

Chapter 17:

Electrochemistry

The study of the interchange of chemical and electrical energy

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Half-Reactions

The overall reaction is split into two **half-reactions**, one involving oxidation and one reduction.



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Review of Terms

oxidation-reduction (redox) reaction: involves a transfer of electrons from the reducing agent to the oxidizing agent.

- **oxidation (氧化):** loss of electrons
- **reduction (還元):** gain of electrons

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17.1 Galvanic Cells

(Voltaic Cell)

A device in which chemical energy is changed to electrical energy

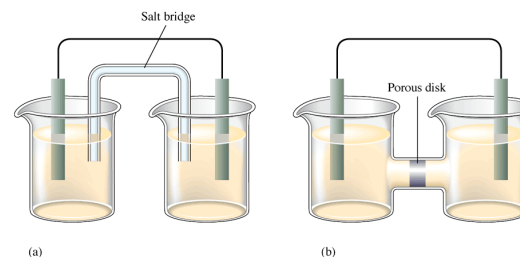
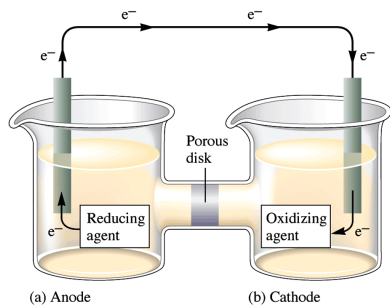


Fig. 17.2: Galvanic cells can contain a salt bridge as in (a) or a porous-disk connection as in (b).

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Fig. 17.3: An electrochemical process involves electron transfer at the interface between the electrode and the solution. (a) The species in the solution acting as the reducing agent supplies electrons to the anode. (b) The species in the solution acting as the oxidizing agent receives electrons from the cathode.

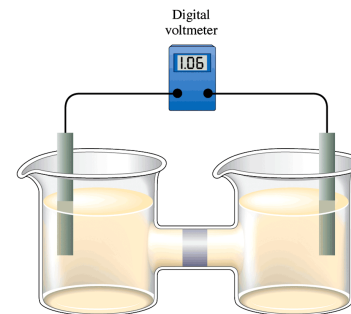


• **Oxidation**
occurs at the
Anode.

• **Reduction**
occurs at the
Cathode.

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Fig. 17.4: Digital voltmeters draw only a negligible current and are convenient to use.



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Cell Potential

Cell Potential or Electromotive Force (emf):
The “pull” or driving force on the electrons.

單位: V (1 V = 1 J/C)

測量工具:

- **Voltmeter:** 有微小電流，造成能量損耗
故所測得之 $V < E_{\text{cell}}$
- **Potentiometer:** 加一反向電壓，直到電流為零
故無能量損耗，測得 $V = E_{\text{cell}}$

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17.2 Standard Reduction Potentials

標準還原電位

The E° values corresponding to reduction half-reactions with all solutes at 1M and all gases at 1 atm.

標準氫電極 (standard hydrogen electrode, SHE)



Where $[\text{H}^+] = 1 \text{ M}$, $P_{\text{H}_2} = 1 \text{ atm}$

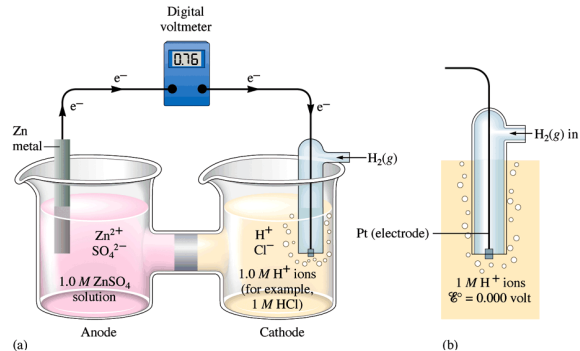
以 SHE 為參考電極可定出其他半反應之電位，例如:



$E^\circ = 0.20 \text{ V vs. SHE}$

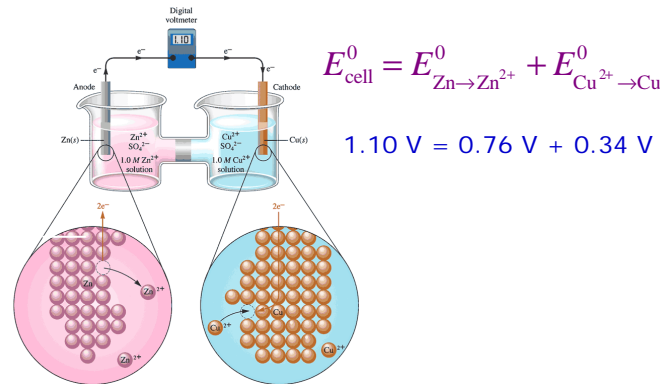
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Fig. 17.5: (a) A galvanic cell involving the reactions $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ (at the anode) and $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (at the cathode) has a potential of 0.76 V. (b) The standard hydrogen electrode where $\text{H}_2(\text{g})$ at 1 atm is passed over a platinum electrode in contact with 1 M H^+ ions. This electrode process (assuming ideal behavior) is arbitrarily assigned a value of exactly zero volts.



