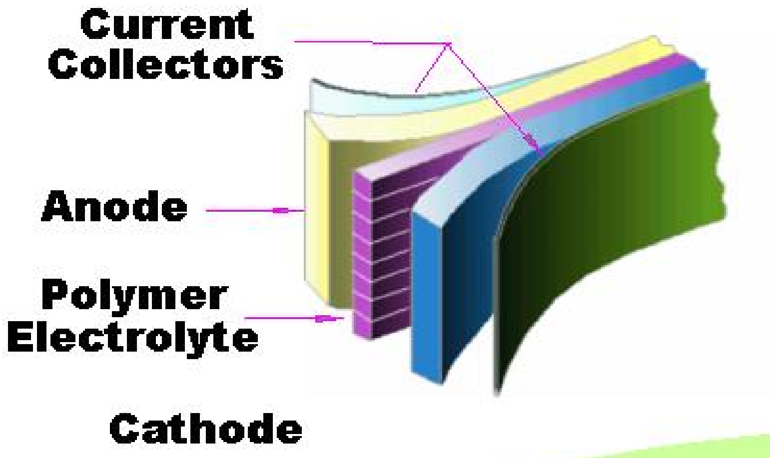
Components of Li polymer battery



- √ Current collector : Cu, Al foil
- √ Anode : Carbon + Polymer binder
- √ SPE : Polymer matrix + (solvent) + Li salt + etc
- √ Cathode : Metal oxide + binder + Carbon black

Commercialized Polymer Electrolytes

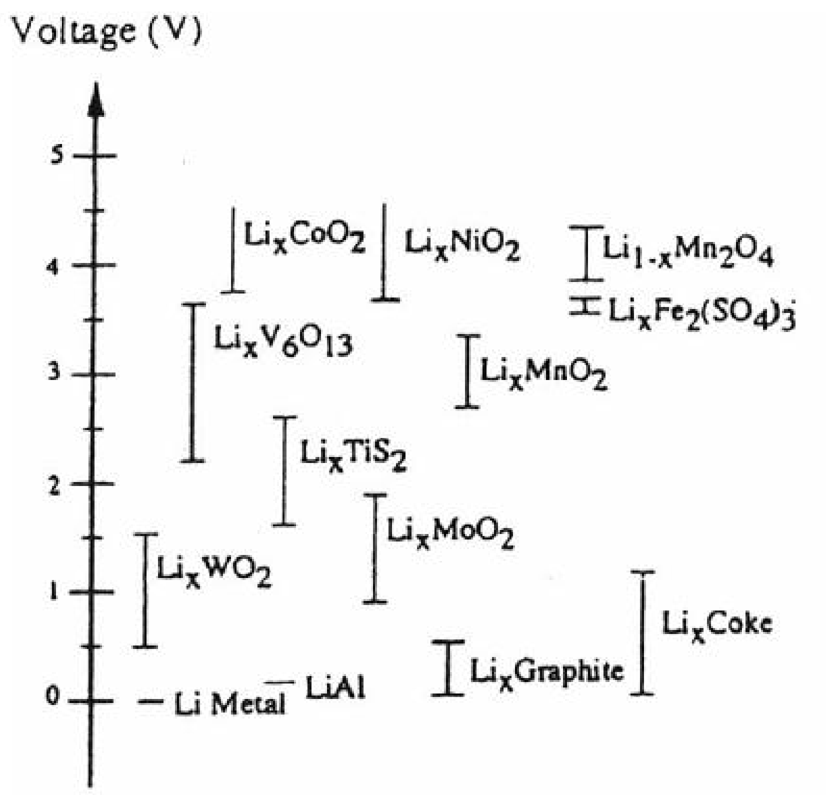
Company	Polymer electrolyte	salt	plasticizer	conductivity [S/cm]	Remarks
Hydro-Quebec (Canada)	Poly(ethylene oxide)	$LiClO_4$	-	3×10^{-5}	Pure solid
		LiTFSI	TESA (10%)	5×10^{-3}	Gel type
Valence (USA)	Poly(ethylene oxide-acrylonitrile)	$LiAsF_6$	PC/EC	4×10^{-3}	Gel type
	Polyacrylonitrile(PAN)	$LiClO_4$	PC 60~80%	1×10^{-3}	Gel type
EIC Lab. (Canada)	Polyacrylonitrile(PAN)	$LiClO_4$	PC/EC (71%)	1.7×10^{-3}	Gel type
	MEEO-EO	LiTFSI	-	6.7×10^{-5}	Gel type
SRI (USA)	siloxane polyelectrolyte $SiO(EO\text{-}ES)CF_3SO_3Li$	-	PC (66%)	5×10^{-4}	Gel type
				1.7×10^{-5}	Gel type

