Lecture Note #14 (Spring, 2022)

Industrial electrolysis

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

Fuller & Harb (textbook), ch.14, Pletcher, ch.3, Oh, ch.11

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

$2Cl^- \rightarrow Cl_2 + 2e^-$ $E^0 = 1.3595$ V

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E^0 = -0.828$ V

Standard potential for full cell : 2.188 V

Fig. 14.1 : a diaphragm cell

Illustration 14.1

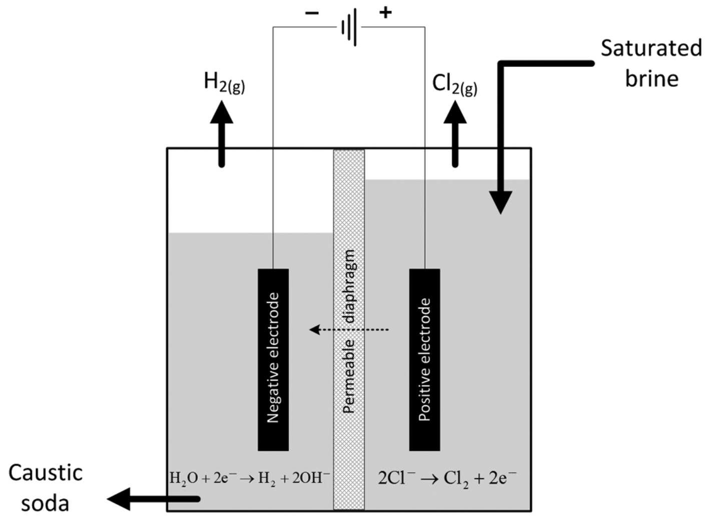
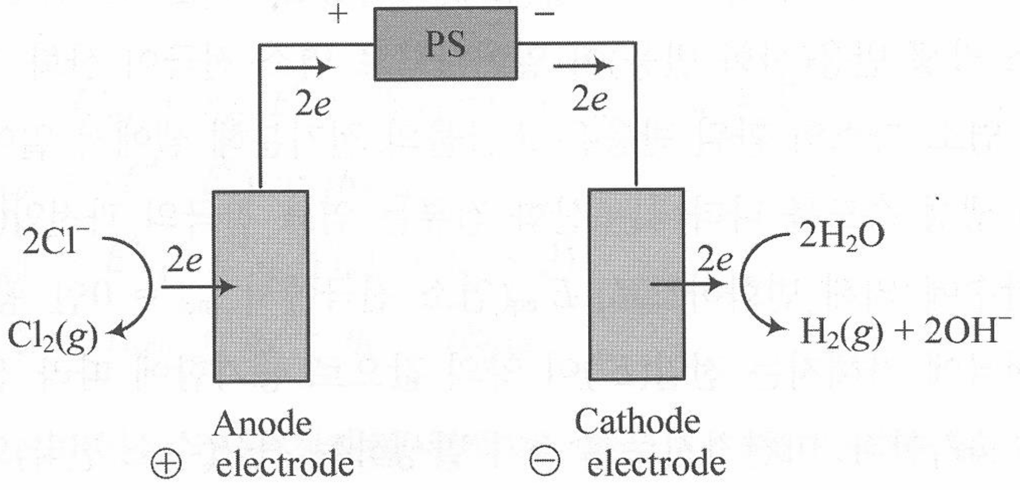
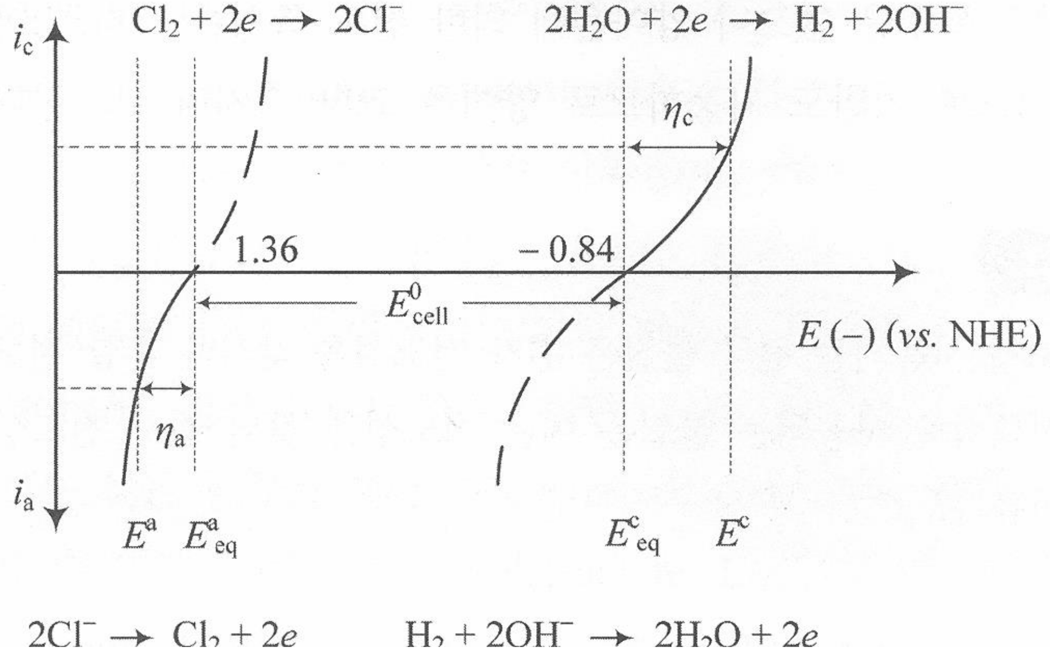


Figure 14.1 Diaphragm cell for the production of chlorine and caustic soda.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

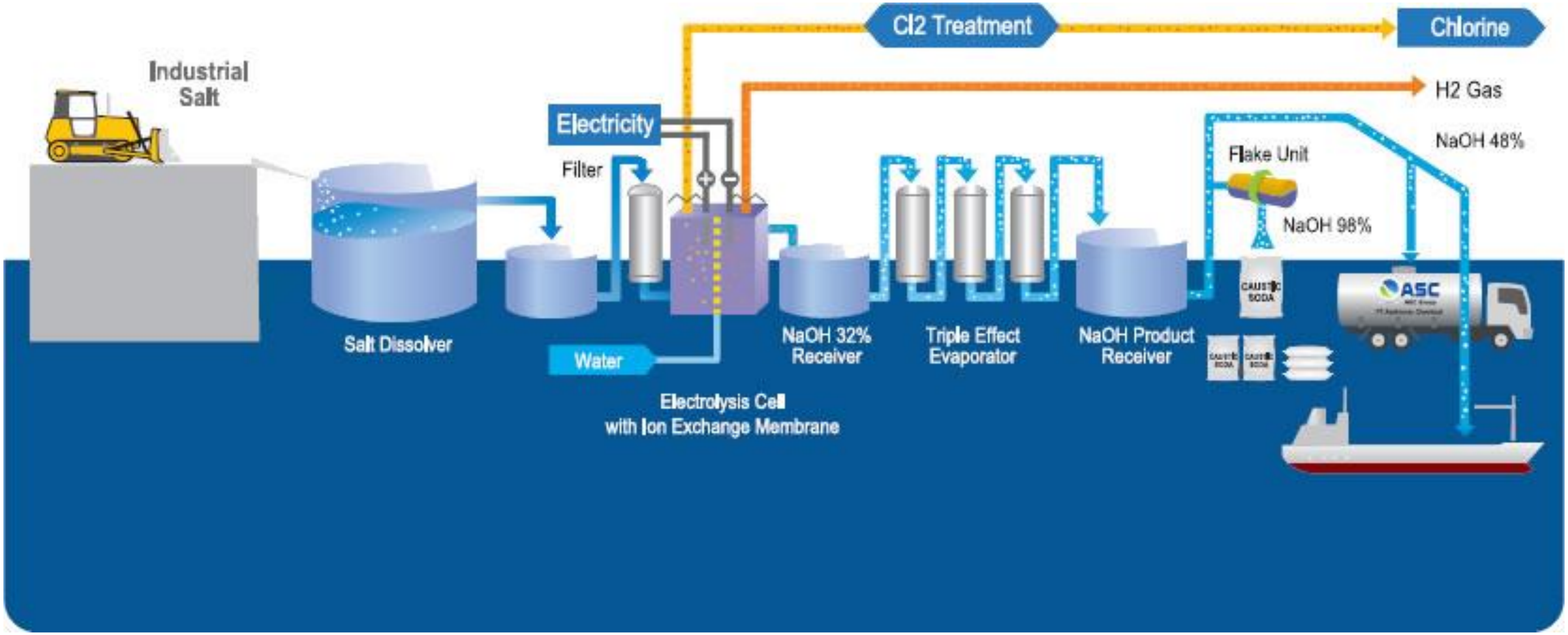
Companion Website: www.wiley.com/go/fuller/electrochemicalengineering


+
PS
−
2e
2e
2Cl⁻
2e
Cl₂(g)
2H₂O
2e
H₂(g) + 2OH⁻
Anode
⊕ electrode
Cathode
⊖ electrode


Cl₂ + 2e → 2Cl⁻
2H₂O + 2e → H₂ + 2OH⁻
i_c
η_c
1.36
− 0.84
E⁰_cell
E (−) (vs. NHE)
η_a
i_a
E^a
E^a_eq
E^c_eq
E^c
2Cl⁻ → Cl₂ + 2e
H₂ + 2OH⁻ → 2H₂O + 2e