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Fig. 17.6: A galvanic cell involving the half-reactions $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ (anode) and $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ (cathode), with $E^0_{\text{cell}} = 1.10 \text{ V}$.



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TABLE 17.1 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	E^0 (V)	Half-Reaction	E^0 (V)
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	2.87	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	0.40
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	1.99	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.34
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	1.82	$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	0.27
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.78	$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	0.22
$\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$	1.70	$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	0.20
$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	1.69	$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	0.16
$\text{MnO}_2 + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO} + 2\text{H}_2\text{O}$	1.68	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
$2\text{e}^- + 2\text{H}^+ + \text{IO}_3^- \rightarrow \text{I}_2 + \text{H}_2\text{O}$	1.60	$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.036
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	1.50	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
$\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$	1.46	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.23
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.36	$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.35
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.40
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.23	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.21	$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.50
$\text{IO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightarrow \frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O}$	1.20	$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.73
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.09	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$	1.00	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83
$\text{AuCl}_4^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{Cl}^-$	0.99	$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	0.96	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
$\text{ClO}_2 + \text{e}^- \rightarrow \text{ClO}_2^-$	0.954	$\text{H}_2 + 2\text{e}^- \rightarrow 2\text{H}^-$	-2.23
$2\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	0.91	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.37
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.80	$\text{La}^{3+} + 3\text{e}^- \rightarrow \text{La}$	-2.37
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	0.80	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	0.77	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.76
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	0.68	$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}$	-2.90
$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	0.56	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.92
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	0.54	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	0.52		

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當結合 2 half-reactions 得到平衡之氧化還原反應式時，有兩點注意事項：

1. The sign of the potential for the reversed half-reaction also must be reversed.
2. The value of E^0 is not changed when a half-reaction is multiplied by an integer.

Sample Exercise 17.1

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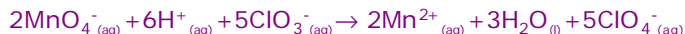
Line notation: to describe electrochemical cells

Anode 寫在左邊、**Cathode** 寫在右邊

例如: a galvanic cell based on



Line notation 為: $\text{Mg}(\text{s})|\text{Mg}^{2+}(\text{aq})||\text{Al}^{3+}(\text{aq})|\text{Al}(\text{s})$



Line notation 為:

$\text{Pt}(\text{s})|\text{ClO}_3^{-}(\text{aq}), \text{ClO}_4^{-}(\text{aq}), \text{H}^{+}(\text{aq})||\text{MnO}_4^{-}(\text{aq}), \text{Mn}^{2+}(\text{aq}), \text{H}^{+}(\text{aq})|\text{Pt}(\text{s})$

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17.3 Cell Potential, Electrical Work, and Free Energy

emf = potential difference (V) = $\frac{\text{work (J)}}{\text{charge (C)}}$

$$E = \frac{-w}{q}$$

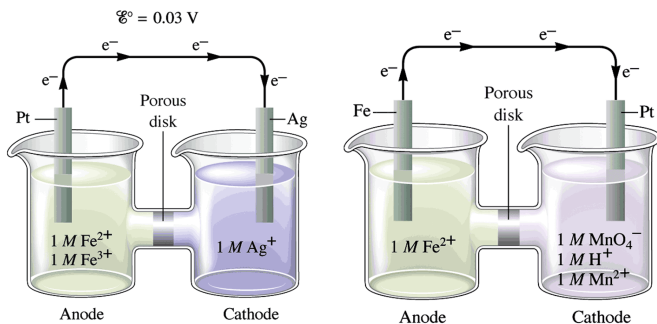
w 是以系統而言，系統對外作功， $w < 0$ ，故加“-”以得正值之 E 。

$$-w_{\text{max}} = qE_{\text{max}} \quad \text{or} \quad w_{\text{max}} = -qE_{\text{max}}$$

In any real spontaneous process, some energy is always wasted – the actual work realized is always less than the calculated maximum.

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Fig. 17.7: The schematic of two galvanic cells



What is the line notation for each cell?

Read textbook!