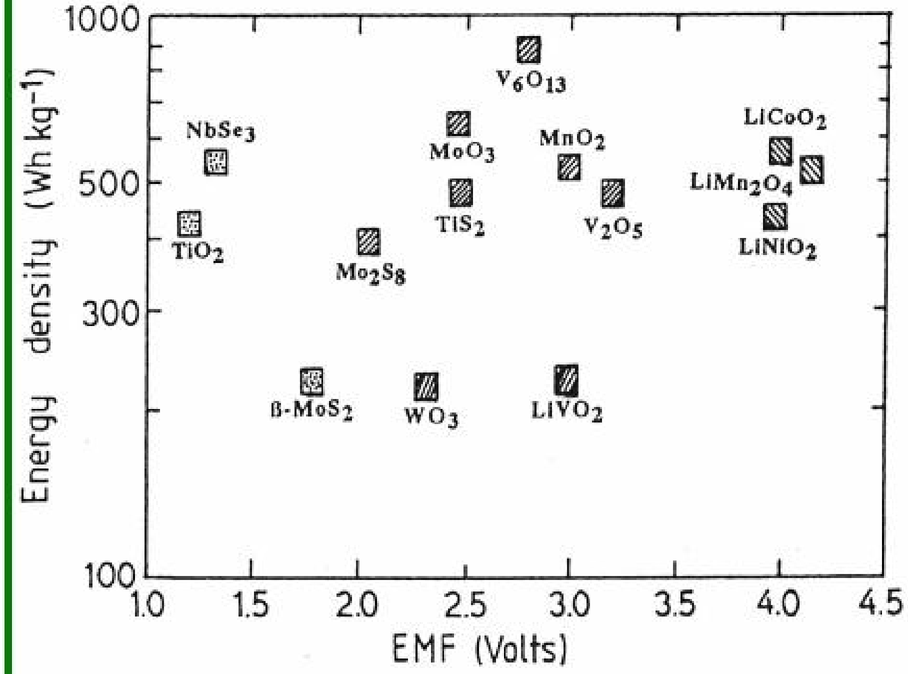
Commercialized Polymer Electrolytes

Company	Polymer electrolyte	Salt	Plasticizer	Conductivity [S/cm]	Remarks
Telcorda (USA)	Poly(vinylidene fluoride) copolymer (PVdF-HFP)	$LiPF_6$	EC	> 1×10^{-5}	Gel type
			EC/PC (60%)	1×10^{-3}	Gel type
Gould (USA)	Poly(ethylene oxide)	$LiClO_4$	PC/EC	2×10^{-3}	Gel type
Battery Eng (USA) Hitachi Maxell (Japan)	2-ethoxyethylacrylate+ ethyleneglycol ethylene carbonate methacrylate +tri(ethyleneglycol)dimethyl acrylate	$LiPF_6$	PC/EC	2×10^{-3}	Gel type
Sony (Japan)	Polyacrylonitrile	$LiPF_6$	EC/PC/γ-BL		Gel type
Asehi kesei (Japan)	poly(vinylideneluoride hexafluoropropylene)	$LiBF_4$	EC/PC		Gel type
Toshiba (Japan)	poly(vinylidenefluoride hexafluoropropylene)	$LiBF_4$	DMC/ sulfone		Gel type

Break ???