From Asahi Kasei

Chloro-alkali process



From ASC AGC Group PT Asahimas Chemical

KCAIA
한국클로르알카리협회
Korea Chlor Alkali Industry Association

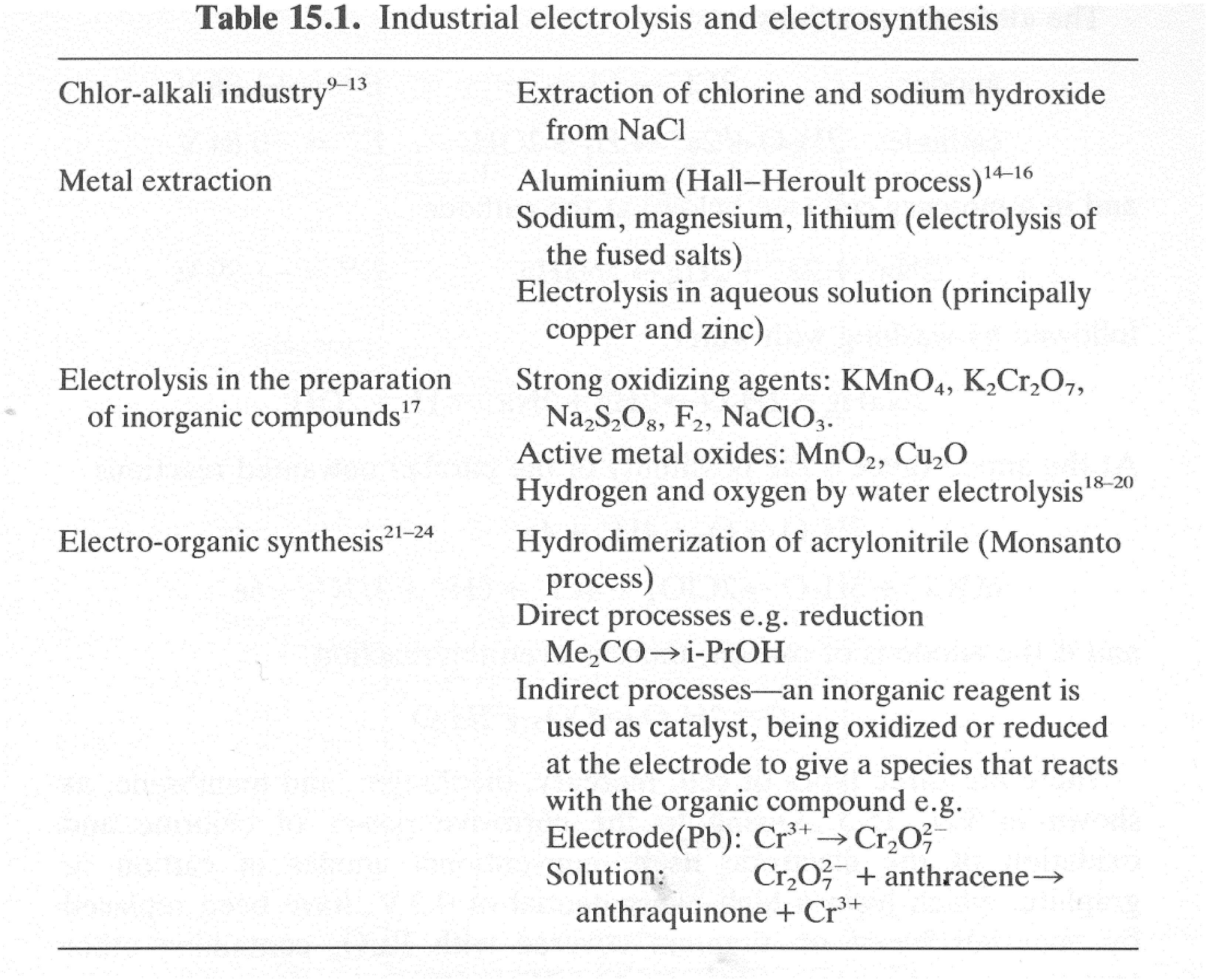


Table 15.1. Industrial electrolysis and electrosynthesis

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: $KMnO_4$, $K_2Cr_2O_7$, $Na_2S_2O_8$, 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 $Me_2CO \rightarrow \text{i-PrOH}$ 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): $Cr^{3+} \rightarrow Cr_2O_7^{2-}$ Solution: $Cr_2O_7^{2-}$ + anthracene → anthraquinone + Cr^{3+}

C. M. A. Brett, A. M. O. Brett, Electrochemistry, Oxford, 1994.

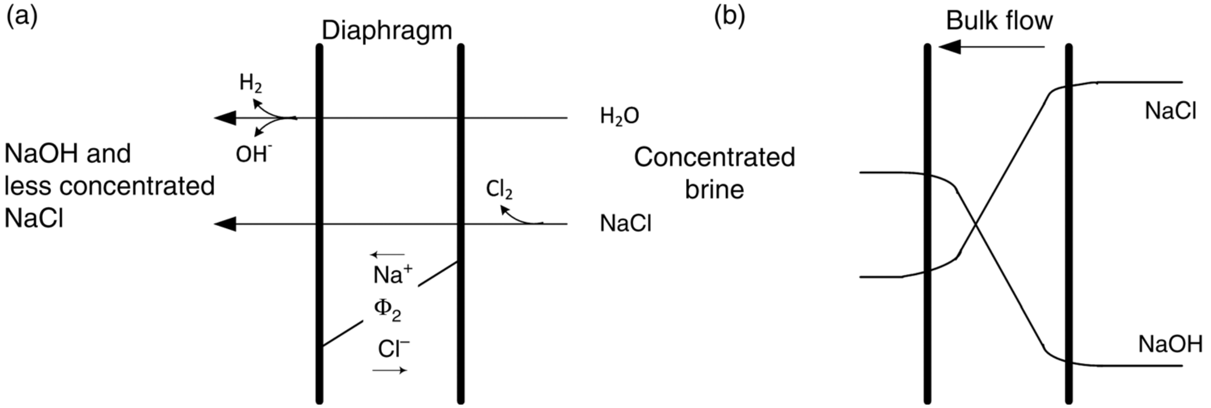


Figure 14.2 Transport in diaphragm separator of a chlor-alkali cell. (a) Movement of species and potential gradient. (b) Concentration profiles.

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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

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

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

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

a_r (specific area for the reactor) → area of the electrode at which the production takes place divided by volume of the reactor, $\mathbf{V}_R$: the reactor volume

- Y unit: $kg \cdot s^{-1} m^{-3}$
- 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

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

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

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

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

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

η_s : surface overpotential ($E-E^0$)
$\eta_{\mathrm{ohmic}} = ih / \kappa = iR_\Omega$, h: a gap of distance

- For a diaphragm cell,
$R_\Omega[\Omega \cdot m^2] = h_a / \kappa + h_d\tau / \kappa\varepsilon_d + h_c / \kappa + R_{\mathrm{leads}}$

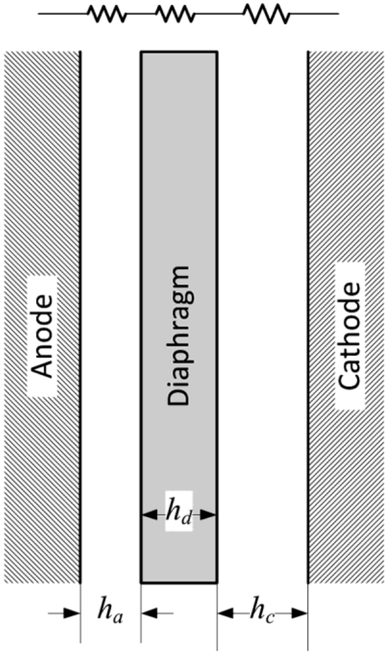

Figure 14.3 Cell resistances.

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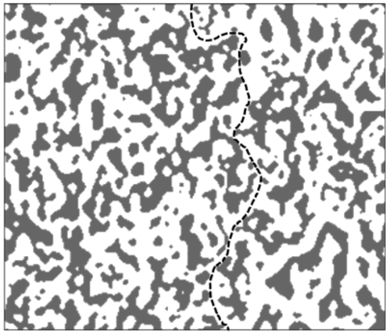

Figure 5.4 Tortuous path through porous media.

τ, tortuosity ε_d, porosity

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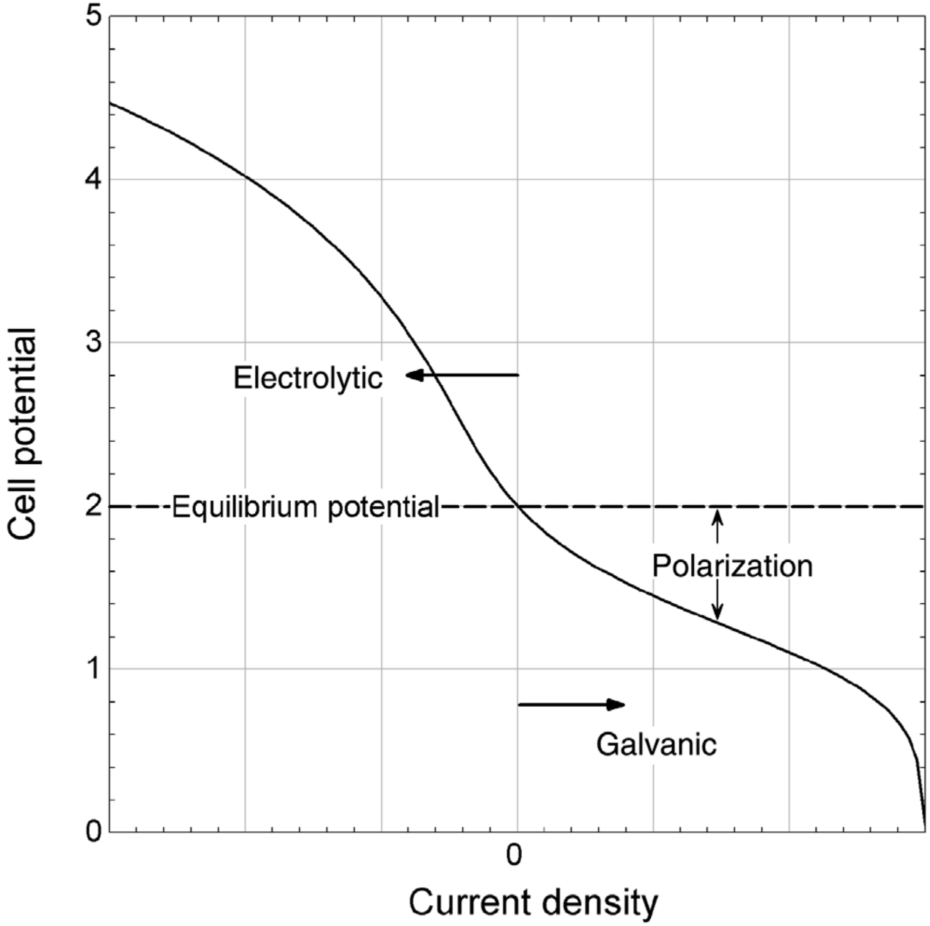

Figure 1.5 Representative relationship between current and potential at steady state. The dividing line between galvanic and electrolytic operation is at a current density of zero.

