

Industrial electrolysis

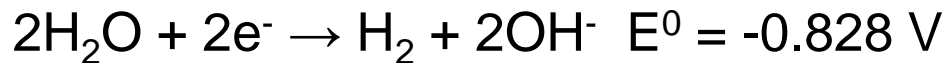
1. Industrial electrolysis
2. Electrochemical reactors
3. Redox-flow battery

Industrial electrochemistry

- Industrial electrolytic processes consume about 6% of US electricity

Industrial electrolysis

- to use electrical energy to convert raw materials into desired products
- e.g. the production of aluminum, chloro-alkali process → 90% of the electricity used in all electrolytic processes
- Chloro-alkali process



Standard potential for full cell : 2.188 V

Fig. 14.1 : a diaphragm cell

Illustration 14.1

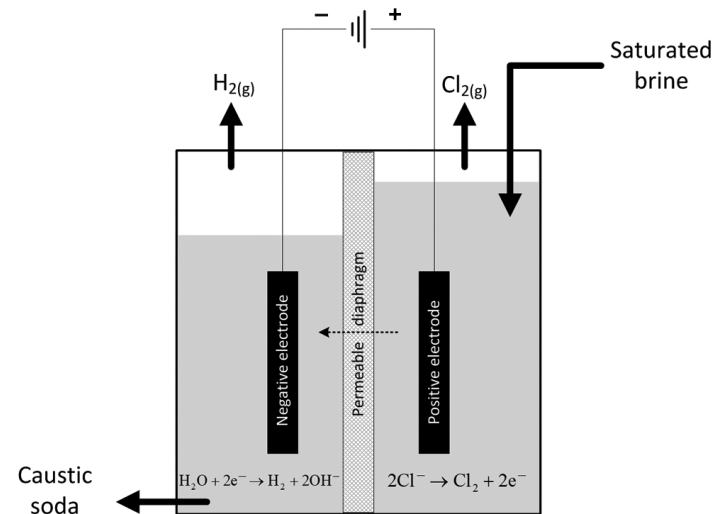


Figure 14.1 Diaphragm cell for the production of chlorine and caustic soda.

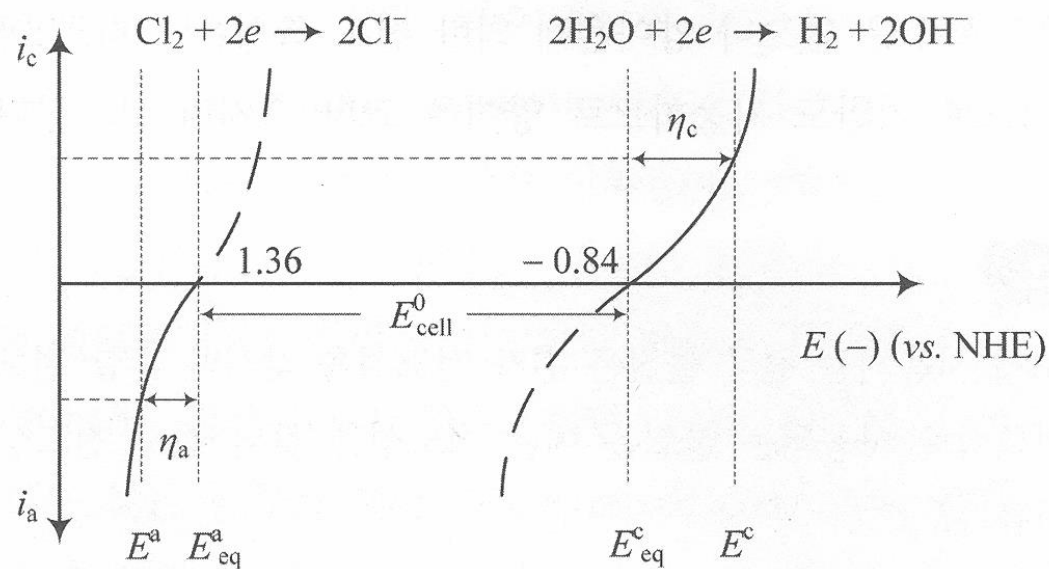
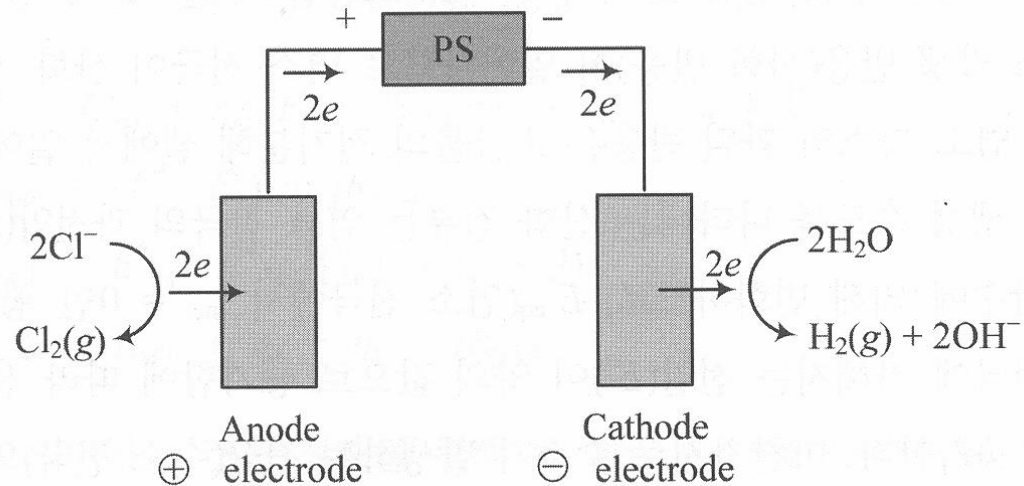


Table 15.1. Industrial electrolysis and electrosynthesis

Chlor-alkali industry ^{9–13}	Extraction of chlorine and sodium hydroxide from NaCl
Metal extraction	Aluminium (Hall–Heroult process) ^{14–16} Sodium, magnesium, lithium (electrolysis of the fused salts) Electrolysis in aqueous solution (principally copper and zinc)
Electrolysis in the preparation of inorganic compounds ¹⁷	Strong oxidizing agents: KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{S}_2\text{O}_8$, F_2 , NaClO_3 . Active metal oxides: MnO_2 , Cu_2O Hydrogen and oxygen by water electrolysis ^{18–20}
Electro-organic synthesis ^{21–24}	Hydrodimerization of acrylonitrile (Monsanto process) Direct processes e.g. reduction $\text{Me}_2\text{CO} \rightarrow \text{i-PrOH}$ Indirect processes—an inorganic reagent is used as catalyst, being oxidized or reduced at the electrode to give a species that reacts with the organic compound e.g. Electrode(Pb): $\text{Cr}^{3+} \rightarrow \text{Cr}_2\text{O}_7^{2-}$ Solution: $\text{Cr}_2\text{O}_7^{2-} + \text{anthracene} \rightarrow \text{anthraquinone} + \text{Cr}^{3+}$