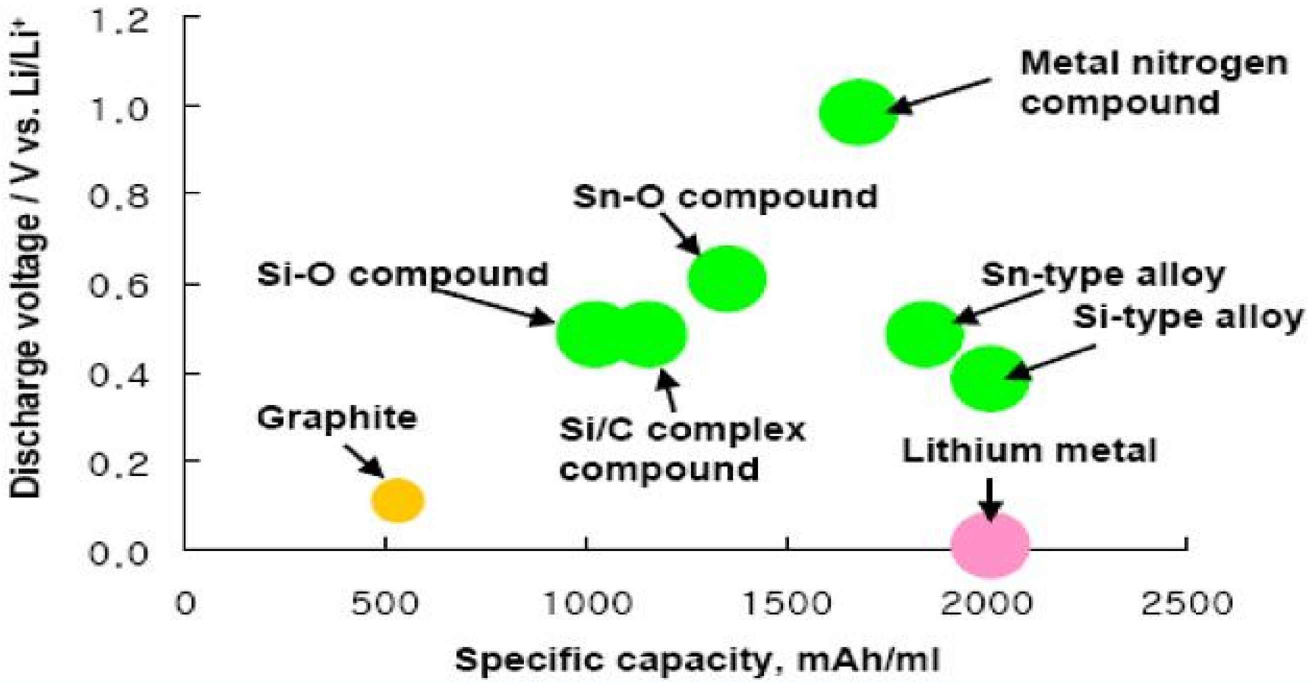
Electrode Materials for Li Batteries





Electrochemical potential ranges of some lithium insertion compounds in reference to metallic lithium.

Anode Materials



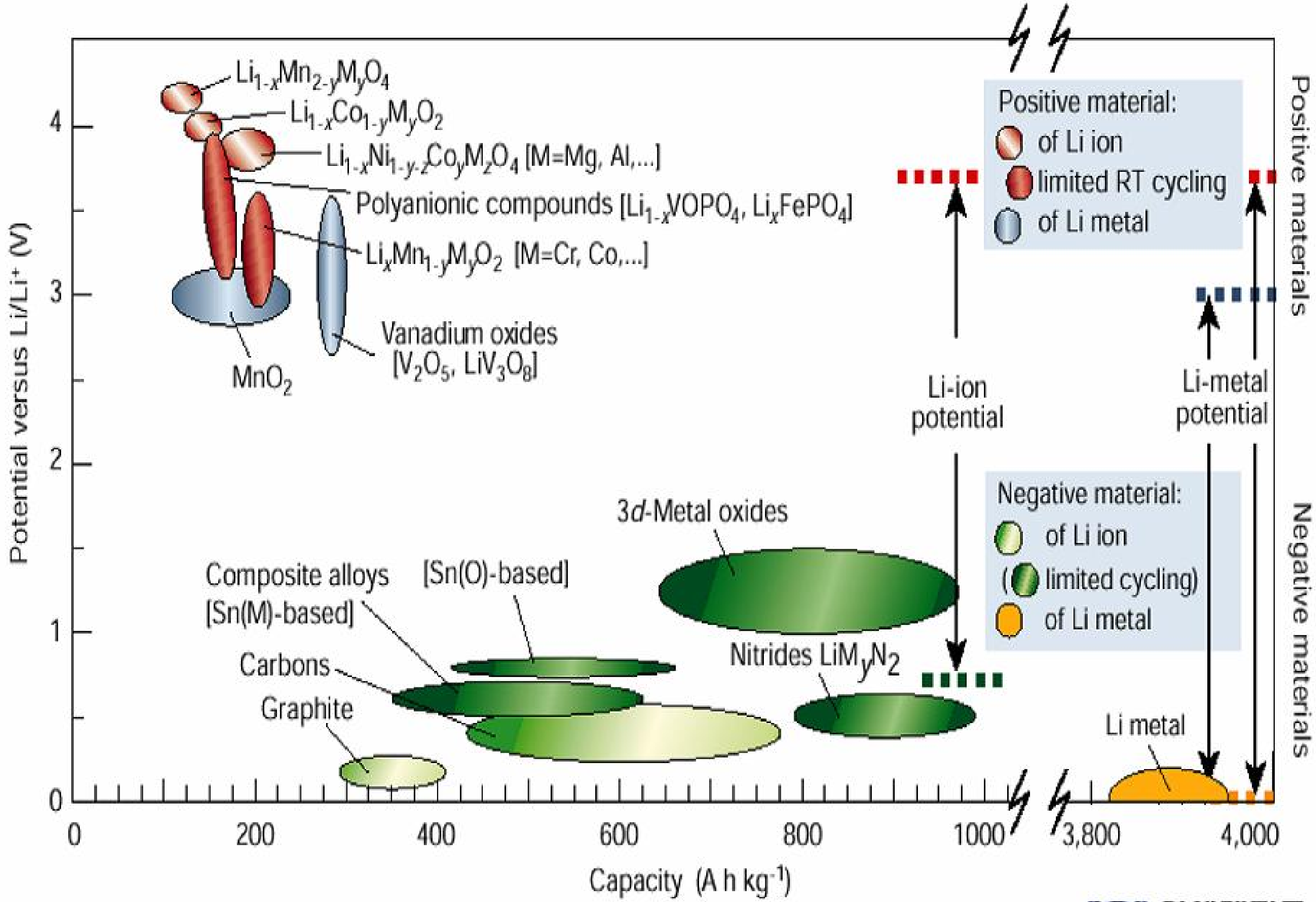
- **Li metals: high density (3860 mAh/g) (+), dendrite formation (-)**
- **Carbon materials: hard carbon, soft carbon, graphite**
- **Alloy (Sn, Al, Si etc)**
- **Nanoparticles, compounds (SnO_x, SiO_x etc)**