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$$\Delta G = -nFE$$

$$\Delta G^\circ = -nFE^\circ$$

n = number of moles of electrons

F = Faraday = 96,485 coulombs per mole of electrons

$$E > 0 \Rightarrow \Delta G < 0 \text{ ----- spontaneous}$$

Sample Exercise 17.3 & 17.4

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Michael Faraday lecturing at the Royal Institution before Prince Albert and others (1855). The faraday was named in honor of Michael Faraday (1791-1867), an English-man who may have been the greatest experimental scientist of the nineteenth century. Among his many achievements were the invention of the electric motor and generator and the development of the principles of electrolysis.

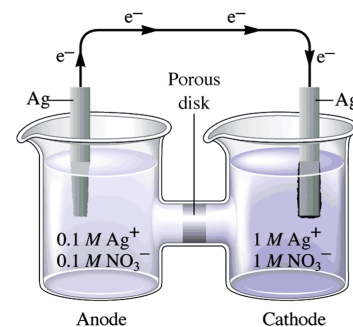


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Concentration Cell

濃度電池: a cell in which both compartments have the same components but at different concentrations.

例如:



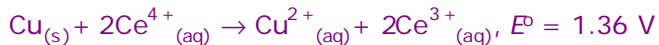
自然會傾向使 [Ag⁺] 相同的方向進行反應。

一般濃度電池的 cell potential 都不大。

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17.4 Dependence of Cell Potential on Concentration

例如:



如果將 [Ce⁴⁺] ↑ (即 [Ce⁴⁺] > 1 M) ⇒ E_{cell} ↑

而若將 [Cu²⁺] or [Ce³⁺] ↑ ⇒ E_{cell} ↓

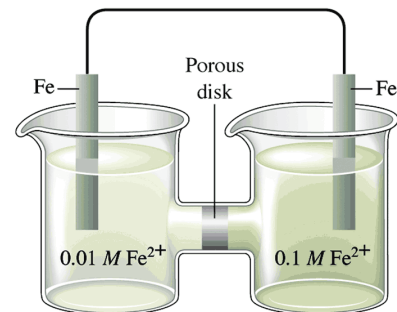
可根據 Le Châtelier's principle 判斷

Sample Exercise 17.5

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Sample Exercise 17.6

Determine the direction of electron flow and designate the anode and cathode for the cell represented below.



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The Nernst Equation

With Nernst equation, we can calculate the potential of a cell in which some or all of the components are not in their standard states.

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

$$\therefore \Delta G = -nFE \text{ and } \Delta G^\circ = -nFE^\circ$$

$$-nFE = -nFE^\circ + RT \ln(Q)$$

$$E = E^\circ - \frac{RT}{nF} \ln(Q) \text{ or } E = E^\circ - \frac{2.303RT}{nF} \log(Q)$$

$$\text{at } 25^\circ\text{C}, E = E^\circ - \frac{0.0591}{n} \log(Q)$$

Sample Exercise 17.7

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Ion-selective electrodes

Cell potential is sensitive to concentrations of the reactants & products

可藉測量 E 來定量特定離子濃度，例如 pH meter。

pH meter 由下列三部份組成：

- (1) a standard electrode of known potential
- (2) a special glass electrode that changes potential depending on the conc. of H^+ in the solution where it is dipped
- (3) a potentiometer

TABLE 17.2

Some Ions Whose Concentrations Can Be Detected by Ion-Selective Electrodes

Cations	Anions
H^+	Br^-
Cd^{2+}	Cl^-
Ca^{2+}	CN^-
Cu^{2+}	F^-
K^+	NO_3^-
Ag^+	S^{2-}
Na^+	

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Calculation of Equilibrium Constants for Redox Reactions

Nernst equation 所計算的 E 為電池放電前之 maximum potential，一旦開始放電，濃度改變， E 亦隨之改變 (\downarrow) 直到達到平衡。

At equilibrium, $Q = K$ and $E_{\text{cell}} = 0$

$$\text{Nernst equation : } E = E^\circ - \frac{RT}{nF} \ln(Q)$$

$$E^\circ = \frac{RT}{nF} \ln(K) \Rightarrow \ln(K) = \frac{nFE^\circ}{RT}, \log(K) = \frac{nFE^\circ}{2.303RT}$$

$$\text{at } 25^\circ\text{C}, \log(K) = \frac{nE^\circ}{0.0591}$$

Sample Exercise 17.8

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17.5 Batteries

A **battery** is a galvanic cell or, more commonly, a group of galvanic cells connected in series.

