能源科技與環境概論

儲能電池導論

Hsing-Yu Tuan（段興宇）

Department of Chemical Engineering, National Tsing-Hua University

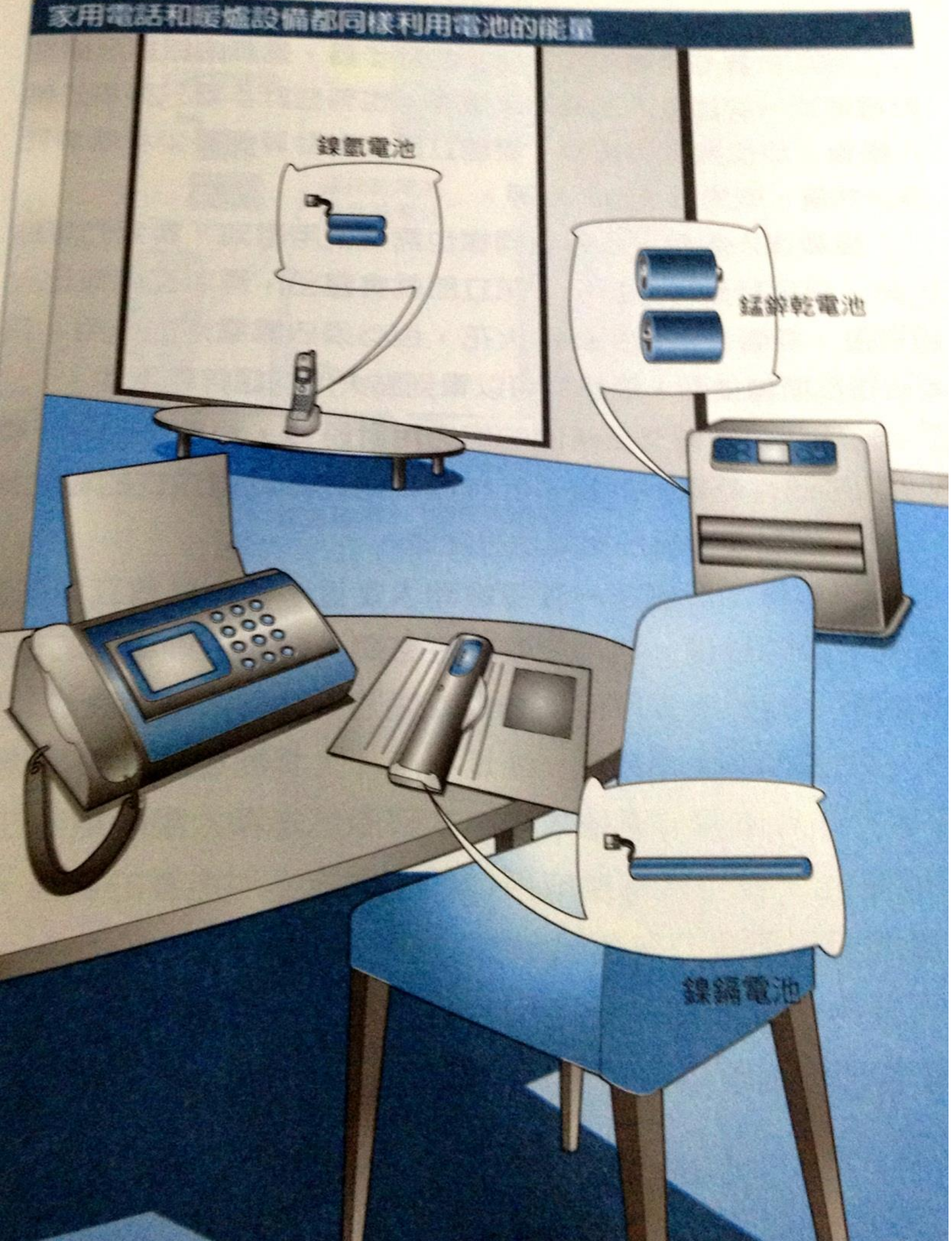
Batteries

- Definition: devices that transform chemical energy into electricity
- Every battery has two terminals:

  positive cathode (+) and the negative anode(-)
- Procedure to produce electricity

Device plug in →chemical reaction started →electron produced →electron travel from (-) to (+)→electrical work is produced