Comparison of Cathode

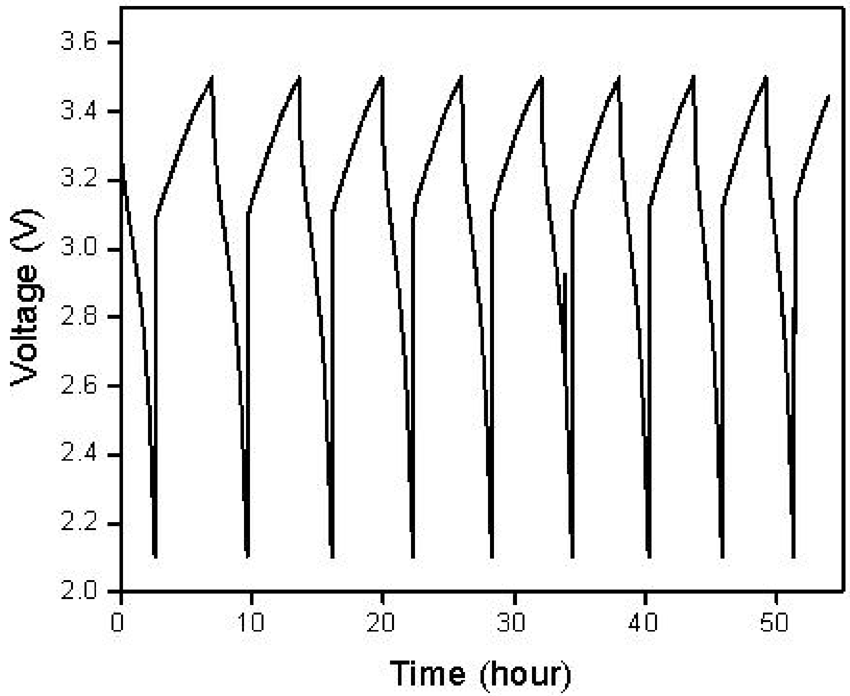
	$LiCoO_2$	$LiNiO_2$	$LiMn_2O_4$
Avg. voltage (V)	3.6	3.4	3.7
Theoretical Capacity (Ah/kg)	273.8	274.5	148.2
Initial capacity	~ 150	~ 200	~ 120
Cycle degradation	Small	Large	Medium
Thermal degradation	Small	Small	Large
Reservation (kg)	Limited (9.0×10^9)	Little limited (1.1×10^{11})	Abundant (5.0×10^{12})
Commercial	Producing	Not yet	Producing
Goal	Lower cost	Improve stability & cycleability by mixing w/ Co	Improve thermal stability & cycleability