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電池設計與原理

電池為一將化學能轉換成電能的裝置，因具有可攜帶、多種組合、高能量密度以及無排放噪音與廢氣的優點，所以在許多的領域受到普遍的應用。

構成電池的四個主要部分為

- **電極 (electrode):** 依其所發生的氧化或還原反應又有陽極 (負極; anode) 與陰極 (正極; cathode) 之分。
- **電解液 (electrolyte)**
- **隔離膜 (separation film):** 為隔離電極的裝置，以避免兩極上的活性物質直接接觸而造成電池內部的短路。
- **罐體 (shell):** 作為電池的外殼，主要用以保護內部結構，所以需要有良好的機械結構、耐熱耐震動耐腐蝕等性能。常見的罐體造型有圓筒型、方型、鈕扣型等。

<http://www.nsc.gov.tw/dept/acro/version01/battery/basictheory.htm> 25

電池的種類

電池可透過電池本身的充放電特性與工作性質大致分類如下：

§ 一次電池 (primary cell)

僅能被使用一次的電池，無法透過充電的方式再補充已被轉化掉的化學能，故稱為一次電池。此類電池常見的有乾電池、水銀電池與鹼性電池等。

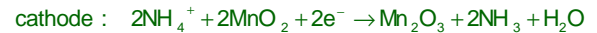
一次電池的應用最早也最為廣泛，市面上販售的不可充電電池幾乎皆屬此類，如鈕扣型水銀電池、1 號、2 號以及 3 號電池等等。



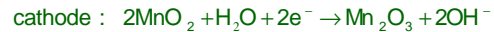
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➤ 乾電池 (dry cell battery), cell potential ~ 1.5 V

Acid version:



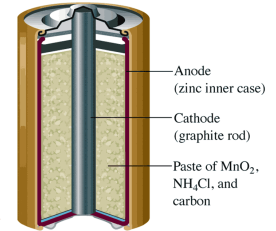
Alkaline version:



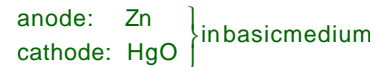
The alkaline dry cell lasts longer mainly because Zn anode corrodes less rapidly under basic conditions.

鋅錳乾電池的保存相當重要，若置於高溫潮濕的環境中，會使陽極的鋅產生腐蝕而造成嚴重的自放電情形。此外，鋅錳乾電池的密封良好度也相當重要；若密封不佳，電解液中的水分會揮發掉，使電池無法放電，另一方面也可能因氧的進入而造成自放電率加劇。

Fig. 17.14: A common dry cell battery ⇒



➤ 水銀電池 (mercury cell), cell potential ~ 1.34 V



因電解液為鹼性故屬鹼性電池，常見除鈕扣型外亦有圓筒型。負極使用 90% 的鋅粉與 10% 的汞製成，正極則為 80~95% 的氧化汞與 5~15% 的石墨組成，電解液是 35~40% 的氫氧化鉀溶液。此類電池放電平穩、開路電壓穩定、易保存且有相當高的體積能量比，於 25 時具有 1.34V 的放電電壓。因此適用於助聽器或相機上。

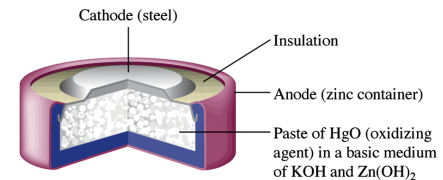


Fig. 17.15: A mercury battery of the type used in calculators.

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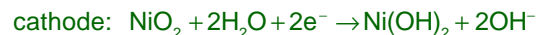
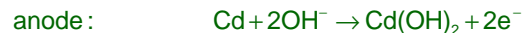
§ 二次電池 (secondary battery)

二次電池所指的就是可以被重複使用的電池。透過充電的過程，可以使得電池內的活性物質再度的回復到原來的狀態，因而能再度的提供電力。這類的電池有鉛蓄電池 (lead storage battery)、鎳鎘電池 (nickel cadmium battery)、鎳氫電池 (nickel hydrogen battery)、二次鋰電池 (secondary lithium battery) 以及鋰離子電池 (lithium ion battery) 和高分子鋰電池 (polymer lithium battery) 等。



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➤ 鎳鎘電池 (nickel-cadmium (Ni-Cd) battery)



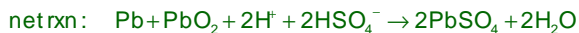
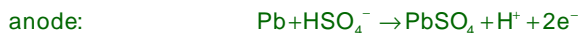
鎳鎘電池電壓值為 1.2V，體積能量密度約 130~200 Wh/L，重量能量密度則在 40~50 Wh/kg 間。因發展已久，成本較低；再加上循環壽命長達 2000~4000 次，及大電流放電的特性、適用溫度範圍廣、自放電率小等優點，故佔有率頗高。不過受到“記憶效應”的影響，效能會隨充放電次數增加而下降。鎳鎘電池的市場佔有率在數年前相當高，但受到環保意識抬頭的影響，有鎘污染疑慮的鎳鎘電池佔有率已逐年下降。