客廳



家用電話
和暖爐設備

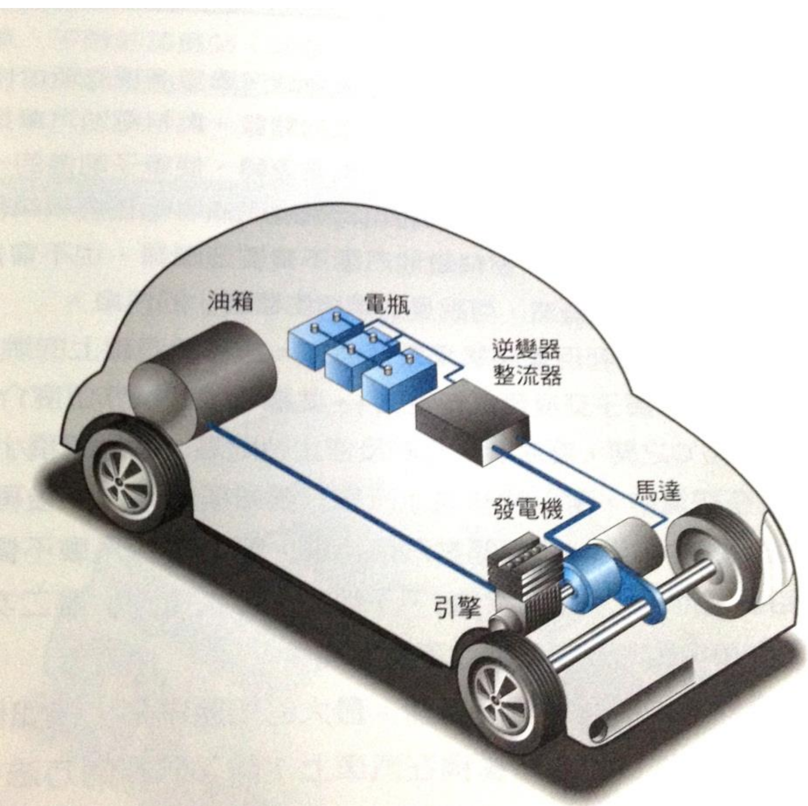
洗臉台等場所使用的電池設備

Mobile

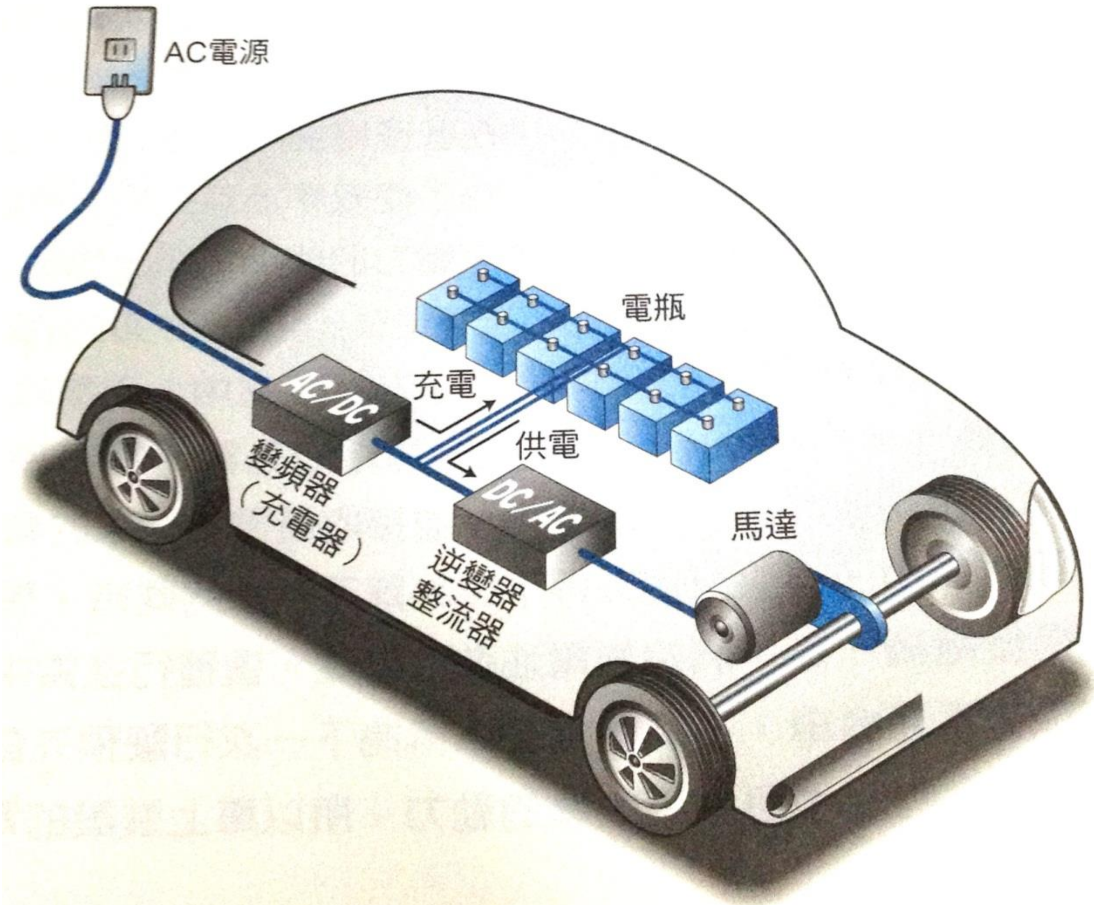
- Mostly Lithium-ion batteries

Hybrid car

- 行進過程，引擎本身附有大型發電機，除了驅動汽車，也會產生電力，為電池充電。

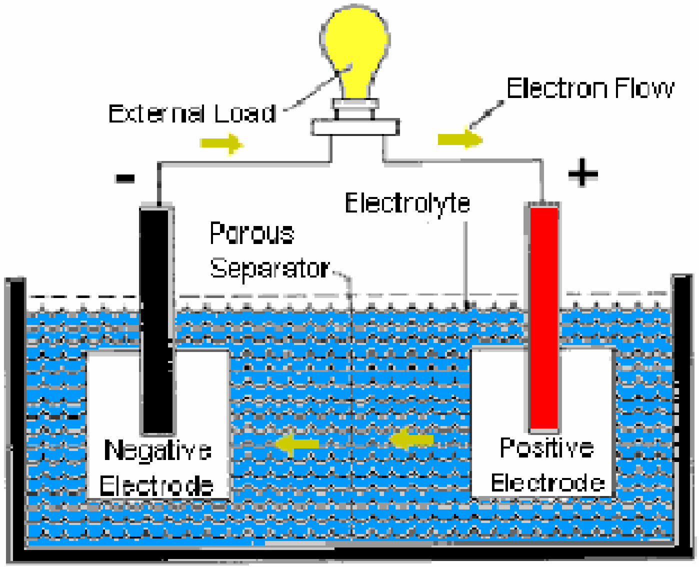


Electrical car



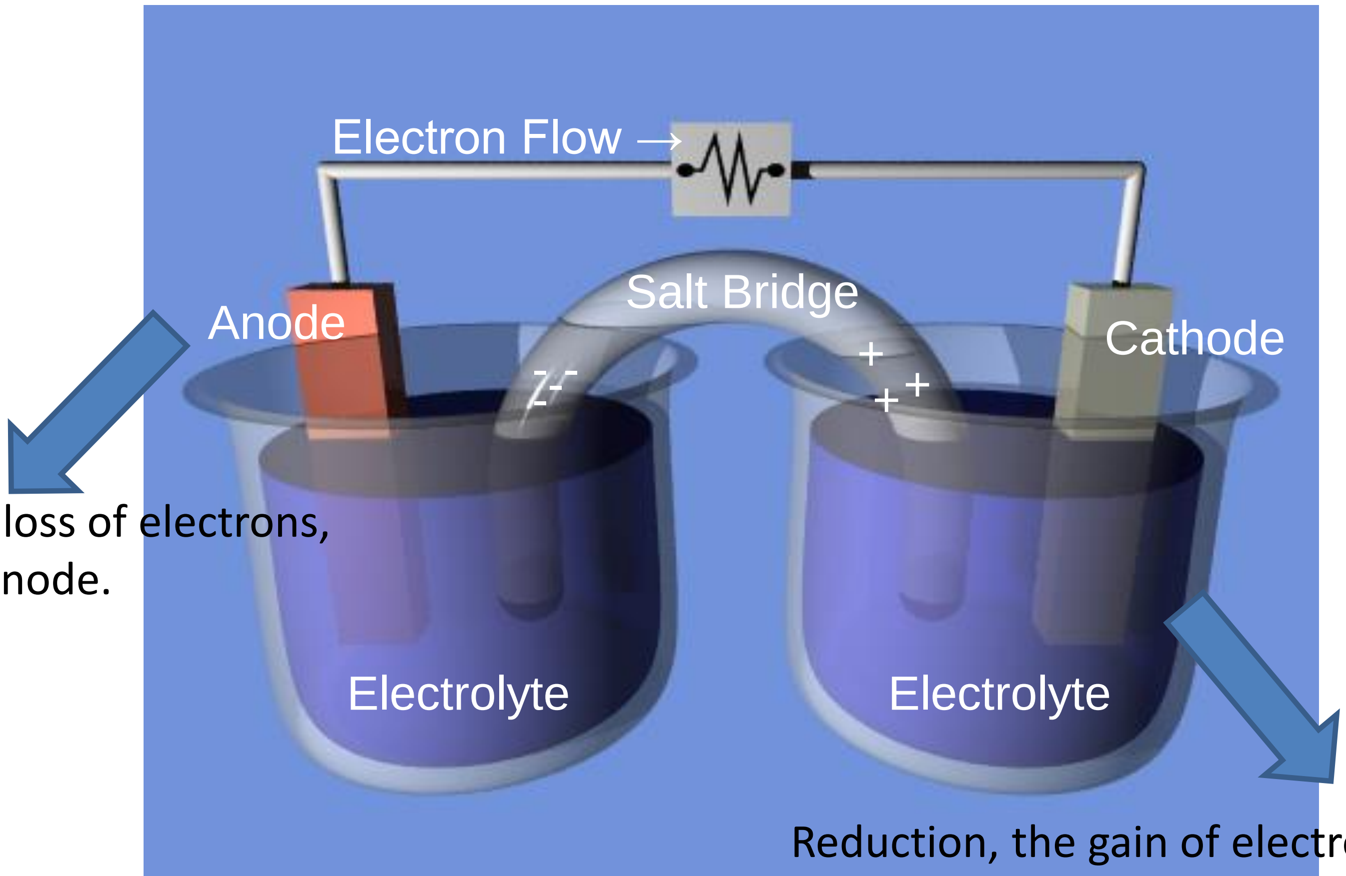
Electrochemical Cell

- An electrochemical cell :
- a negative electrode to which anions (-) migrate – donates electrons to the eternal circuit as the cell discharge (anode)
- A positive electrode to which cations migrate (cathode)
- Electrolyte solution containing dissociated salts, which enable ion transfer between the two electrodes, providing a mechanism for charge to flow between positive and negative electrodes.
- A separator which electrically isolates the positive and negative electrodes.



How Electrochemical Batteries Work

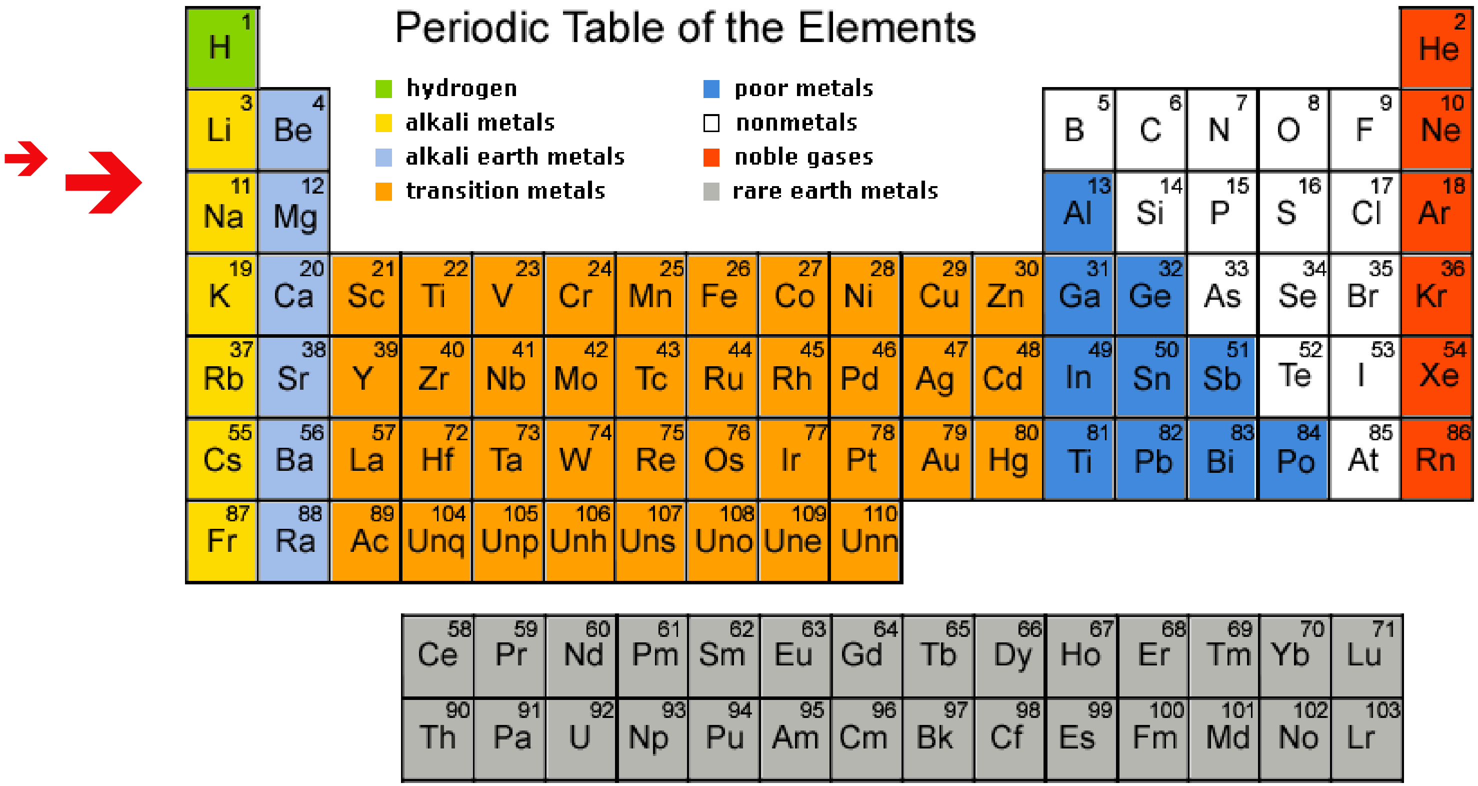
- REDOX Reaction



Oxidation, the loss of electrons, occurs at the anode.

Reduction, the gain of electrons, occurs at the cathode.

The Periodic Table: choose the electrode

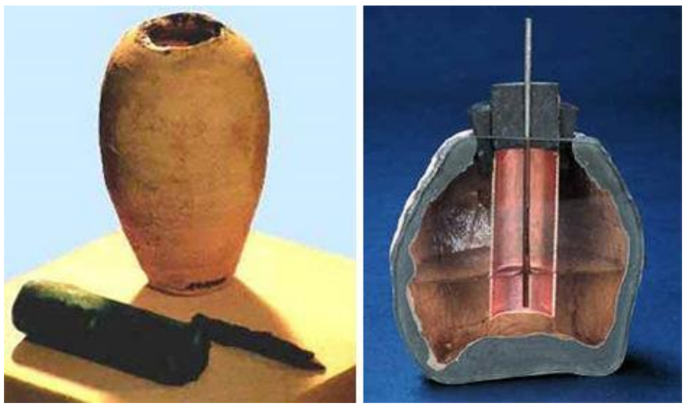


Combination of electrodes to make a variety types of batteries:
lithium ion battery、nickel-zinc、zinc air、Nickel cadmium、Ni iron、Silver zinc、Mercury cell

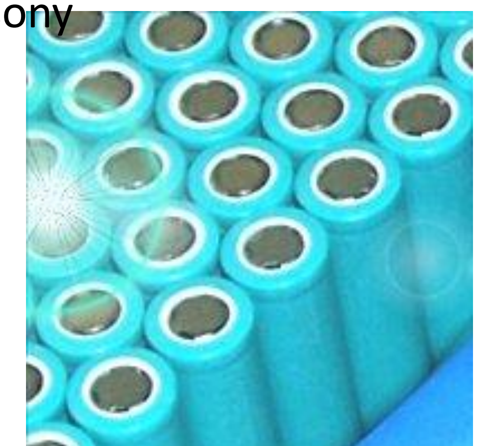
The History of Battery

Volta piles

Baghdad battery

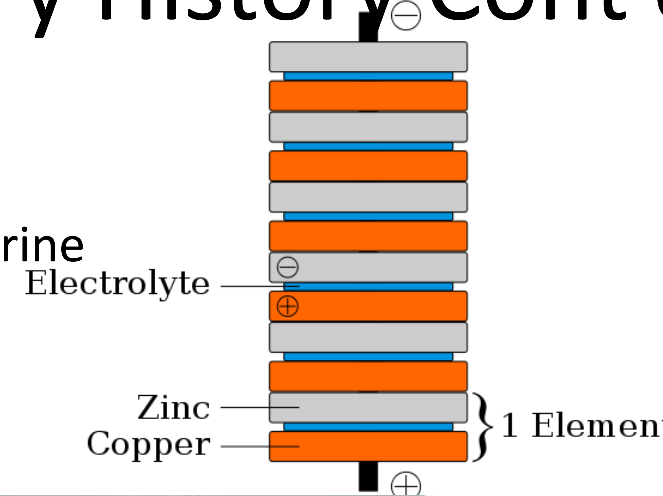


Lithium ion battery -sony



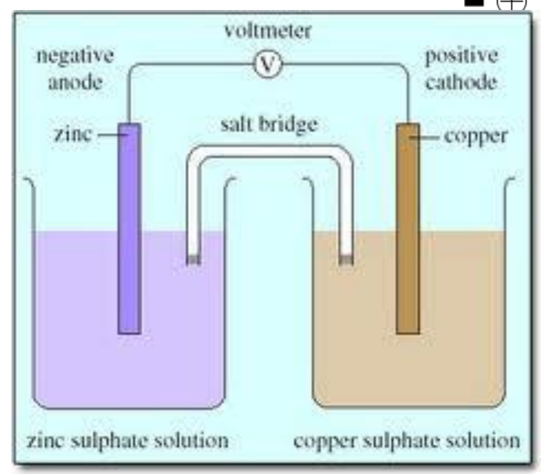
Time	Event	Name
200 B.C.	Baghdad battery	??
1791	Frog leg experiment	Galvani
1800	Voltaic piles	Volta
1802	Mass pr[illegible] battery	Cruickshank
[illegible]	Giant battery (2,000 cells)	Davy
1820	Electricity from magnetism	Ampere
1827	Ohm's law	Ohm
1833	Ionic mobility in Ag_2S	Faraday
1836	$Cu/CuSO_4$, $ZnSO_4/Zn$	Daniell
1839	Principle of the air cell	Grove
1859	Lead acid battery	Planté
1868	$Zn/NH_4Cl/C$ wet battery	Leclanché
1874	Telegraph	Edison
1878	Air Cell	Maiche
1880	High capacity lead/acid	Faure
1881	$Zn/NH_4Cl/C$ encapsulated	Thiebault
1885	Zinc-bromine	Bradley
1887	$Zn/NH_4Cl/C$ dry battery	Gassner
1891	Thermodynamics of dry cells	Nernst
1899	Nickel cadmium battery	Jungner
1900	Ni Storage batteries	Edison
1905	Ni iron batteries	Edison
1911	Automobile self-starter	Kettering
1927	Silver zinc	Andre
1930	Nickel-zinc battery	Drumm
1943	Cuprous chloride battery	Adams
1945	Mercury cell	Ruben
1950	Sealed mercury Cell	Ruben
1956	Alkaline fuel cell	Bacon
1959	Alkaline primary cell	Urry
1983	Lithium metal rechargeable	Moli
1991	Commercial lithium ion	Sony
1992	Reusable alkaline	Kordesch
1995+	Recent developments	..

Electrochemical Battery History Cont'd



- The Voltaic Pile
  - Invented by Alessandro Volta in 1800
  - Zinc and Copper with a cloth soaked in brine
  - Technical Flaws:
    - Compressing of cloth created shorts
    - Short battery life

- The Daniel Cell
  - Invented in 1836 by John Daniell



- The lead-acid cell
  - Invented in 1859 by Gaston Planté
  - First rechargeable battery

- The zinc-carbon cell
  - Invented in 1887 by Carl Gassner

Electrochemical Battery History Cont'd

- The Nickel-Cadmium Battery
  - Invented in 1899 by Waldmar Jungner.