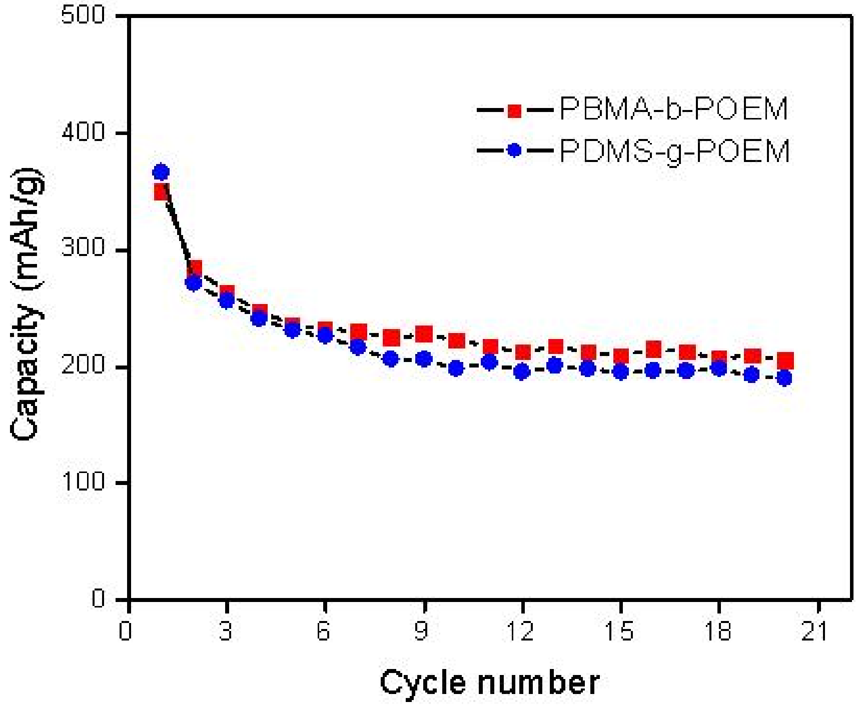
- F ; 96500 C (A·sec) or 26.8 Ah : charge carried by one mole of ion
- Theoretical Capacity = F/M_w

Electrode Materials



Graph of Voltage and Capacity





Capacitity decreases with cycle No.

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Polymer Electrolytes

- **Solid: polyether-*g*-polyester, polysiloxane, polyphosphazene**

- **Gel polymer electrolyte: polymer + organic electrolyte**
  - **Porous PVDF: P(VDF-co-HFP)**

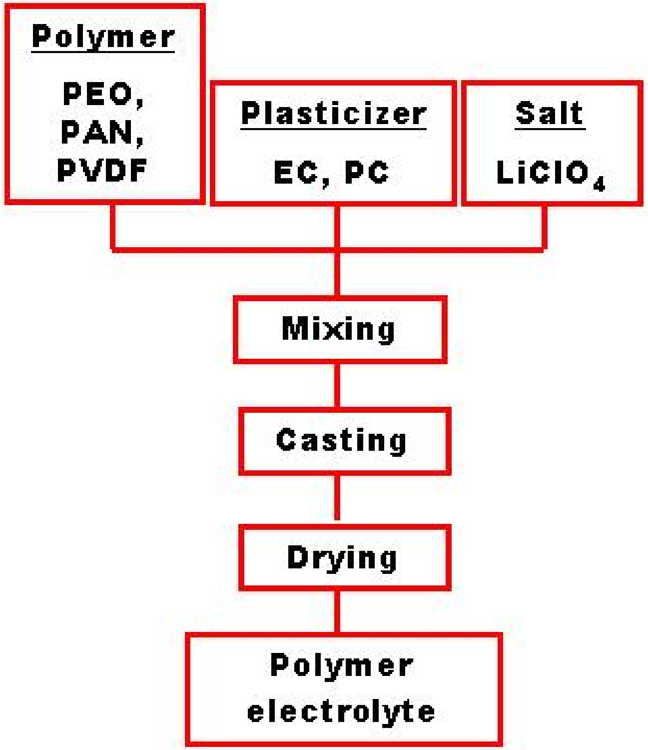
    → **VDF (crystallinity, mechanical property)**

    → **HFP (compatibility w/ electrolyte) (Bellcore, Valence, Ultralife)**
  - **PAN (EIC, Sony)**
  - **Polyacrylate (Hitachi, Sanyo)**
  - **PEO (Yuasa, 3M)**

