

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

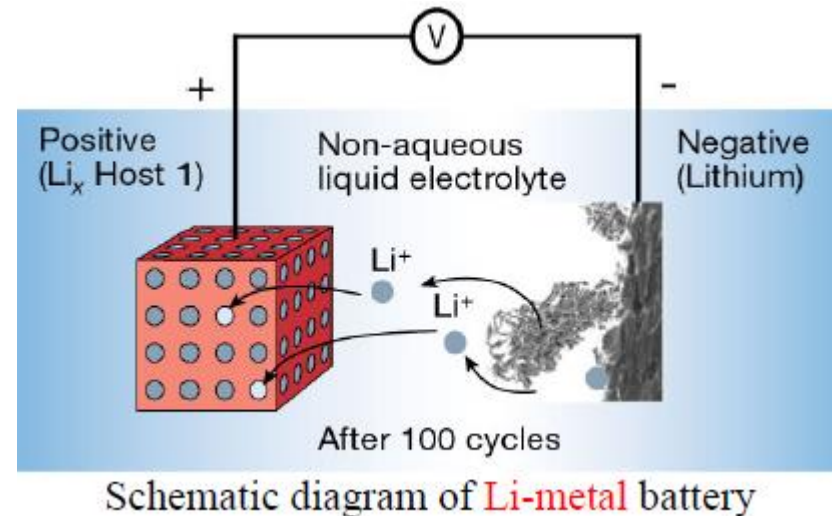
- 正極
- 活性物質(LiCoO_2 \ LiMnO_2 \ $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$) 導電劑、溶劑、粘合劑、基體
- 負極 活性物質(石墨、MCMB) 粘合劑、溶劑、基體
- 隔膜(PP+PE)
- 電解液(LiPF_6 + DMC EC EMC)
- 外殼五金件(鋁殼、蓋板、極耳、絕緣片)

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 began in 1912 by G. N. Lewis but it was not until the early 1970's when the first non-rechargeable lithium batteries became commercially available
- In the 1970's Lithium metal was used but its instability rendered it unsafe

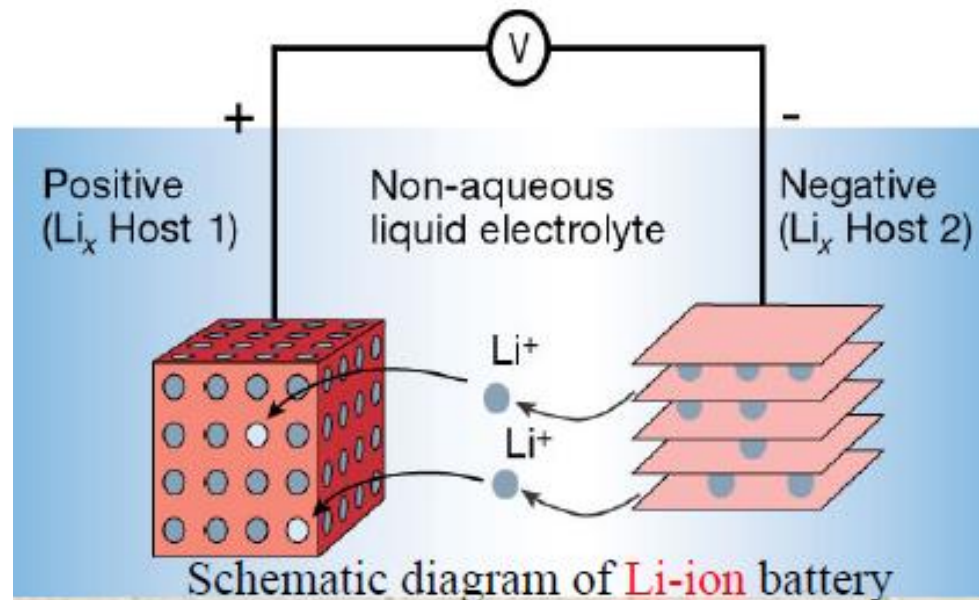


Why lithium-ion other than Lithium

- 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

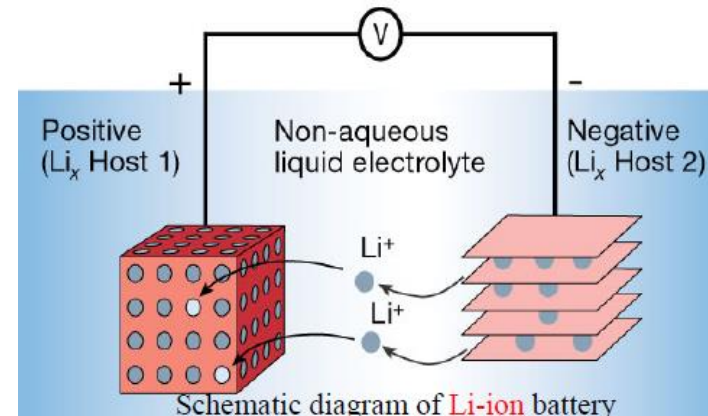
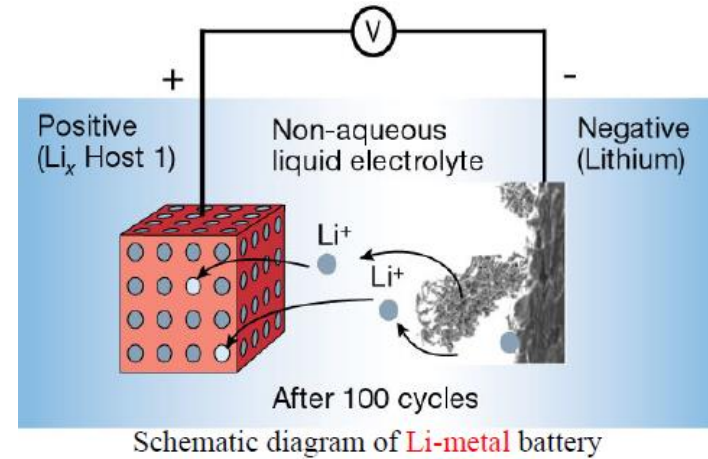
- Attempts to develop rechargeable lithium batteries followed in the eighties, but failed due to safety problems
- The lithium ion battery has a slightly lower energy density than lithium metal, but it is much safer. Introduced by Sony 1991



Lithium secondary battery

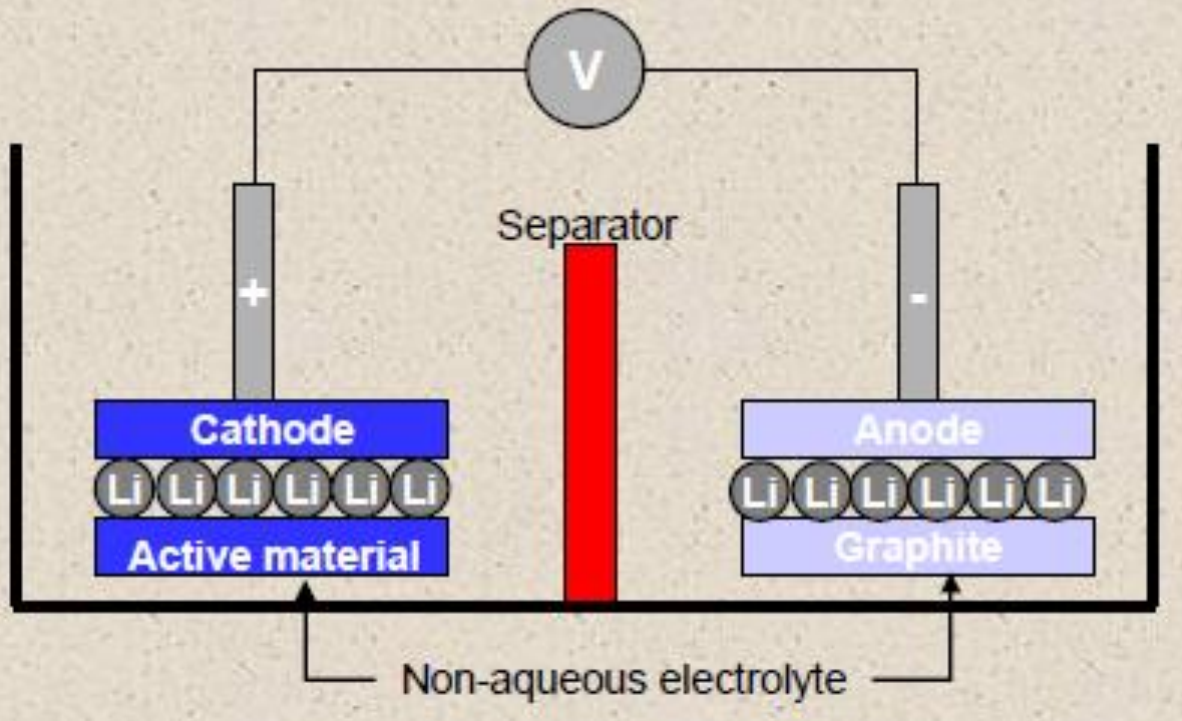
- A chemical intercalation reaction
- Intercalation is the reversible inclusion of a molecule between two other molecules

Ex: graphite intercalation compounds



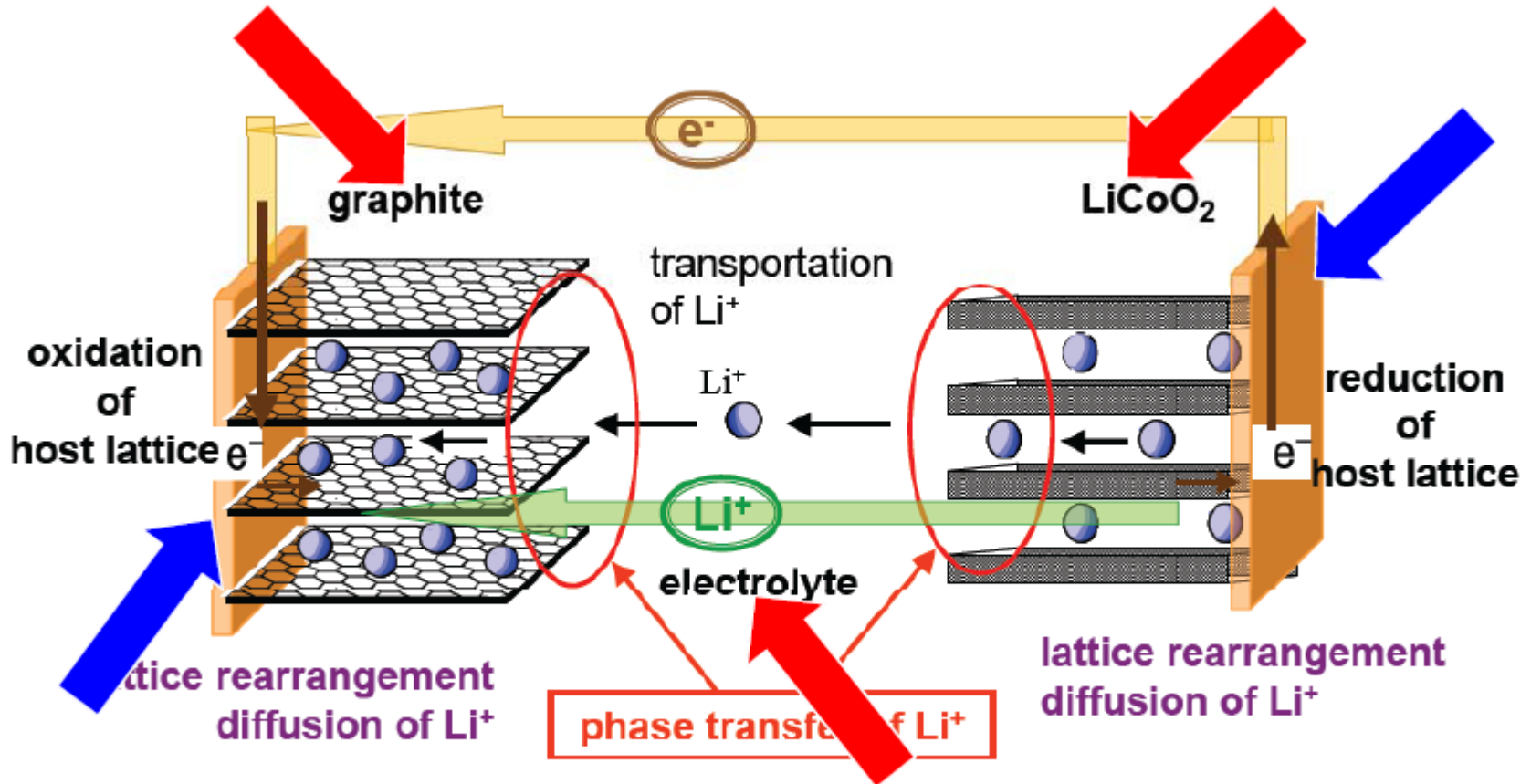
The operation principle of a Li-Ion battery

To a large extent, the cathode material limits the performance of current Li-ion batteries



- 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

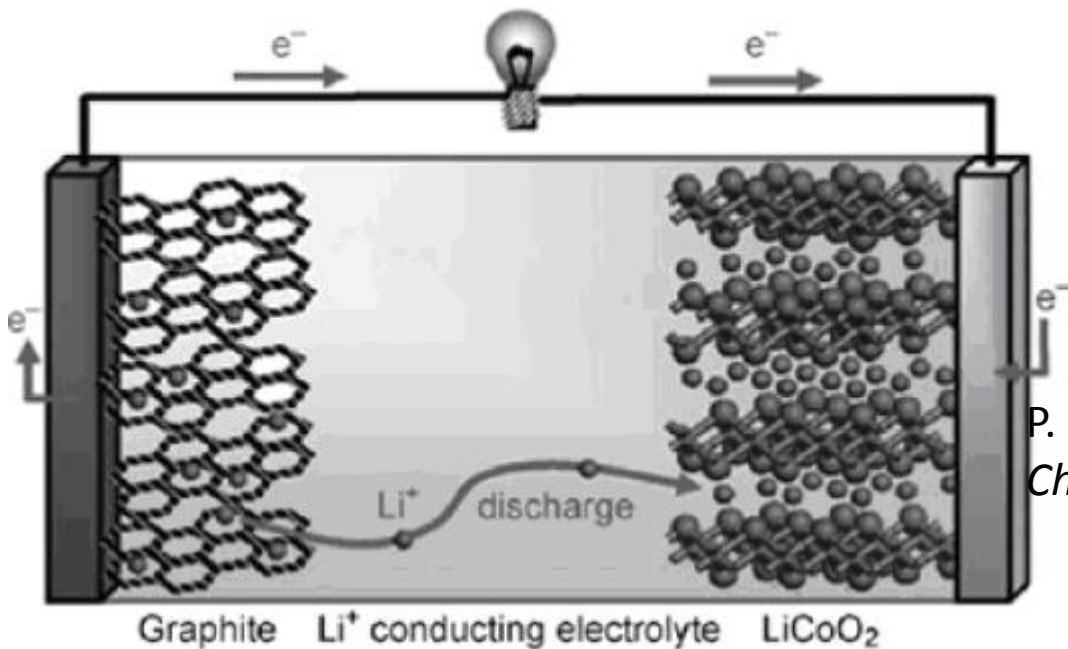


Lithium ion phase transfer

充電時，鋰離子從 LiCoO_2 脫出、 Co^{+3} 氧化為 Co^{+4} ；放電池鋰離子則嵌入 LiCoO_2 ，則 $\text{Co}^{+4} \rightarrow \text{Co}^{+3}$