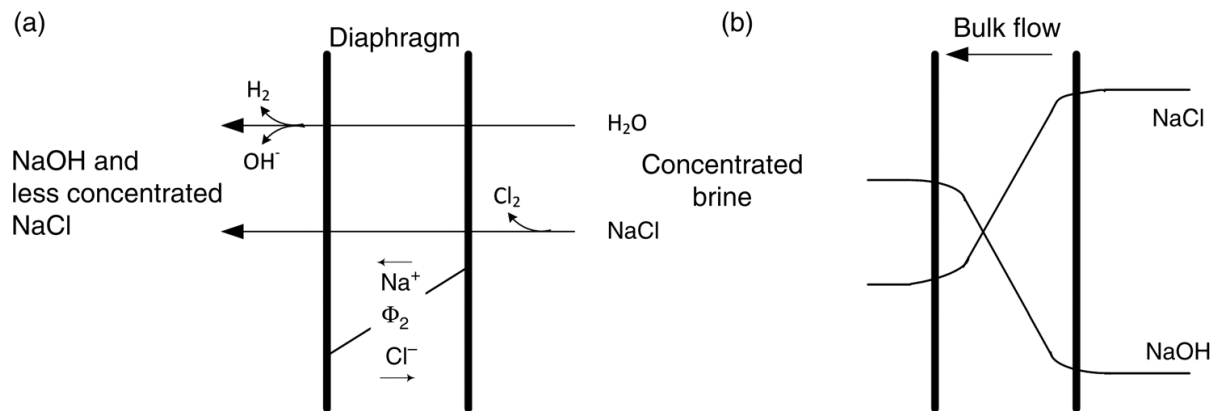


Figure 14.2 Transport in diaphragm separator of a chlor-alkali cell. (a) Movement of species and potential gradient. (b) Concentration profiles.



Performance measures

(1) Faradaic efficiency : the ratio of the product mass to the amount that could be obtained based on the current and Faraday's law

$$\eta_f = \text{mass of product} / \text{theoretical mass from Faraday's law} \\ = m_i / (QM_i / nF) = \dot{m}_i / (IM_i / nF)$$

m_i : mass of the product, Q : total charge passed during electrolysis, \dot{m}_i : mass flow rate of the desired product, I : total current, M_i : molecular weight

- η_f for the Cl_2 reaction for a diaphragm cell ~0.96 or 96%
to use electrical energy to convert raw materials into desired products
- Lower η_f for side reactions, contaminants (that react with the desired products)

(2) **Space-time yield** : the rate of production per volume of reactor → reactor efficiency

$$Y = \dot{m}_i / V_R = \eta_f \times (IM_i / nF) / V_R = \eta_f \times (ia_r M_i / nF)$$

a_r (specific area for the reactor) → area of the electrode at which the production takes place divided by volume of the reactor, V_R : the reactor volume

- Y unit: $\text{kg} \cdot \text{s}^{-1} \text{m}^{-3}$
- ia_r : current per unit volume of the reactor

(3) **Energy efficiency** : the product of the faradaic efficiency and the ratio of the equilibrium potential to the cell potential

$$\eta_{\text{energy}} = \eta_f \times (E^0 / E_{\text{cell}})$$

E^0 / E_{cell} : voltage efficiency defined for an electrolytic cell (η_v)

- η_{energy} : the theoretical power required to complete the chemical conversion ($I_{\text{Rx}} E^0$) divided by the actual power used ($I V_{\text{cell}}$) $V_{\text{cell}} = E_{\text{cell}}$

Illustration 14.2, 14.3, 14.4

Voltage losses and the polarization curve

- Relationship between the potential of the cell and the current density for an electrolytic cell

$$E_{\text{cell}} = E_{\text{cell}}^0 + |\eta_{\text{s,anode}}| + |\eta_{\text{s,cathode}}| + |\eta_{\text{conc,anode}}| + |\eta_{\text{conc,cathode}}| + |\eta_{\text{ohmic}}|$$

η_{s} : surface overpotential ($E - E^0$)

$\eta_{\text{ohmic}} = ih / \kappa = iR_{\Omega}$, h : a gap of distance

- For a diaphragm cell,

$$R_{\Omega}[\Omega \cdot \text{m}^2] = h_a / \kappa + h_d / \kappa \epsilon_d + h_c / \kappa + R_{\text{leads}}$$

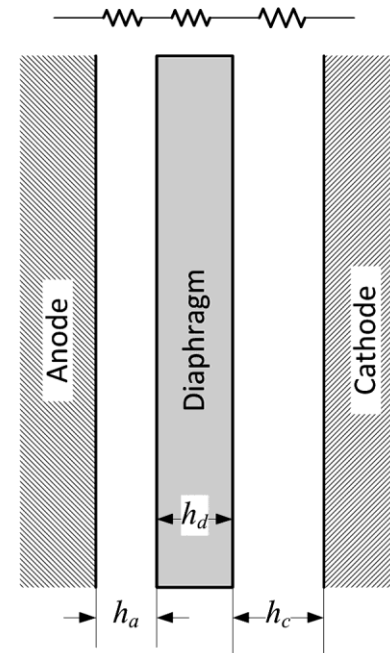


Figure 14.3 Cell resistances.