- **Others: plasticized polymer, networks, ionic rubber, polymeric alloy**

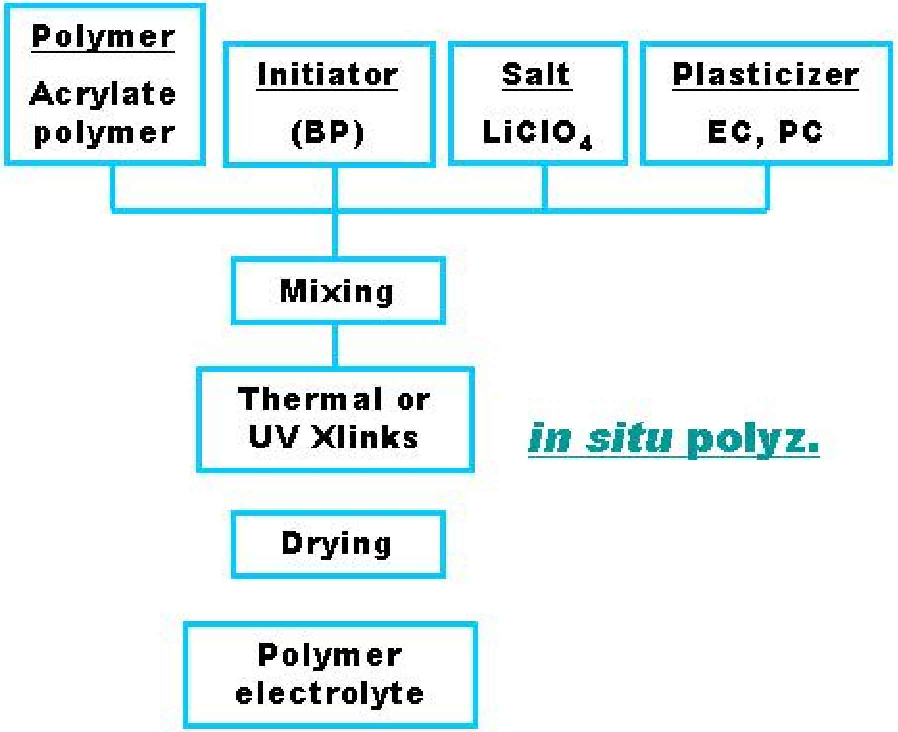
Preparation of gel polymer electrolyte

Physical gel



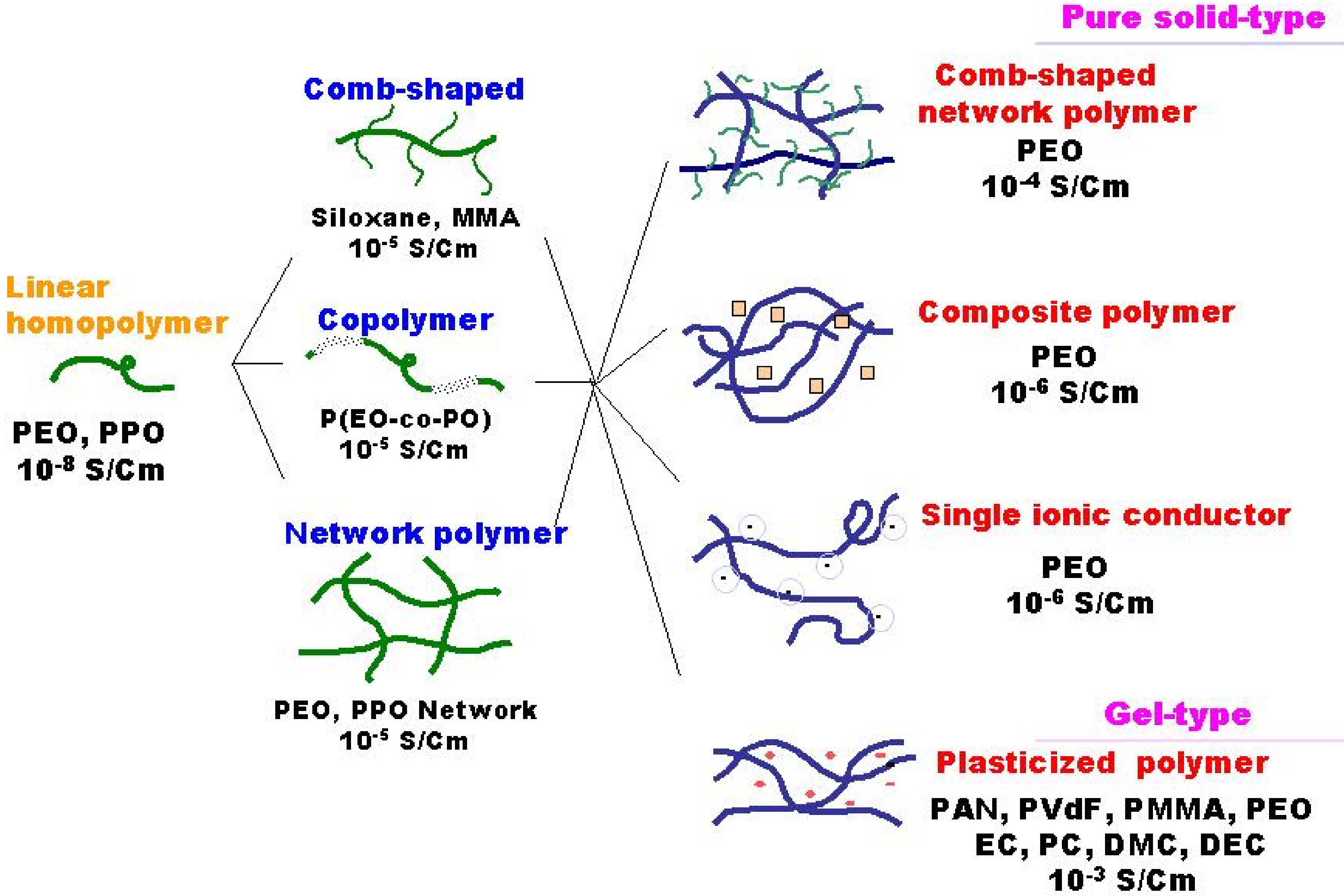
2nd bond (HB, dipole, Ionic bond)