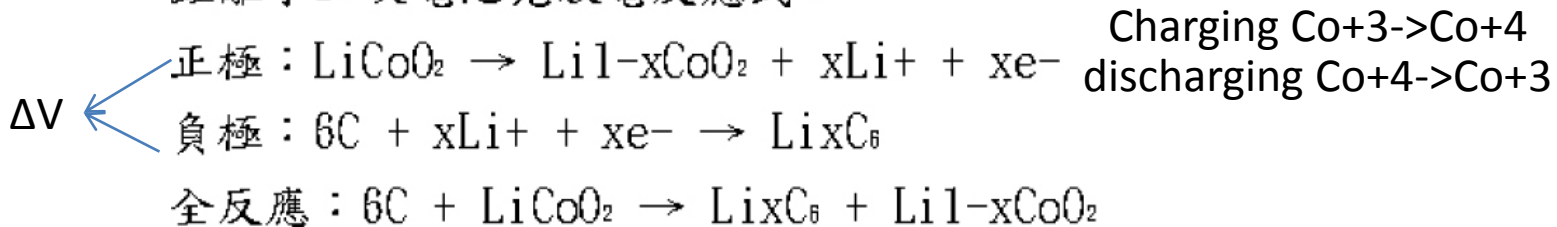
。換句話說，充電時由外界輸入能量而迫使鋰離子由低能量之正極材料往負極材料移動，而成為能量較高之狀態；而放電時，鋰離子將會自然地由高能量之負極材料移動至較低能量之正極材料之中，並同時對外釋出能量

Overall reaction of Li-ion battery

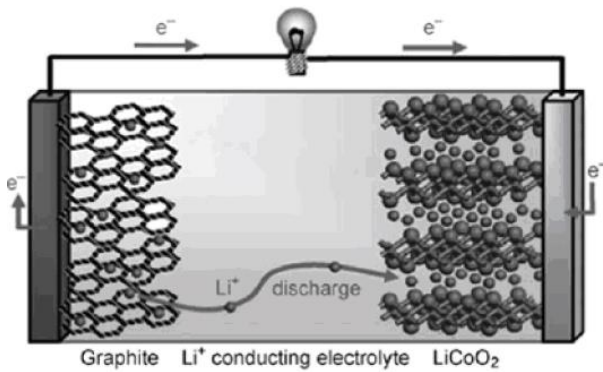


P. G. Bruce, B. Scrosati, J. M. Tarascon, *Angew. Chem. Int. Ed.*, **2008**, 47, 2930

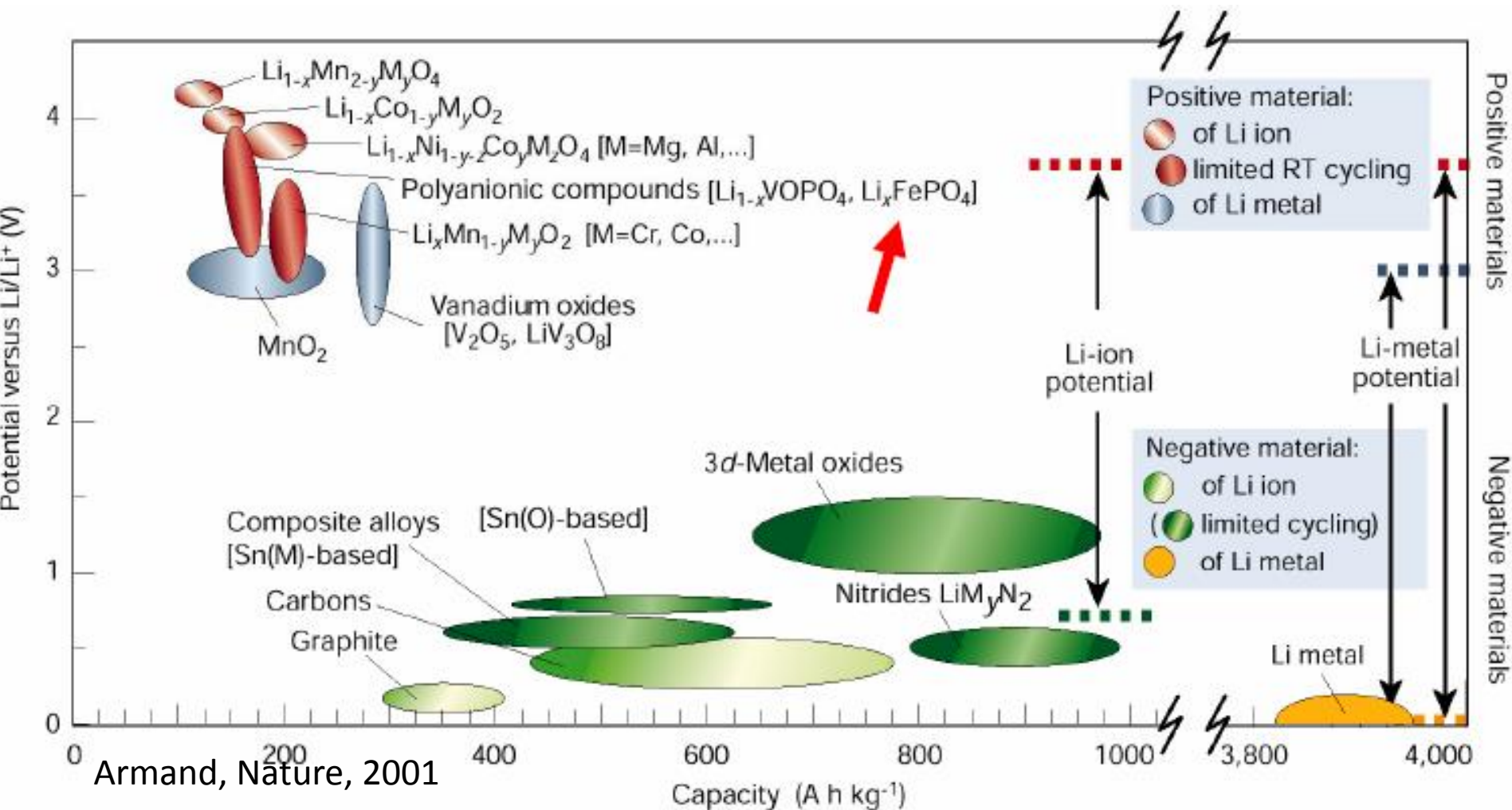
鋰離子二次電池充放電反應式：



Rocking-chair technology

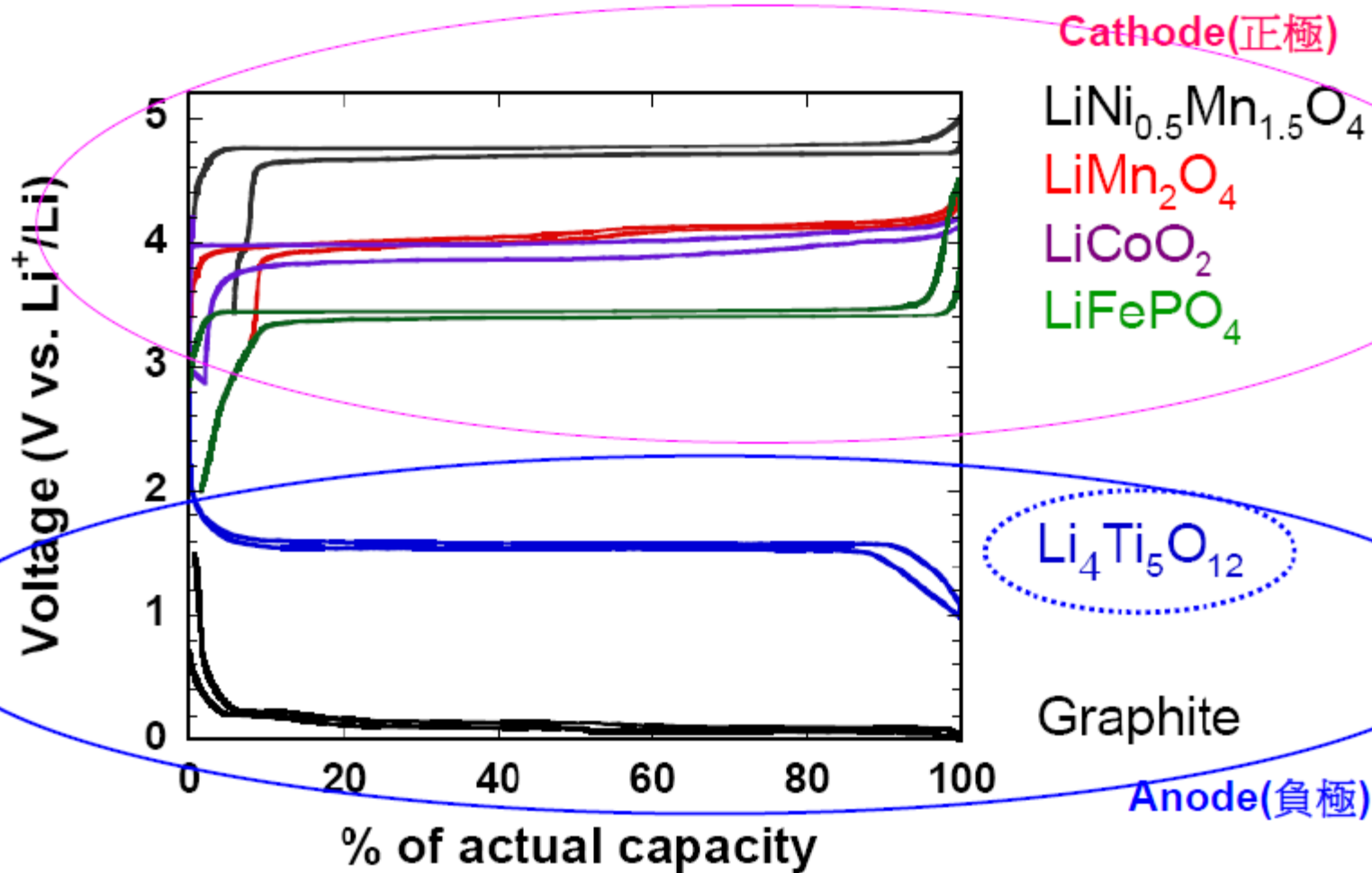


Combination of positive materials and negative materials for Lithium batteries



Voltage of a cell

$$V(\text{battery}) = V_{\text{正}} - V_{\text{負}}$$

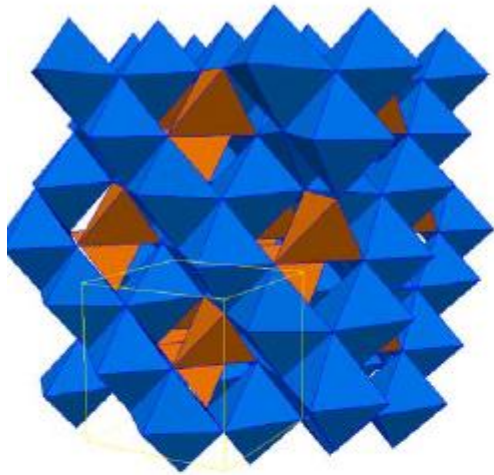


Capacity

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

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

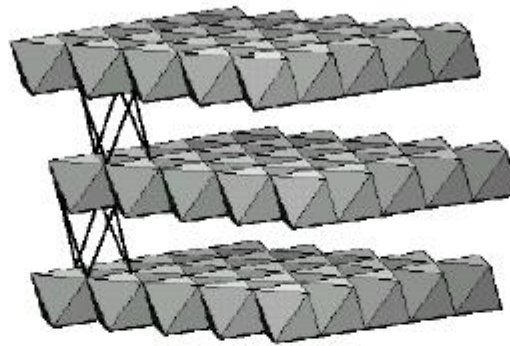


正方晶系

3D frameworks

Spinel

Fd3m



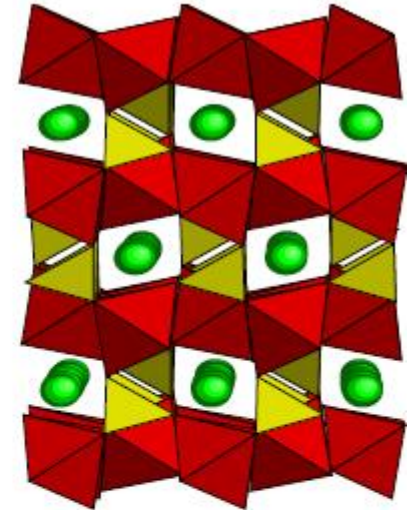
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2D channel

Lamellar LiCoO₂

R3m

LiFe^{II}PO₄



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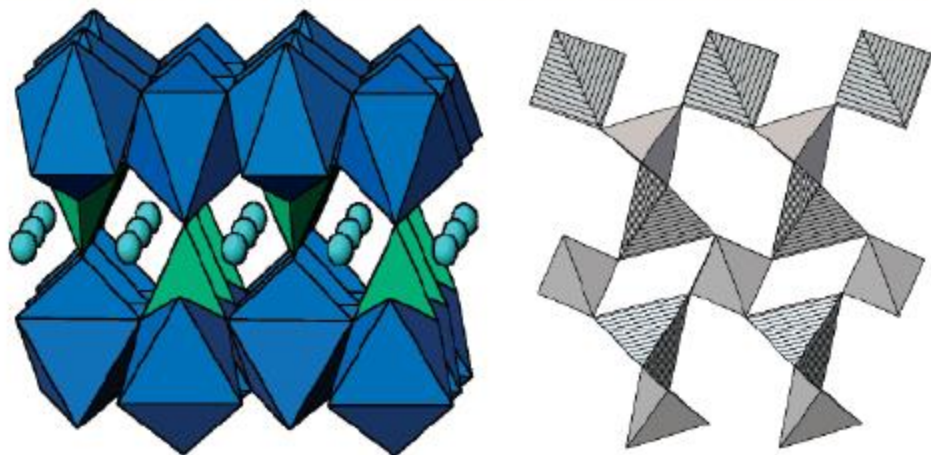
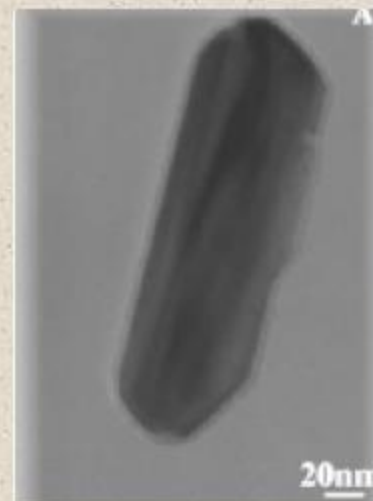
Pnma

Cathode materials in Lithium-ion batteries

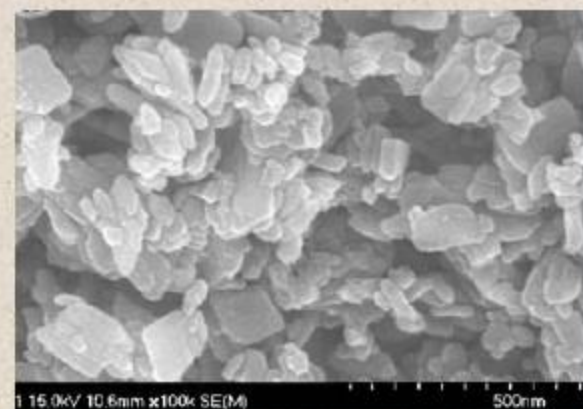
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層狀氧化物 (layered Oxides)	2D	LiCoO_2 $\text{Li}(\text{Co-Ni})\text{O}_2$ $\text{Li}(\text{Ni-Mn})\text{O}_2$ $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$	273	160 180 160 190	3.6~3.7	尚可	高	小型電池 & 動力電池及大型電池
尖晶石 (Spinel)	3D	LiMn_2O_4	148	110	3.7	佳	低	動力電池及大型電池

LiFePO₄ 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...