- The common Alkaline Battery
  - Invented in 1955 by Lewis Urry

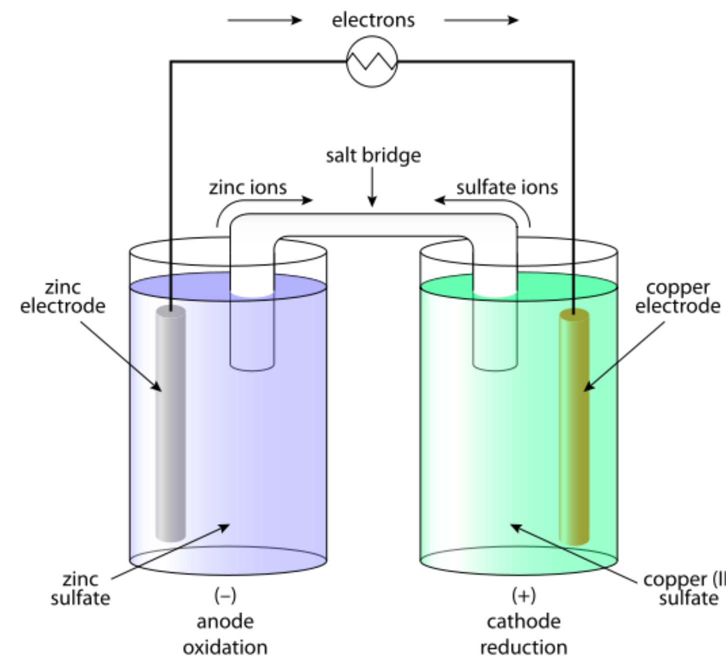
- The Nickel Metal-Hydrid Battery
  - NiMH batteries for smaller applications started to be on the market in 1989.

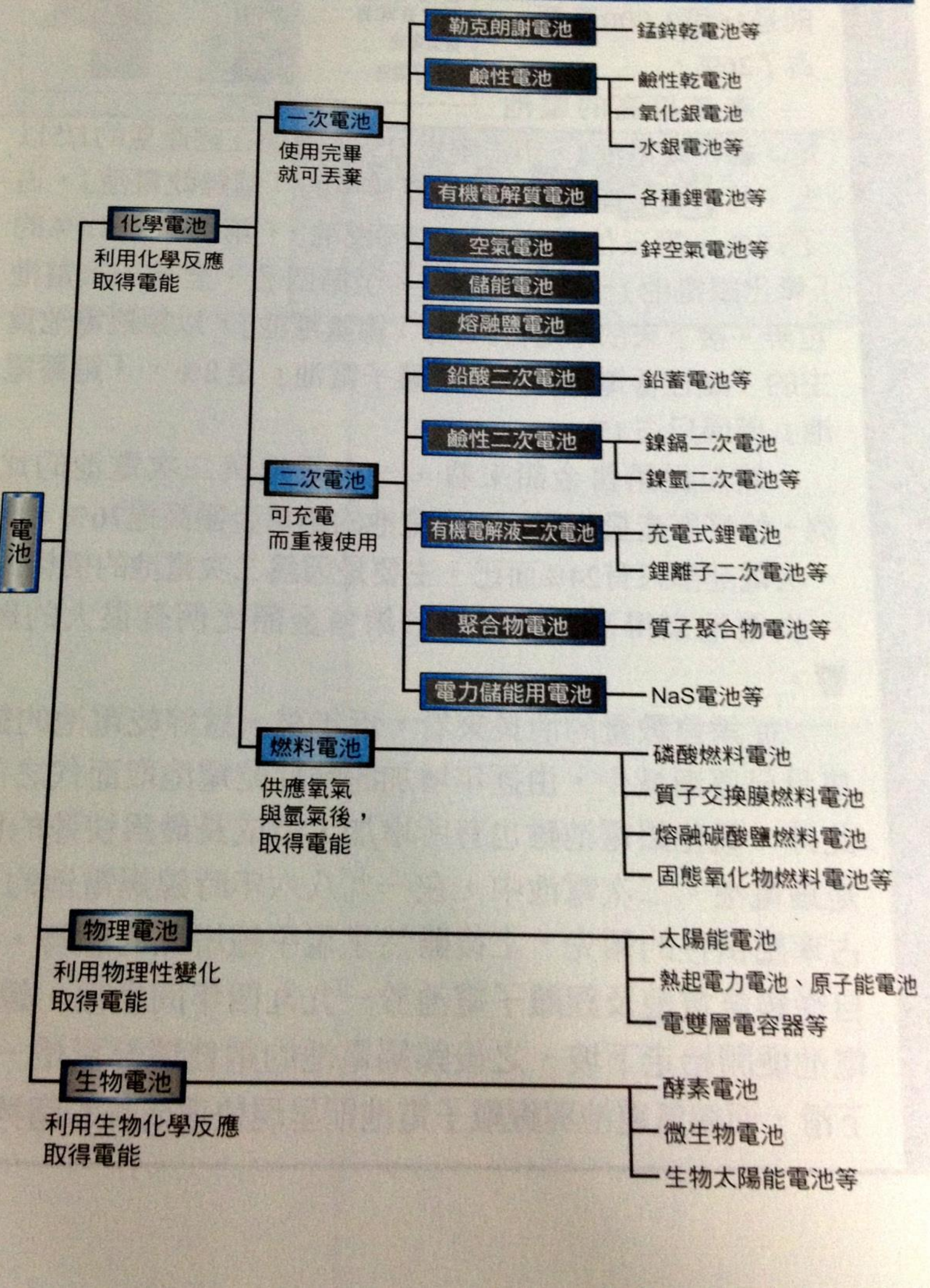
- Lithium and Lithium-ion Batteries
  - First lithium batteries sold in the 1970s
  - First lithium-ion batteries sold in 1991 → portable electronic devices
  - First lithium-ion polymer batteries released in 1996

伏特電池的原理

- 在稀硫酸中插入銅板和鋅版兩種電極
- 鋅金屬變成鋅離子溶出Zn+2 鋅變成負電
- 銅板不會融化，但因電子被H+帶走帶著一點正電

以導線連接鋅版和銅板則會產生電流，直到鋅版耗盡。





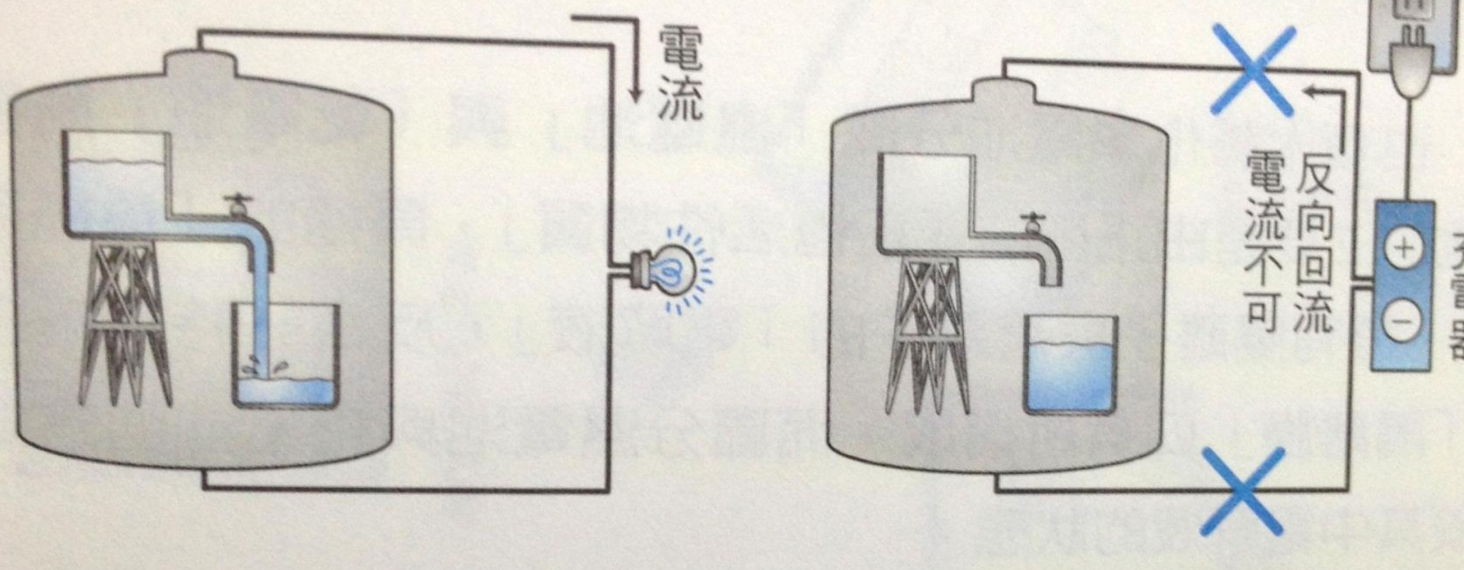
Various kinds of batteries

Primary vs. Secondary Batteries

- Primary batteries are disposable：their electrochemical reaction cannot be reversed.
- Secondary batteries are rechargeable, because their electrochemical reaction can be reversed by applying a certain voltage to the battery in the opposite direction of the discharge.

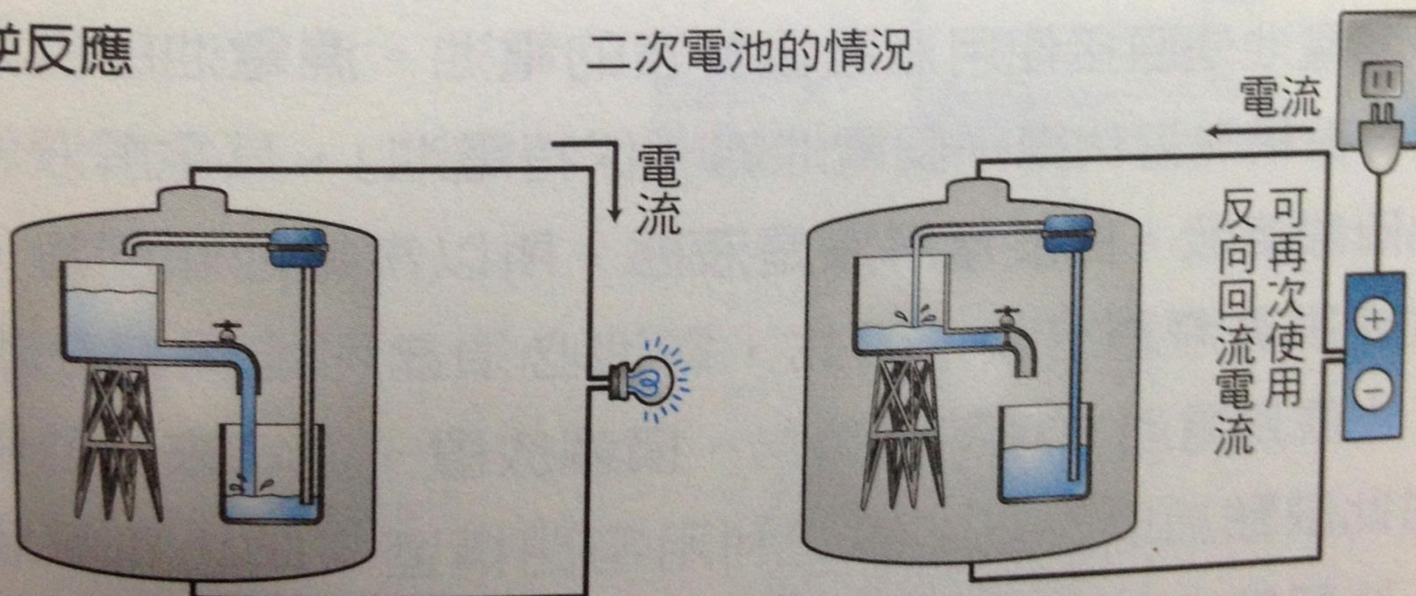
不可逆反應

一次電池的情況



可逆反應

二次電池的情況



Terminology and Units

- Primary Batteries – Disposable
- Secondary Batteries – Rechargeable
- emf – Electromotive force, voltage
- Ampere·hour (Ah) = 3600 coulombs, a measure of electric charge
- Watt ·hour (Wh) = 3600 joules, a measure of energy
- Ah = (Wh) / emf

Theoretical Cell voltage

- Anode (oxidation potential)+ cathode (reduction potential)=standard cell potential

$Zn+Cl_2 \rightarrow ZnCl_2$

$Zn \rightarrow Zn^{+2} +2e$ -(-0.76 V)

$Cl_2 \rightarrow 2Cl^- \;\; -2e$ 1.36V

E^o = 2.12 V → theoretical voltage

Theoretical capacity

- Zn + Cl2 → ZnCl2

0.82 Ah/g 0.76 Ah/g

1.22g/Ah 1.32g/Ah = 2.54 gAH or 0.394/Ah/g

Primary Alkaline Batteries

- Can lose 8 – 20% charge every year at room tempurature.
- Discharge performance drops at low temperatures.