Chemical crosslinking



Covalent bond

Advanced polymer electrolytes



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Studied gel-type polymer electrolyte

Polymer	Salt	Solvent	Conductivity [S/cm]
Poly(ethylene oxide)	$LiClO_4$	EC:PC, 20mol%	10^{-3}
	$LiClO_4$	PC, 50%	8×10^{-4}
Poly(vinylidene floride) (PVDF)	$LiN(CF_3SO_2)_2$	EC:PC, 75%	1.5×10^{-3}
Poly(ethylene glycol acrylate)	$LiClO_4$	PC, 1M	10^{-3}
Poly(p-phenylene terephalamide)	$LiBF_4$	PC:EC = 25:25 (mol%)	2.2×10^{-3}
Poly(ethylene glycol dimethacrylate)	$LiClO_4$	PC, 1M	2×10^{-3}
Poly(acrylonitrile) (PAN)	$LiClO_4$	EC:PC = 38-33:21 (mol%)	10^{-3}
	$LiAsF_6$	BL	6.1×10^{-3}
	$LiN(CF_3SO_2)_2$	BL/PC	4.0×10^{-3}
	$LiCF_3SO_3$	EC/PC	1.4×10^{-3}
Poly(VdF-HEP)	LiPF6	EC/PC	3×10^{-3}
		EC/DMC	3×10^{-3}
Poly(ethylene glycol) diacrylate	$LiCF_3SO_3$	PC	1×10^{-3}

Energetics of batteries

● Three major characteristics

(1) the operating voltage

(2) the current that can be drawn at a usable voltage

(3) how long it will last

Reaction → $\Delta G^0 = -nFE^0$, F ; 96500 C or 26.8 Ah

● Cell voltage

Actual voltage (E) < $\Delta G/-nF$

; overpotential associated with the reaction

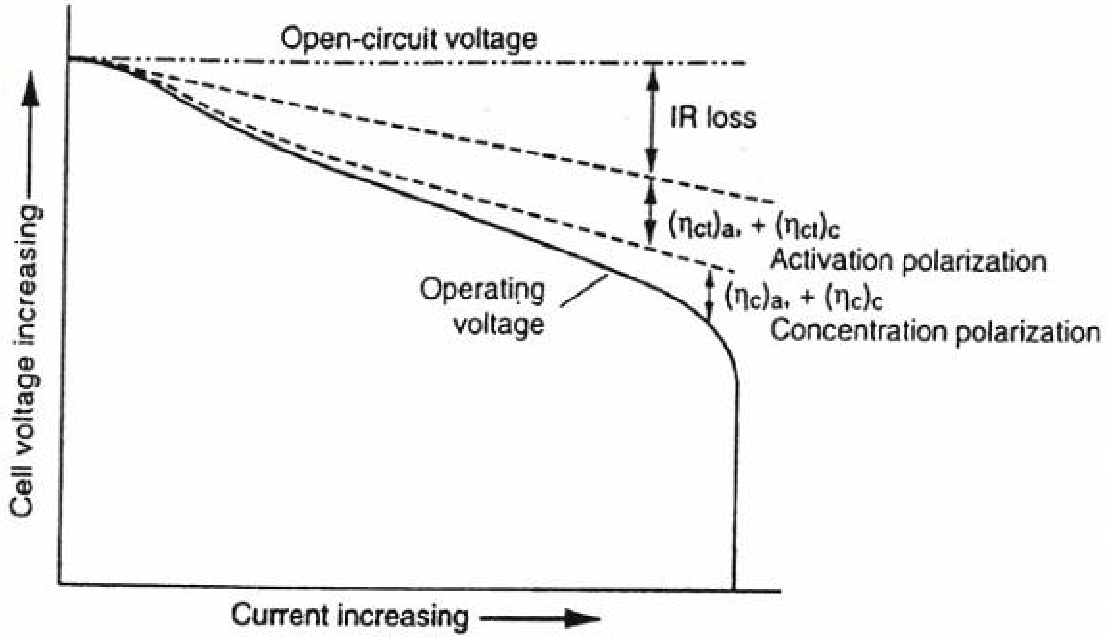
● Overpotential

- voltage shift caused by each kind of polarization

1) **Ohmic polarization**: resistance loss of electrolytes in the cell

2) **Activation polarization**: slow electrode reaction

3) **Conc. polarization**: difference btn. electrode surface & bulk conc. gives the maximum possible potential



Cell polarization as a function of operating current.