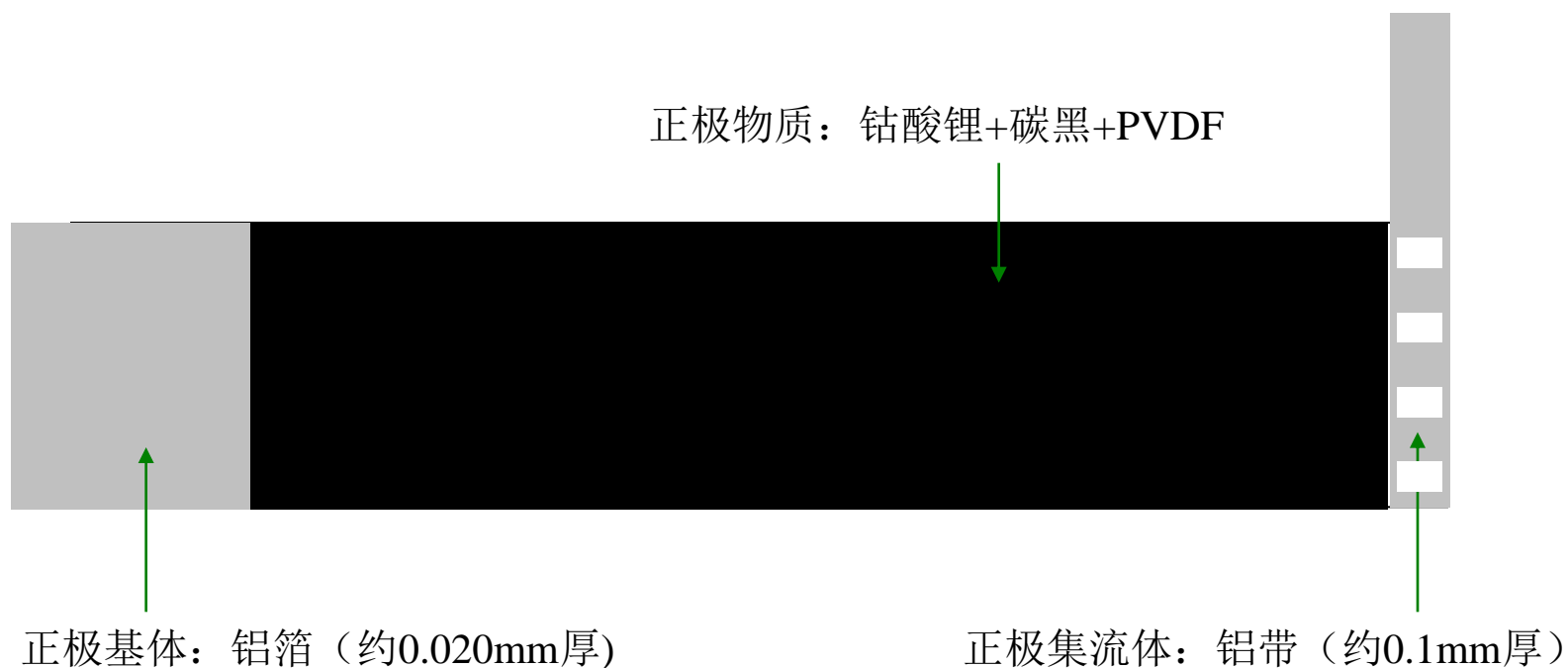


Structures of orthorhombic LiFePO₄ and trigonal quartz-like FePO₄.



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.

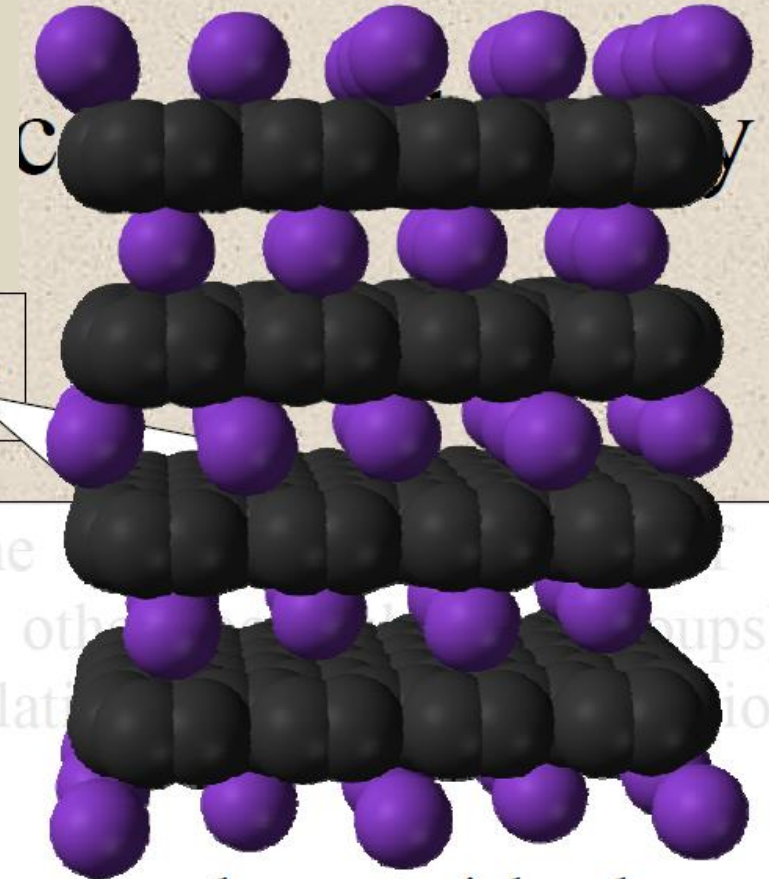
锂离子电池结构——正极



Cathode Materials Challenges

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

Anode materials: Carbon



1972 Define the concept of **chemical intercalation**

In chemistry, intercalation is the insertion of a molecule (or group) between two other groups). Examples include DNA intercalation compounds, etc.

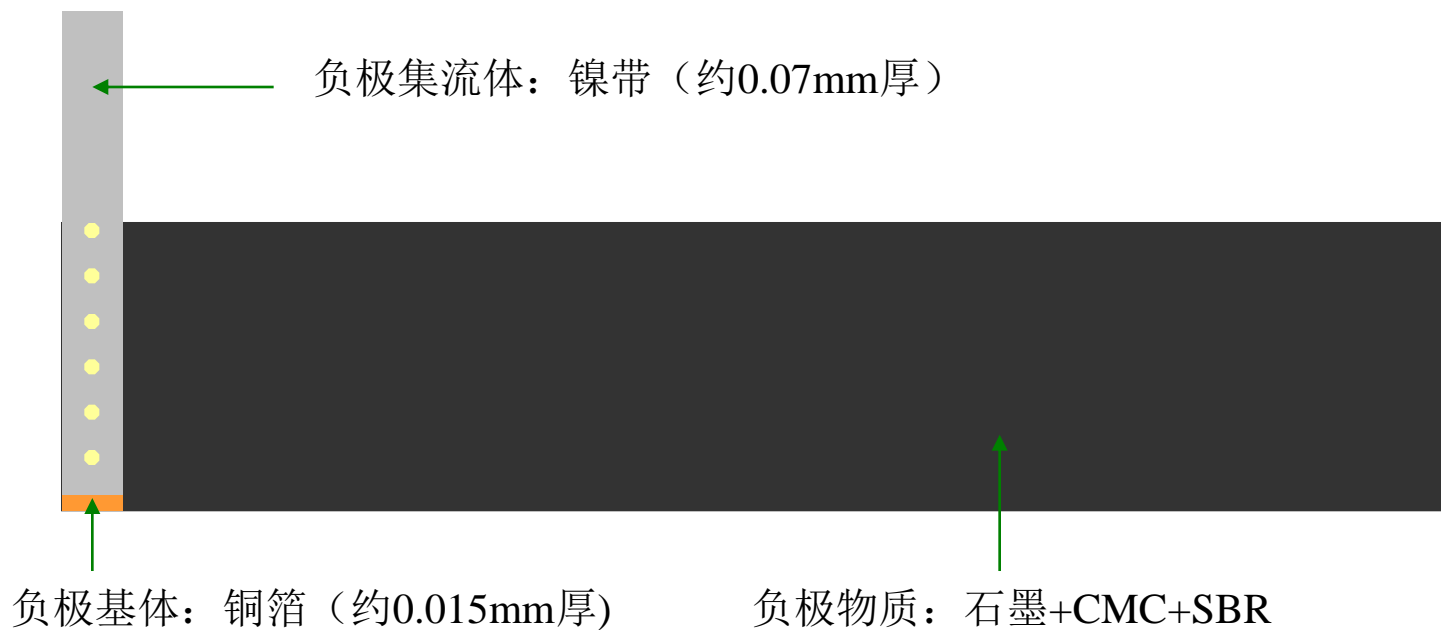
Graphite intercalation compounds are complex materials where an atom, ion, or molecule is inserted (intercalated) between the graphite layers. In this type of compound the graphite layers remain largely intact and the guest species are located in between

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

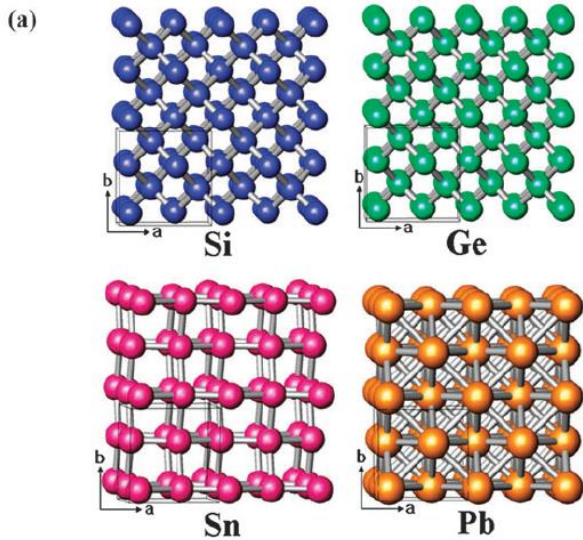
Anode materials

Anode material	Fully lithiated material	Theoretical Specific capacity (mAh/g)	Volumetric capacity* (mAh/cm ³)
Al	LiAl	993	1374
Sb	Li ₃ Sb	660	1881
Sn	Li ₂₂ Sn ₅	994	2025
SiO	Li ₁₅ Si ₄	>2000	~200
Si	Li ₁₅ Si ₄	3579	2200
Li ₄ Ti ₅ O ₁₂	Li ₇ Ti ₅ O ₁₂	175	350
C, graphite	LiC ₆	372	760

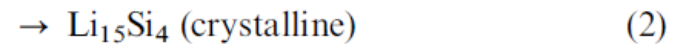
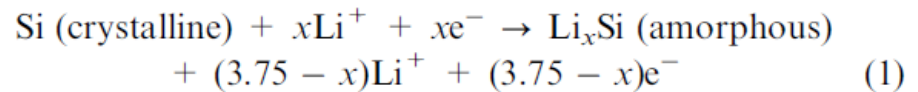
锂离子电池结构——负极



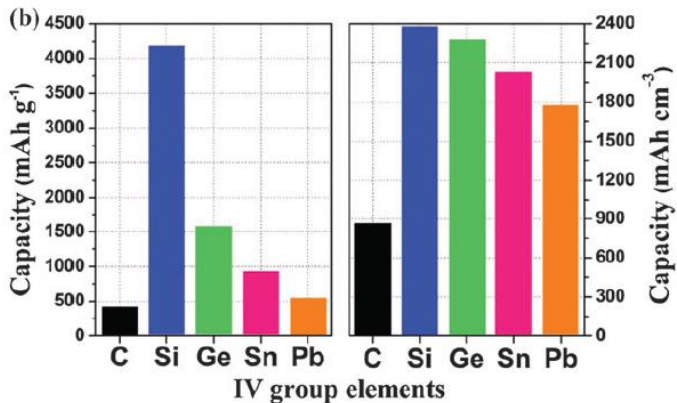
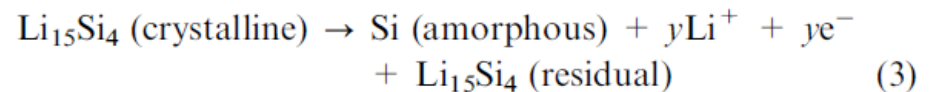
Li-alloy based anode materials for Li secondary batteries



During discharge:



During charge:



Anode capacity for total specific capacity

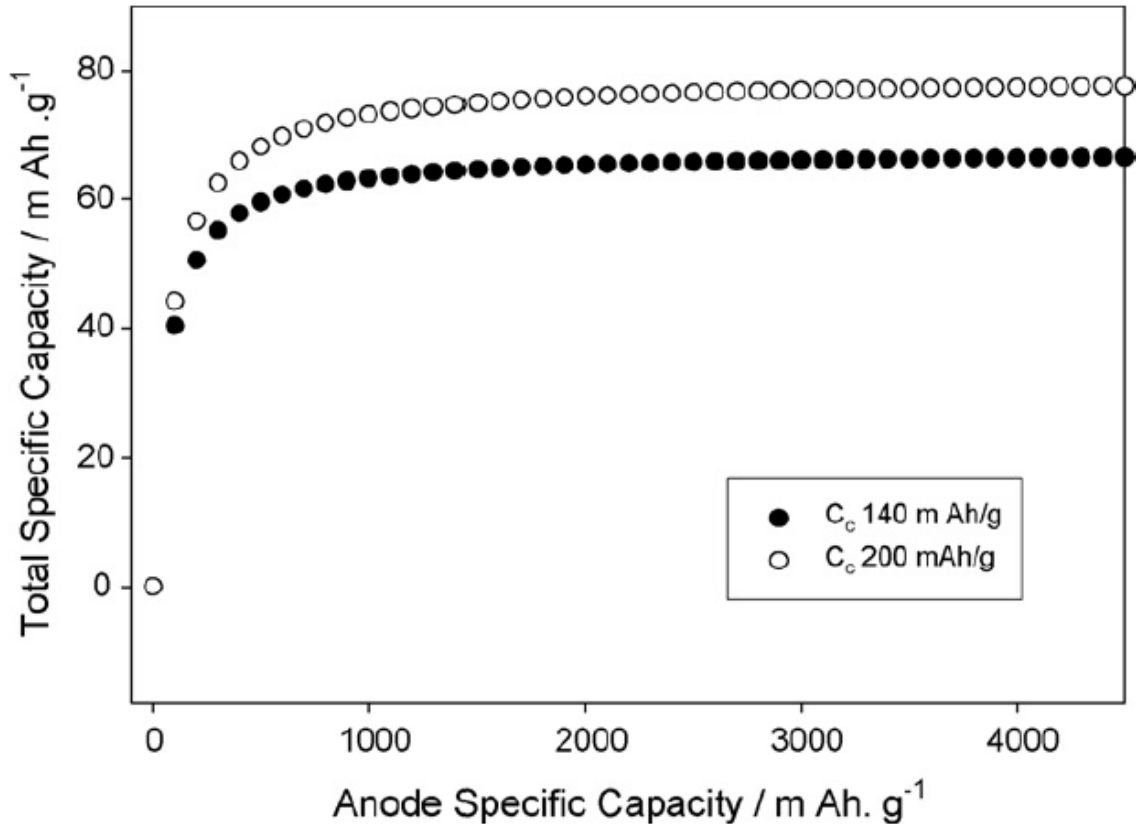
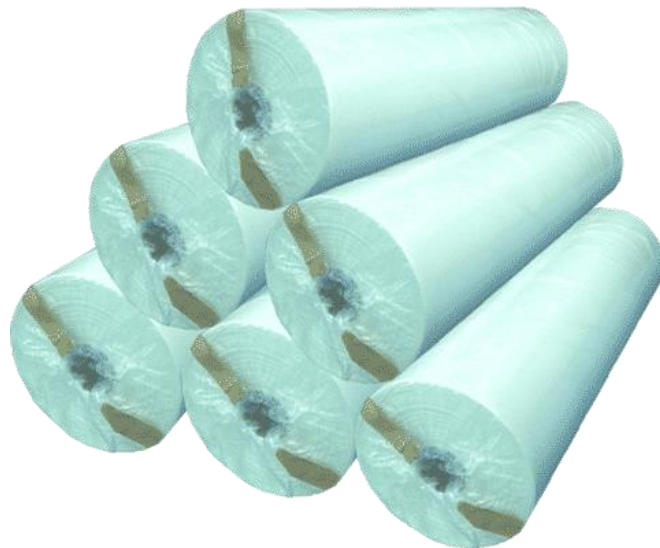


Fig. 1. Total capacity of 18650 Li-ion cell as a function of anode capacity (C_A), including masses of other required internal components and case. Capacities of cathodes considered were 140 and 200 mAh g⁻¹.

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) LiPF6 濃度 1mol/l
- 品質指標: 密度(25°C) 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°C) 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.

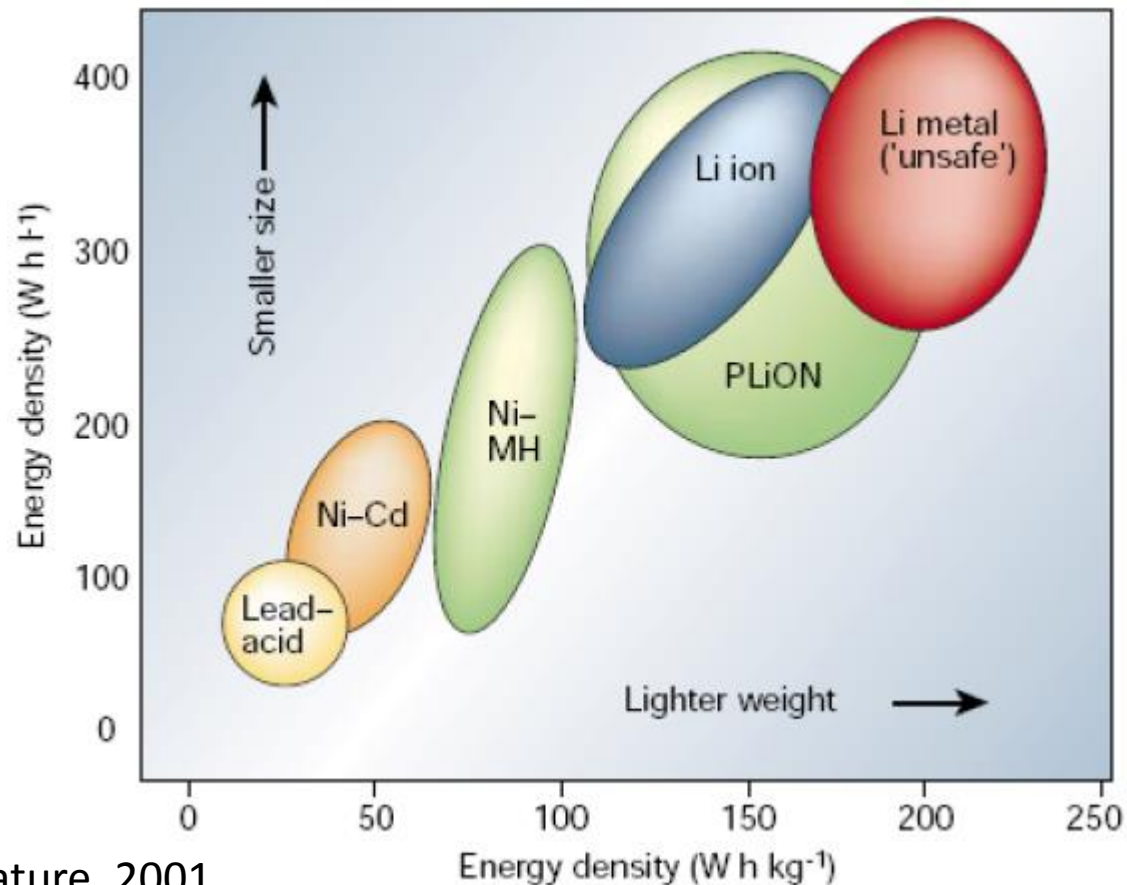


表 1：鋰離子電池/鎳鎘電池/鎳氫電池主要性能比較

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

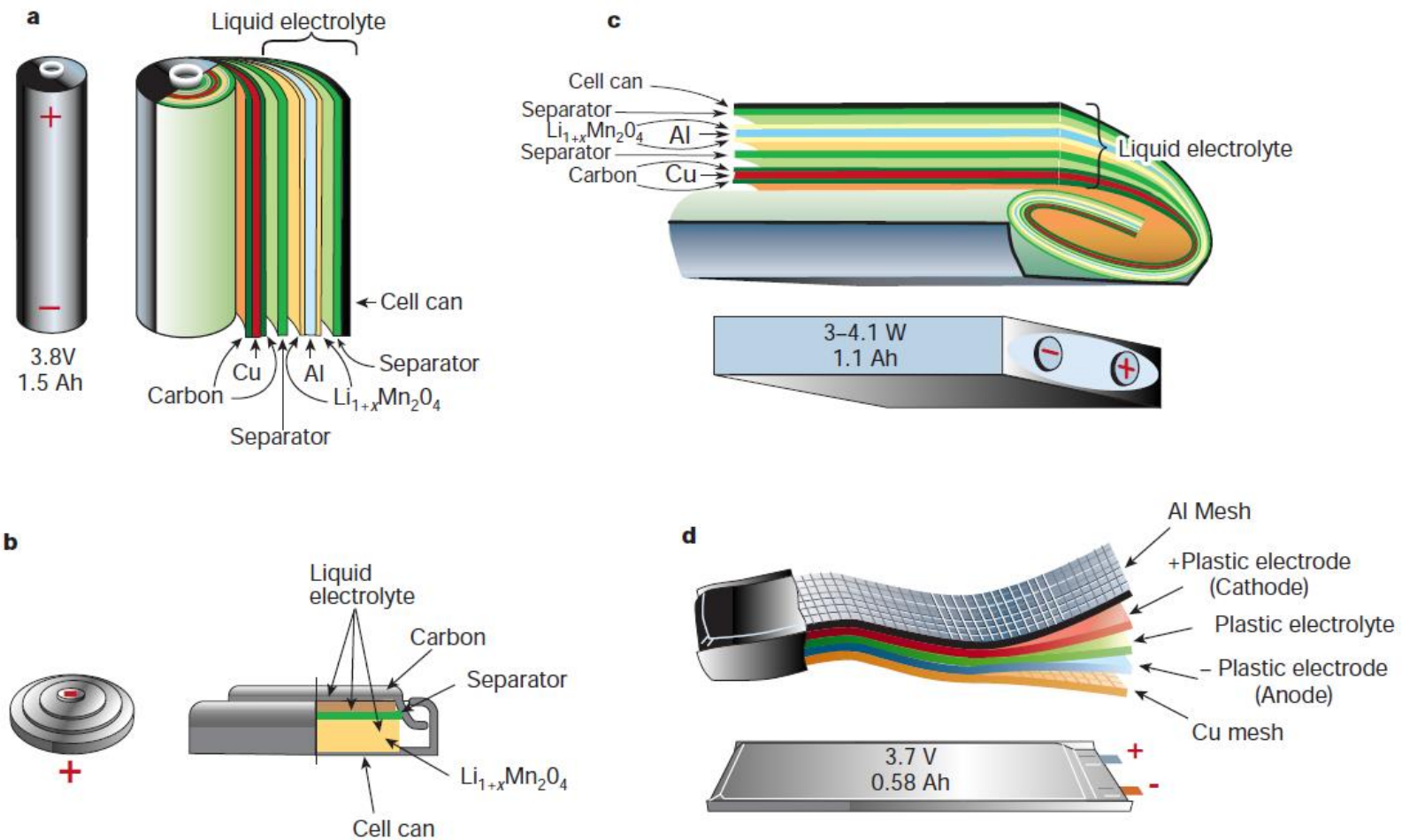


Figure 4 Schematic drawing showing the shape and components of various Li-ion battery configurations. **a**, Cylindrical; **b**, coin; **c**, prismatic; and **d**, thin and flat. Note the

unique flexibility of the thin and flat plastic LiION configuration; in contrast to the other configurations, the PLiON technology does not contain free electrolyte.

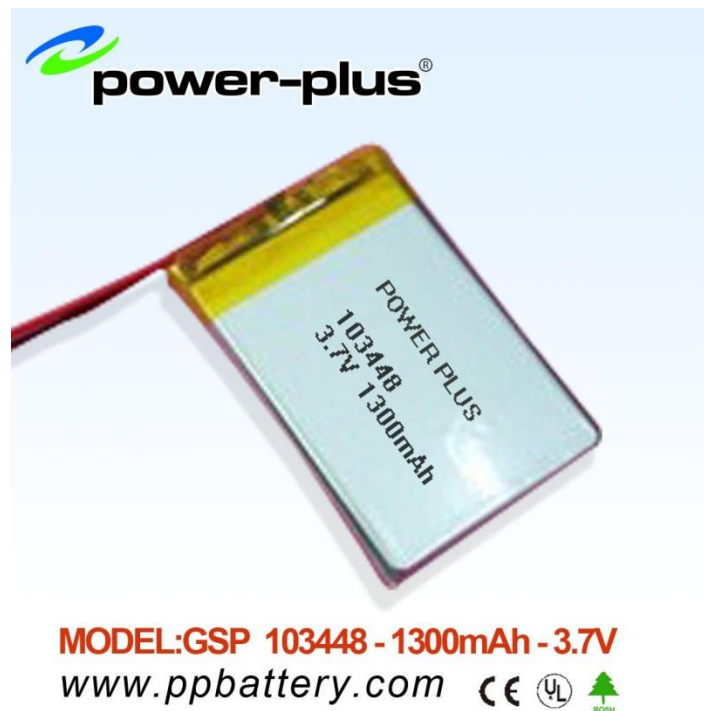
Types of lithium-ion batteries

- 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



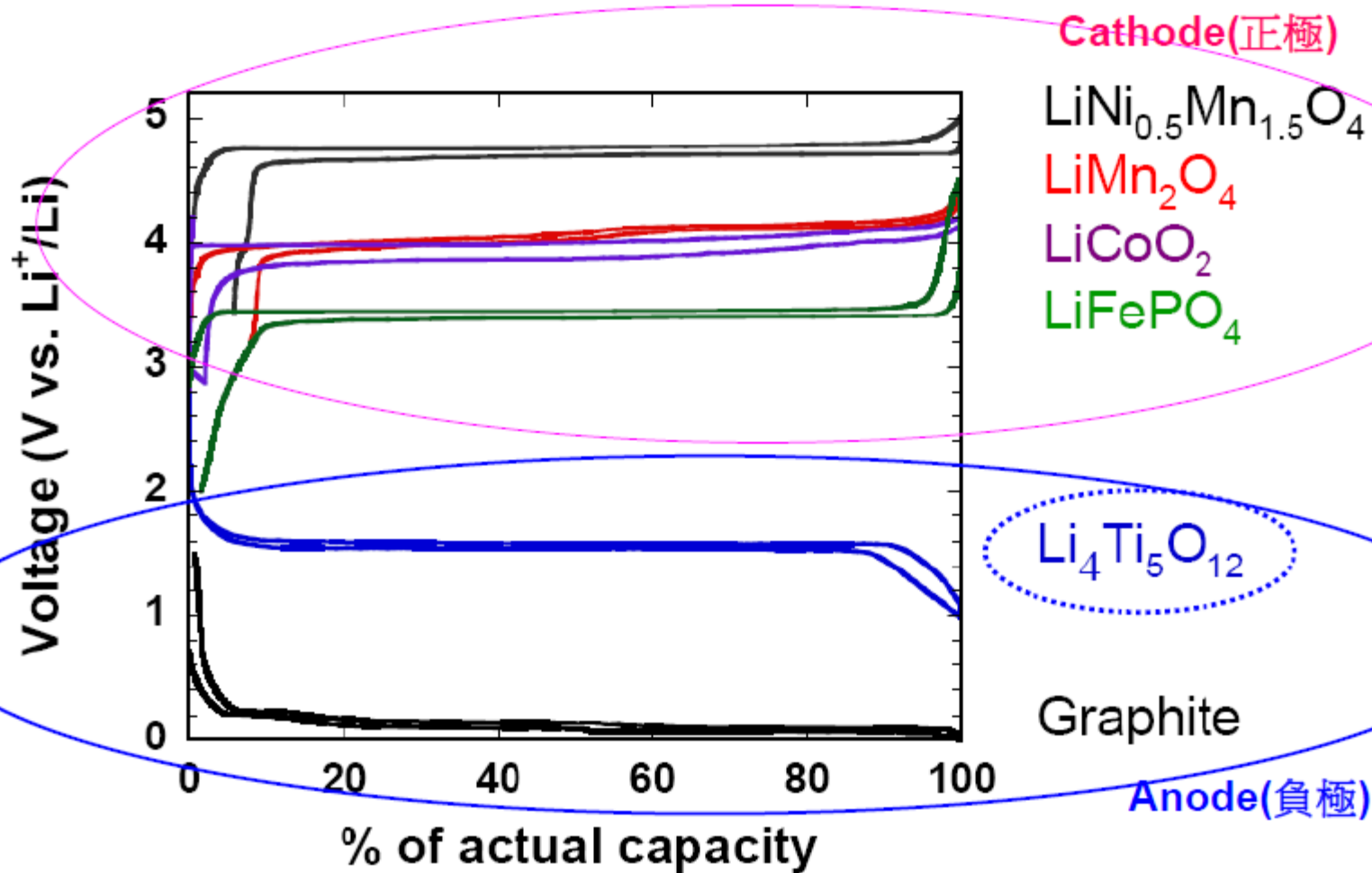
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- 方形：六位數。前兩位電池厚度、中間兩位為電池寬度，後面兩位為電池長度。
083448：厚度8mm、寬度:34mm、長度48mm