	AAA	AA	9V	C	D
Capacity (Ah)	1.250	2.890	0.625	8.350	20.500
Voltage	1.5	1.5	9	1.5	1.5
Energy (Wh)	1.875	4.275	5.625	12.525	30.75

Secondary Alkaline Batteries

- Self-discharge more quickly than primary batteries

	Low-Capacity NiMH (1700-2000 mAh)	High-Capacity NiMH (2500+ mAh)	NiCd
Charge Cycles	1000	500	1000

- Must not overcharge because that will damage the batteries. Quick charges will also damage the batteries.
- Must not over-discharge.
- NiCd has "memory effect."
- NiCd is better for applications where current draw is less than the battery's own self-discharge rate.
- NiMH have a higher capacity, are cheaper, and are less toxic than NiCd.

Recharge-ability & the “memory effect”

- Recharge-ability: basically, when the direction of electron discharge (negative to positive) is reversed, restoring power.
- the Memory Effect:

- The battery appears to "remember" the smaller capacity
- the term 'memory' came from an aerospace nickel-cadmium application in which the cells were repeatedly discharged to 25% of available capacity by exacting computer control, then recharged to 100% capacity **without overcharge**. This long-term, repetitive cycle regime, with no provision for overcharge, resulted in a loss of capacity beyond the 25% discharge point. Hence the birth of a "memory" phenomenon, whereby nickel-cadmium batteries purportedly lose capacity if repeatedly discharged to a specific level of capacity.

Source: wiki

Types of Batteries

- Zinc-Carbon: used in all inexpensive AA, C, and D dry-cell batteries. The electrodes are zinc and carbon, with an acidic paste between them serve as the electrolyte (disposable)

- Alkaline: Curalcell or Energizer cell batteries. The electrodes are zinc and manganese-oxide, with an alkaline electrolyte (disposable)

Modern batteries

- Lead-Acid: used in cars: the electrodes are lead and lead-oxide, with an acidic electrolyte (rechargeable)

- Lithium-ion batteries

  - rechargeable and no memory effect

- Fuel cells

碳鋅電池

- 電壓：1.5V
- 正極：二氧化錳
- 負極：鋅
- 電解液：NH4Cl、ZnCl2

Battery Aspects

- Energy Density: total amount of energy that can be stored per unit mass or volume →how long will your laptop run by a fully-charged cell.
- Power Density: Maximum rate of energy discharge per unit mas or volume. Low power: laptop, ipod high power car
- Safety: could sustain at high temperatures
- Life: stability of energy density and power density with repeated cycling is needed for the long life required in many applications.
- Cost: Must compete with other energy storage technologies

Lithium ion battery








Lithium

- Periodic Table Symbol: Li
- Atomic Weight: 3 (light!)
- Like sodium and potassium, an alkali metal. (Group 1 – #s 1 through 7)
- Highly reactive, with a high energy density.
- Used to treat manic-depression because it is particularly effective at calming a person in a “manic” state.
- The most electropositive (-3.04V versus standard hydrogen electrode

鋰離子電池的結構

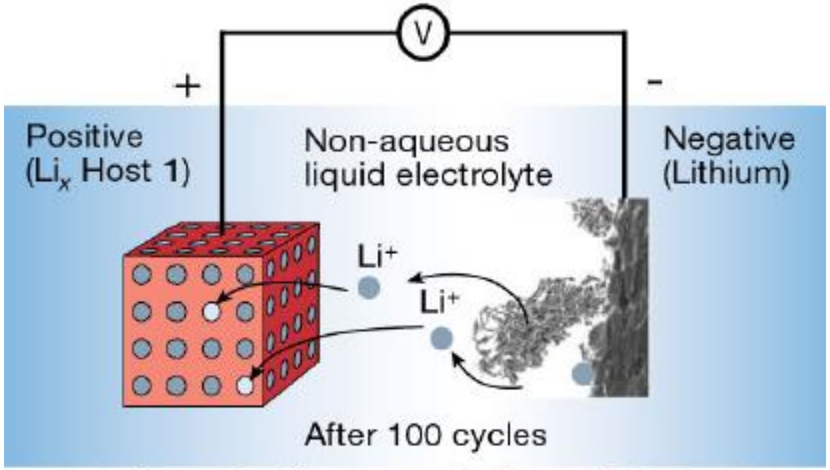
- 正極
- 活性物質(LiCoO2\LiMnO2\LiNixCo1-xO2) 導電劑、溶劑、粘合劑、基體
- 負極 活性物質(石墨、MCMB) 粘合劑、溶劑、基體
- 隔膜(PP+PE)
- 電解液(LiPF6 + DMC EC EMC)
- 外殼五金件(鋁殼、蓋板、極耳、絕緣片)

Composition of Li-ion batteries

Electrode Component	Role	Anode(負極) Example	Cathode(正極) Example
Active Material	Reversibly stores chemical energy	Graphite	$LiCoO_2$ or LMO2
Binder	Stabilizes electrode coating (holds it together)	PVDF or SBR (Polyvinylidene fluoride)	
Current Collector	Supports electrode material Leads to electronic circuitry	Copper	Aluminum
Additives	Improves electrode performance	Carbon Black, Graphite	
Electrolyte	Li-ion transportation	**Salt:**LiPF6 + **Solvent:** Carbonates	

Lithium Ion Battery Development

- Pioneering work for the lithium battery bagan in 1912 by G. N. Lewis but it was not until the early 1970’s when the first non-rechargeable lithium batteries became commercially availble
- In the 1970’s Lithium metal was used but its instability rendered it unsafe



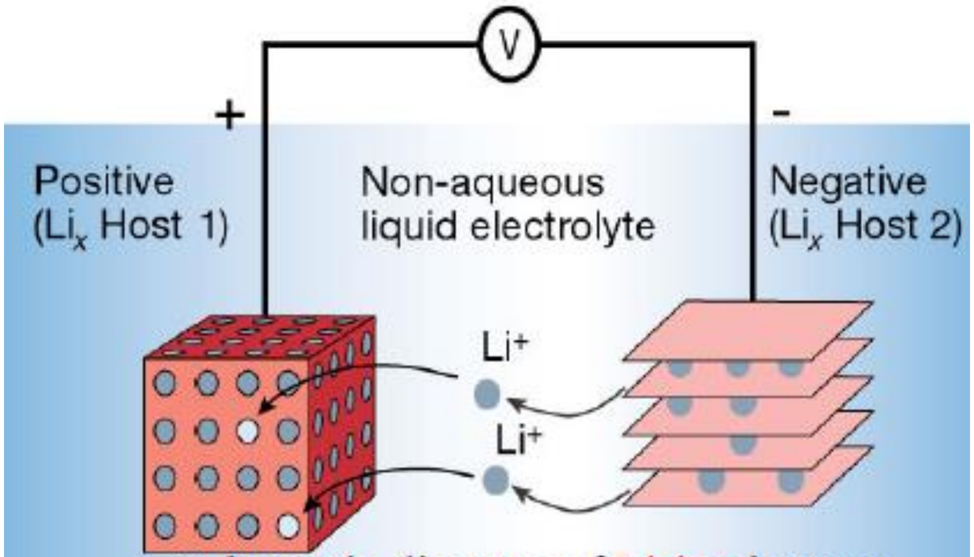
Schematic diagram of Li-metal battery

Why lithium-ion other than Lithium

- 鋰電池的負極採用金屬鋰，在充電過程中金屬鋰會在鋰負極上沉積，產生枝晶鋰，造成電池內部短路產生爆炸。
- 鋰離子電池則採用了碳材料代替純鋰做為負極。

Lithium Ion Battery Development

- Attempts to develop recharageable lithium batteries followed in the eithties, but failed due to safty problems
- The lithium ion battery has a slightly lower energy density than lithium metal, but it is much safer. Introduced by Sony 1991

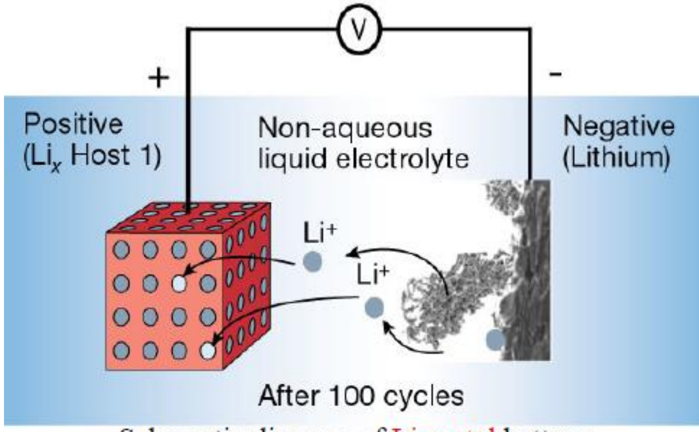


Schematic diagram of Li-ion battery

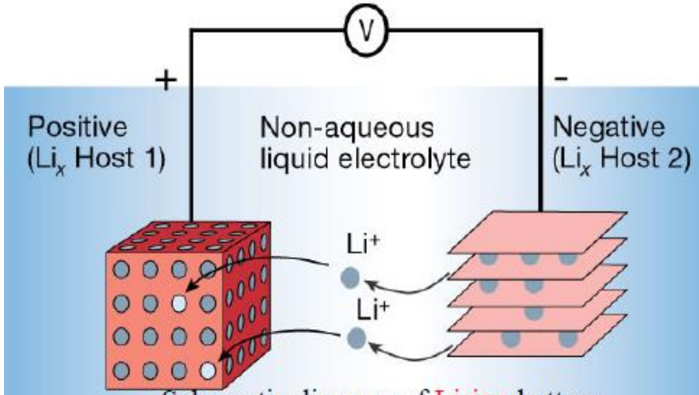
Lithium secondary battery

- A chemical intercalation reaction
- Intercalation is the reversible inclusion of a molecule between two other molecules