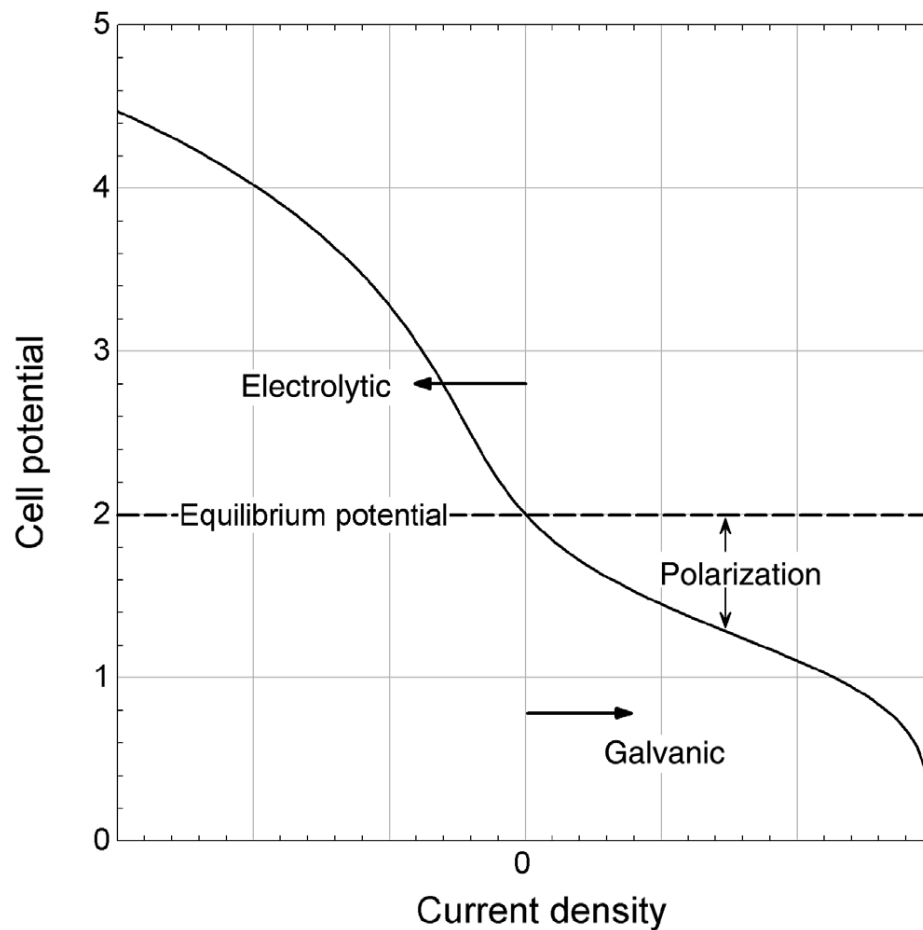


Figure 1.5 Representative relationship between current and potential at steady state. The dividing line between galvanic and electrolytic operation is at a current density of zero.

- Gas evolution → increasing ohmic loss

$$\kappa_{eff} = \kappa(1 - \epsilon_g)^{3/2}$$

ϵ_g : volume fraction of gas

For a diaphragm cell,

$$R_{\Omega}[\Omega \cdot m^2] = h_a / \kappa + h_d T / \kappa \epsilon_d + h_c / \kappa + R_{leads}$$

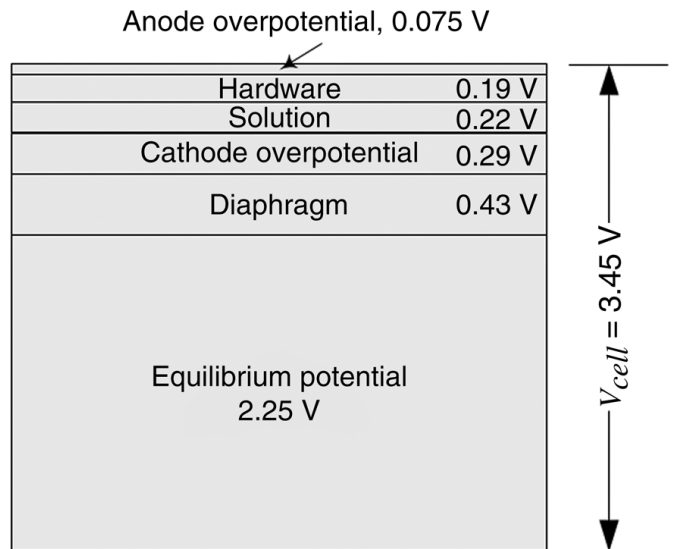


Figure 14.5 Polarization in an operating diaphragm chlor-alkali cell.

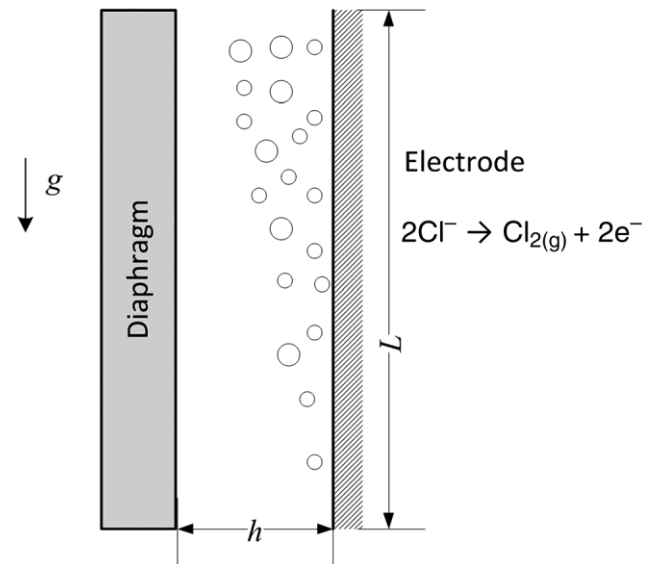


Figure 14.4 Evolution of gas on an electrode.

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Dimensionally stable anode (DSA)

- One of the most significant advancements in industrial electrochemistry is the development of stable oxide electrodes or DSA. The first anodes for chloro-alkali were carbon and then graphite, both of which were consumed over time, increasing the electrode gap and requiring costly maintenance. Titanium is stable in the harsh environment of chloro-alkali cell, but forms a nonconducting oxide. The key innovation was the application of conductive oxides on Ti to produce a “nonconsumable,” dimensionally stable electrode. Also, with titanium as a support, the electrode could be constructed in the form of meshes and expanded metals. The open structure allowed gases to be removed more easily, thus allowing the gap to be reduced.

Design of electrochemical reactors

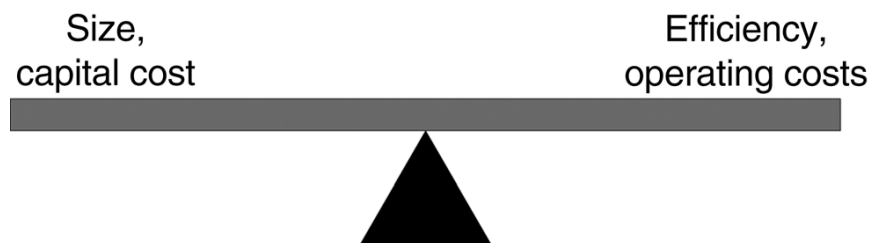


Figure 14.6 Trade-off between size and efficiency is essential part of design.

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Table 14.1 Eight Key Variables for an Electrochemical Reactor

Variable	Units	Description	Comments
\dot{m}_i	$\text{kg}\cdot\text{s}^{-1}$ metric tons $\cdot\text{yr}^{-1}$	Rate of production of desired material	Size scales with production rate
i	$\text{A}\cdot\text{m}^{-2}$	Current density	These three along with the <i>configuration of the cell</i> would be optimized simultaneously
V_{cell}	V	Potential of an individual cell	
η_{energy}	–	Energy efficiency	
A	m^2	Total electrode area, sometimes referred to as the separator area	Follows directly from Faraday's law once i is established
V_s	V	Voltage of the DC power system	Follows directly, $m = \frac{V_s}{V_{\text{cell}}}$
m	–	Number of cells that are connected in series	
A_c	m^2	Area of individual electrodes	Cells may be placed in parallel

Electrical configurations

- Number of series connections is established from the system voltage (V_s) and potential of an individual cell (V_{cell})

$$\text{number of cells in series} = m = V_s / V_{\text{cell}} \quad (14.17)$$

- Two general methods for making electrical connections: **monopolar and bipolar**

(1) monopolar: a separate electrical connection is made to each electrode. Many electrode pairs can be combined in a single cell. All the anodes are at the same potential, as are all of the cathodes. The voltage between each anode and cathode pair is the same and equal to the cell voltage.