➤ 鎳氫電池

鎳氫電池與鎳鎘電池相似，但鎳氫電池的陰極活性物質則是儲氫合金。所能提供的電壓約為 1.2 V，具有不錯的能量密度 (50 ~ 60 Wh/kg or 250 ~ 300 Wh/L)，及良好的循環壽命。因不含鎘，不會像鎳鎘電池有鎘污染的問題。但鎳氫電池在高溫下效能較差，且在一般使用上有自放電率高及記憶效應的問題。

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➤ 鉛蓄電池 (lead storage battery)



鉛蓄電池在 25 時能提供 ~2V 的電壓。具有電動勢大、操作溫度廣、結構簡單、技術成熟與價格低廉等的優勢，再加上良好的循環壽命，使得此種電池的產量與產值在電池產出中具有相當重要的地位。其應用以汽機車領域為主，或用於 UPS、無線電機、緊急照明設備、通信電機以及工業用電機設備等處。此外，也使用於電廠中，作為緊急的電力來源之用。

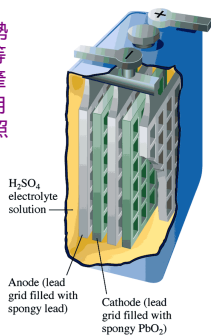
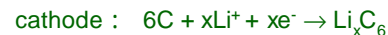
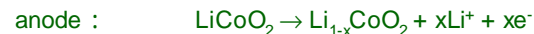


Fig. 17.13: One of the six cells in a 12-V lead storage battery. The anode consists of a lead grid filled with spongy lead, and the cathode is a lead grid filled with lead dioxide. The cell also contains 38% (by mass) sulfuric acid.

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➤ 鋰離子電池 (lithium ion battery)

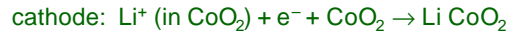
鋰離子電池以鋰鈷氧化物、鋰錳氧化物、鋰鎳氧化物等作為陽極活性材料，在陰極材料的部分則為碳材料，電解質也有許多種可能 LiPF₆、LiClO₄、LiBF₄等，使用有機電解液。電壓可達到3.6V，而能量密度為 250~300 Wh/L(或90~110 Wh/kg)。該電池具有相當高的能量密度及工作電壓，再加上長循環壽命與較無記憶效應的特性，使得鋰離子二次電池佔有率日益上升。但其成本過高，過充、放電時有安全顧慮而需保護迴路等問題仍是需要克服的缺點。



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➤ 高分子鋰離子電池 (polymer lithium ion battery)

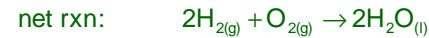
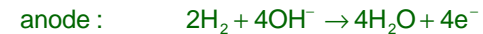
高分子鋰離子電池以高分子電解質取代液態鋰離子電池所使用的有機電解液，以避免後者容易揮發燃燒與造成漏液的現象，使高分子鋰電池有更佳的安全性。此種高分子電解質，一方面可作為傳導離子的媒介、一方面又可作為隔離膜用，再加上與鋰金屬的反應性低，故在安全性方面受到的質疑較小，也因此受到廣泛研究與開發。分類上，高分子鋰離子電池因所使用的高分子電解質有不同而有完全固態的固態高分子電解質與加入可塑劑的膠態高分子電解質兩類。



the most promising new reusable battery

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➤ 氫氧燃料電池 (hydrogen oxygen fuel cell)



此種 fuel cells 已用於 space vehicles

Cars powered by fuel cells are being tested.

H₂ 目前多來自於分解天然氣中的 CH₄，可直接使用 CH₄ 之新型 fuel cell 正在開發中。

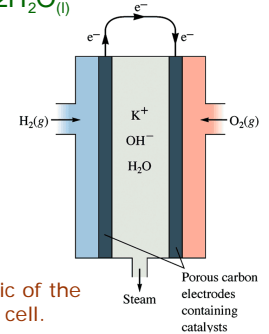


Fig. 17.16: Schematic of the hydrogen-oxygen fuel cell.