Ex: graphite intercalation compounds



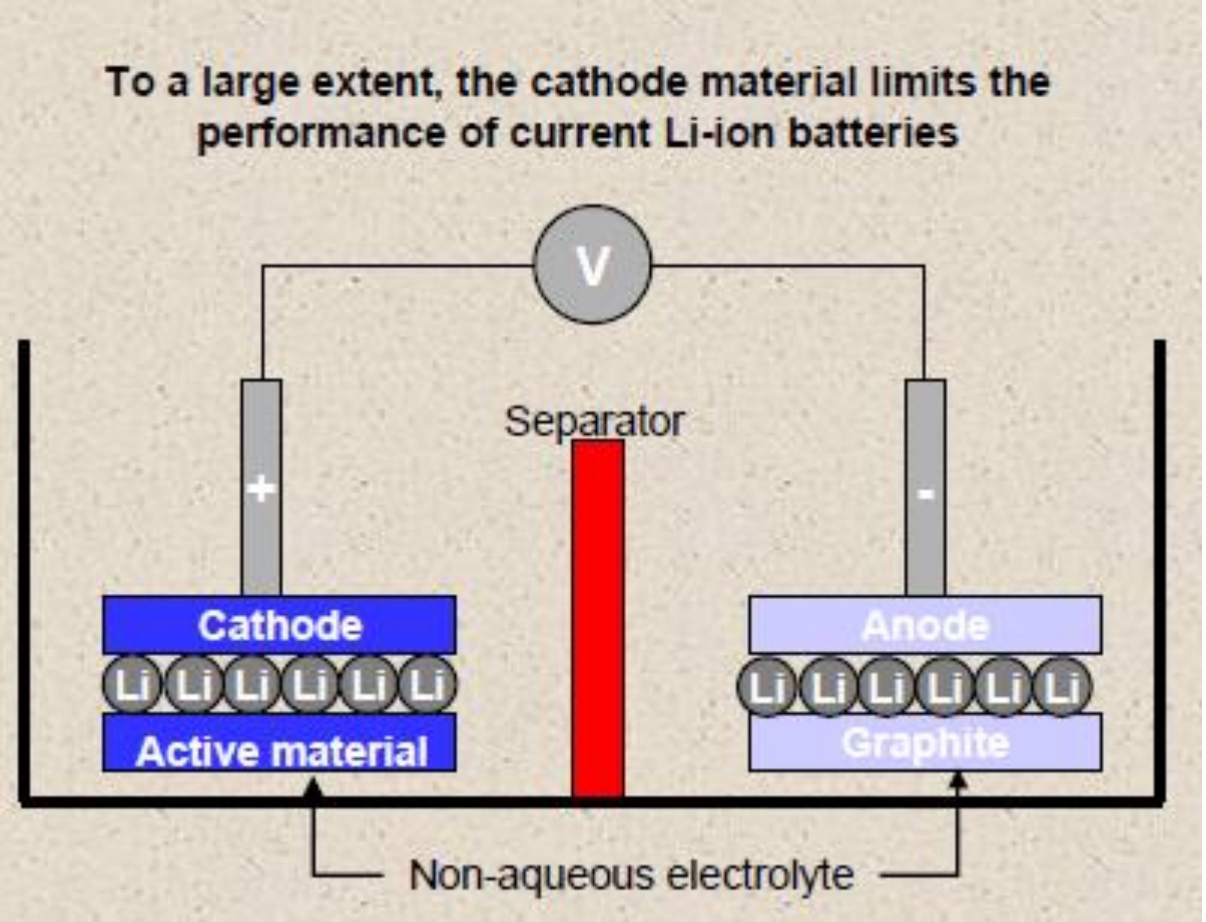
Schematic diagram of Li-metal battery



Schematic diagram of Li-ion battery

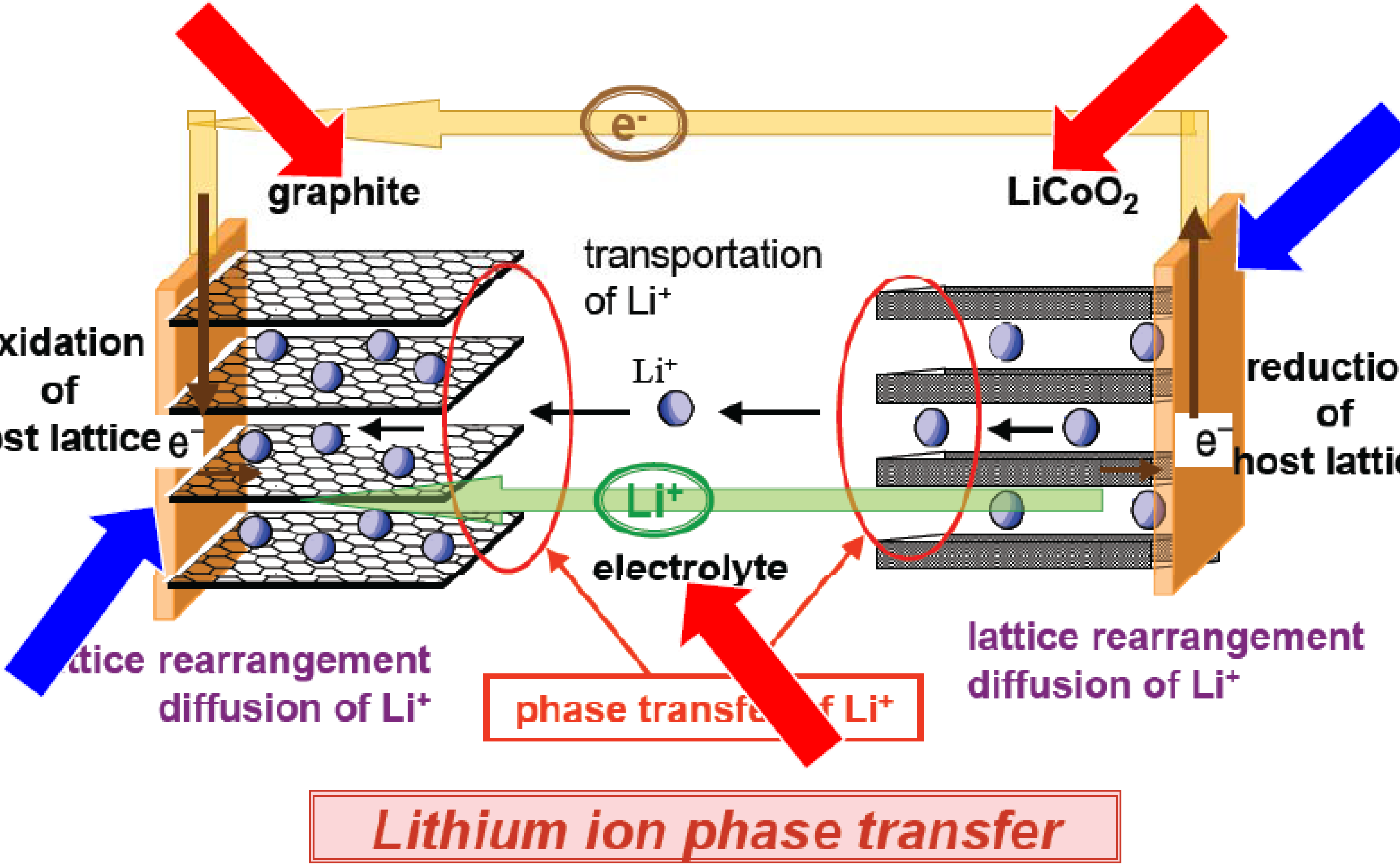
Armand, Nature, 2001

The operation principle of a Li-Ion battery



- During charging an external voltage source pulls electrons from the cathode through an external circuit to the anode and causes Li-ions to move from the cathode to the anode by transport through an liquid electrolyte.
- During discharge the processes are reversed. Li-ions move from the anode to the cathode through the electrolyte while electrons flow through the external circuit from the anode to the cathode and produce power.

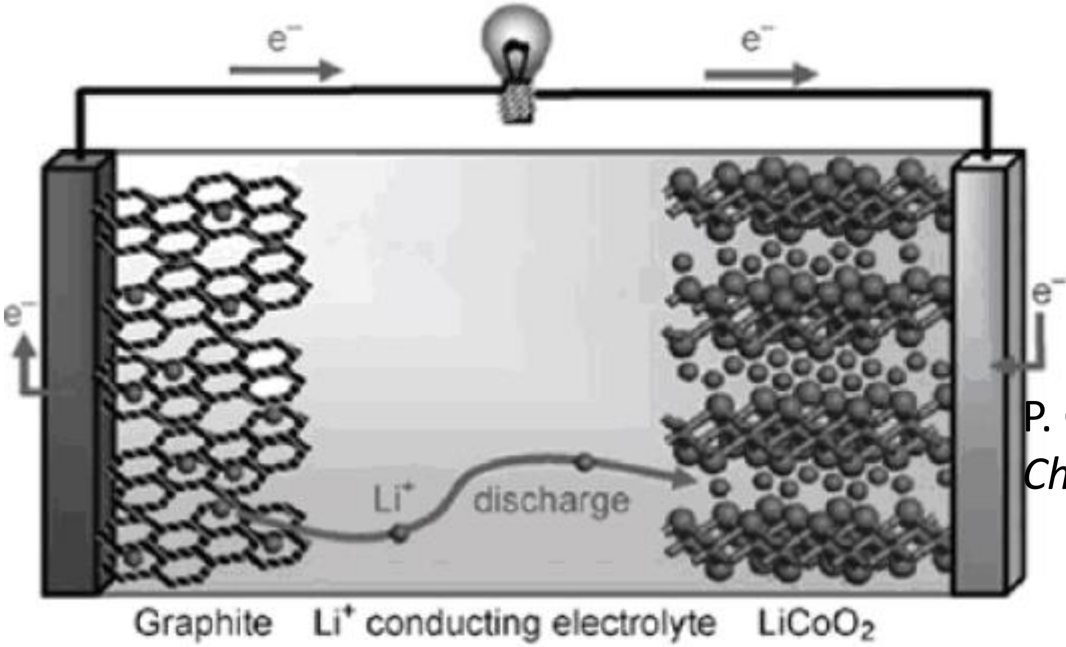
Intercalation process



充電時，鋰離子從LiCoO2脫出、Co+3氧化為Co+4; 放電池鋰離子則嵌入LiCoO2, 則Co+4 →Co+3

。換句話說，充電時由外界輸入能量而迫使鋰離子由低能量之正極材料往負極材料移動，而成為能量較高之狀態；而放電時，鋰離子將會自然地由高能量之負極材料移動至較低能量之正極材料之中，並同時對外釋出能量

Overall reaction of Li-ion battery



P. G. Bruce, B. Scrosati, J. M. Tarascon, *Angew Chem. Int. Ed.*, **2008**, 47, 2930

鋰離子二次電池充放電反應式：

正極：$LiCoO_2 \rightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$

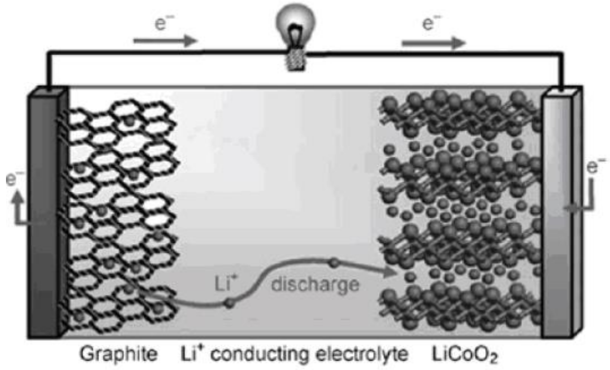
負極：$6C + xLi^+ + xe^- \rightarrow Li_xC_6$

ΔV

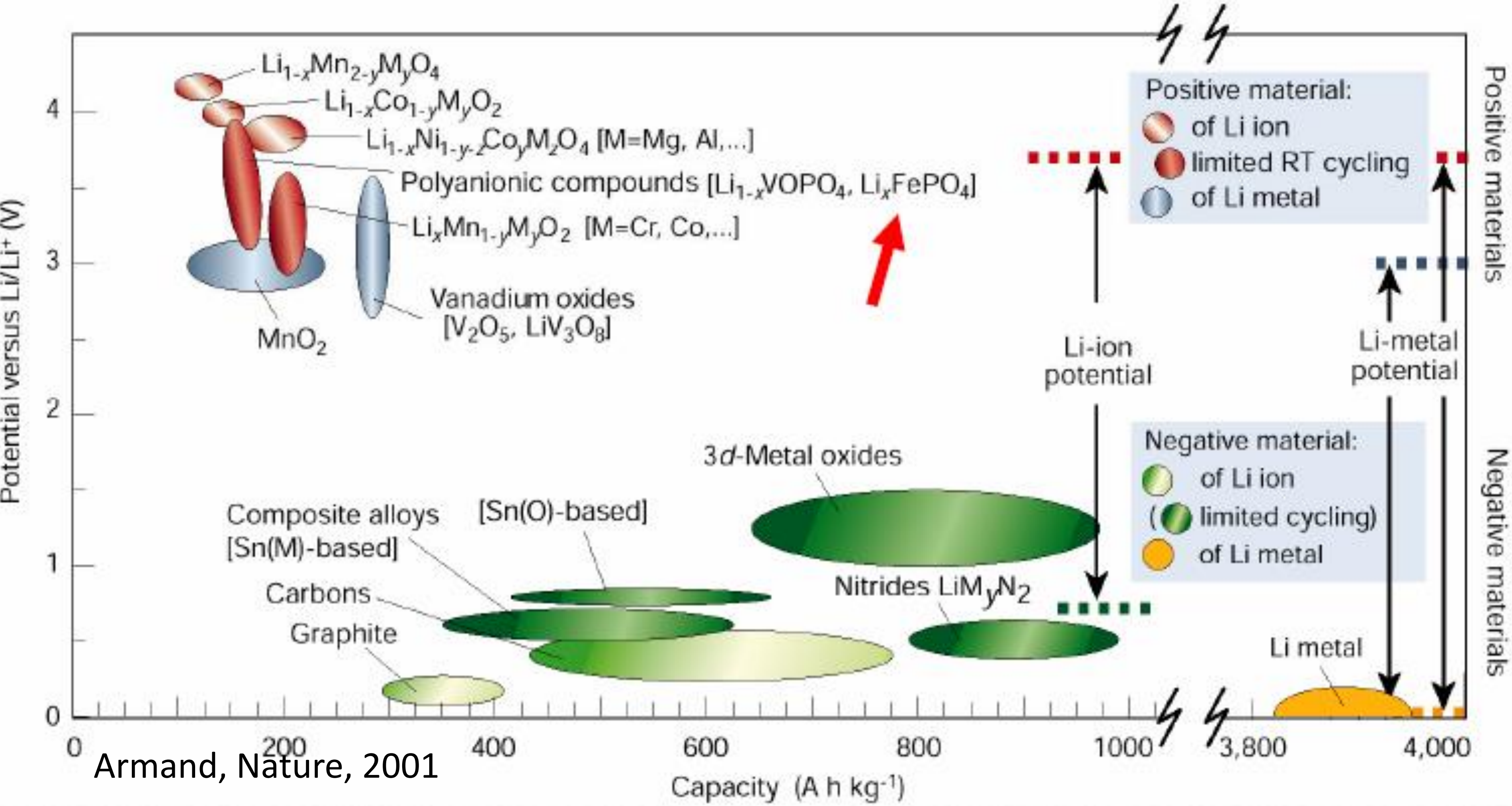
全反應：$6C + LiCoO_2 \rightarrow Li_xC_6 + Li_{1-x}CoO_2$