(2) bipolar: current in a bipolar stack flows straight through the stack. Failure of one cell results in failure of the entire stack. It is possible for a portion of the current to skip one or more cells and flow directly to another cell downstream, referred as a *bypass* or *shunt current*.

→ standard in fuel cells and redox-flow batteries, but used less frequently in industrial electrolysis

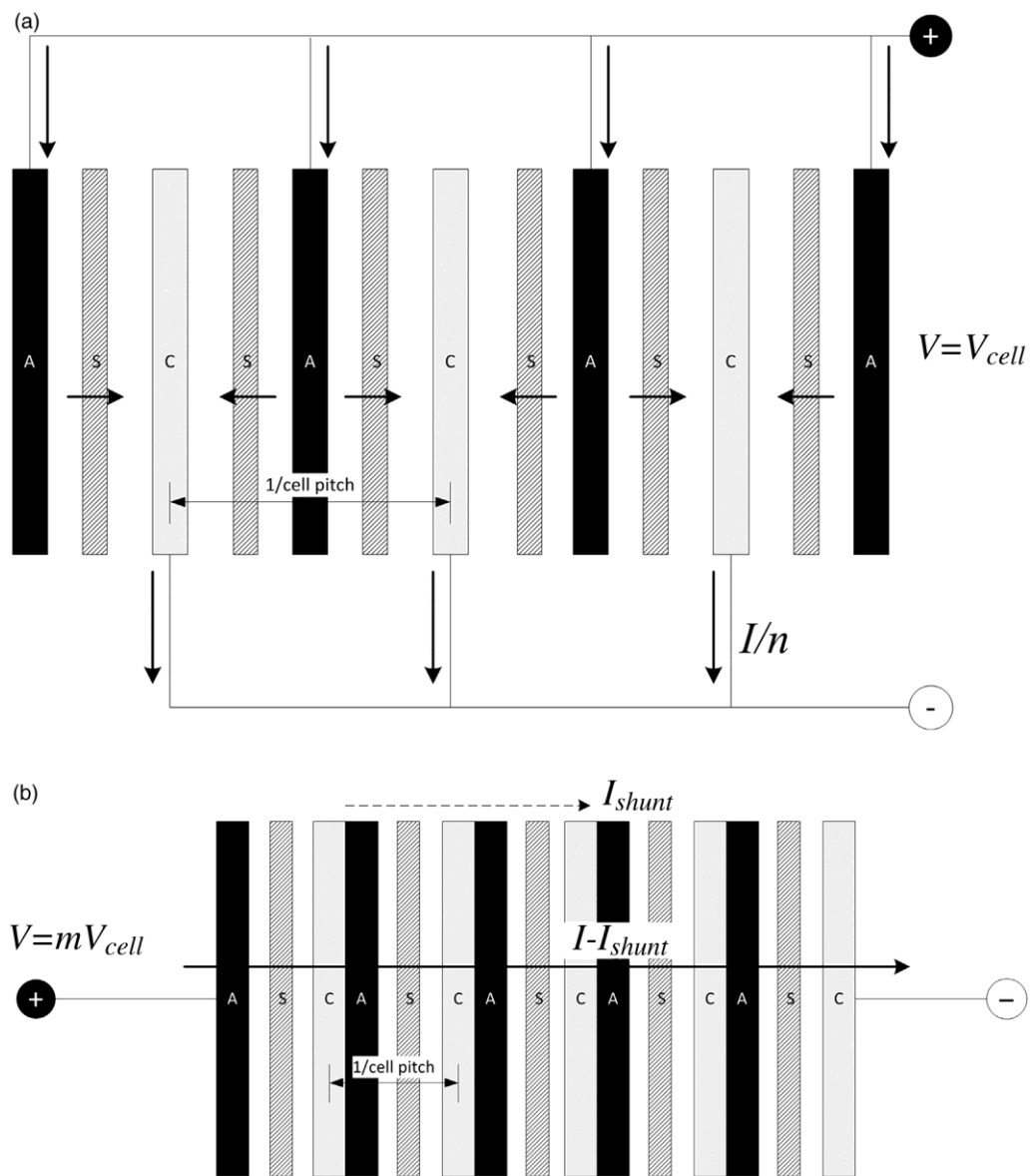


Figure 14.7 Monopolar (a) shown with a separator and bipolar (b) configurations. Current flow is shown for electrolysis. Cell pitch is the number of electrode pairs per unit length.

Flow configurations

- Industrial electrochemical reactors are usually flow reactors → streams of reactants into and out of the reactor
- Two principal flow arrangements: **parallel flow** and **series flow**
- (1) Parallel flow: a lower pressure drop
- (2) Series flow: problem associated gas evolution
- hybrids of parallel and series possible

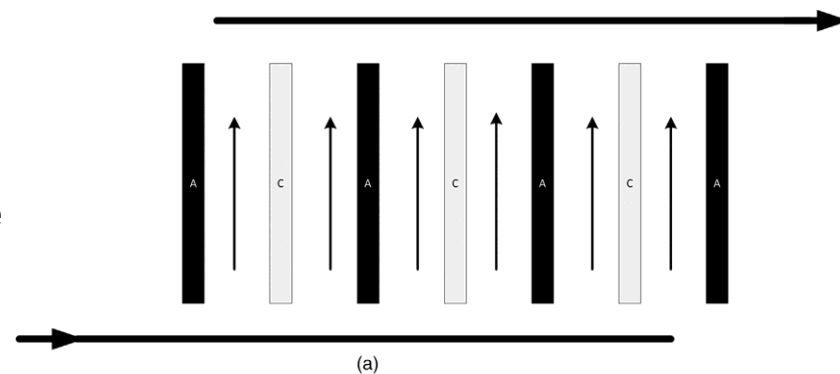


Illustration 14.8

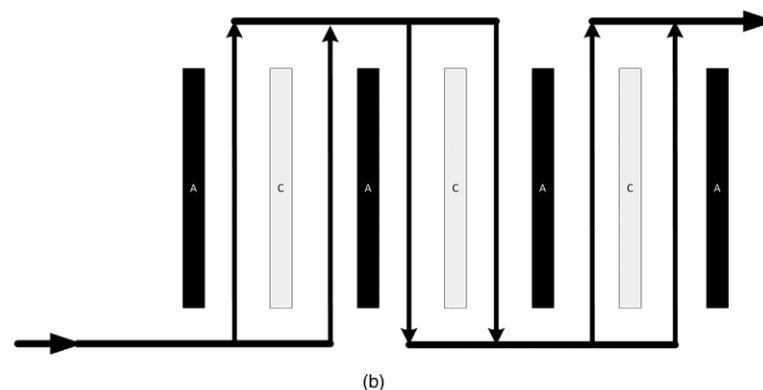


Figure 14.8 Basic flow arrangements. (a) Parallel flow. (b) Series flow.