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Battery Evaluations

● Capacity (C or Ah)

- the amount of charge that may be delivered by a battery
- theoretical capacity

$$C = nF\ (W/M_W)$$

W: weight of active electrode material

F; 96500 C or 26.8 Ah

● Theoretical capacity

1 mol : 96500 C/mol

e.g.

Li: M_W 6.941g → 26.8 Ah/6.941 g = 3.861 Ah/g

$LiCoO_2$: MW 97.871g → 26.8 Ah/97.871 g = 273.7 mAh/g

Efficiency of 2nd Battery

1) **Coulometric efficiency**: $q_{Ah} = Q_{discharge}/Q_{charge}$

For LIB: 95 -100%

2) **Energy efficiency** : $q_{wh} = q_{Ah} \times V_{discharge}/V_{charge}$

- difference btn. required energy to charge a battery & the energy delivered by the battery in use

3) **Current efficiency**

- the ratio btn. the electricity obtained from a battery & that used to charge it

Cycle life

- discharged partially or completely, then recharged, and this should be feasible an infinite number of times
- practically not (∵ not the same electrode, electrolyte, separator after charge)
- irreversibility in the electrochemical reaction
- Usually 60-80% of initial capacity

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● Rate Performance

- Discharge rate
- a measure of the rate at which charge is drawn from the cell
- quoted as "C/n or n-hour rate", the current to discharge the nominal capacity C of the battery in n hours.

  e.g., 300 mAh capacity battery: 300 mA in 1 h "c-rate"

  c/5-rate, 5 h discharge

- High Rate performance: possible commercialization

  (e.g.: at C-rate, 95% discharge > 60% discharge)

● Economics of Batteries

i) Shelf life: self-discharge

ii) Reliability; e.g., pacemaker

iii) Overcharge

iv) Economic & environmental factors

Nomenclature of Li 2nd Battery

▶ Cylindrical shape: ABCxxyyy (e.g.: ICR18650)

A: anode (L for lithium metal or alloy, I for intercalation material)

B: cathode (C for Co, N for Ni, M for Mn, V for V based)

C: shape of cell (R for round, C for cylindrical)

xx: approximate cell diameter in mm

yyy: approximate cell height in tenth of mm

▶ Square shape: ABCxxyyzz (e.g.: ICP103448)

A: anode (L or I)

B: cathode (C, N, M, V)

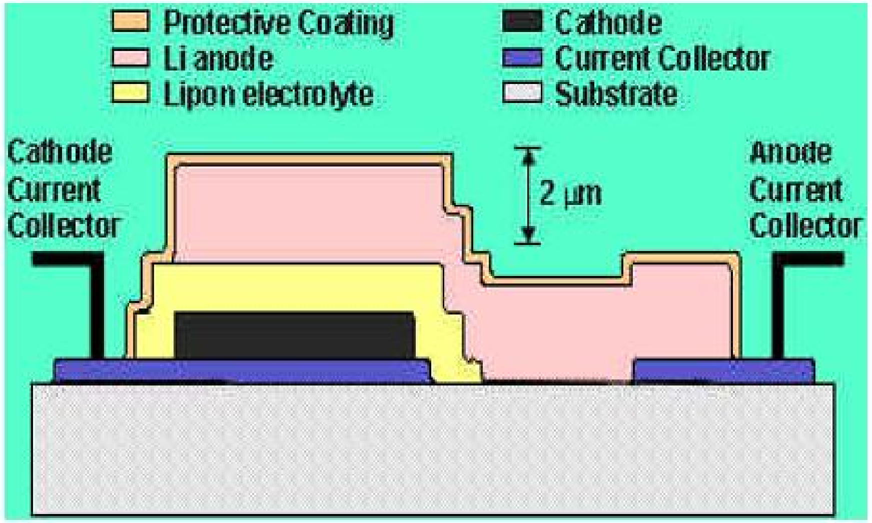
C: shape of cell (P for prismatic, R for rectangular)

xx: approximate cell width in mm

yy: approximate cell height in mm

zz: approximate cell length in mm

Thin film battery



Advantages

- Variable size/power : thin film/layer
- Semiconductor process: reliable
- All solid state: stability, no sealing
- Long life : good cycle life
- Microbattery: small size
- Good thermal stability
- Low resistance due to thin film

Disadvantages

- Low current densities due to high internal resistance of the cell.
- Low ionic conductivity of the electrolyte

Applications

- Smart Card: chip + TFB → e-business, medical, ID card
- Hazard card: sensor + TFB → industry
- Computer: CMOS, On-chip memory backup
- MEMS device: military, medical
- Micro-robotics
- High power electronics
- Solar cell + TFB : maintenance-free battery