Charging Co+3->Co+4
discharging Co+4->Co+3

Rocking-chair tecnology

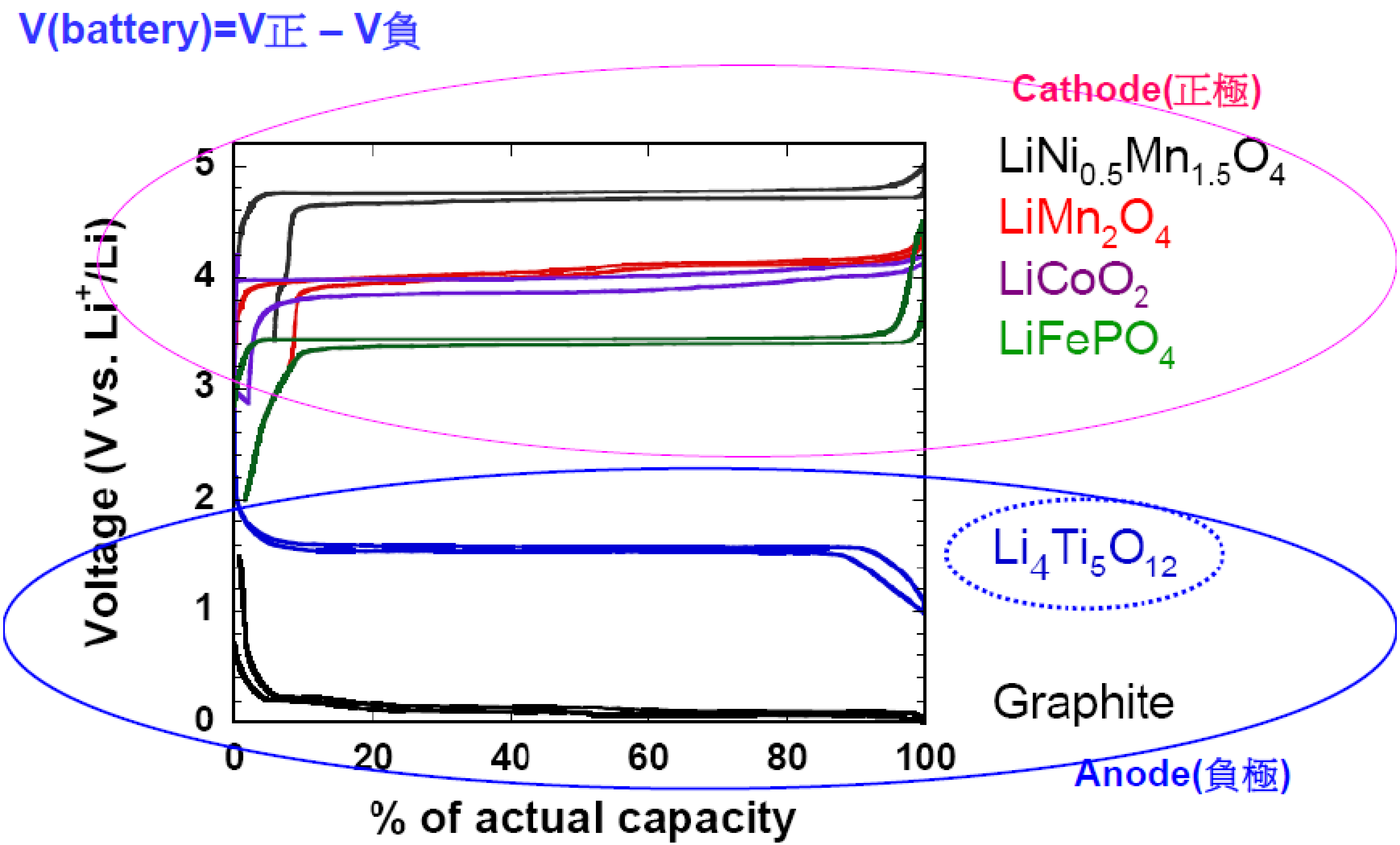


Combination of positive materials and negative materials for Lithium batteries



Armand, Nature, 2001

Voltage of a cell



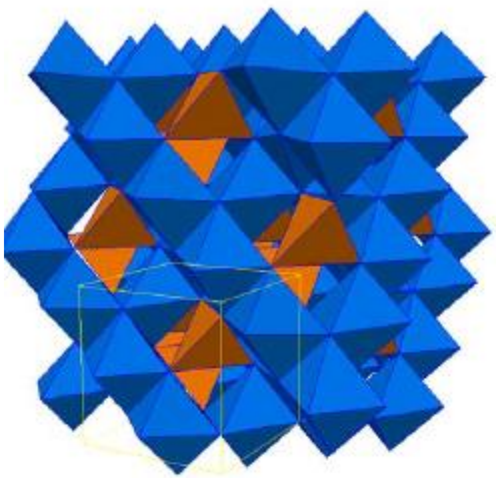
Capacity

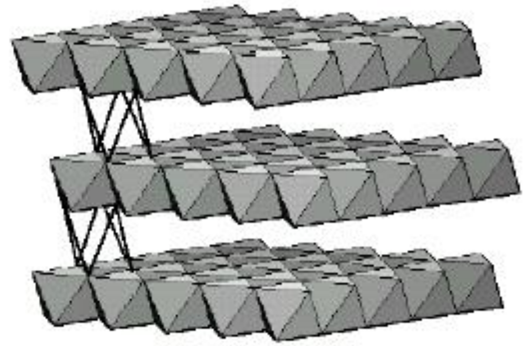
$$\text{Total cell (mAh g}^{-1}) = \frac{1}{(1/C_A) + (1/C_c) + (1/Q_M)}$$
$$= \frac{C_A C_C Q_M}{C_A Q_M + C_C Q_M + C_A C_C}$$

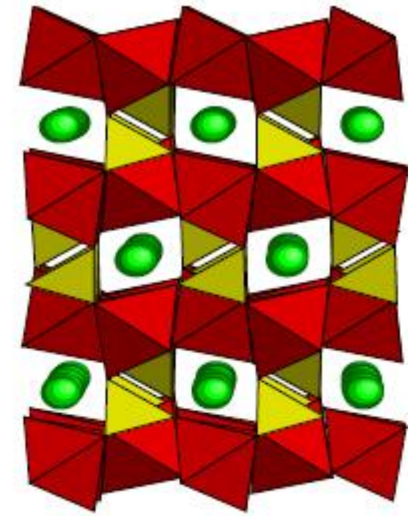
where C_A and C_C are the theoretical specific capacities of the cathode and anode materials, respectively, and $1/Q_M$ is the specific mass of other cell components (electrolyte, separator, current collectors, case, etc.) in g mAh^{-1}. $1/Q_M$ will vary with cell geometry and dimensions, and will include any failure to obtain the theoretical capacity values and any other excess required, e.g., to provide excess cathode material for formation of the surface electrolyte interphase (SEI) film at the anode. For carbon, C_A is 372 mAh g^{-1}, and for $LiCoO_2$, C_C is 135 mAh g^{-1}. For the Sony 18650G8 cell (2550 mAh, 46 g), Q_M may be calculated to be 130.4 mAh g^{-1}. A similar calculation may be performed in terms of mAh cm^{-3}.

Cathode materials

$LiFe^{II}PO_4$







正方晶系
3D frameworks

Spinels
Fd3m

六方晶系
2D channel

Lamellar $LiCoO_2$
R3m

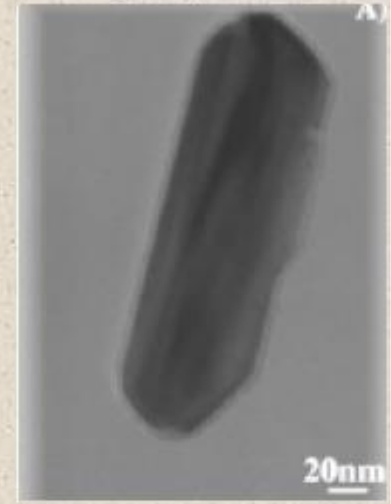
斜方晶系
1D channel

Olivine
Pnma

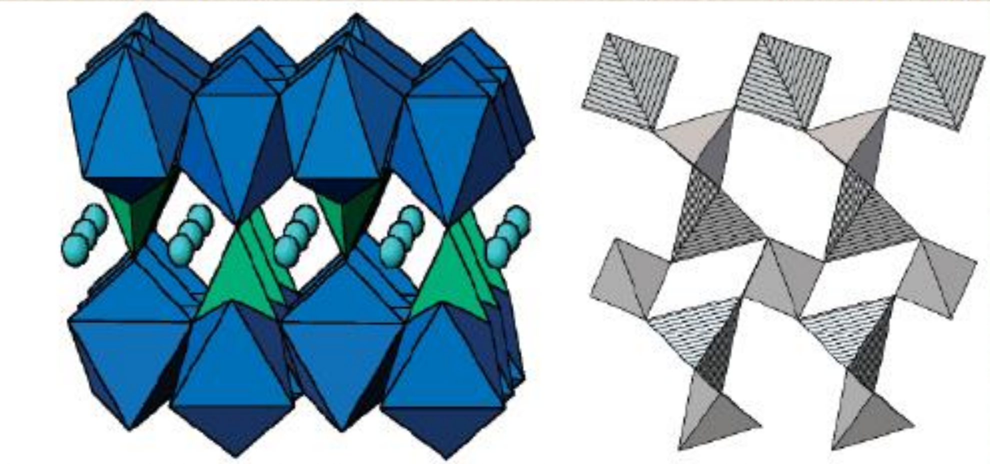
Cathode materials in Lithium-ion batteries

材料結構	鋰遷入/出空間	主要產品開發	理論電容量 (mAh/g)	預估電容量 (mAh/g)	平均工作電壓(V)	安全性	成本	主要產品應用
橄欖石 (Olivine)	1D	$LiFePO_4$	170	140-150	3.4	優	中	動力電池及大型電池
層狀氧化物 (layered Oxides)	2D	$LiCoO_2$ $Li(Co\text{-}Ni)O_2$ $Li(Ni\text{-}Mn)O_2$ $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$	273	160 180 160 190	3.6~3.7	尚可	高	小型電池 & 動力電池及大型電池
尖晶石 (Spinel)	3D	$LiMn_2O_4$	148	110	3.7	佳	低	動力電池及大型電池

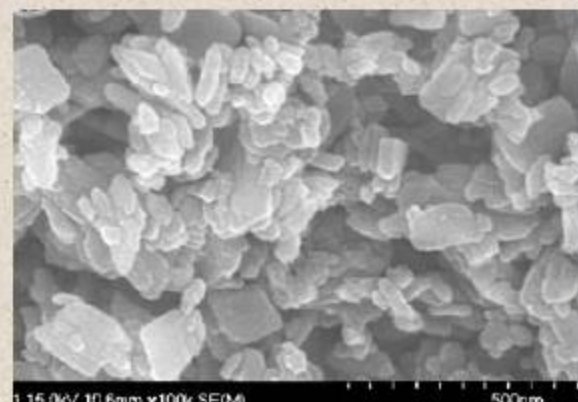
$LiFePO_4$ *active material for lithium batteries*



- Potentially low cost and plentiful elements;
- Environmentally benign;
- Theoretical capacity = 170 mAh/g
- Different synthetic methods: sol-gel, solid state, hydrothermal...

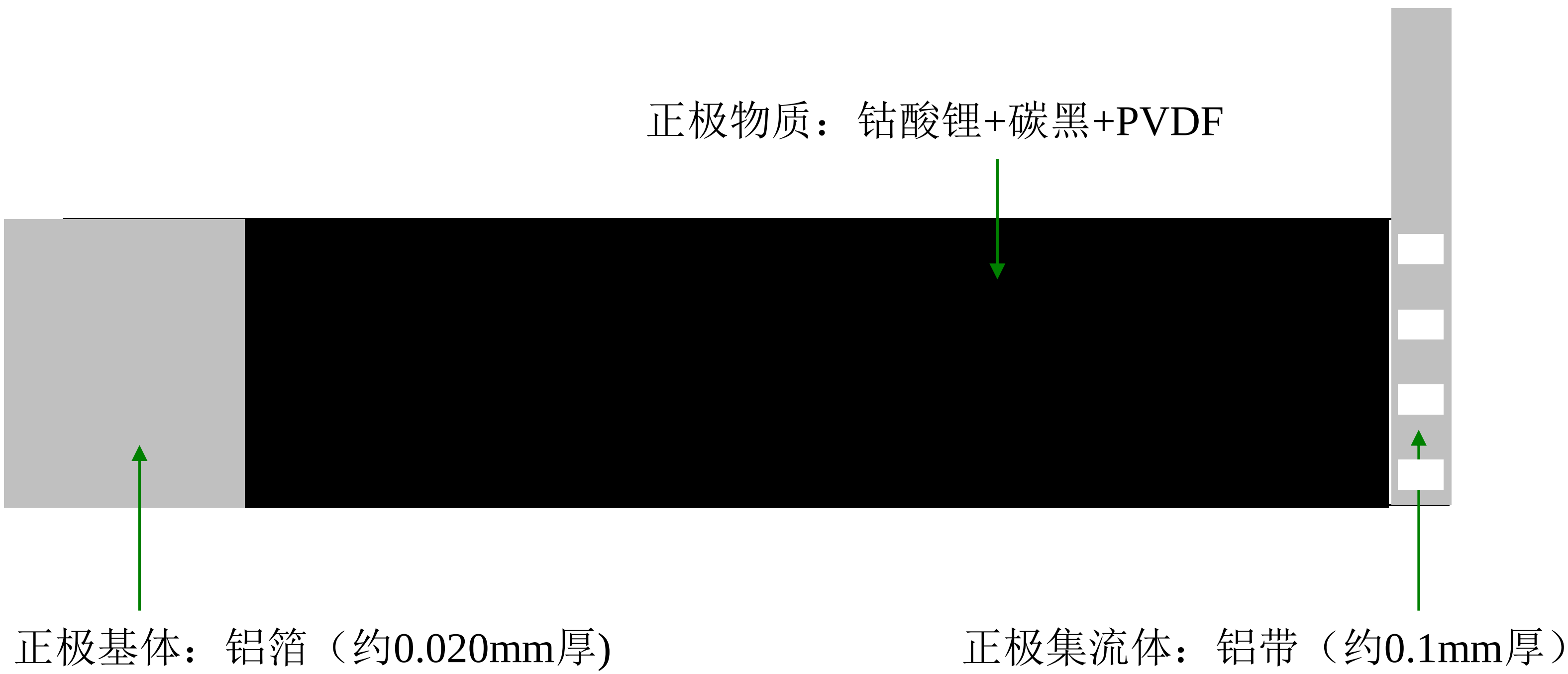


Structures of orthorhombic $LiFePO_4$ and trigonal quartz-like $FePO_4$.