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§ 燃料電池 (fuel cell)

與前述兩者有相當大的不同，又被稱為連續電池。特色是陰陽兩極並無活性物質的存在，而是透過外部的系統提供，所以只要持續地提供活性物質，電池就可以持續的放電。在陽極部分，真正進行氧化反應的是空氣或是氧氣；而陰極部分則是以氫或者是煤氣等為主。此類電池如氫氧燃料電池 (hydrogen oxygen fuel cell) 等。

此類電池尚在發展中，且受限於其較大的體積，主要用在發電機組上或最為備用能源。近來由於技術的提昇，有逐漸小型化的趨勢，並運用於電動車輛等領域。

§ 其他

太陽能電池 (solar cells)、熱起電力電池等

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A gathering of several cars powered by fuel cells (Los Angeles Memorial Coliseum).

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17.6 Corrosion

- Corrosion involves oxidation of the metal.
- ~1/5 年產之鋼鐵是用以 replace rusted metal.
- 由 Table 17.1 可看出除了Au外，常用為 structural or decorative 用之金屬的 standard reduction potentials 均比 O₂ 小 (less positive).
- Some metals, such as copper, gold, silver and platinum, are relatively difficult to oxidize. These are often called noble metals.



⇒ 故 Au 在空氣中不會氧化

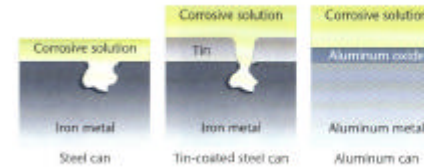
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Prevention of Corrosion

☆ 改變鐵的“體質” – 添加鉻 (Cr) & 鎳 (Ni)，即為不鏽鋼

☆ 覆蓋“金鐘罩”

- 鍍金、銀等貴重金屬
- 鍍鋁以於表面形成緻密氧化鋁層
- 犧牲打 (galvanizing): 鍍活性較高之金屬，如鋅或錫
- 塗佈無機鹽類，上釉
- 塗佈油漆

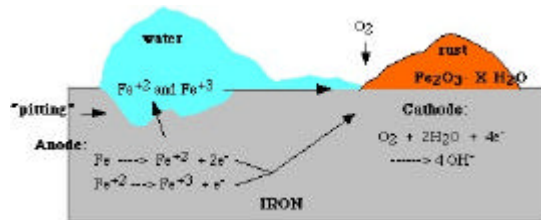


A tin coating offers some protection to the iron. However, if a hole or crack develops in the thin tin coating, the underlying iron corrodes rapidly. A tin-coated steel can will degrade completely in about 100 years. The aluminum oxide coating on an aluminum can is tough and closely packed. It protects the underlying aluminum from further corrosion so that the can will take about 400 years to degrade.

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Corrosion of Iron

鐵鏽形成的 3 要件: 鐵、氧氣、水



- $\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^{-}$
 - $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^{-}$
 - $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^{-} \rightarrow 4\text{OH}^{-}(\text{aq})$
- $$2\text{Fe}^{3+}(\text{aq}) + 6\text{OH}^{-}(\text{aq}) \rightarrow \text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$$

酸與鹽分均會加速鐵的生鏽

Fe₂O₃ 的水合 (hydration) 程度會影響鐵鏽的顏色

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☆ “cathodic protection” – a method most often employed to protect steel in buried fuel tanks and pipelines

▷ 以 active metal (如 Mg) 以導線連接至欲保護之 tank or pipeline，因為 Mg 比 Fe 為更好之 reducing agent，可防止 Fe 被氧化，但 Mg anode 須定期更換；ship’s hull 亦以類似法防鏽 (用 Ti)。

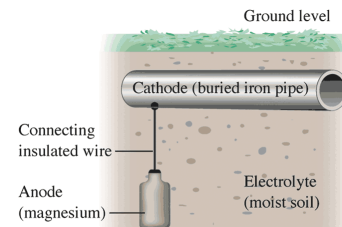
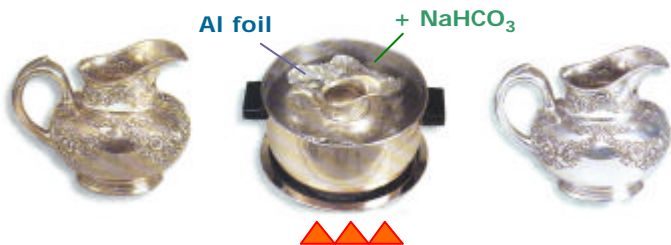


Fig. 17.18: Cathodic protection of an underground pipe.

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生活小撇步

銀器變黑了怎麼辦?



加 NaHCO_3 的目的:

- to help remove any aluminum oxide coating that forms
- to make the cleaning solution more conductive

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Stoichiometry of electrolysis

How much chemical change occurs with the flow of a given current for a specified time?