Reactor volume

- Specific area of reactor (a_r)
- Cell pitch: the number of electrode pairs per unit length when the repeating units are stacked together

cell pitch = 1 / center to center distance between electrodes of the same type

$$\begin{aligned} a_r &= \text{electrode area} / \text{total volume} \\ &= 2(\text{length})(\text{width}) / [(\text{length})(\text{width})/\text{cell pitch}] = 2 \times \text{cell pitch} \end{aligned}$$

- the factor of 2 accounts for the two active faces of the electrode

Illustration 14.9

Scale up

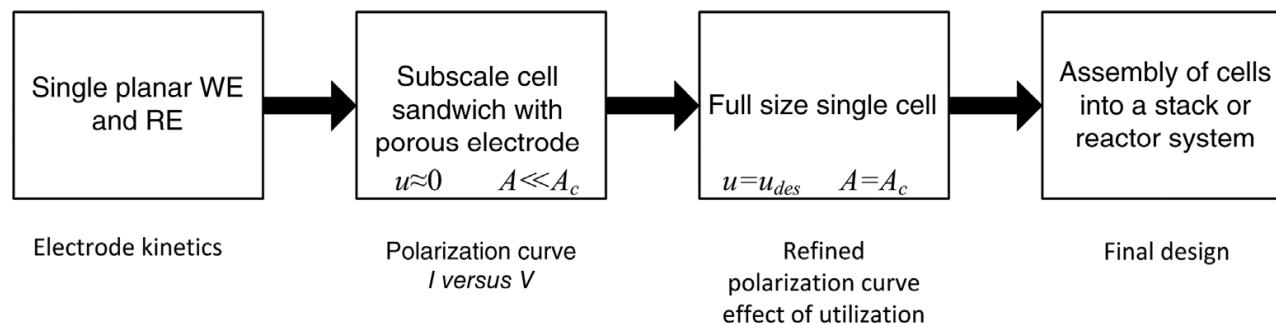
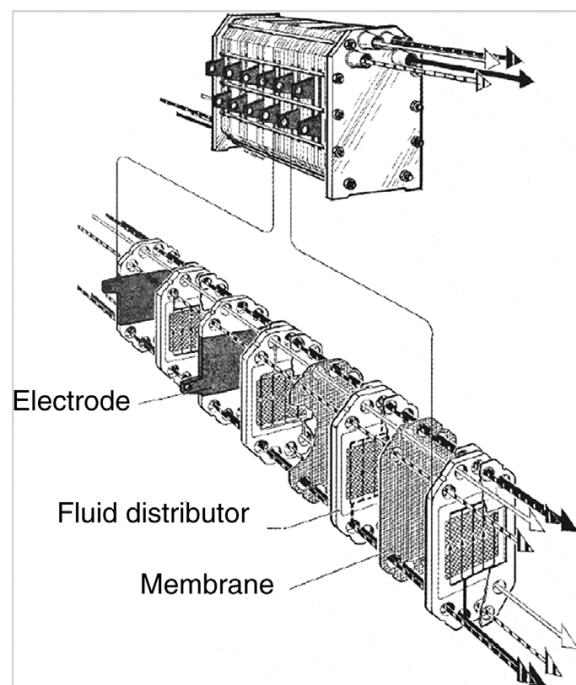


Figure 14.9 One possible scale-up process from fundamental electrochemistry to prototype reactor.



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u = amount reacted / amount supplied
 A_c : full size

Figure 14.10 Plate-and-frame system that is commercially available for process evaluation. Image provided by ElectroCell A/S.



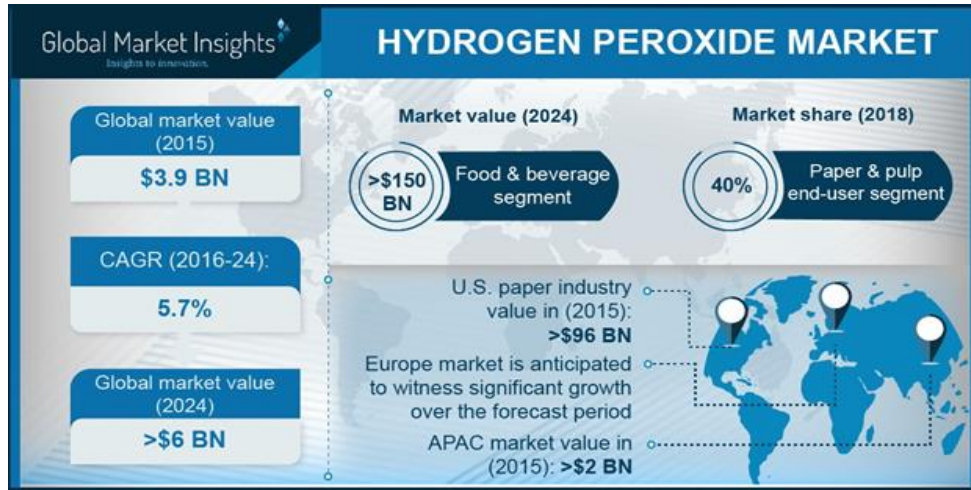
Examples of industrial electrolytic processes

Synthesis of inorganic chemicals

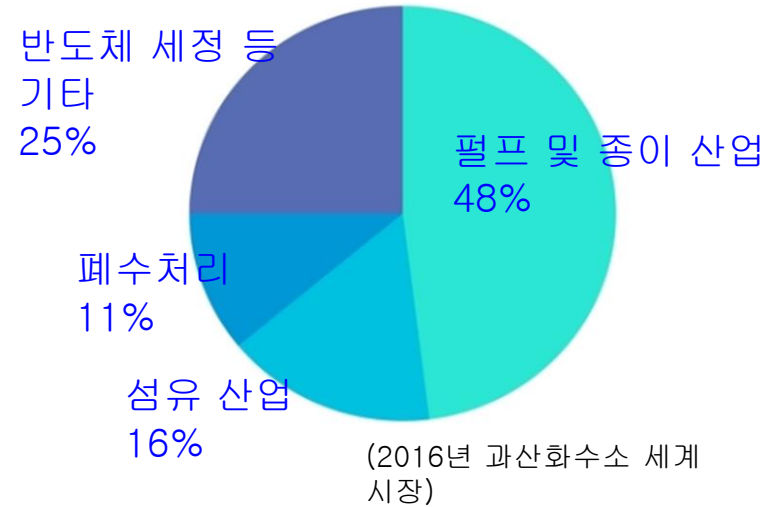
- The largest electrolytic industry: chloro-alkali process → chlorine, sodium hydroxide, (hydrogen) from a salt solution → two types of cells dominated: diaphragm cell, mercury cell → third type (new type): a membrane cell
- Production of chlorine and hydrogen from hydrochloric acid using diaphragm cell and membrane cell → process converting byproduct HCl due to serious environmental concerns
- Other examples of industrial electrolysis: fluorine gas, strong oxidizing agents such as KMnO_4 , H_2O_2 , $\text{Na}_2\text{S}_2\text{O}_8$ (sodium persulfate) → recently, hydrogen peroxide (H_2O_2) has been produced in situ by electrolysis at the quantity needed for optimal use
- MnO_2 production by electrolysis for battery applications
- Hot issue: water electrolysis to produce hydrogen and oxygen gas at high purity