Source: M. Stanley Whittingham. Chemical Reviews, 104 (2004) 4271-4301; R. Dominko,et al. Journal of The Electrochemical Society, 152 (2005) A607-A610; Bo Jin et al. J Solid State Electrochem (2008) 12:1549–1554.

锂离子电池结构——正极

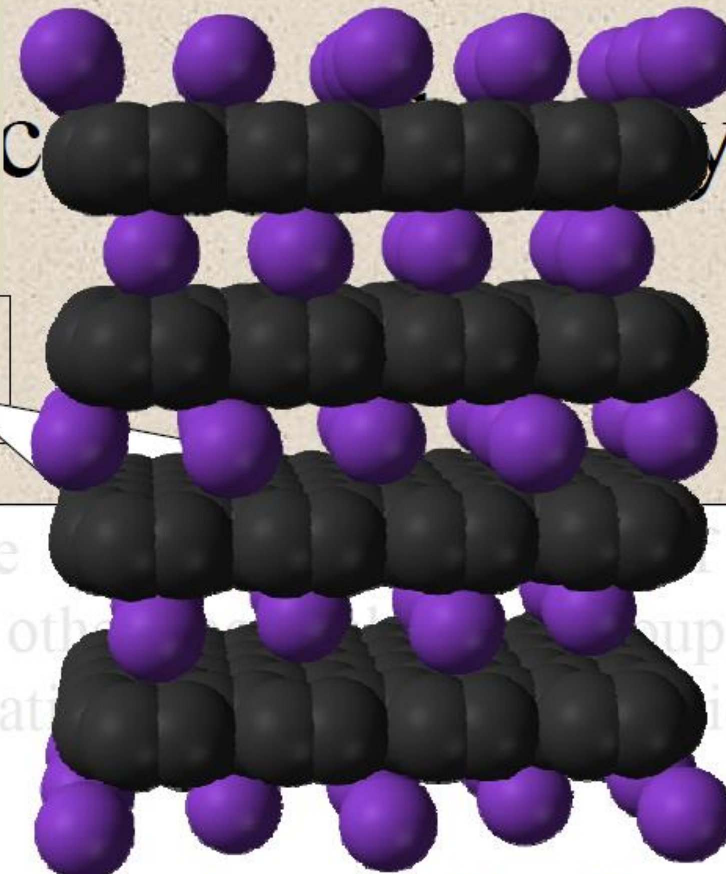


Cathode Materials Challenges

- The most desirable cathode materials are strong oxiding agents that can react with and decompose organic electrolytes
- In extreme cases, problems with internal shorts or improper voltages can trigger exthermic reactions, leading to thermal runaway and catastropic falure

Anode materials: Carbon

1972 Define the concept of chemical intercalation



In chemistry, intercalation is the ... a molecule (or group) between two oth... ups). Examples include DNA intercalat... ion compounds, etc.

Graphite intercalation compounds are complex materials where an atom, ion, or molecule is inserted (intercalated) between the graphite layers. In this type of compound the graphite layers remain largely intact and the guest species are located in between

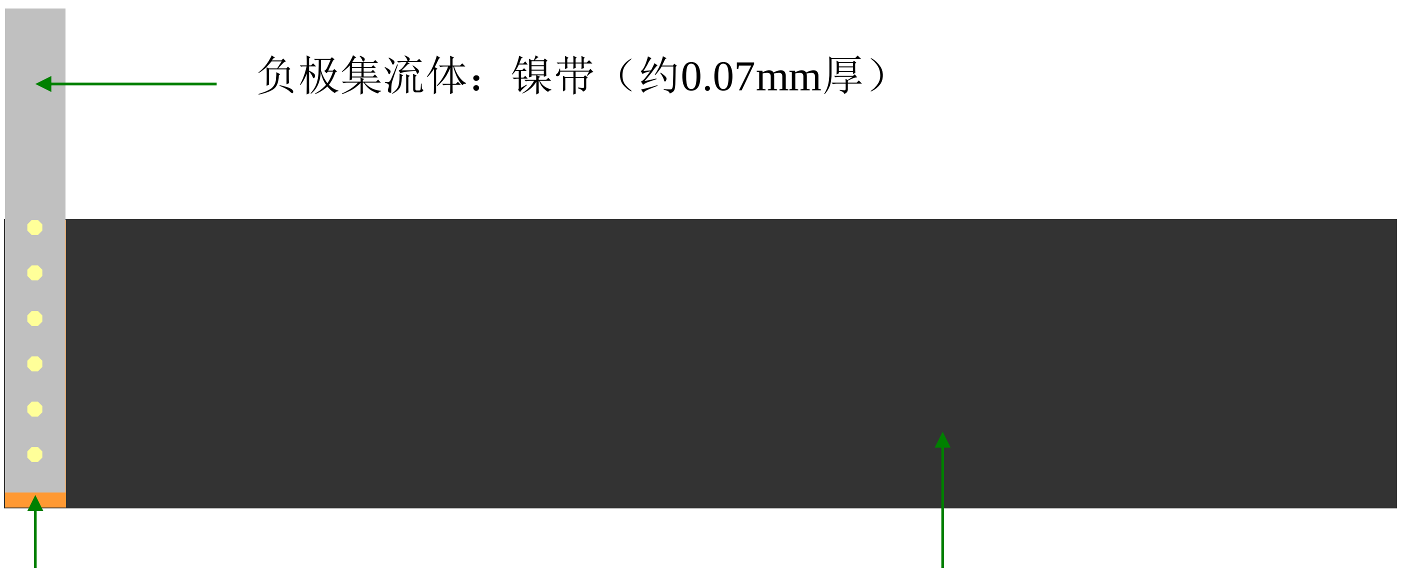
However, its theoretical capacity (LiC_6) is only 372 $mAhg^{-1}$

Figure:Space filling model of potassium graphite KC8 (side view) from: http://en.wikipedia.org/wiki/Graphite_intercalation_compound

Anode materials

Anode material	Fully lithiated material	Theoretical Specific capacity (mAh/g)	Volumetric capacity* (mAh/cm³)
Al	LiAl	993	1374
Sb	Li_3Sb	660	1881
Sn	$Li_{22}Sn_5$	994	2025
SiO	$Li_{15}Si_4$	>2000	~200
Si	$Li_{15}Si_4$	3579	2200
$Li_4Ti_5O_{12}$	$Li_7Ti_5O_{12}$	175	350
C, graphite	LiC_6	372	760

锂离子电池结构——负极

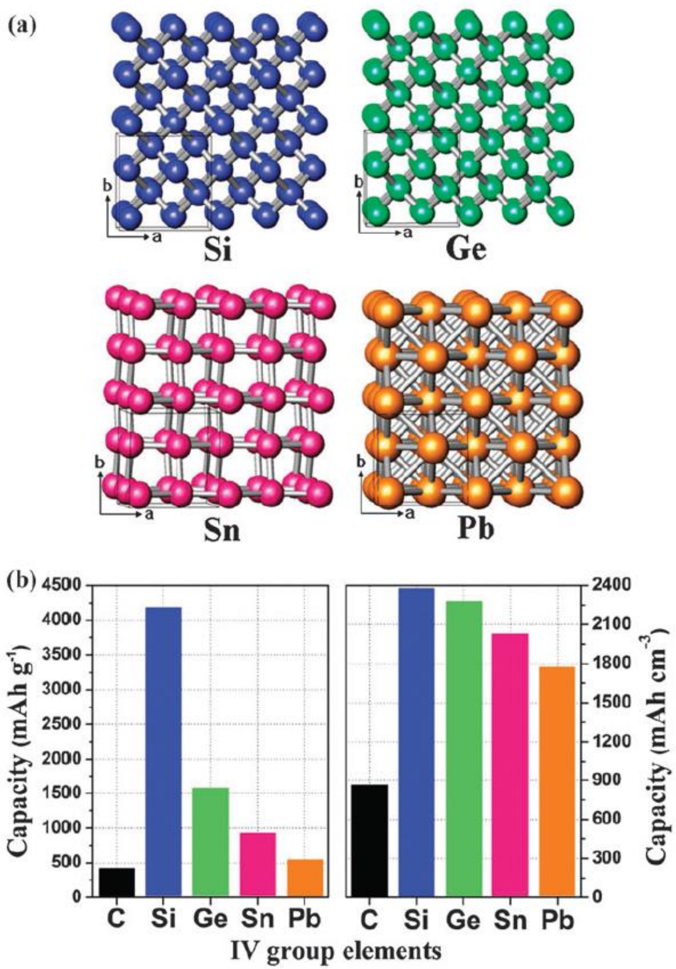


负极集流体：镍带（约0.07mm厚）

负极基体：铜箔（约0.015mm厚)

负极物质：石墨+CMC+SBR

Li-alloy based anode materials for Li secondary batteries



During discharge:

$$\text{Si (crystalline)} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Si (amorphous)} + (3.75 - x)\text{Li}^+ + (3.75 - x)e^- \quad (1)$$

$$\rightarrow \text{Li}_{15}\text{Si}_4 \text{ (crystalline)} \quad (2)$$

During charge:

$$\text{Li}_{15}\text{Si}_4 \text{ (crystalline)} \rightarrow \text{Si (amorphous)} + y\text{Li}^+ + ye^- + \text{Li}_{15}\text{Si}_4 \text{ (residual)} \quad (3)$$