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- Gas evolution → increasing ohmic loss

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

ε_g: volume fraction of gas

For a diaphragm cell,
$R_\Omega[\Omega \cdot m^2] = h_a / \kappa + h_d\tau / \kappa\varepsilon_d + h_c / \kappa + R_{leads}$

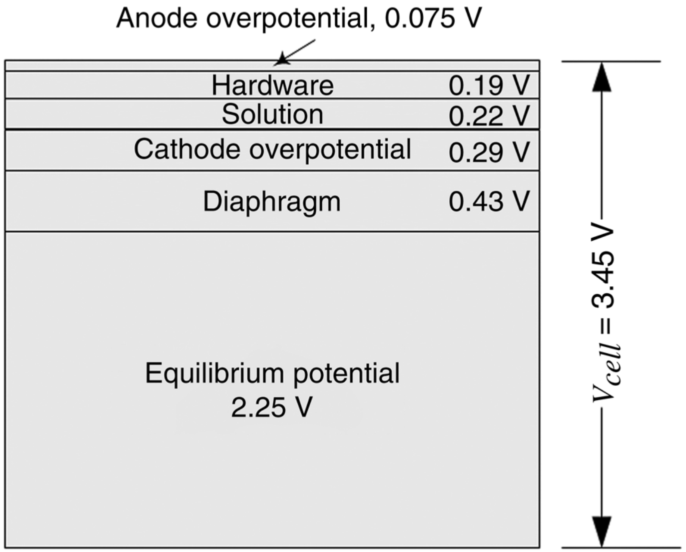

Figure 14.5 Polarization in an operating diaphragm chlor-alkali cell.

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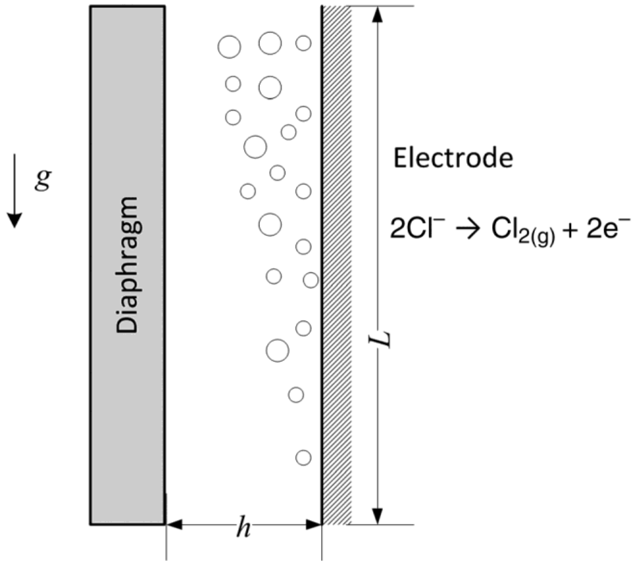

Figure 14.4 Evolution of gas on an electrode.

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Illustration 14.5

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.

From Wikipedia

Design of electrochemical reactors

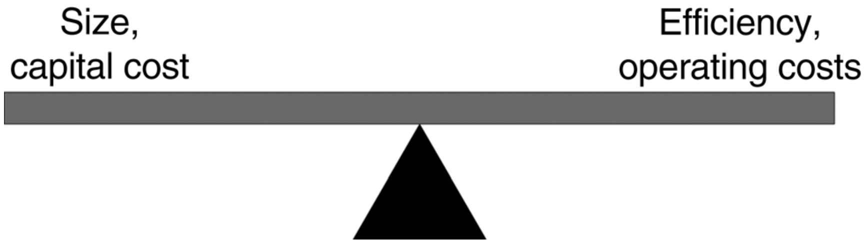

Figure 14.6 Trade-off between size and efficiency is essential part of design.

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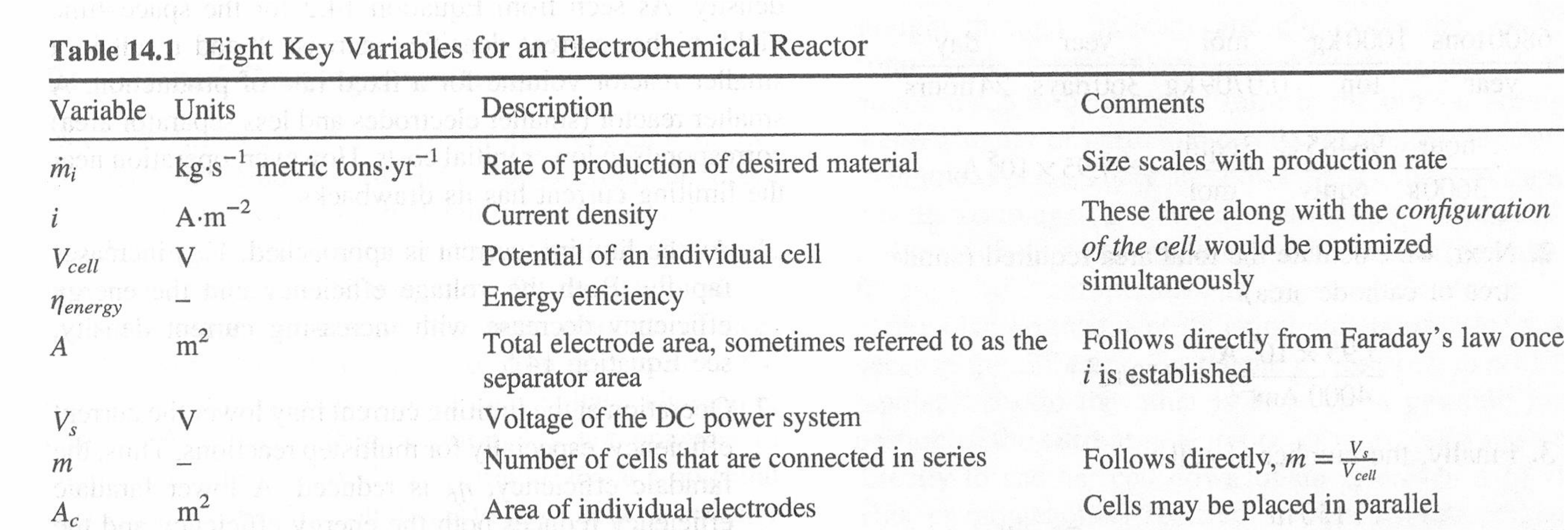

Table 14.1 Eight Key Variables for an Electrochemical Reactor

Variable	Units	Description	Comments
$\dot{m}_i$	$kg \cdot s^{-1}$ metric $tons \cdot yr^{-1}$	Rate of production of desired material	Size scales with production rate
i	$A \cdot m^{-2}$	Current density	These three along with the *configuration of the cell* 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	
m	–	Number of cells that are connected in series	Follows directly, $m = \frac{V_s}{V_{cell}}$
A_c	m^2	Area of individual electrodes	Cells may be placed in parallel