1. $Q = I \times t$ $1\text{A} = 1\text{C/s}$
2. $Q/F = \text{moles of } e^{-}$
3. 由 e^{-} 轉移數 \Rightarrow 求得 moles of species
4. 求出 mass of species

Sample Exercise 17.9 43

17.7 Electrolysis

- An electrolytic cell uses electrical energy to produce a chemical change that would otherwise not occur spontaneously.
- 生活中的重要例子: 電池充電、製鋁、chrome plating 等

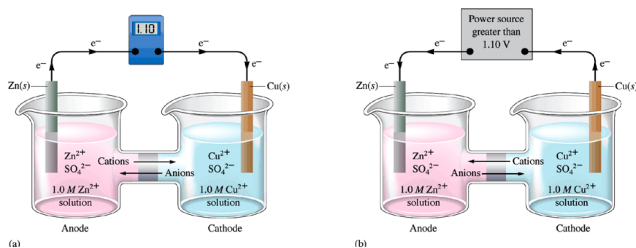
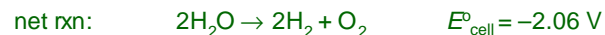
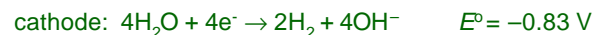
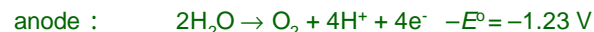


Fig. 17.19: A standard galvanic cell vs. a standard electrolytic cell.

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Electrolysis of water



於 pure water $[\text{H}^+] = [\text{OH}^-] = 10^{-7}\text{ M}$, 上述反應之 $E = -1.23\text{ V}$ 而實際上, 若以 Pt 為電極接 6V 電池, 放入純水中, 觀察不到任何反應 (ions 太少)。

加入少量電解質 (salts) 則可
加快反應進行。



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Electrolysis of mixture of ions

Suppose 某一溶液含 Cu^{2+} 、 Ag^+ 、 Zn^{2+} 。若外加電壓逐漸 turn up, metals being plated out onto the cathode 順序為何?



reduction of Ag^+ 最容易發生, 即氧化力: $\text{Ag}^+ > \text{Cu}^{2+} > \text{Zn}^{2+}$, 此亦為金屬於 cathode 析出之順序。

以 E° 預測電解產物時須注意 “overvoltage” 問題

例如: electrolysis of $\text{NaCl}_{(\text{aq})}$, 於 anode 產生 Cl_2 而非 O_2



因為氧化水須要施加比預期高許多之電壓, 此即稱 “overvoltage”, 過電壓之成因複雜。

Sample Exercise 17.10₅

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Production of aluminum

因為鋁的活性太高, 在自然界中和各種不同元素(尤其是氧)緊密地結合在一起, 很難提煉出來。鋁的生產, 初期是使用化學法, 利用活性高之鈉或鎂金屬將鋁還原出來; 法國於1855年採用化學法開始工業生產, 是世界最早生產鋁的國家。

以化學法煉鋁的成本極高, 在西元1886年之前, 鋁的價值甚至超過銀和金! 直到西元1886年, 年輕的美國歐柏林大學學生 Charles M. Hall 和法國化學家 Paul L. T. Héroult 於同年發現以電解法來提煉鋁的廉價方法, 大量地生產純鋁, 而使鋁的價格「一落千丈」。

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17.8 Commercial Electrolytic Processes

- Production of aluminum
- Electrorefining of metals
- Metal plating
- Electrolysis of sodium chloride
-

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TABLE 17.3
The Price of Aluminum over the Past Century

Date	Price of Aluminum (\$/lb)*
1855	100,000
1885	100
1890	2
1895	0.50
1970	0.30
1980	0.80
1990	0.74



Fig. 17.21: Charles Martin Hall (1863-1914)

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鋁礦砂 (bauxite): 主成分為 Al_2O_3

Al_2O_3 : m.p. = 2050 °C

$\text{Al}_2\text{O}_3 + \text{cryolite (Na}_3\text{AlF}_6) \Rightarrow \text{m.p.} = \sim 1000 \text{ °C}$

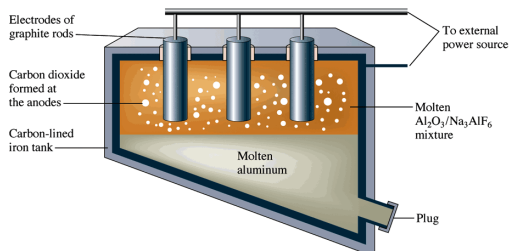


Fig. 17.22: A schematic diagram of an electrolytic cell for producing aluminum by the Hall-Heroult process.