Voltage of a cell

$$V(\text{battery}) = V_{\text{正}} - V_{\text{負}}$$

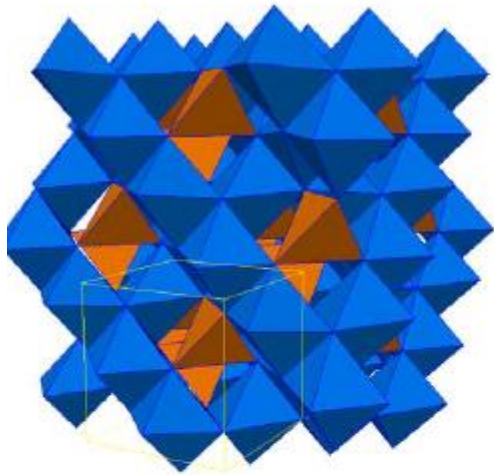


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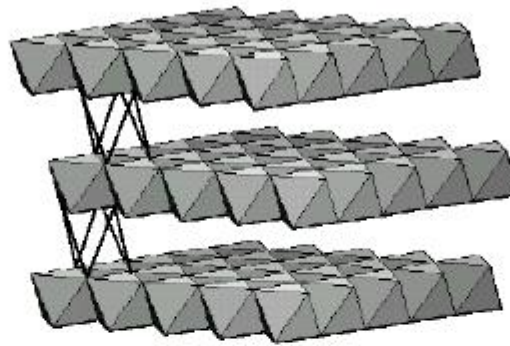


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Fd3m



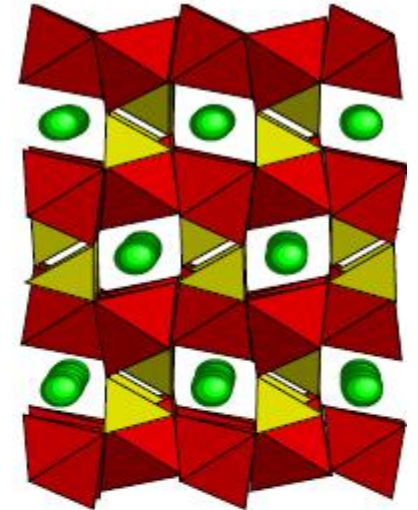
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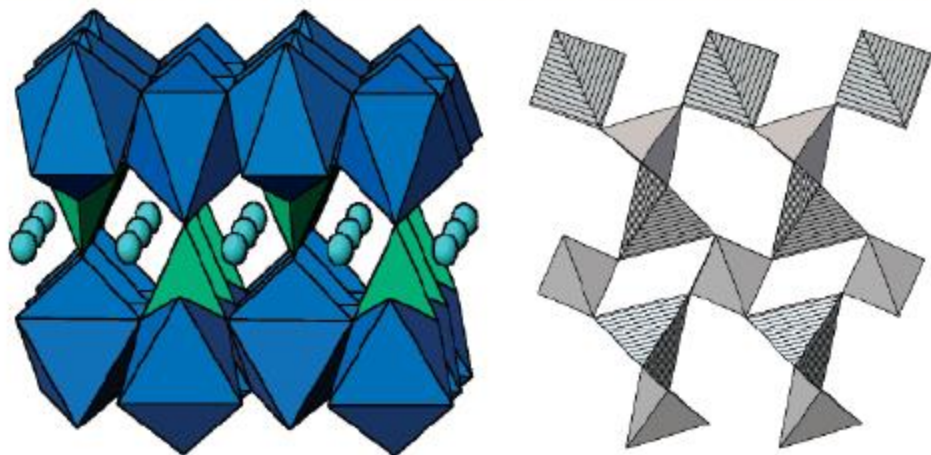
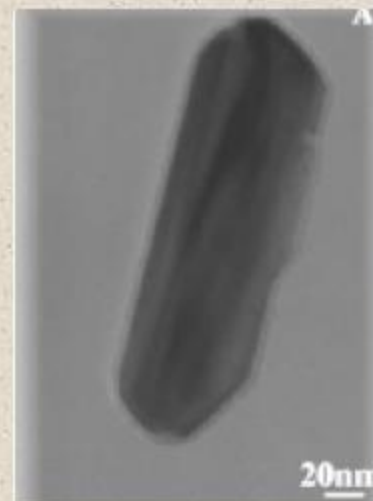
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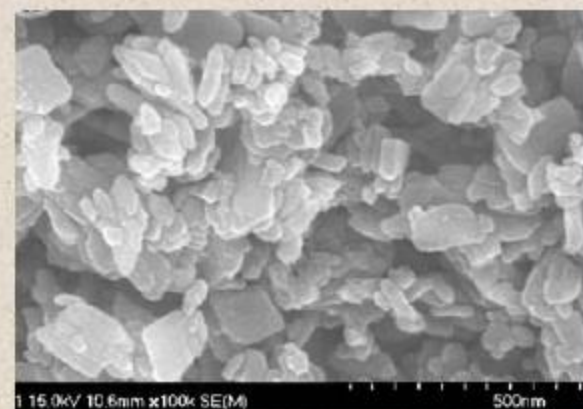
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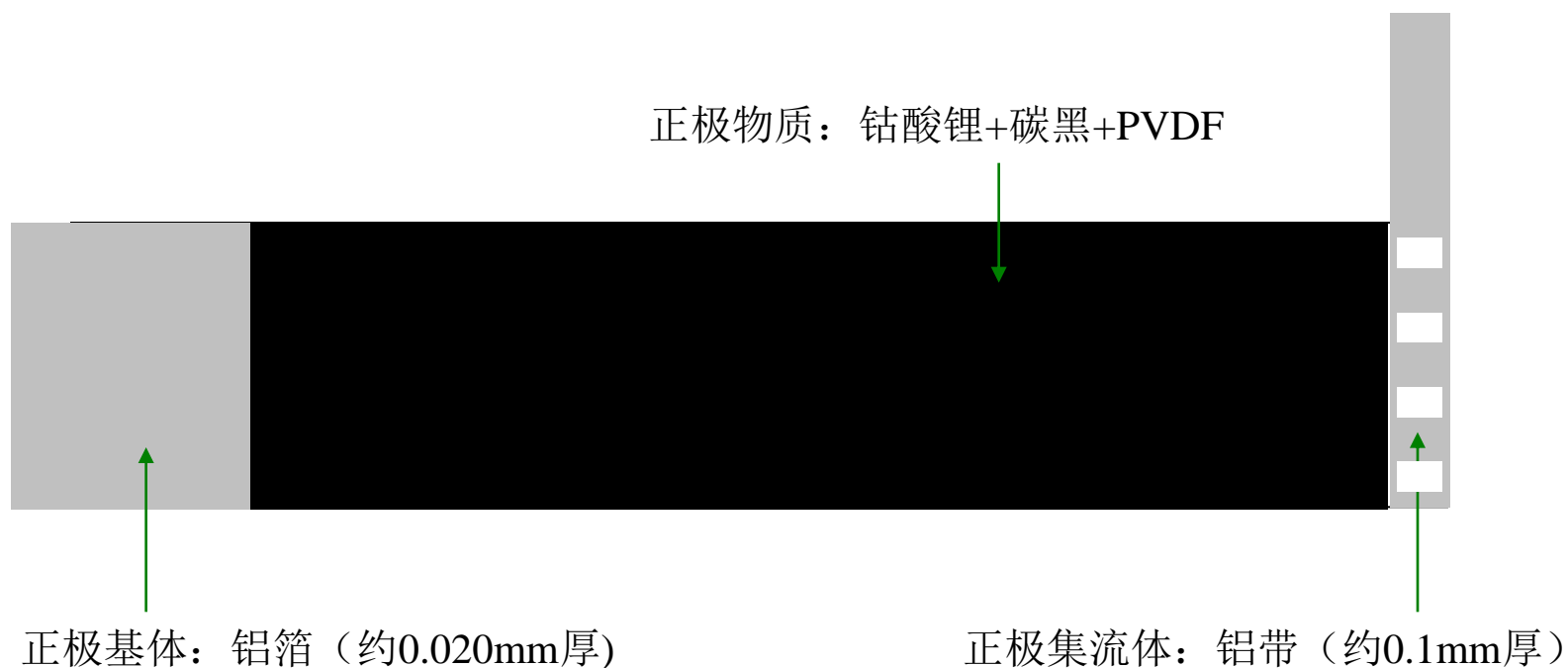
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Structures of orthorhombic LiFePO₄ and trigonal quartz-like FePO₄.



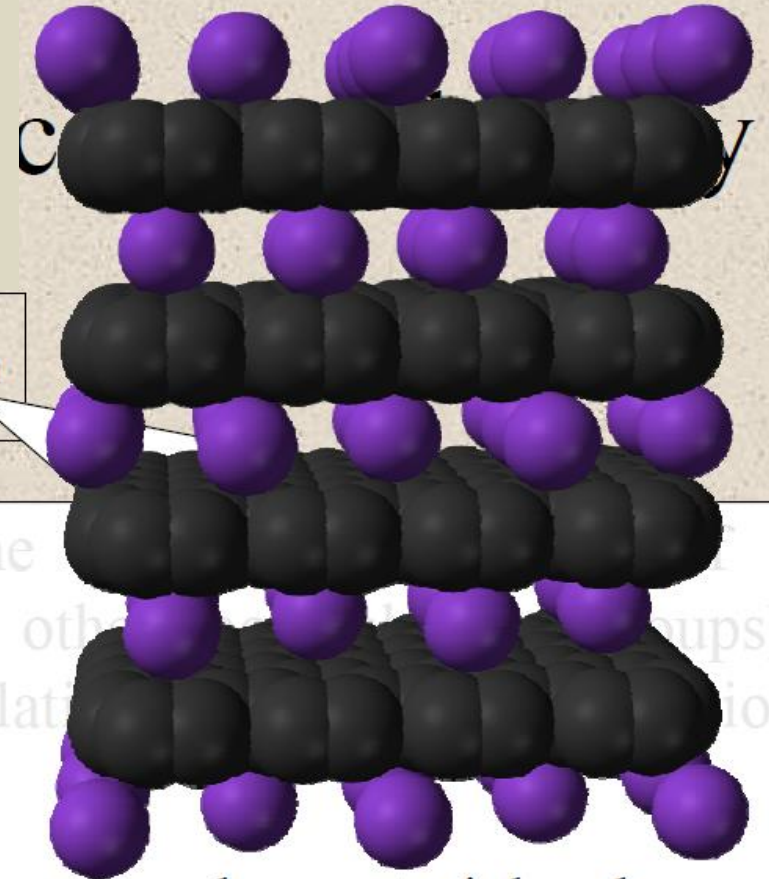
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1972 Define the concept of **chemical intercalation**

In chemistry, intercalation is the insertion of a molecule (or group) between two other groups). Examples include DNA intercalation compounds, etc.

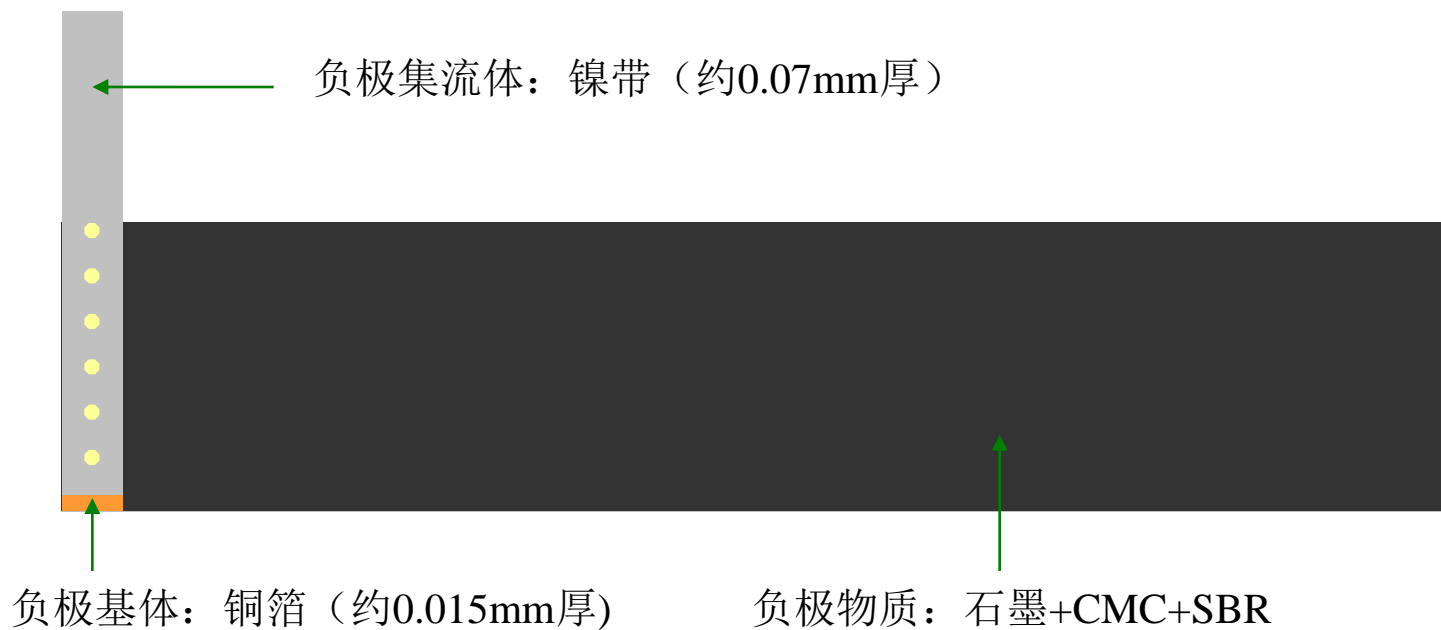
Graphite intercalation compounds are complex materials where an atom, ion, or molecule is inserted (intercalated) between the graphite layers. In this type of compound the graphite layers remain largely intact and the guest species are located in between

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

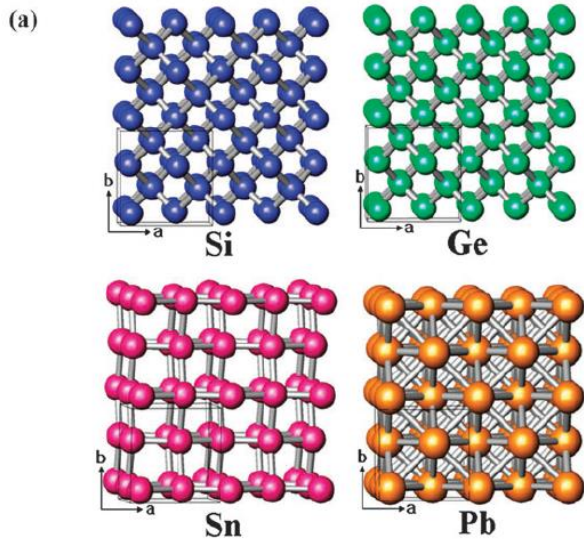
Anode materials

Anode material	Fully lithiated material	Theoretical Specific capacity (mAh/g)	Volumetric capacity* (mAh/cm ³)
Al	LiAl	993	1374
Sb	Li ₃ Sb	660	1881
Sn	Li ₂₂ Sn ₅	994	2025
SiO	Li ₁₅ Si ₄	>2000	~200
Si	Li ₁₅ Si ₄	3579	2200
Li ₄ Ti ₅ O ₁₂	Li ₇ Ti ₅ O ₁₂	175	350
C, graphite	LiC ₆	372	760