Illustration 14.6

Electrical configurations

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

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

- 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

Illustration 14.7

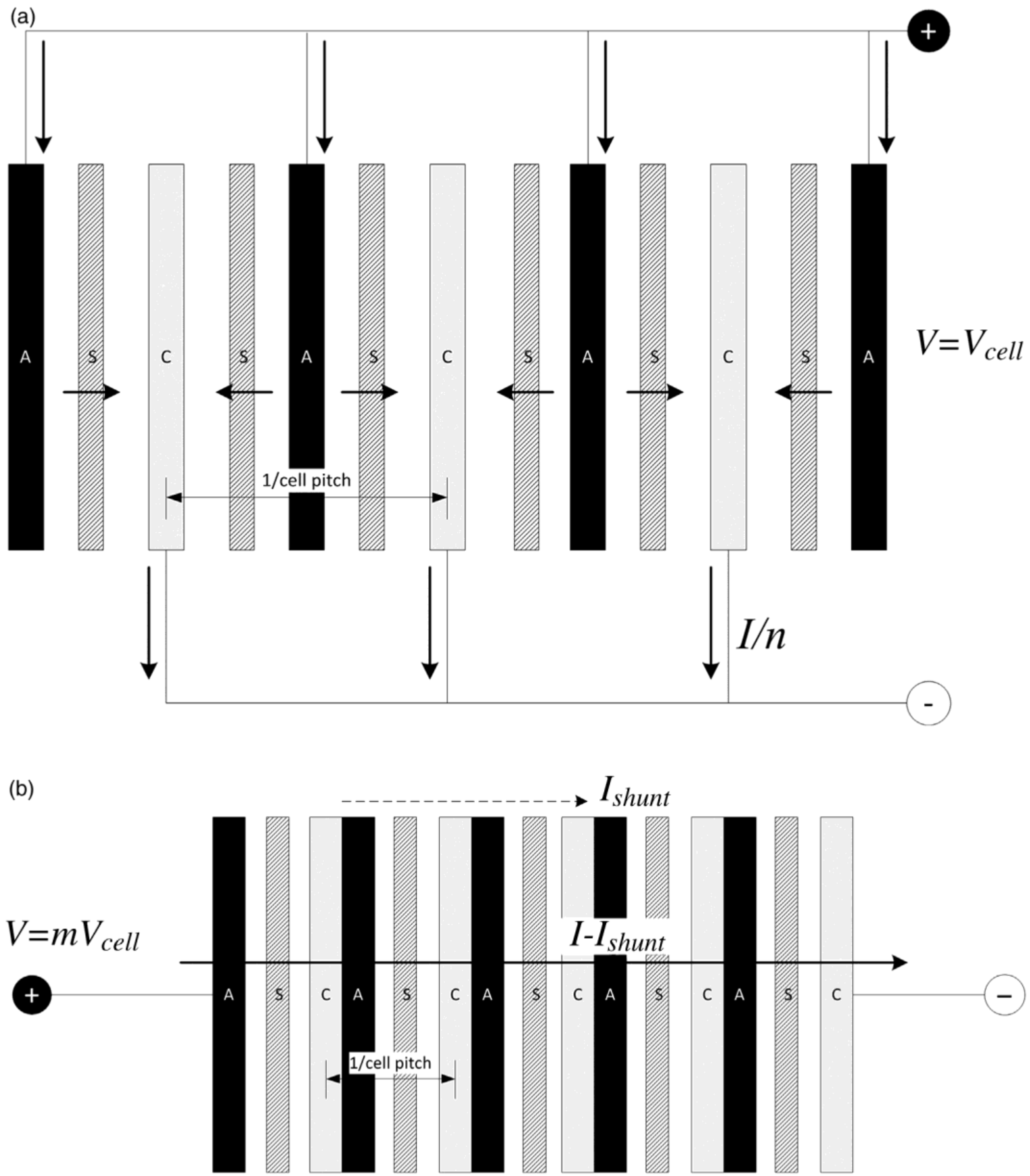

Figure 14.7 Monopolar (a) shown with a separator and bipolar (b) configurations. Current flow is shown for electrolysis. Cell pitch is the number of electrode pairs per unit length.

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Flow configurations

- Industrial electrochemical reactors are usually flow reactors → streams of reactants into and out of the reactor

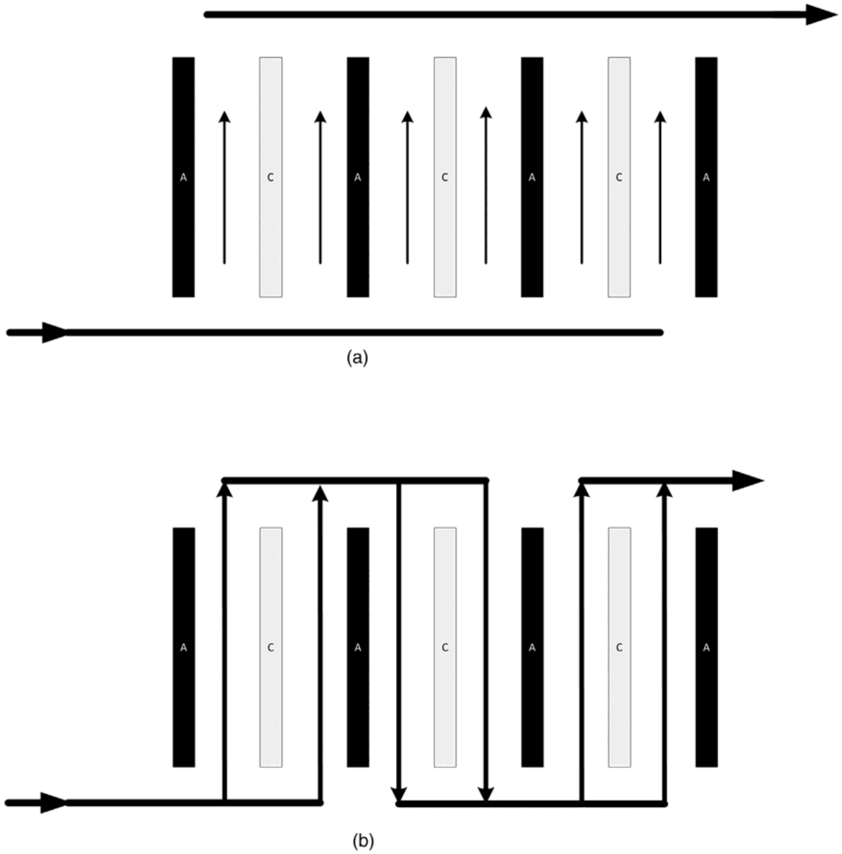
- Two principal flow arrangements: parallel flow and series flow

(1) Parallel flow: a lower pressure drop

(2) Series flow: problem associated gas evolution

→ hybrids of parallel and series possible

Illustration 14.8



(a)

(b)

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

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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

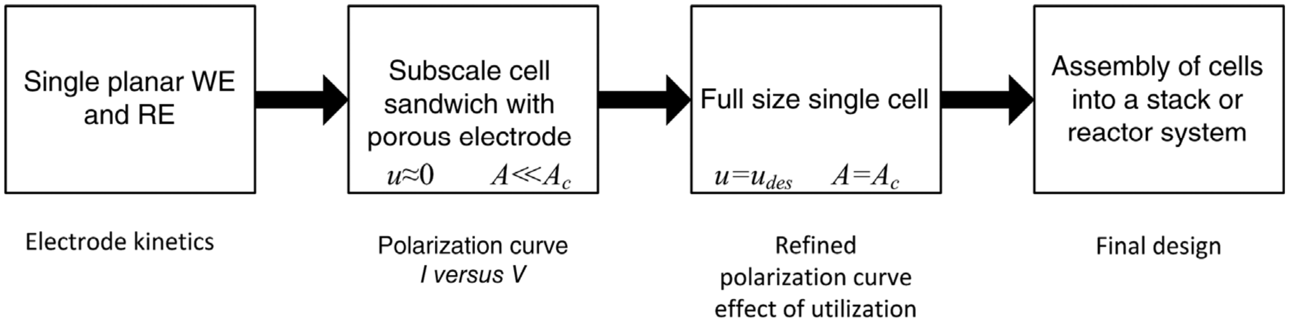
cell pitch = 1 / center to center distance between electrodes of the same type

a_r = electrode area / total volume
= 2(length)(width) / [(length)(width)/cell pitch] = 2 x cell pitch

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

Illustration 14.9

Scale up



Single planar WE and RE

Subscale cell sandwich with porous electrode

$u \approx 0$ $A \ll A_c$

Full size single cell

$u = u_{des}$ $A = A_c$

Assembly of cells into a stack or reactor system

Electrode kinetics

Polarization curve
I versus V

Refined
polarization curve
effect of utilization

Final design

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

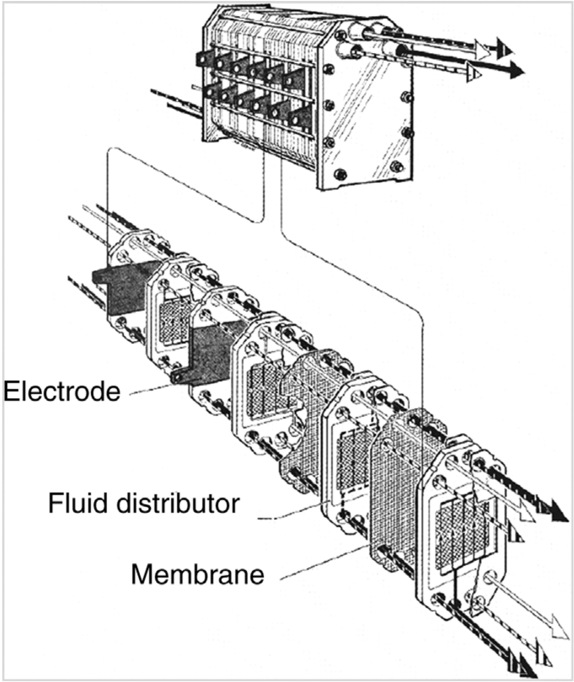


Figure 14.10 Plate-and-frame system that is commercially available for process evaluation. Image provided by ElectroCell A/S.