Overall cell reaction: $2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al} + 3\text{CO}_2$

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Fig. 17.23: Ultrapure copper sheets that serve as the cathodes are lowered between slabs of impure copper that serve as the anodes into a tank containing an aqueous solution of copper sulfate (CuSO_4).

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Electrorefining of metals

Purification of metals is an important application of electrolysis. 例如: 銅的精煉純化

Anode: impure Cu $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$

Cathode: thin sheet of ultrapure Cu $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \underline{\text{Cu}}$

Electrolyte: $\text{CuSO}_4(\text{aq})$ 99.95% pure

於 anode 上, 除 Cu 被氧化外, 其他如 $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ 、 $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ 等亦會發生, 而 noble metal impurities 在所施電壓下則不會被氧化, 沉澱在底下形成 sludge, 為煉銅之重要副產品。

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Metal plating

例如: “tin cans” – steel cans with a thin Sn coating, chrome-plated steel bumper for cars 等

Anode: plating metal (欲鍍上之金屬)

Cathode: object to be plated (被鍍物)

Electrolyte: 含欲鍍金屬之 ions

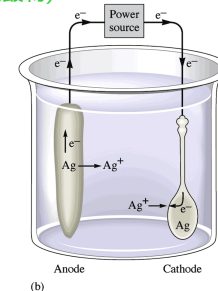


Fig. 17.24: (a) A silver-plated teapot. (b) Schematic of the electroplating of a spoon.

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Electrolysis of sodium chloride

電解熔融之 NaCl

NaCl: m.p. = 800°C

NaCl + CaCl₂ ⇒ m.p. = ~600°C

anode :



cathode:



Na must be stored in an inert solvent, such as mineral oil, to prevent its oxidation.

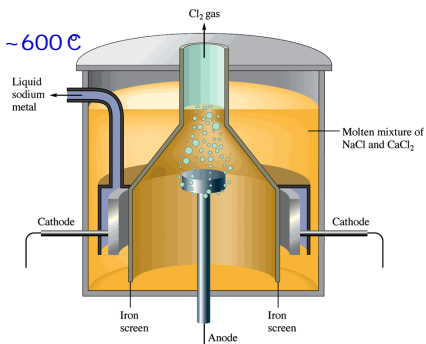
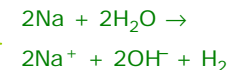
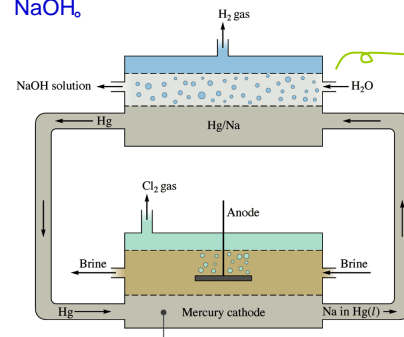


Fig. 17.25: The Downs cell for the electrolysis of molten sodium chloride.

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chlor-alkali process: 使用汞作為cathode，因 H₂ 對於汞電極有很高之overvoltage，cathode 上將會還原出鈉：Na⁺ + e⁻ → Na。鈉即與汞形成鈉汞齊液態合金，再於另一槽中與 H₂O 反應生成 NaOH。



因環保考量，此法已逐漸被淘汰，改用薄膜隔離 the anode and cathode compartments in brine electrolysis cells，此 membrane 只可使陽離子通過，不讓陰離子通過，故不會有 NaOH 被 NaCl 污染的問題。

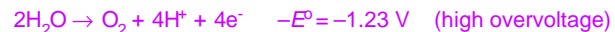
Fig. 17.26: The mercury cell for production of chlorine and sodium hydroxide.

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電解 NaCl 水溶液 (brine):

為工業上製備 Cl₂ & NaOH 之重要方法

Anode:

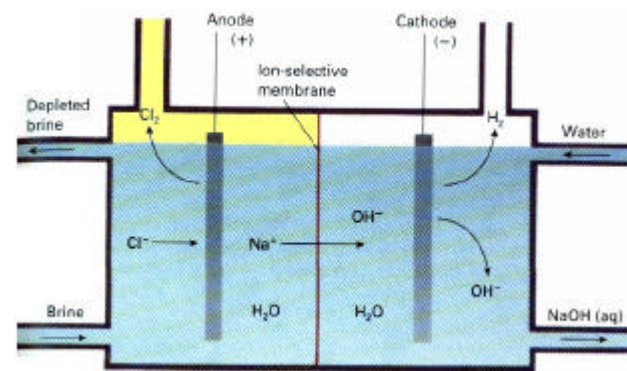


Cathode:



如此之電解槽中含有混合之 NaOH and NaCl

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