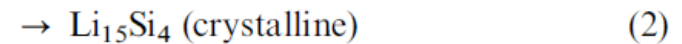
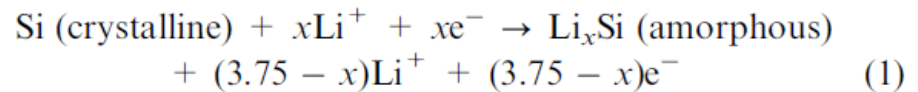
锂离子电池结构——负极



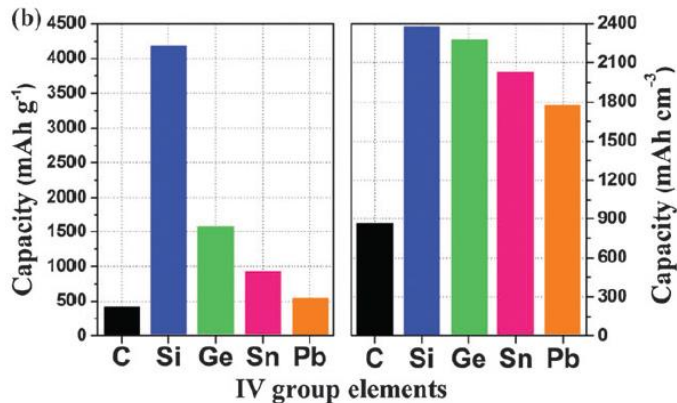
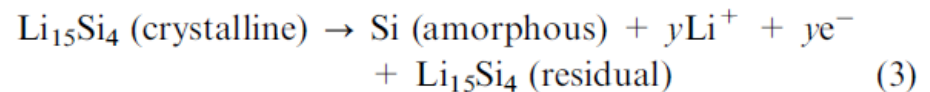
Li-alloy based anode materials for Li secondary batteries



During discharge:



During charge:



Anode capacity for total specific capacity

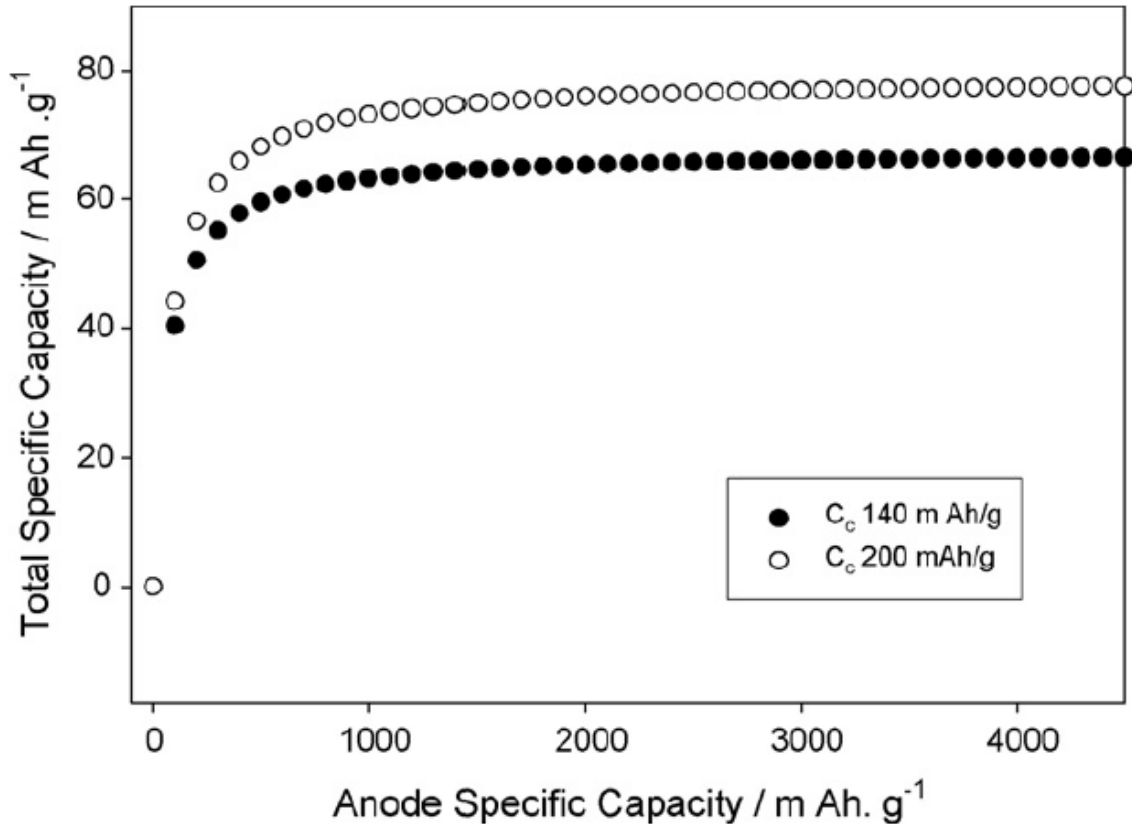
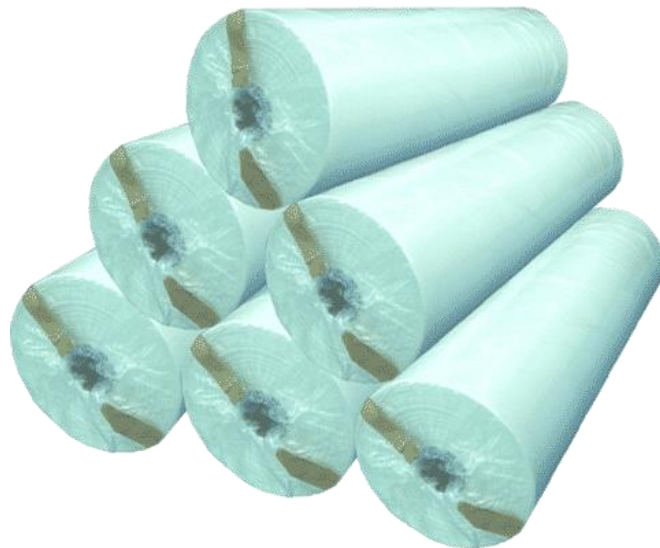


Fig. 1. Total capacity of 18650 Li-ion cell as a function of anode capacity (C_A), including masses of other required internal components and case. Capacities of cathodes considered were 140 and 200 mAh g⁻¹.

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) LiPF6 濃度 1mol/l
- 品質指標: 密度(25°C) 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°C) 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.

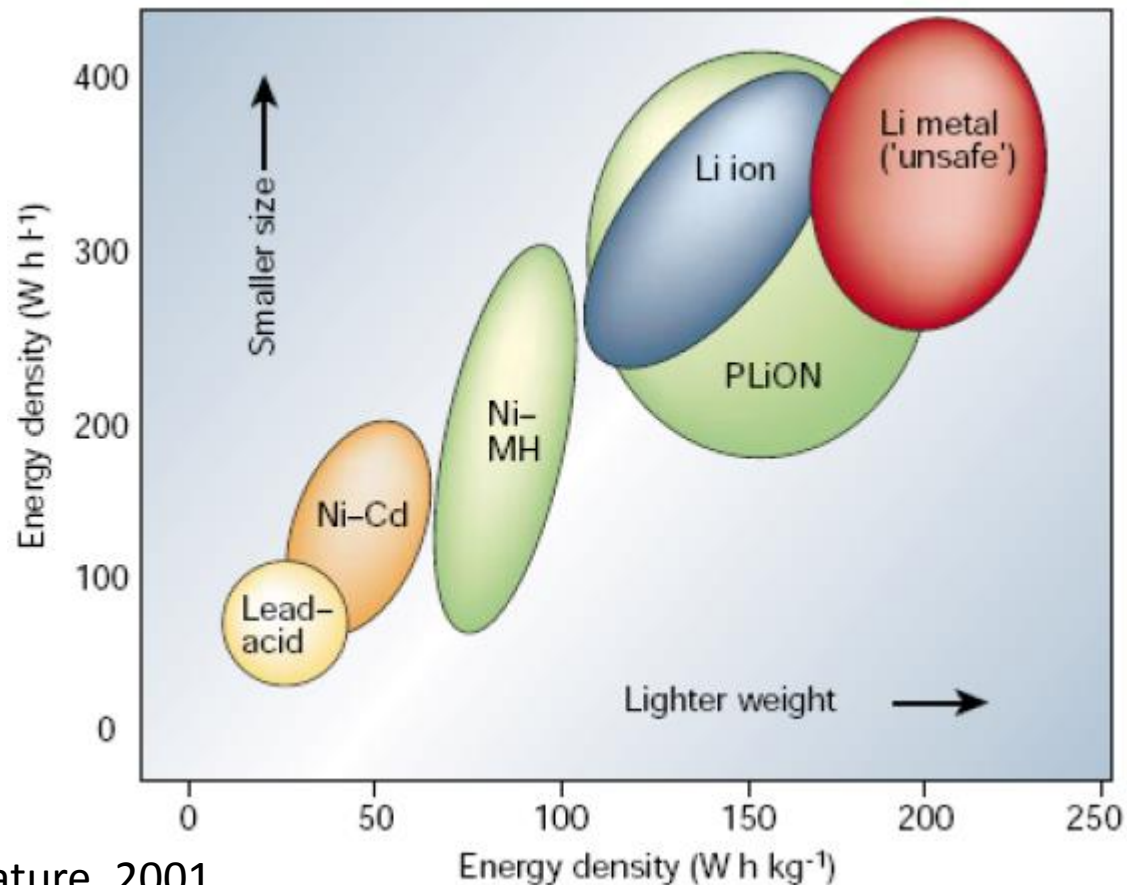


表 1：鋰離子電池/鎳鎘電池/鎳氫電池主要性能比較

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

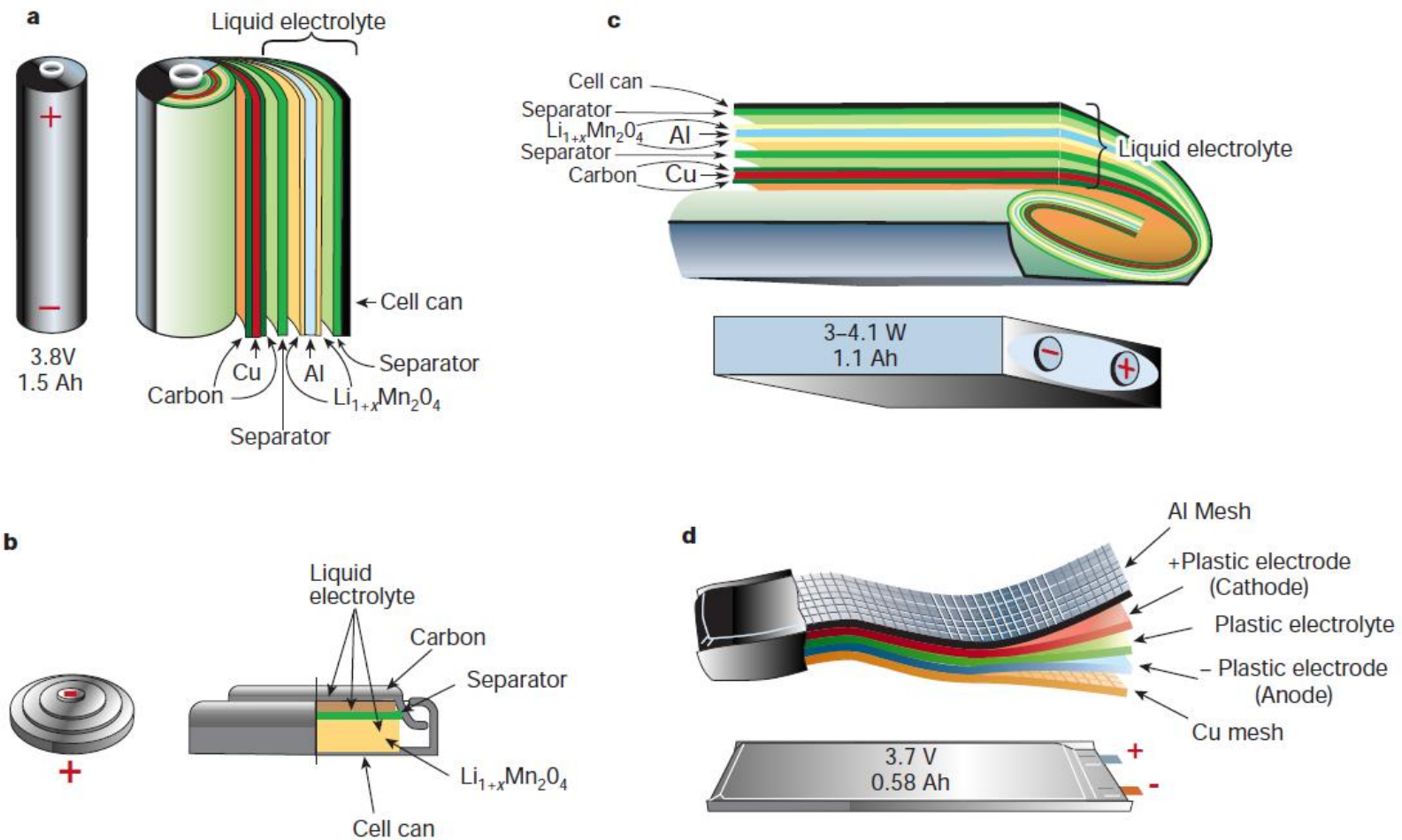


Figure 4 Schematic drawing showing the shape and components of various Li-ion battery configurations. **a**, Cylindrical; **b**, coin; **c**, prismatic; and **d**, thin and flat. Note the

unique flexibility of the thin and flat plastic LiION configuration; in contrast to the other configurations, the PLiON technology does not contain free electrolyte.