CSR, 2010

Anode capacity for total specific capacity

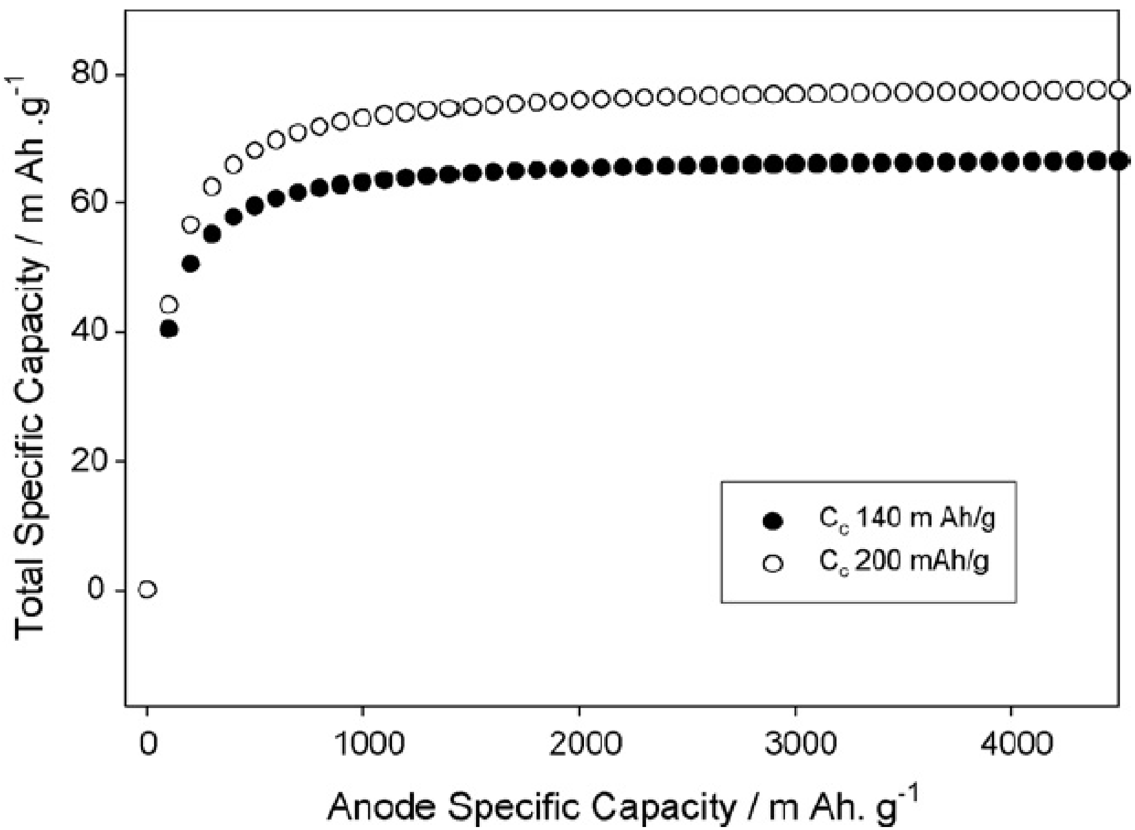
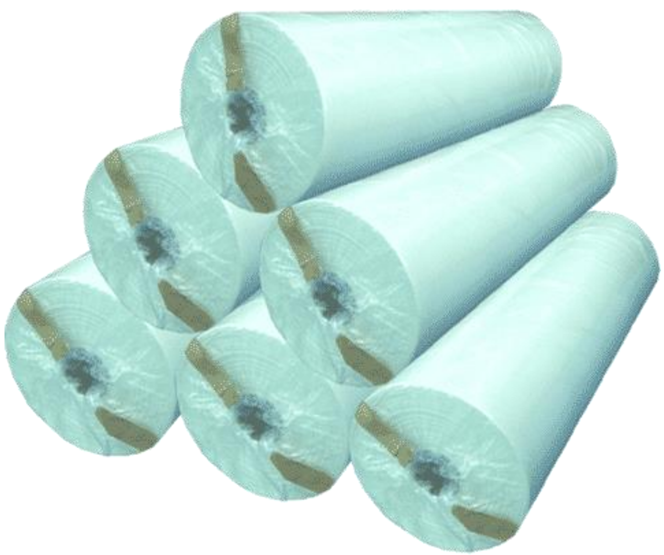


Fig. 1. Total capacity of 18650 Li-ion cell as a function of anode capacity (C_A), including masses of other required internal components and case. Capacities of cathodes considered were 140 and 200 mAh g^{-1}.

Electro Acta

隔離膜

- 材質:單層PE(聚乙烯)或者 三層複合PP(聚丙烯) +PE+PP
- 厚度:單層一般為0.016~0.020mm 三層一般為0.020~0.025mm



電解液

- 性質: 無色透明液體,具有較強吸濕性。
- 應用: 主要用於可充電鋰離子電池的電解液,只能在乾燥環境下使用操作(如環境水分小於20ppm的手套箱內)。
- 規格: 溶劑組成 DMC:EMC:EC =1:1:1 (重量比) $LiPF_6$ 濃度 1mol/l
- 品質指標: 密度(25℃)g/cm3 1.23±0.03 水分(卡爾費休法) ≤20ppm 游離酸(以HF計) ≤50ppm 電導率(25℃) 10.4±0.5 ms/cm

Electrolyte challenges:

- Liquid electrolyte （LiPF6/EC+DMC)
- Problems: leakage, non-flexibility of the cells, side reactions with charged electrodes
- Explosions

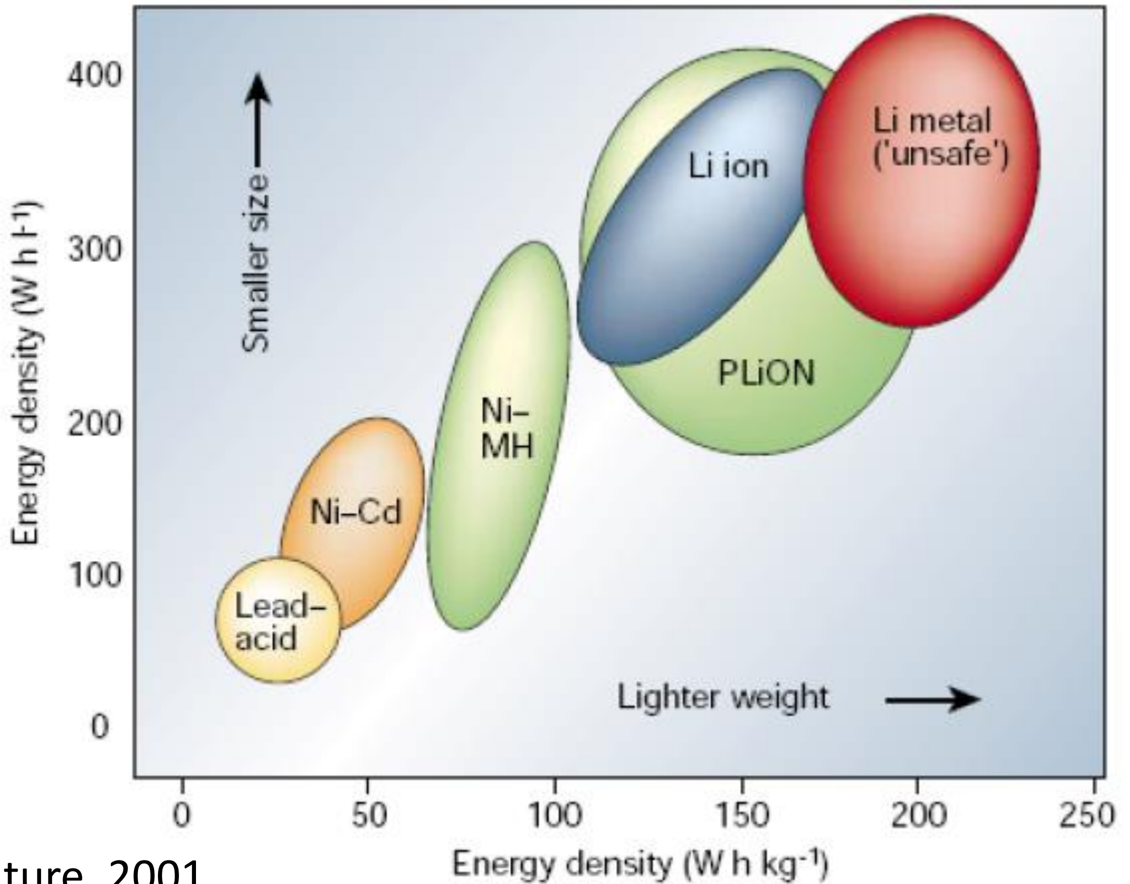
新型電解液

- 非水溶液系，如離子溶液
- 化學和電化學穩定性好，與電極材料和集流體以及隔離膜不發生反應
- 較高的離子導電性
- 沸點高、冰點低（在-40~70C保持液態）
- 高熱穩定性
- 較寬電化學視窗

Lithium-Ion and Lithium-Ion Polymer Batteries

- Great energy-to-weight ratio (~160 Wh/kg compared to 30-80 Wh/kg in NiMH)
- No memory effect.
- Slow self-discharge rate.
- Battery will degrade from moment it is made.
- Protection circuits are required to protect the battery.
- Li-Ion Polymer batteries are significantly improved.
  - Higher energy density.
  - Lower manufacturing costs
  - More robust to physical damage
  - Can take on more shapes.

Comparison of the different battery technologies in terms of volumetric and gravimetric energy density.



Armand, Nature, 2001

表 1：鋰離子電池/鎳鎘電池/鎳氫電池主要性能比較

參數/電池種類	鋰離子	鎳鎘	鎳氫
單位重量能量密度（W－Hr/kg）	90	40	60
單位體積能量密度（W-Hr/l）	210	100	140
額定電壓（V）	3.6	1.2	1.2
充電次數	1000	1000	800
自放電率（%/月）	6	15	20

Disadvantages of Li-Ion

EXPENSIVE -- 40% more than NiCd.

DELICATE -- battery temp must be monitored from within (which raises the price), and sealed particularly well.

REGULATIONS -- when shipping Li-Ion batteries in bulk (which also raises the price).

- Class 9 miscellaneous hazardous material
- UN Manual of Tests and Criteria (III, 38.3)

Schematic drawing of Li-ion batteries

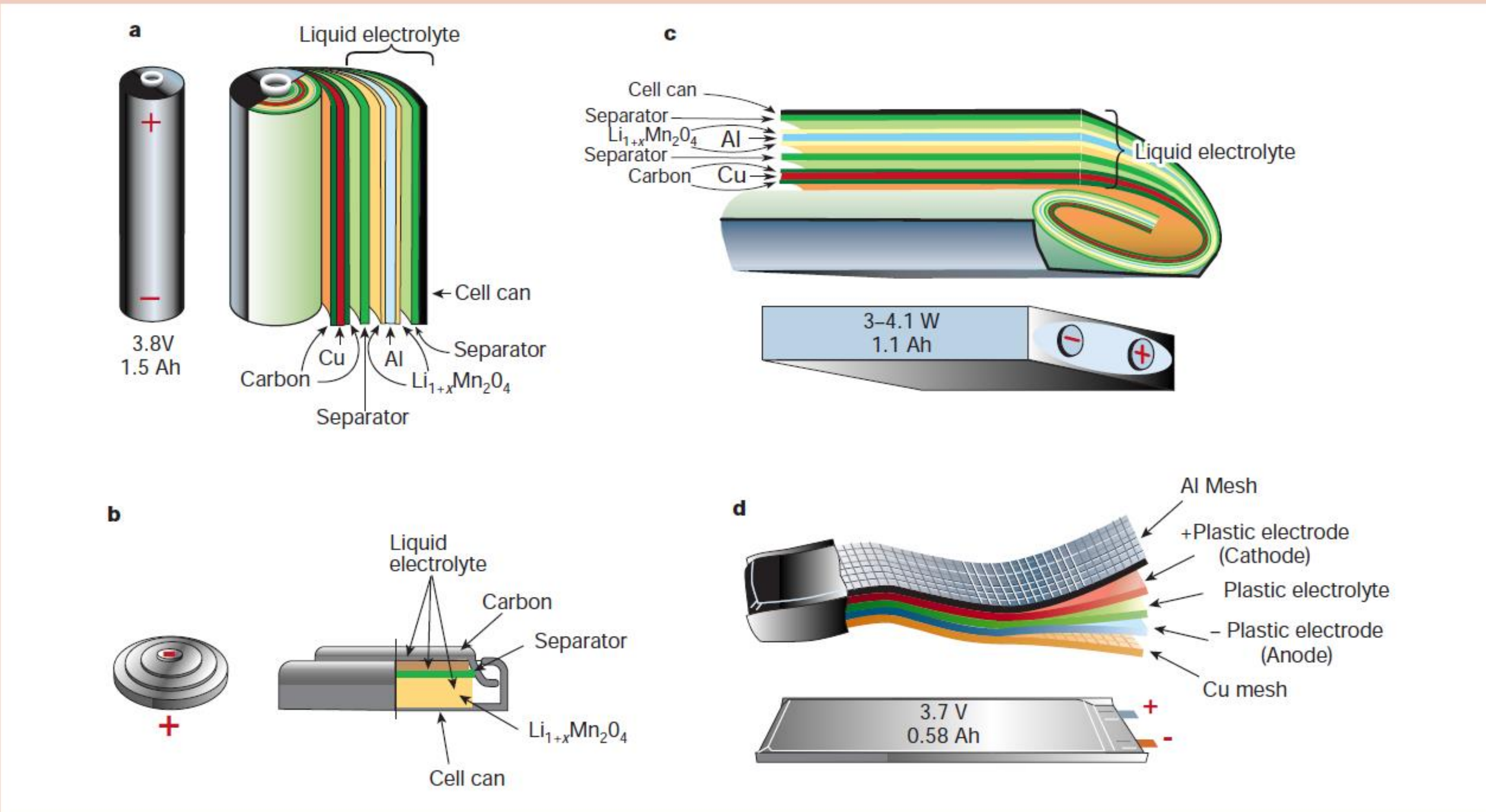


Figure 4 Schematic drawing showing the shape and components of various Li-ion battery configurations. **a**, Cylindrical; **b**, coin; **c**, prismatic; and **d**, thin and flat. Note the unique flexibility of the thin and flat plastic LiION configuration; in contrast to the other configurations, the PLiION technology does not contain free electrolyte.

Types of lithium-ion batteries

- 圓柱型：5位數 前兩位為直徑，後兩位數為高度。18650 型電池，直徑18mm, 高度65mm

Types of lithium-ion batteries

- 方形：六位數。前兩位電池厚度、中間兩位為電池寬度，後面兩位為電池長度。083448：厚度8mm、寬度:34mm、長度48mm