과산화수소

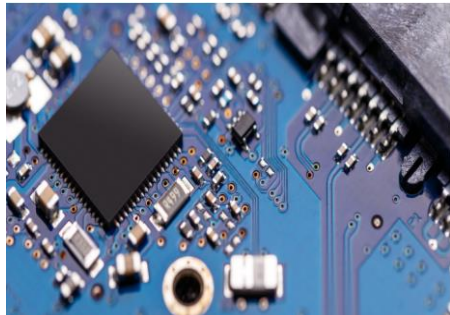
글로벌 시장 가치: 7조 4500억 (2024),
연간 성장률: 5.7 %



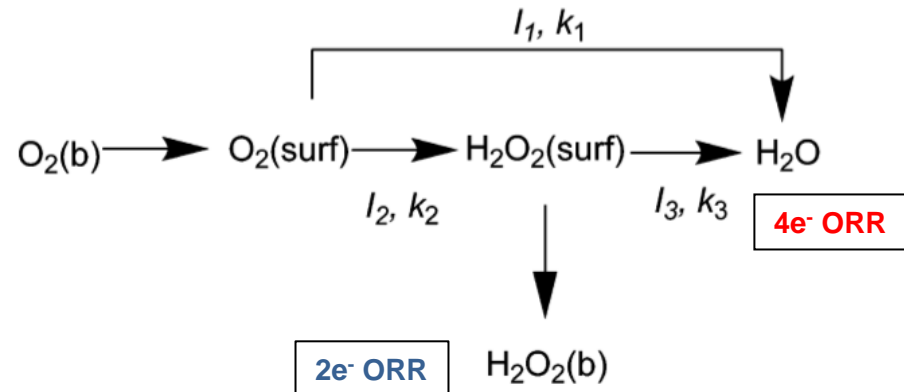
과산화수소의 산업적 중요성



반도체 산업 세정제

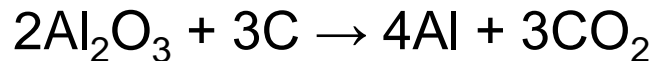


의료현장의 멸균제



Electrowinning of metals 전해제련

- The production of metals from ores by electrodeposition from a melt or solution
- The most important industrial electrowinning process: production of aluminum using Hall-Heroult process



- Li, Mg, Na from a molten salt (typically chloride-based salts)
- Cu, Zn from aqueous solutions

Illustration 14.10

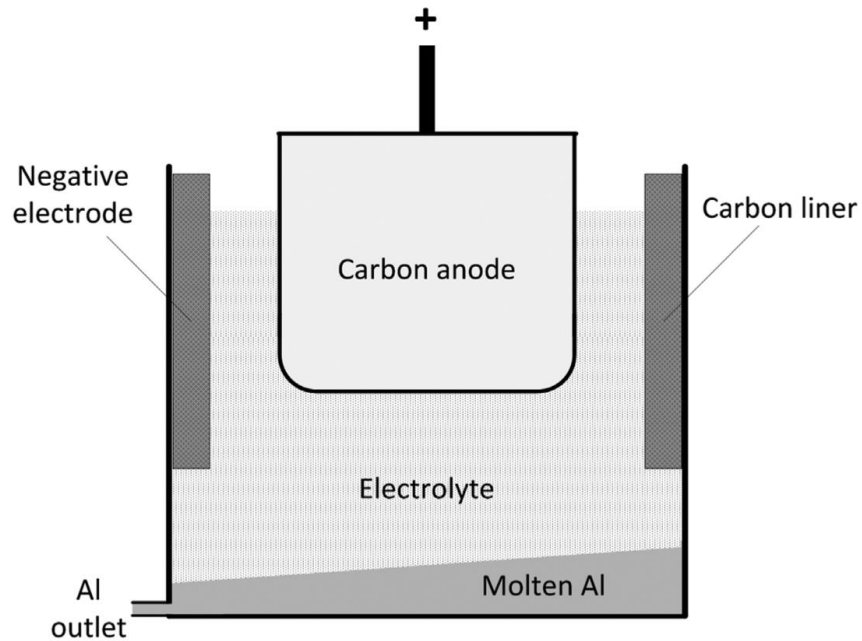


Figure 14.11 Hall-Héroult process for the production of aluminum.

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Electrorefining

- To purify the metal (rather than to recover the metal)
- Cu: Cu anode is dissolved and Cu is plated at the cathode → active impurities are dissolved but not plated at the cathode → high purity copper at the cathode (e.g. 99.999%)
- Ni, Co, Pb, Sn in aqueous solution
- Al in a molten salt electrolyte

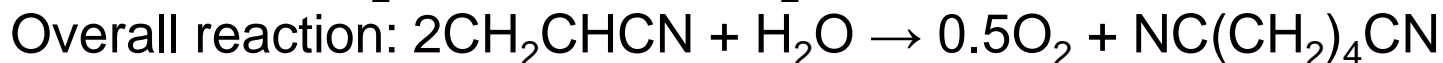
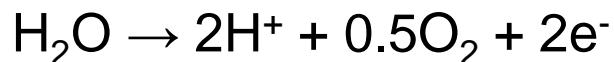
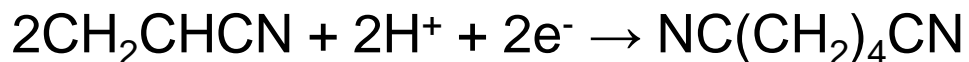
Electrosynthesis of organic compounds

- Types of reactions: oxidation and reduction of functional groups, cleavage, substitutions (e.g. halogenation), additions (e.g. hydrogenation), coupling (e.g. dimerization), rearrangement

Reductions: $\text{Sn}^{4+}/\text{Sn}^{2+}$, $\text{Cr}^{3+}/\text{Cr}^{2+}$, $\text{Ti}^{4+}/\text{Ti}^{3+}$, Zn^{2+}/Zn , Na^+/NaHg

Oxidations: $\text{Ce}^{3+}/\text{Ce}^{4+}$, $\text{Cr}^{3+}/\text{Cr}^{6+}$, $\text{Mn}^{2+}/\text{Mn}^{3+}$, $\text{Mn}^{2+}/\text{Mn}^{4+}$, $\text{Ni}(\text{OH})_2/\text{NiOOH}$, I^-/I_2 , Br^-/Br_2 , Cl^-/ClO^-