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engineering

u = amount reacted / amount supplied

u: utilization

A_c: full size

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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

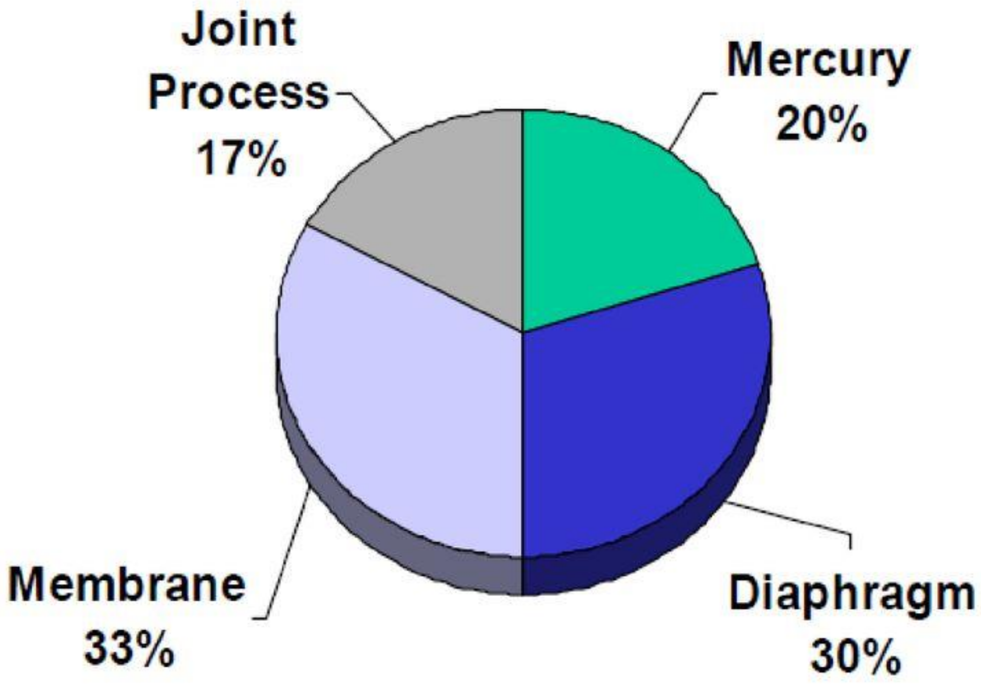
- Production of chlorine and hydrogen from hydrochloric acid using diaphragm cell and membrane cell → process converting byproduct HCl due to serious environmental concerns

- Other examples of industrial electrolysis: fluorine gas, strong oxidizing agents such as $KMnO_4$, H_2O_2, $Na_2S_2O_8$(sodium persulfate) → recently, hydrogen peroxide(H_2O_2) has been produced in situ by electrolysis at the quantity needed for optimal use

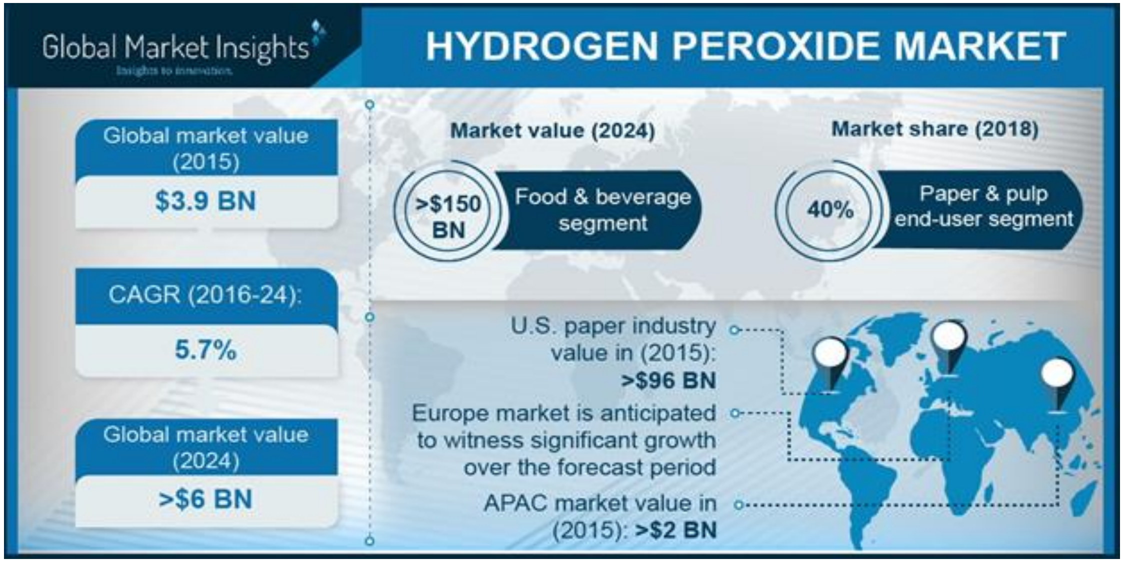
- MnO_2 production by electrolysis for battery applications

- Hot issue: water electrolysis to produce hydrogen and oxygen gas at high purity

Chlor-Alkali Production by Process Type



Hydrogen Peroxide(과산화수소)



Global Market Insights
Insights to innovation

HYDROGEN PEROXIDE MARKET

Global market value (2015)
$3.9 BN

CAGR (2016-24):
5.7%

Global market value (2024)
>$6 BN

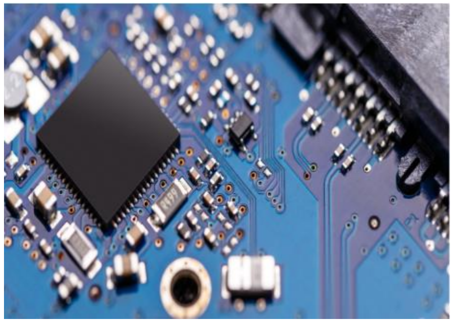
Market value (2024)
>$150 BN Food & beverage segment

Market share (2018)
40% Paper & pulp end-user segment

U.S. paper industry value in (2015): **>$96 BN**

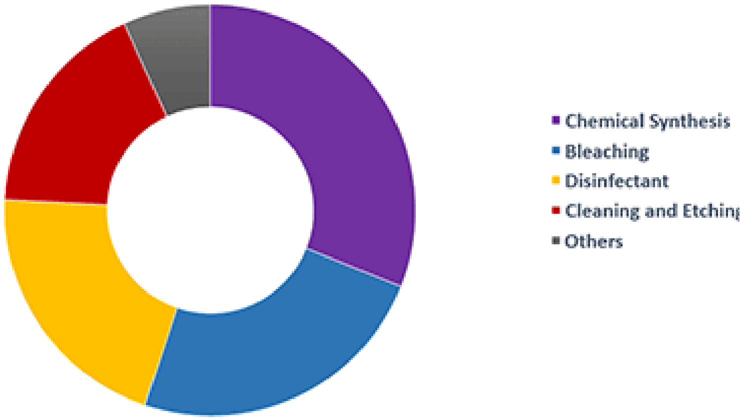
Europe market is anticipated to witness significant growth over the forecast period

APAC market value in (2015): **>$2 BN**

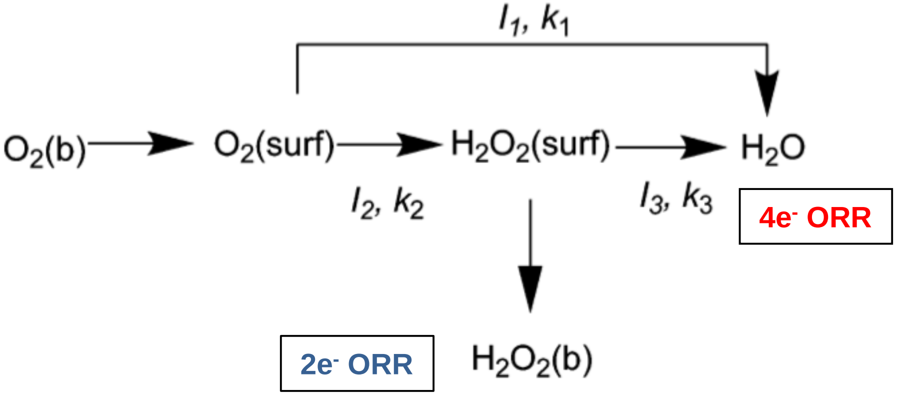


Global Hydrogen Peroxide Market

Market Share by Application (%)



Source: www.expertmarketresearch.com



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

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

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

Illustration 14.10

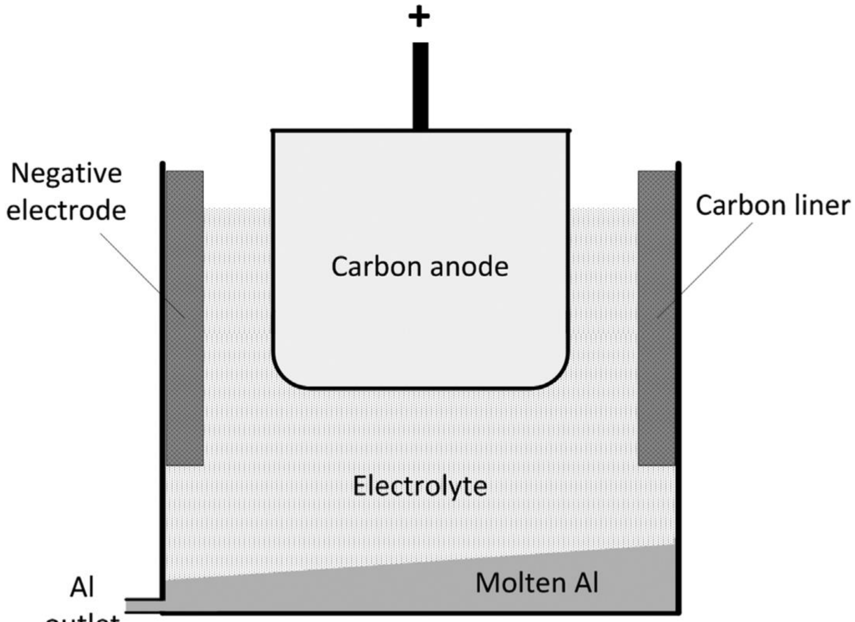


Figure 14.11 Hall–Héroult process for the production of aluminum.