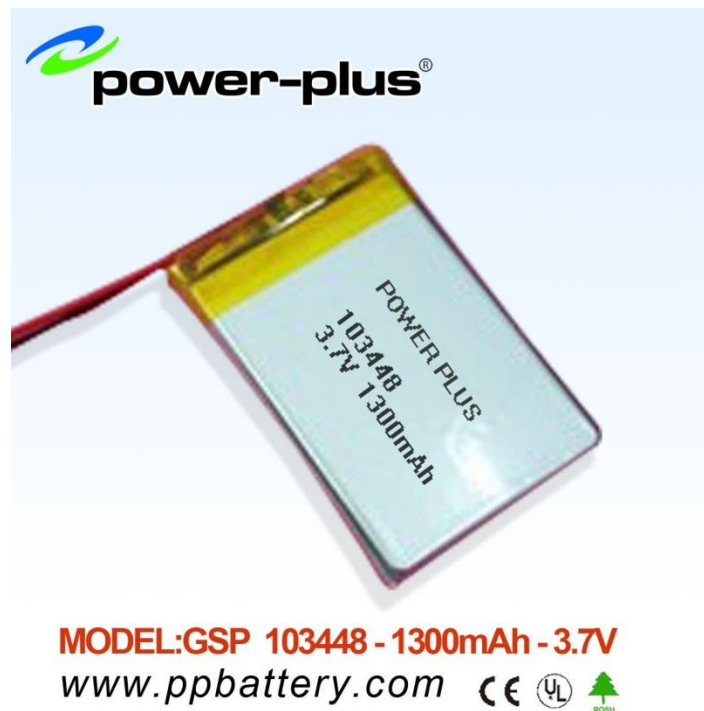
Types of lithium-ion batteries

- 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



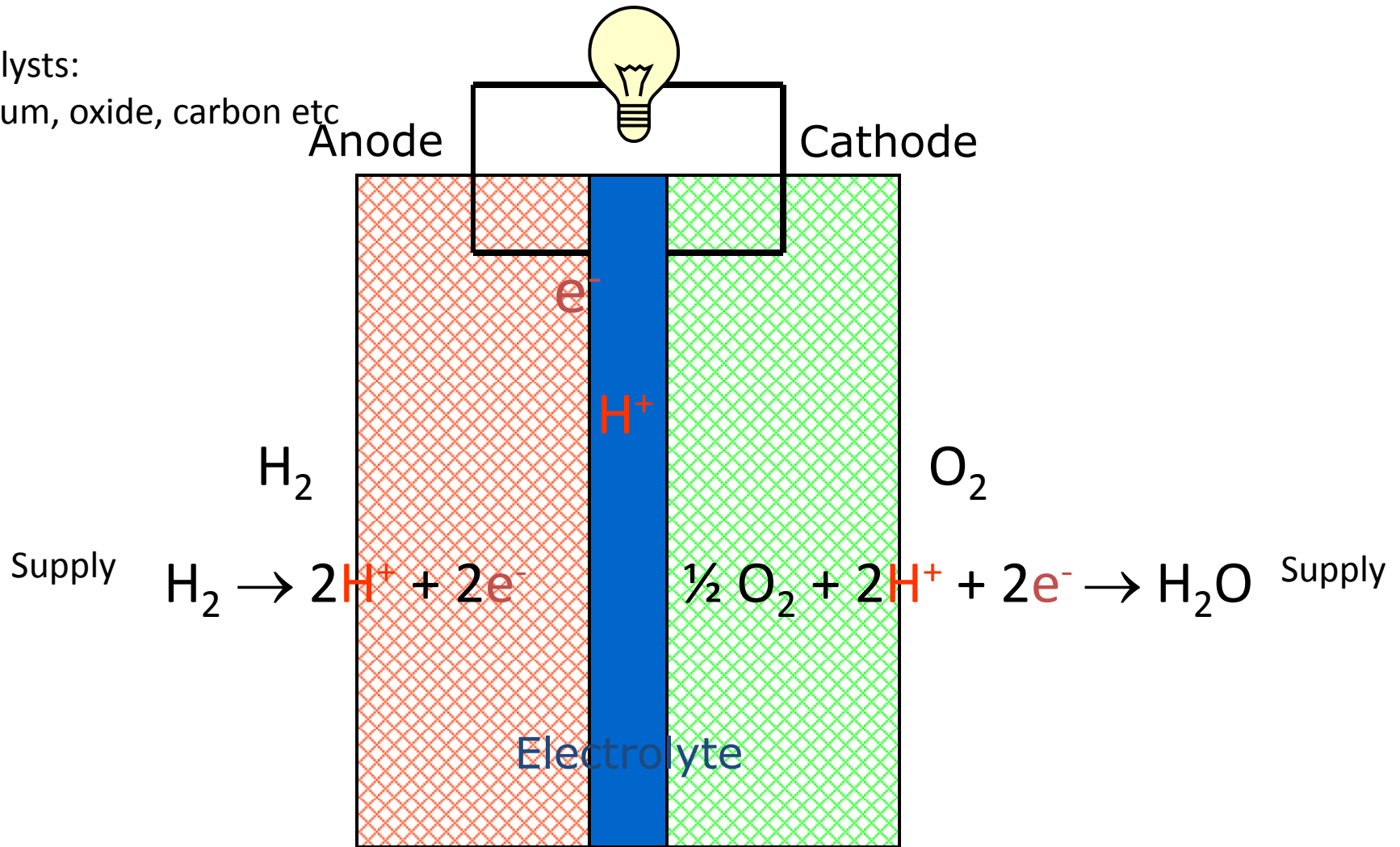
燃料電池 (Fuel Cell)

- 電池經由外界源源不絕提供可產生反應的物質，藉此持續產生能量。
- 燃料電池電極本身不具活性物質，只是個電催化元件。
- 燃料電池獲得未發生化學反應的物質（燃料）的供應，並製造出電能後，就會將發生過化學反應的物質排出，不會囤積在電池內部，只要能持續提供燃料，即可持續的製造出電能

Fuel Cell: Principle of Operation

Catalysts:

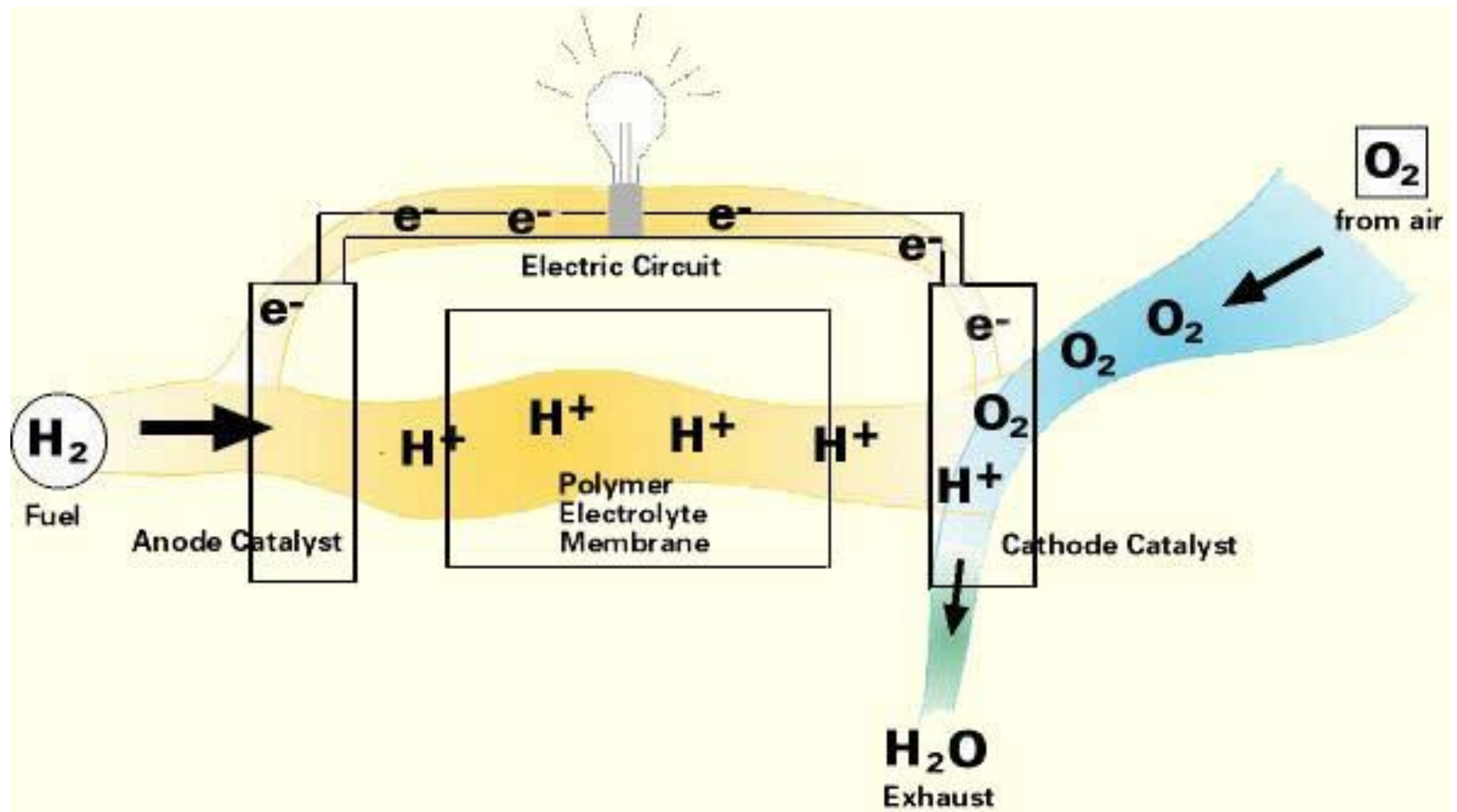
Platinum, oxide, carbon etc



燃料電池發展史

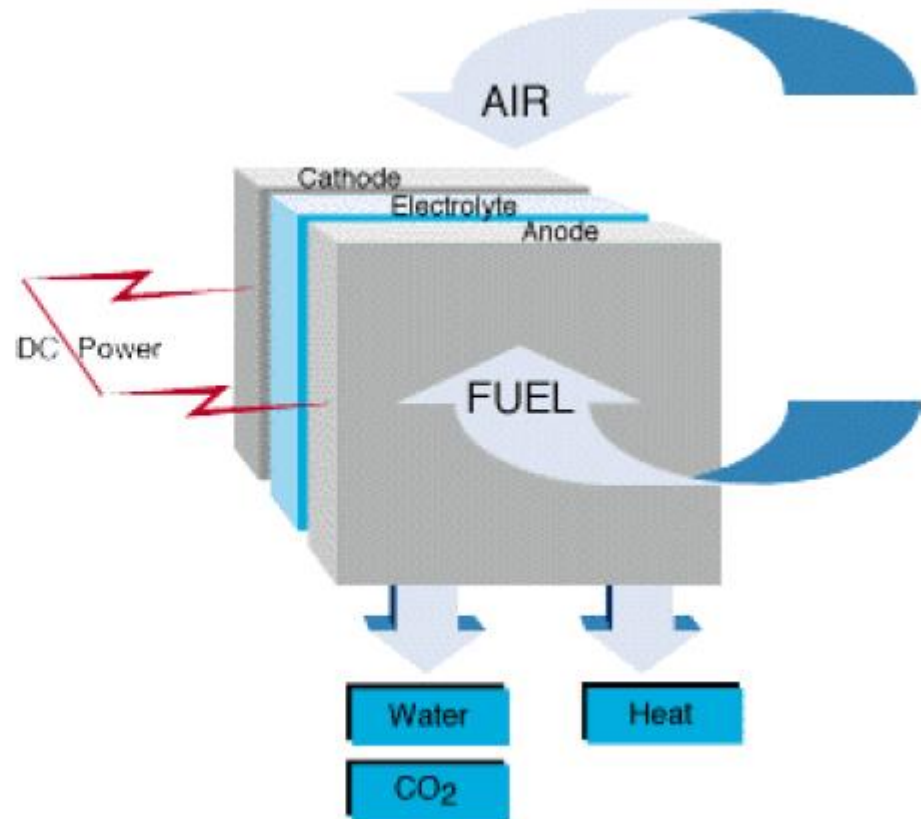
	1800	
Schoenbein (1838) Grove (1839)		發現燃料電池原理 發明燃料電池(當時稱作「氣體電池」)
	1850	
Mond and Langer (1889)		「氣體電池」正名為「燃料電池」
	1900	
Reid (1902)		提出鹼性燃料電池概念(專利)
Schmid (1923) Heise (1932)		提出氣體擴散電極概念 開發出以蠟為疏水劑之疏水電極
	1950	
Bacon (1959) Allis-Chalmers (1959)		開發出可工作之 6 kW 鹼性燃料電池 開發出鹼性燃料電池農用曳引機
GE, Grubb and Niedrach (1960)		開發出「Grubb-Niedrach 燃料電池」
GE, Gemini Space Mission (1962)		應用高分子電解質燃料電池於雙子星太空任務
GE and Union Carbide (1965)		應用 Teflon [®] 於疏水氣體擴散電極
P&W, Apollo Space Mission (1965)		應用鹼性燃料電池於阿波羅太空任務
Dupont (1972)		杜邦開發出 Nafion [®] 質子交換膜
P&W, TARGET (1967-1976)		普惠主導「目標」之磷酸燃料電池開發計畫
Moonlight Project (1981-1992)		「月光計畫」—— 日本首度進行之燃料電池開發計畫
Jet Propulsion Laboratory (1992)		JPL 首度將 Nafion [®] 膜應用於直接甲醇燃料電池
Ballard Power System (1993)		巴拉德推出質子交換膜燃料電池電動車
CaFCP (1998)		「加州燃料電池夥伴聯盟」成立
	2000	
Toyota & Honda (2002)		以租用方式正式推出燃料電池乘客車
Hydrogen Fuel Initial (2003)		美國政府推出「自由車」燃料電池電動車發展計畫
Freedom Fuel (2003)		美國政府推出「燃料解放」氫能發展計畫
International Partnership for the Hydrogen Economy (2003)		17 個國家地區組成氫能經濟國際合作組織

How does a Fuel Cell work?



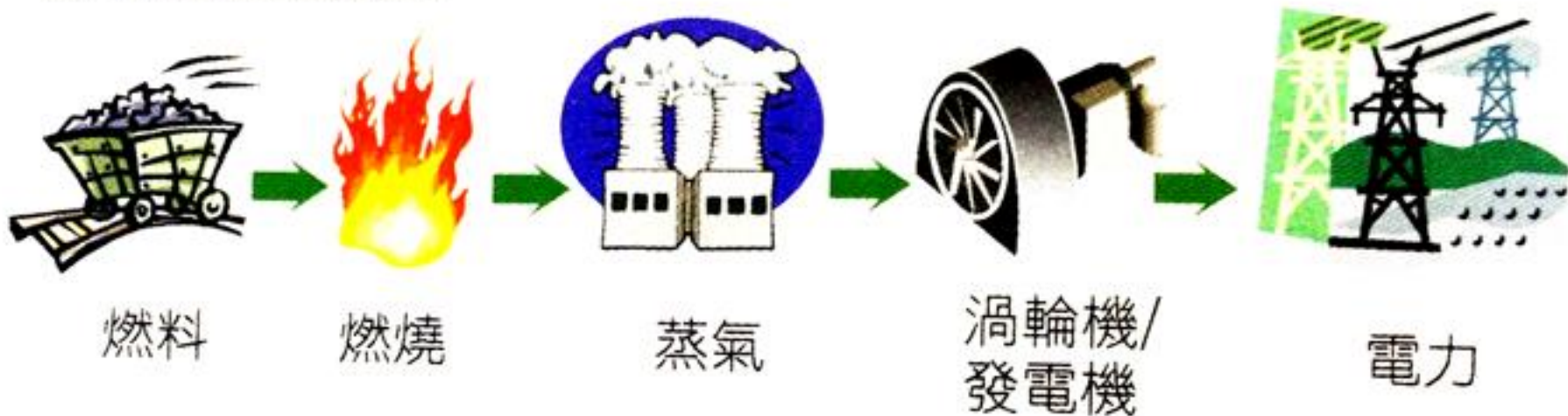
How a fuel cell function

- Unlike battery, fuel cell **does not run down or require recharging**.
- Fuel cell consists of two electrodes sandwiched around an electrolyte.
- Encouraged by catalysts, **H₂ (fuel)** and **O₂ (air)** occur anodic and cathodic reaction (with electrons create a separate current) then generate **electricity, water** and **heat** by chemical reaction.