- The most significant industrial process: production of adiponitrile, an intermediate in the production of Nylon
→ cathode reaction: electro-hydro-dimerization of acrylonitrile, and oxygen is evolved at the anode (using aqueous sulfuric acid electrolyte)



- Electrochemical synthesis of ethylene glycol

Thermal management and cell operation

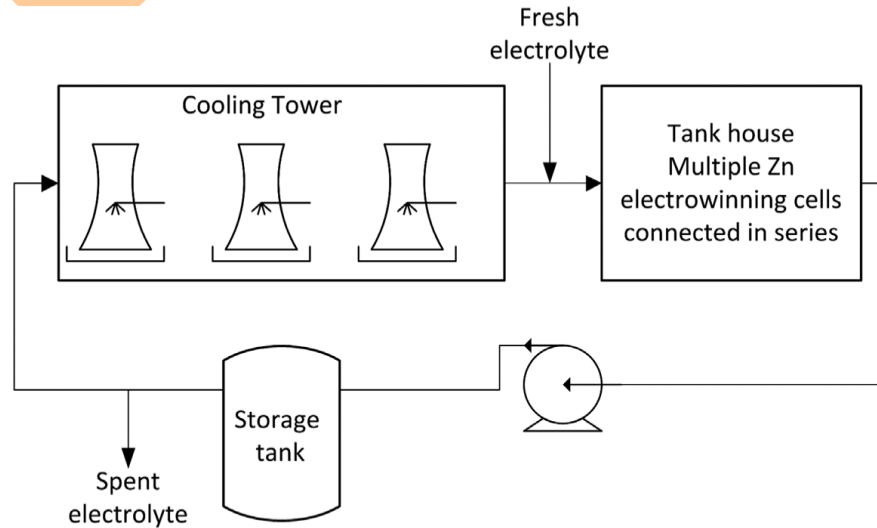


Figure 14.12 Process diagram for Zn electrowinning that emphasizes cooling of the electrolyte.

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$$mC_p \frac{dT}{dt} = \sum_m \dot{n}_m H_{in,m} - \sum_p \dot{n}_p H_{out,p} + \dot{q} - \dot{W} - \sum_j r_i \Delta H_{Rx,j}, \quad (14.22)$$

where

m = mass of the system, assumed constant [kg]

C_p = average heat capacity of the system [$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$]

$H_{out,p}$ = enthalpy of outlet stream p [$\text{J} \cdot \text{mol}^{-1}$]

$H_{in,m}$ = enthalpy of inlet stream m [$\text{J} \cdot \text{mol}^{-1}$]

\dot{n}_m = molar flowrate of inlet stream m , [$\text{mol} \cdot \text{s}^{-1}$]

\dot{n}_p = molar flowrate of outlet stream p , [$\text{mol} \cdot \text{s}^{-1}$]

\dot{q} = heat transferred to the system from the environment [W]

\dot{W} = Rate of work done by the system on the environment [W]

r_i = Rate of reaction of species i [$\text{mol} \cdot \text{s}^{-1}$]

$\Delta H_{Rx,j}$ = Heat of reaction j per mole of species i [$\text{J} \cdot \text{mol}^{-1}$]



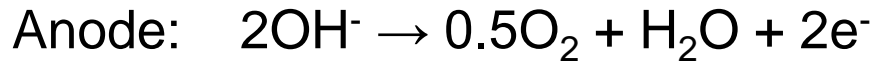
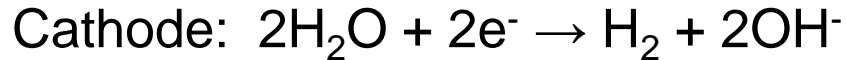
Electrolytic processes for a sustainable future

Electrolytic fuel generation

- Solar fuels such as hydrogen: Hydrogen production using photoelectrochemical cell (ch.15 in the textbook)

Water electrolysis

- A fuel cell in reverse → three principal types of electrolyzers: alkaline, PEM(proton exchange membrane), solid oxide
- Alkaline electrolyzer: most commercial water electrolyzer



- Water electrolysis as a function of T
→ $T \uparrow \rightarrow \text{potential} \downarrow$

$$U = E_{\text{cell}}^0$$

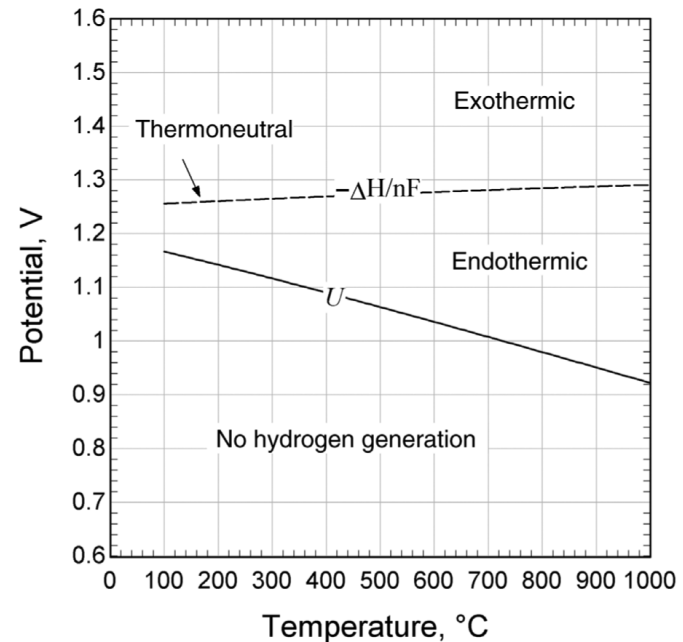


Figure 14.13 Equilibrium and thermoneutral potentials assuming gaseous water.

- Voltage losses as a function of current density in a typical alkaline electrolyzer → overpotentials for both the anodic and cathodic reactions are significant, ohmic losses become more important at the high current densities
- Commercial electrolyzers typically operate at below 2 V and current densities between 1000 and 3000 A·m² (note at 25°C, $E = 1.229$ V, and thermoneutral potential is 1.481 V assuming liquid water)
- electrolyte: 25-30% KOH
- 60~100°C, >15 years