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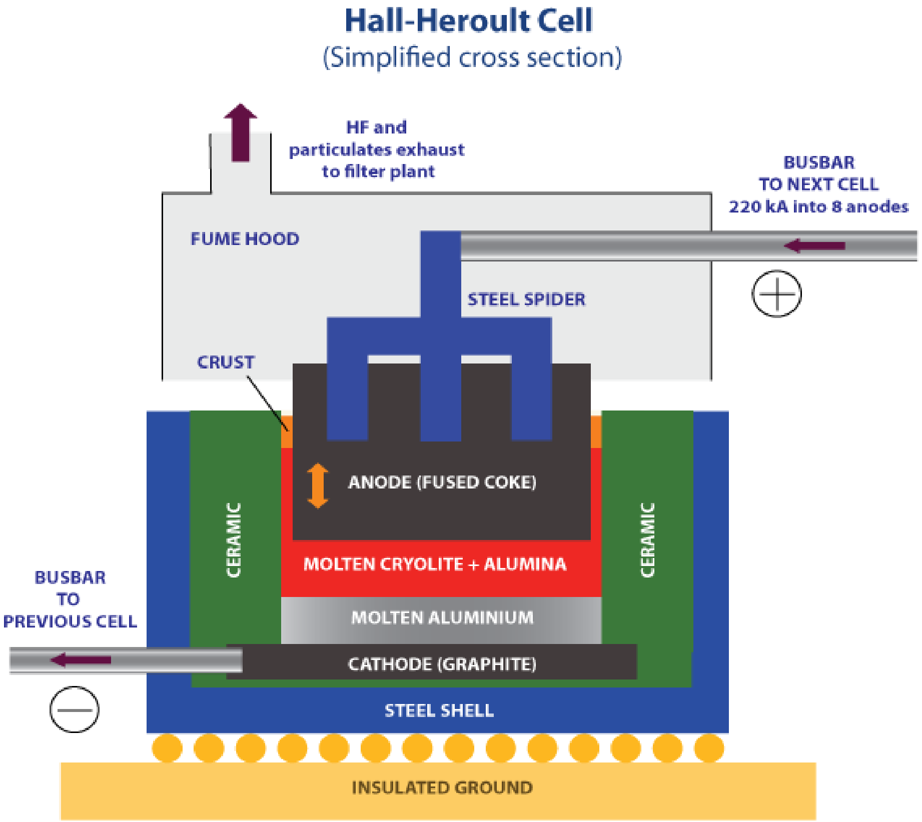
$$\text{Cathode: } 4Al^{3+} + 12e^{-} \rightarrow 4Al$$

$$\text{Anode: } 6O^{2-} + 3C \rightarrow 3CO_2 + 12e^{-}$$

$$\text{Overall: } 2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$



From Wikipedia

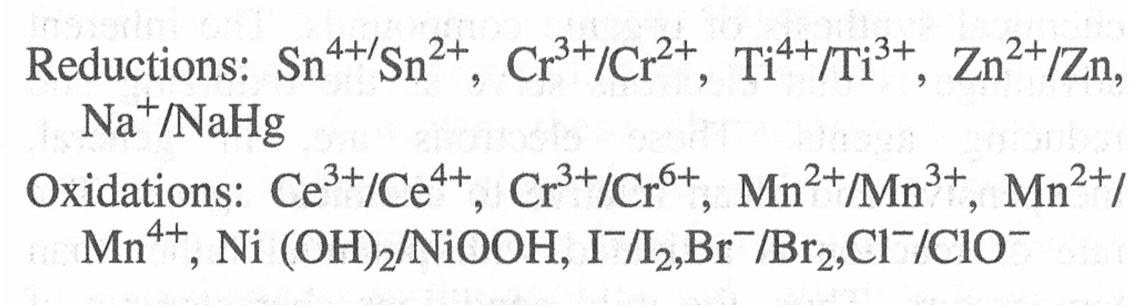
From EGA

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

Oxidations: Ce^{3+}/Ce^{4+}, Cr^{3+}/Cr^{6+}, Mn^{2+}/Mn^{3+}, Mn^{2+}/Mn^{4+}, $Ni\,(OH)_2/NiOOH$, 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)

$$2CH_2CHCN + 2H^+ + 2e^- \rightarrow NC(CH_2)_4CN$$

$$H_2O \rightarrow 2H^+ + 0.5O_2 + 2e^-$$

$$\text{Overall reaction: } 2CH_2CHCN + H_2O \rightarrow 0.5O_2 + NC(CH_2)_4CN$$

- Electrochemical synthesis of ethylene glycol

Illustration 14.11

Thermal management and cell operation

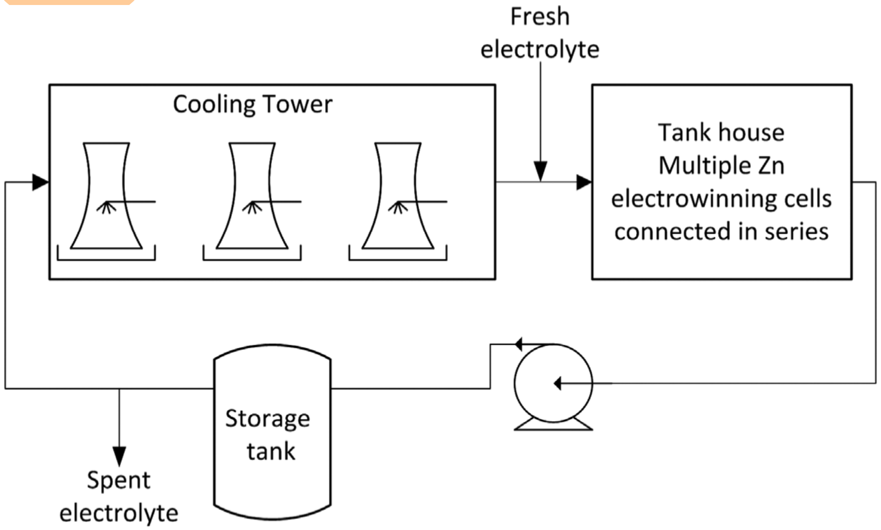


Figure 14.12 Process diagram for Zn electrowinning that emphasizes cooling of the electrolyte.

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energy balance

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

where

m = mass of the system, assumed constant [kg]
C_p = average heat capacity of the system [J·kg^{-1}·K^{-1}]
$H_{out,p}$ = enthalpy of outlet stream p [J·mol^{-1}]
$H_{in,m}$ = enthalpy of inlet stream m [J·mol^{-1}]
$\dot{n}_m$ = molar flowrate of inlet stream m, [mol·s^{-1}]
$\dot{n}_p$ = molar flowrate of outlet stream p, [mol·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 [mol·s^{-1}]
$\Delta H_{Rx,j}$ = Heat of reaction j per mole of species i [J·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

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Anode: $2OH^- \rightarrow 0.5O_2 + H_2O + 2e^-$

- Water electrolysis as a function of T
→ T↑ → potential↓

$U = E^0_{cell}$

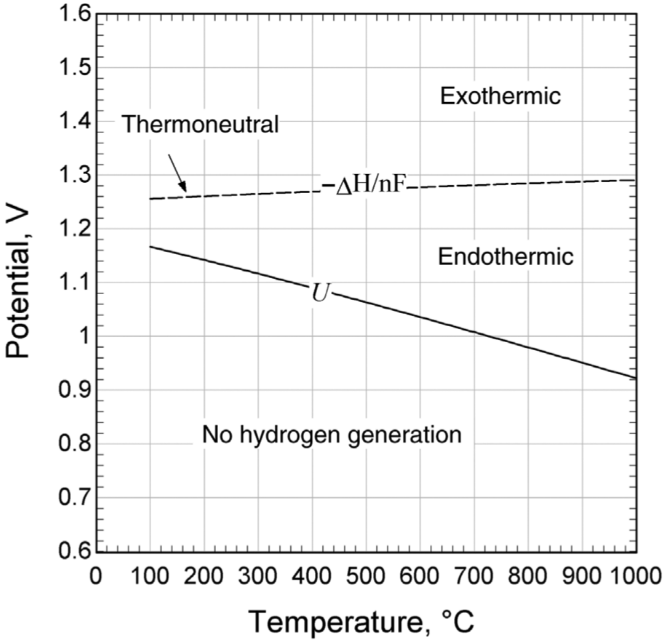

Figure 14.13 Equilibrium and thermoneutral potentials assuming gaseous water.

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- 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·m^2

(note at 25ºC, E = 1.229 V,
and thermoneutral potential is 1.481 V
assuming liquid water)

- electrolyte: 25-30% KOH
- 60~100ºC, >15 years

Illustration 14.13

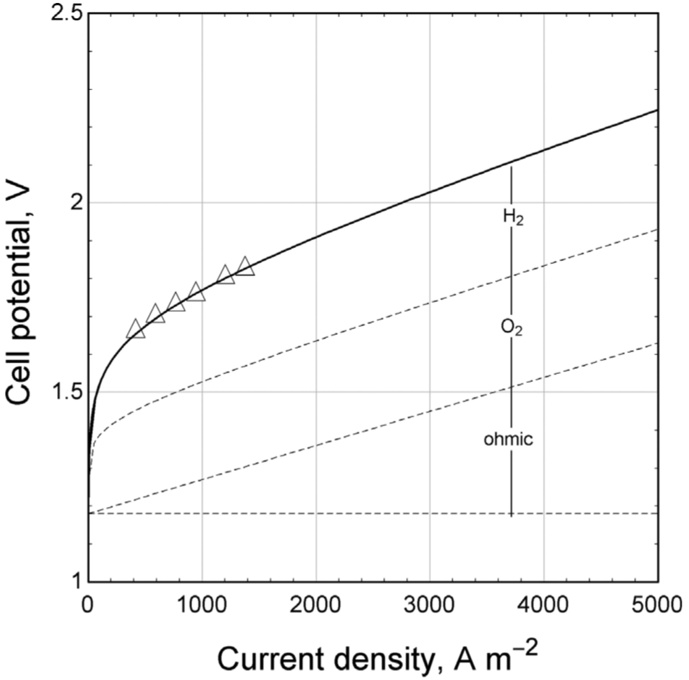


Figure 14.14 Electrolysis of water at 40 °C.
Source: Adapted from Ulleberg 2003.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