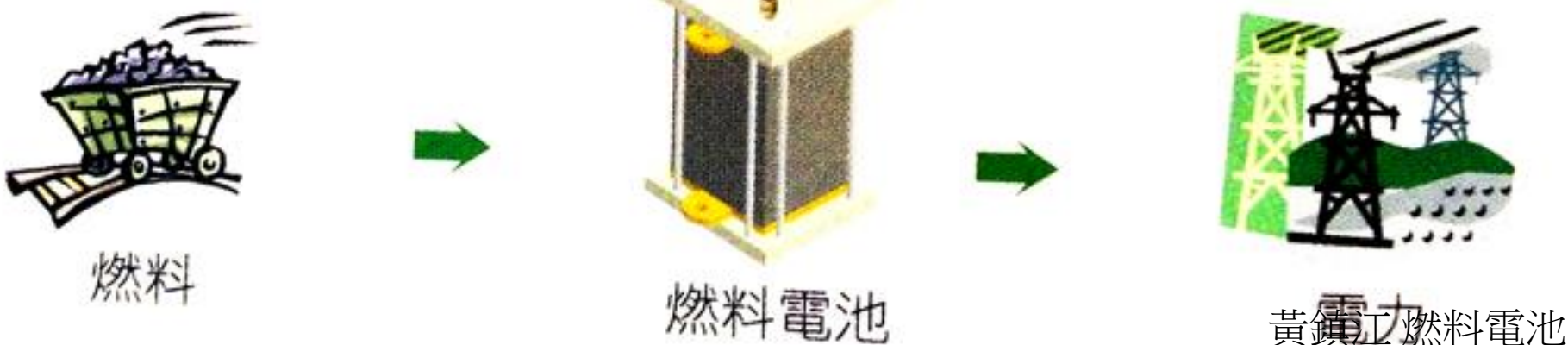


燃料電池與傳統熱機的火力發電比較

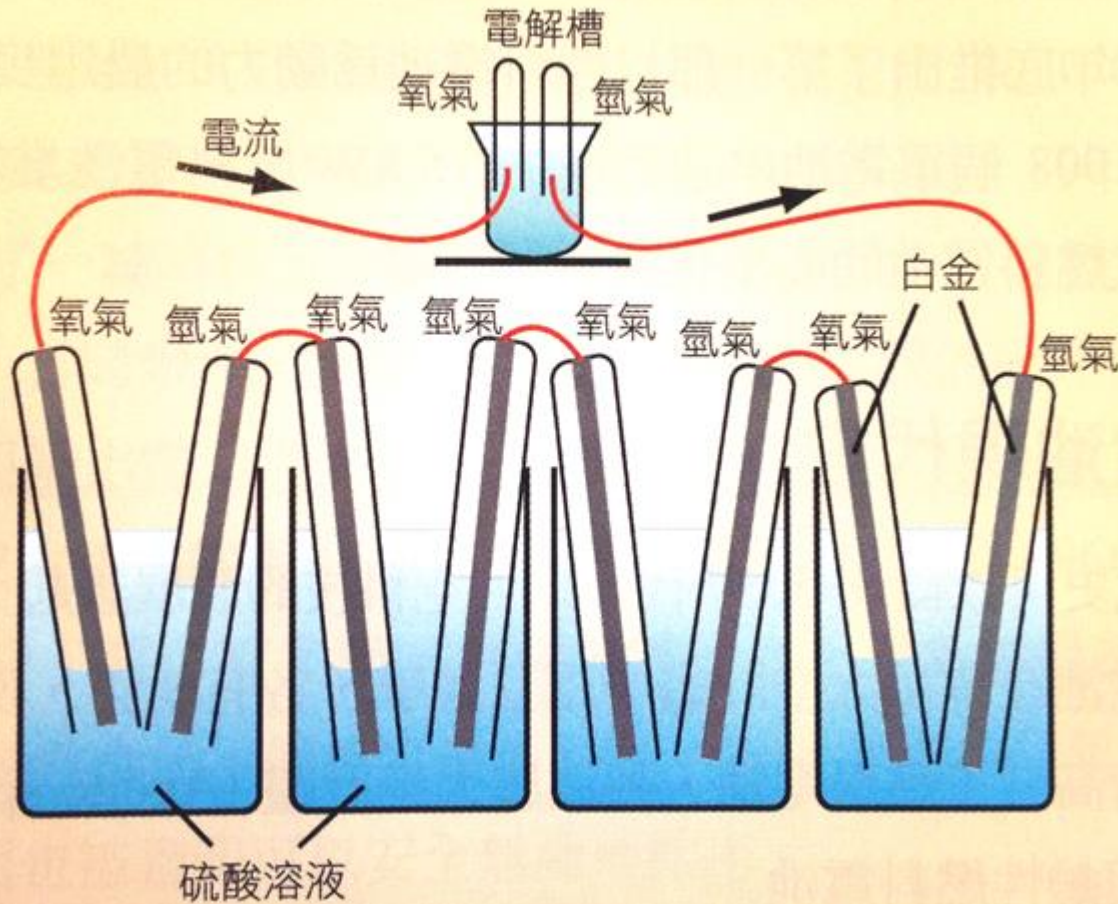
(a) 傳統熱機發電



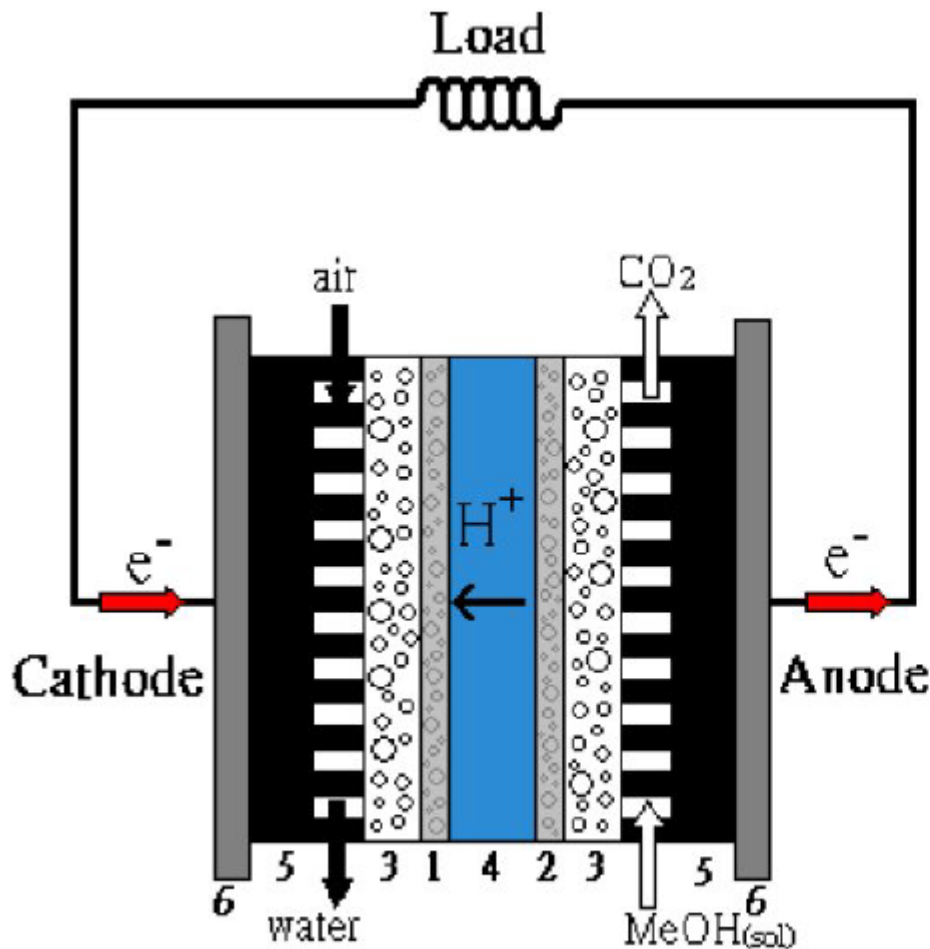
(b) 燃料電池發電



Willam R. Grove 進行的氣體電池實驗



DMFC, direct methanol fuel cell



Anode

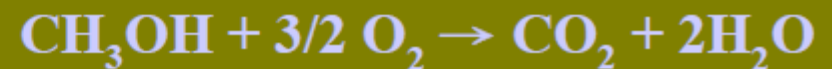


Electrolyte

Cathode



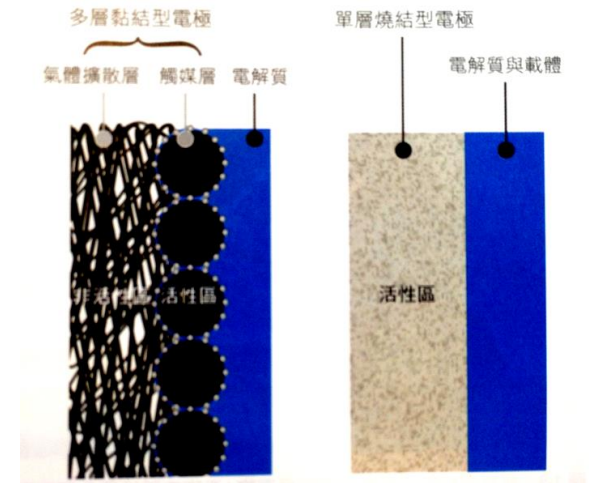
Overall



觸媒與多孔氣體擴散電極

表 1-5 燃料電池使用觸媒電極結構之比較

種類	AFC	PEMFC	PAFC	MCFC	SOFC
陽極觸媒	雷尼鎳、鉑/碳	鉑/碳	鉑/碳、鉑鈣/碳	鎳-鉻合金、鎳-鋁合金	鎳/YSZ
陰極觸媒	雷尼鎳、鉑/碳	鉑/碳	鉑/碳	鋰化-氧化鎳	摻錫錳酸鎳
電極結構	單層雷尼鎳電極或 多層黏結型電極	多層黏結型電極	多層黏結型電極	單層燒結型電極	單層燒結型電極



- 主要可分為單層燒結型電極以及多層的黏結型電極
- 單層：將金屬觸媒與電解質之混合粉末以燒結方式製作多孔結構
- 多層：在高分散型觸媒內填加黏結劑 (PTFE)後黏貼至氣體擴散層上。擴散區為非活性區

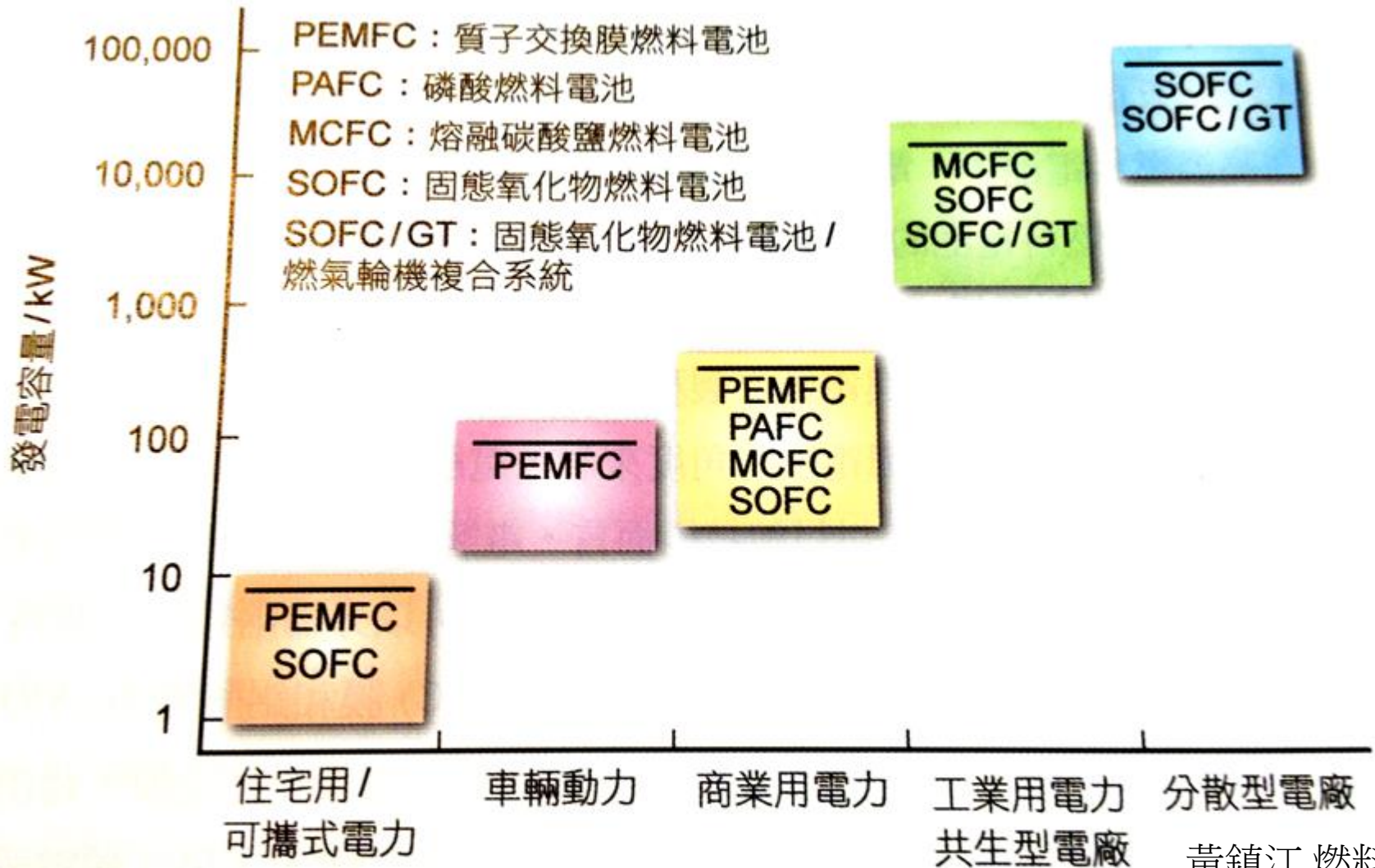
燃料電池用燃料系統之比較



燃料電池的分類

- 依電解液性質可分為五類
 - 1) 鹼性燃料電池 (alkaline fuel cell, AFC)
 - 2) 磷酸燃料電池 (phosphoric acid fuel cell, PAFC)
 - 3) 質子交換燃料電池 (proton exchange membrane fuel cell, PEMFC)
 - 4) 熔融碳酸鹽燃料電池 (molten carbonate fuel cell, MCFC)
 - 5) 固態氧化物燃料電池 (solid oxide fuel cell, SOFC)

燃料電池發電容量與適用範圍



燃料電池特點

- 效率高：目前工作的燃料電池效率可達**40-60%**，平均單位質量燃料所產生的電能，僅次於核能
- 噪音低：結構簡單且沒有運轉機件
- 污染低：氫氣為主要燃料。
- 進料廣：只要含有氫原子的物質都可以當作燃料來源，包括天然氣、石油、燃煤、酒精、甲醇。
- 用途多：可提供的電力範圍在**1W~1000MW**間

Fuel Cell