Illustration 14.13

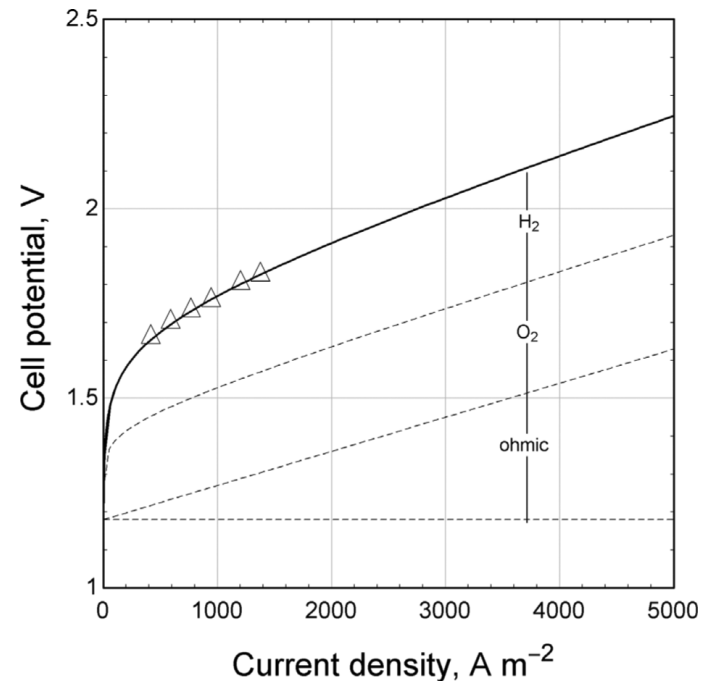
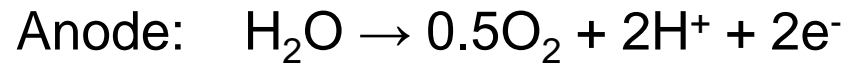
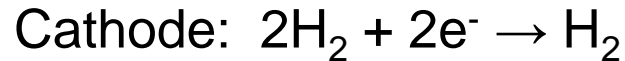


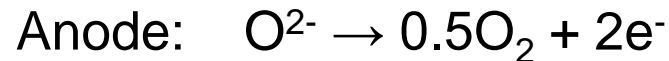
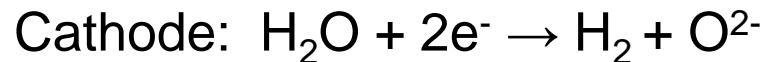
Figure 14.14 Electrolysis of water at 40 °C.

Source: Adapted from Ulleberg 2003.

- PEM(proton exchange membrane) electrolyzer: similar to PEM fuel cell



- Solid oxide electrolyzer: similar to solid oxide fuel cell → operate at high T and utilize a solid, ceramic O^{2-} conducting electrolyte



수전해 (Water Electrolysis)



Other electrolysis processes

- Advantages over water electrolysis:

- (1) Use of a waste stream to produce the desired fuel and perhaps other valuable products while simultaneously cleaning up the stream

- (2) Reduction of the voltage, hence the energy, required for hydrogen production

- Hydrogen generation using the electrolysis of HCl and the electrolysis of $\text{NH}_3 \rightarrow \text{H}_2$ production + cleaning up the stream

- $E^0_{\text{cell}} = 0.06 \text{ V}$ of electrolysis of $\text{NH}_3 \rightarrow$ lower than water electrolysis (1.229 V) \rightarrow hydrogen production from ammonia waste streams require less energy

- Urea-contaminated wastewater electrolysis ($E^0_{\text{cell}} = 0.37 \text{ V}$)



Wastewater treatment

- The use of electrochemical reactors in environment friendly ways to produce useful products while simultaneously cleaning up waste streams
- Another use of electrochemical technologies is for the cleanup of industrial effluent streams containing dilute concentrations of toxic materials: toxic metal ions, pharmaceutical residues

Illustration 14.14

Redox-flow batteries

- A battery in the sense that it is used to store and release energy → it operates like a combination of fuel cell (discharge) and an electrolyzer (charge) → the reactants and products in a flow battery are contained within the electrolyte, which circulates through the cells
- Vanadium redox-flow battery (VRB):
two vanadium redox couples
for the negative (V^{3+}/V^{2+})
and positive electrodes (VO_2^+/VO^{2+})

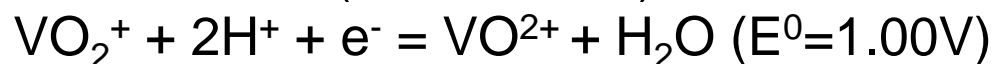
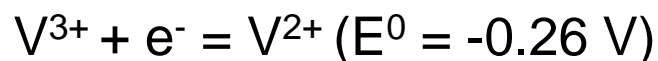


Illustration 14.14

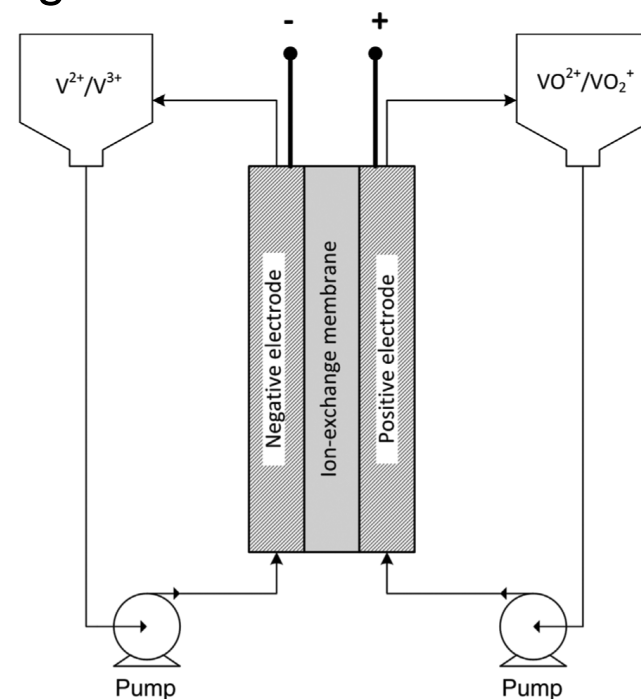


Figure 14.16 Vanadium redox-flow battery. Reactions and transport are shown for discharging.

- charge-discharge curve

$$E = E_0 + (RT/2F)\ln[(c_{V^{2+}}^2 c_{VO_2^+}) / (c_{V^{3+}}^2 c_{VO^{2+}})]$$

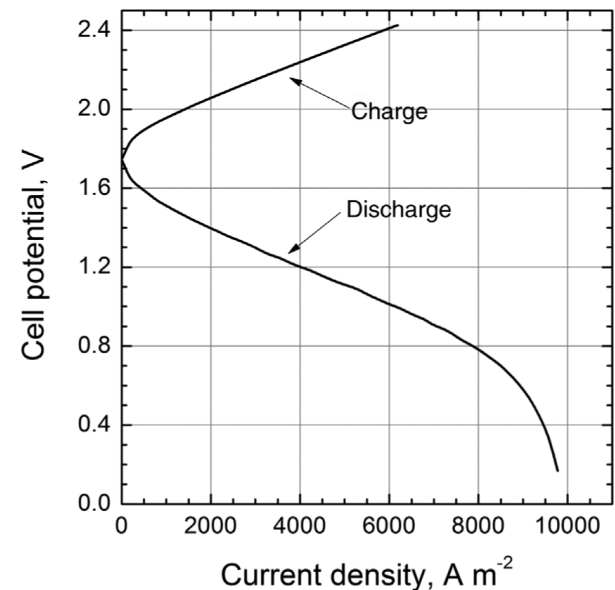


Illustration 14.15

Figure 14.17 Example of polarization curve for the vanadium redox-flow battery at a high state of charge.