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

Cathode: $2H^+ + 2e^- \rightarrow H_2$

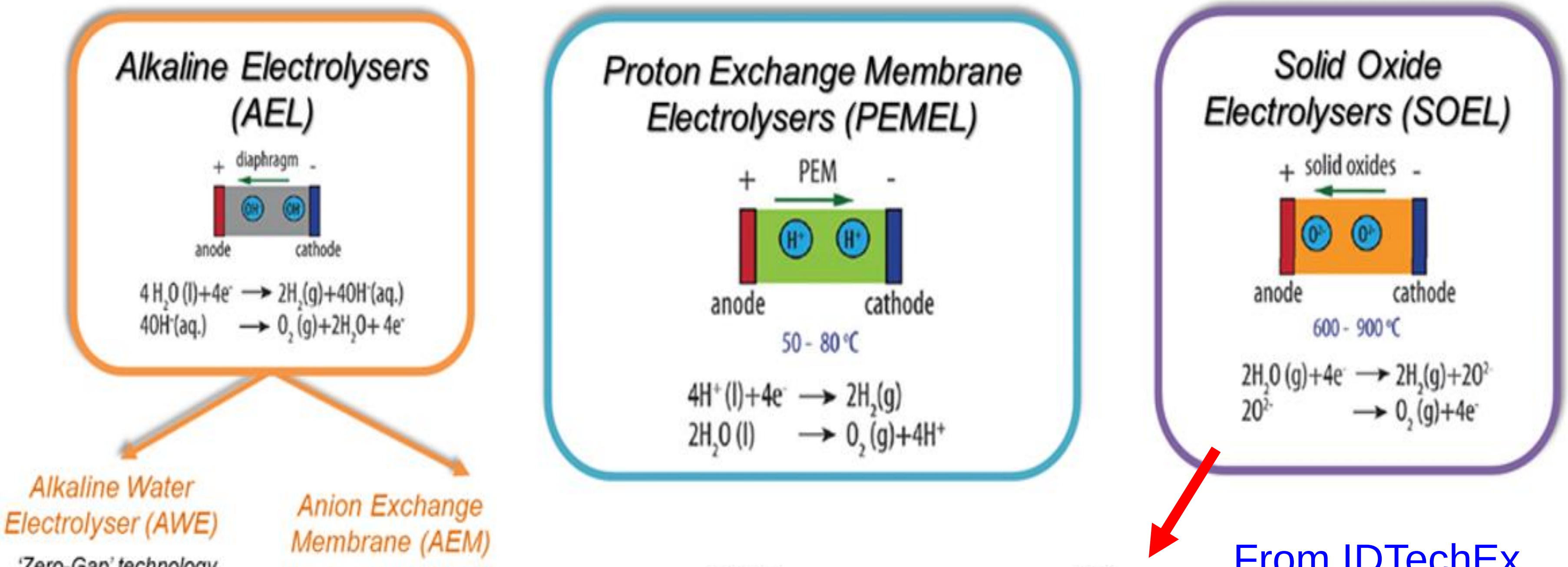
Anode: $H_2O \rightarrow 0.5O_2 + 2H^+ + 2e^-$

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

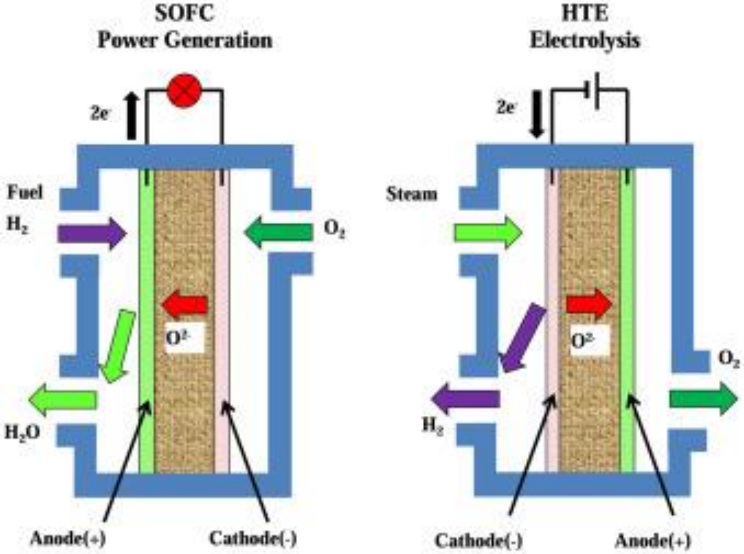
Cathode: $H_2O + 2e^- \rightarrow H_2 + O^{2-}$

Anode: $O^{2-} \rightarrow 0.5O_2 + 2e^-$

Electrolyser Systems



From IDTechEx

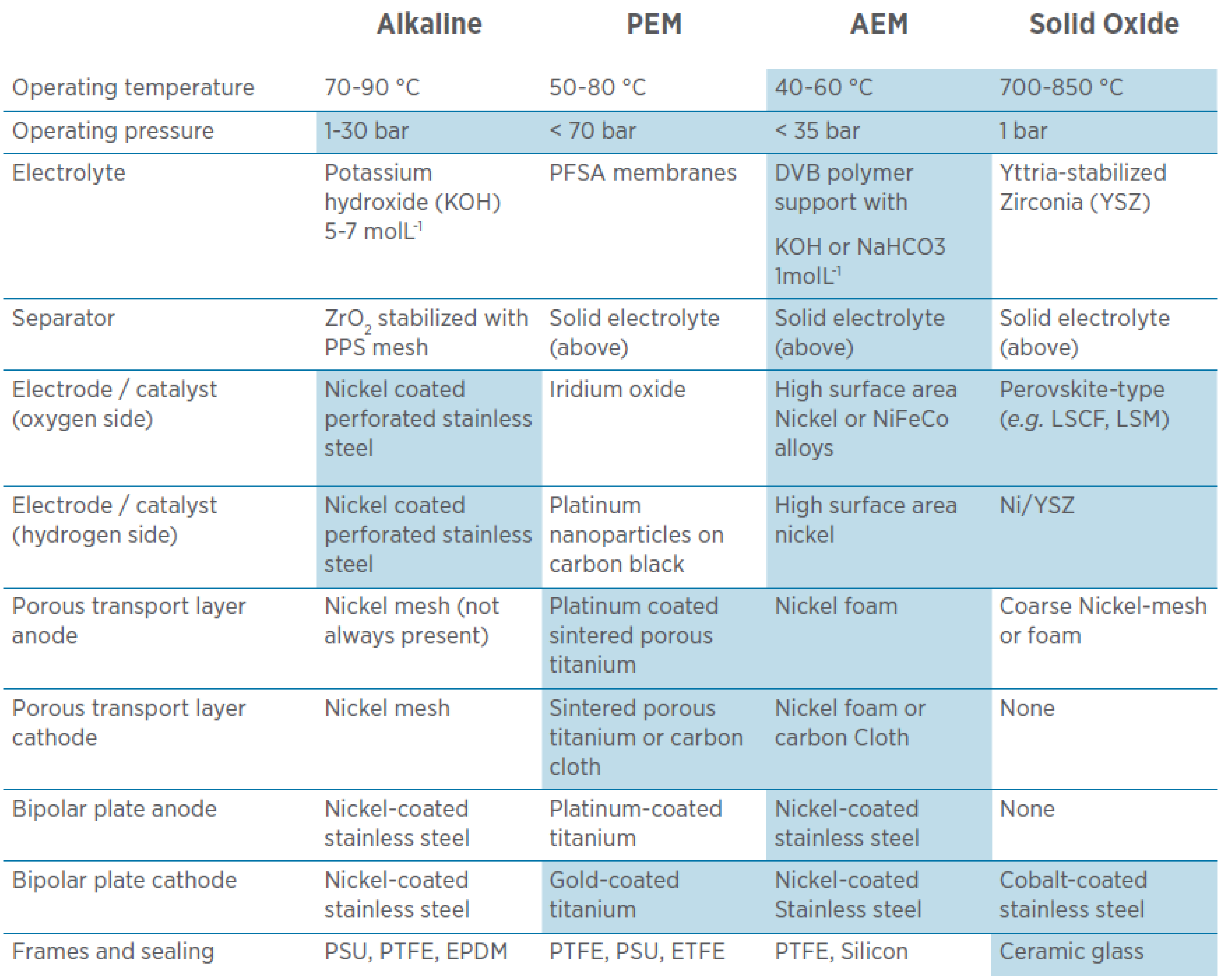


High Temperature Electrolyzer

e.g. Nuclear Hydrogen Producction

Table 1. Characterisation of the four types of water electrolysers.

Blue color: low technology maturity



	Alkaline	PEM	AEM	Solid Oxide
Operating temperature	70-90 °C	50-80 °C	40-60 °C	700-850 °C
Operating pressure	1-30 bar	< 70 bar	< 35 bar	1 bar
Electrolyte	Potassium hydroxide (KOH) 5-7 molL^{-1}	PFSA membranes	DVB polymer support with KOH or NaHCO3 1molL^{-1}	Yttria-stabilized Zirconia (YSZ)
Separator	ZrO_2 stabilized with PPS mesh	Solid electrolyte (above)	Solid electrolyte (above)	Solid electrolyte (above)
Electrode / catalyst (oxygen side)	Nickel coated perforated stainless steel	Iridium oxide	High surface area Nickel or NiFeCo alloys	Perovskite-type (*e.g.* LSCF, LSM)
Electrode / catalyst (hydrogen side)	Nickel coated perforated stainless steel	Platinum nanoparticles on carbon black	High surface area nickel	Ni/YSZ
Porous transport layer anode	Nickel mesh (not always present)	Platinum coated sintered porous titanium	Nickel foam	Coarse Nickel-mesh or foam
Porous transport layer cathode	Nickel mesh	Sintered porous titanium or carbon cloth	Nickel foam or carbon Cloth	None
Bipolar plate anode	Nickel-coated stainless steel	Platinum-coated titanium	Nickel-coated stainless steel	None
Bipolar plate cathode	Nickel-coated stainless steel	Gold-coated titanium	Nickel-coated Stainless steel	Cobalt-coated stainless steel
Frames and sealing	PSU, PTFE, EPDM	PTFE, PSU, ETFE	PTFE, Silicon	Ceramic glass

Source: IRENA (2020)

Water Electrolysis(수전해)

Other electrolysis processes

- Advantages over water electrolysis:
(1) Use of a waste stream to produce the desire 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 NH_3 → H_2 production + cleaning up the stream
- $E^0_{cell} = 0.06$ V of electrolysis of NH_3 → lower than water electrolysis (1.229 V) → hydrogen production from ammonia waste streams require less energy
- Urea-contaminated wastewater electrolysis ($E^0_{cell} = 0.37$ V)

$NH_3 \rightarrow 3/2H_2$ (cathode) + $1/2N_2$ (anode)

$CO(NH_2)_2 + H_2O \rightarrow 3H_2$ (cathode) + N_2 (anode) + CO_2

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+})

$V^{3+} + e^- = V^{2+}$ ($E^0 = -0.26$ V)
$VO_2^+ + 2H^+ + e^- = VO^{2+} + H_2O$ (E^0=1.00V)

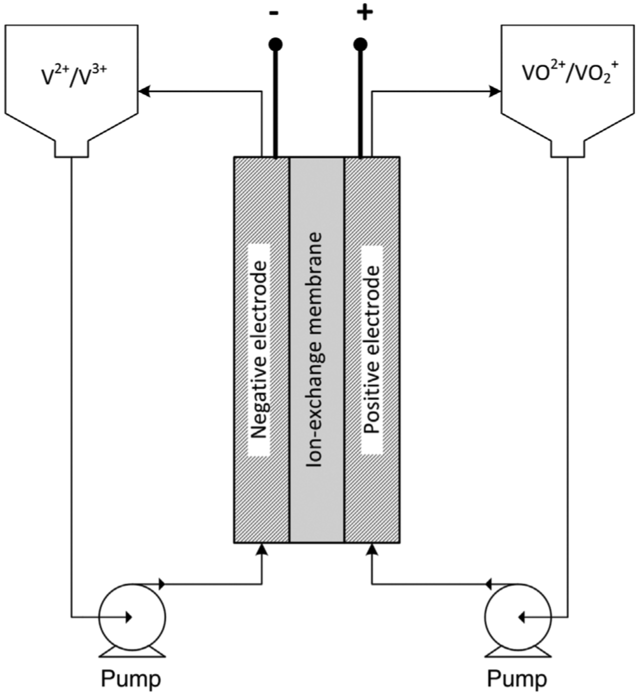


Figure 14.16 Vanadium redox-flow battery. Reactions and transport are shown for discharging.

Illustration 14.14

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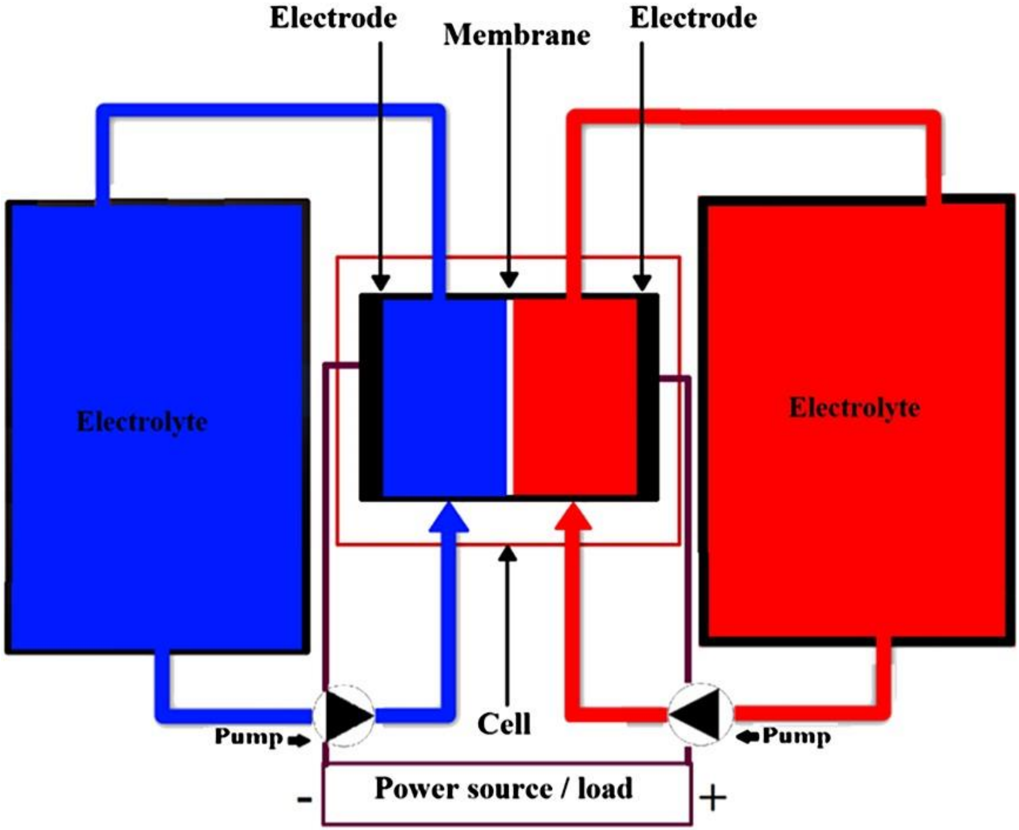
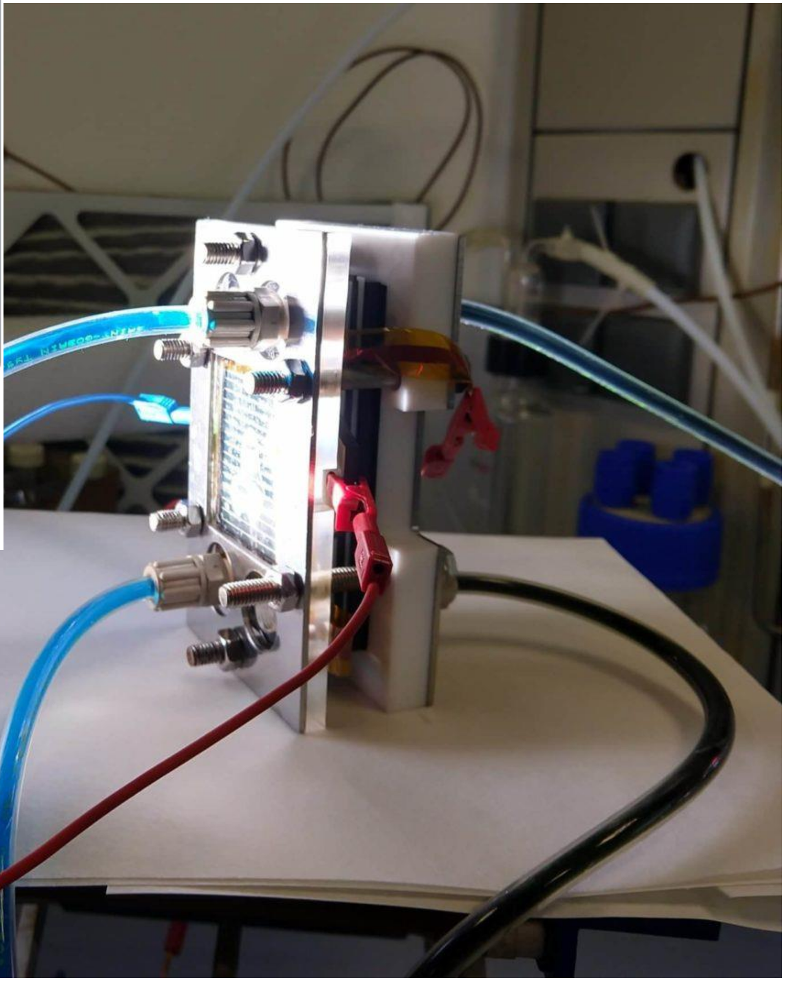


A. Kunha *et al*,
Int. J. Energy Research (2014)



PV Magazine (Dec. 21, 2020)

- charge-discharge curve

$$E = E^0 + (RT/2F)\ln[(c^2_{V2+}\, c_{VO2}{}^{+}) / (c^2_{v3+}\, c_{VO}{}^{2+})]$$

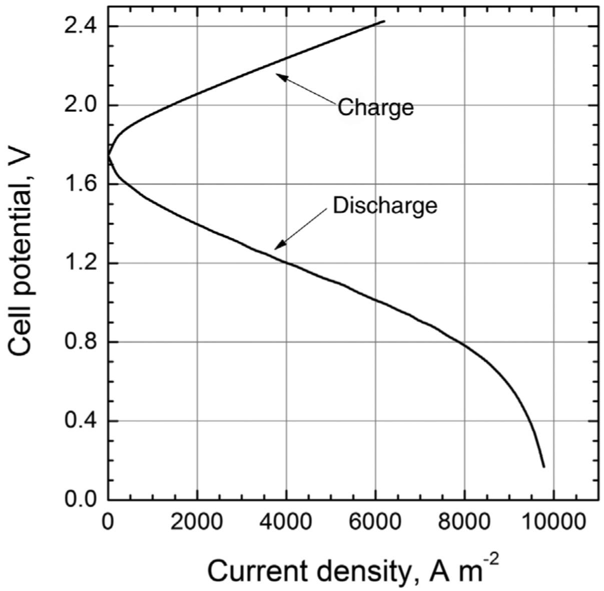


Figure 14.17 Example of polarization curve for the vanadium redox-flow battery at a high state of charge.

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Illustration 14.15