

Syllabus

2018 Fall, 4582-608 (WCU Program)

Electrochemical Energy Engineering, 전기화학에너지공학

LECTURER: Professor Yung-Eun Sung (성영은)

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OUTLINE

This class deals with electrochemical principles of the electrochemical energy devices and systems such as fuel cells, batteries & solar cells and, photoelectrochemical devices.

TEXTBOOKS

Mathew M. Mench, *Fuel Cell Engines*, Wiley, 2008.

Robert A. Huggins, *Advanced Batteries*, Springer, 2009.

(e-book in library, also in Korean)

SCHEDULE

1. Fuel cell: electrochemical principles (Mench, ch. 2)
2. Thermodynamics of fuel cell systems (Mench, ch. 3)
3. Performance characterization of fuel cell systems ((Mench, ch. 4)
4. Transport in fuel cell systems ((Mench, ch. 5)

5. Battery: electrochemical principles ((Huggins, ch. 1-5)
6. Negative electrodes in lithium cells ((Huggins, ch. 6-8)
7. Positive electrodes in lithium systems ((Huggins, ch. 9)
8. Other topics on electrodes ((Huggins, ch. 12)

9. Photoelectrochemical devices (special lecture)

GRADING (B⁺ & above ~ 80%, B⁰ & below ~ 20%)

Midterm Exam 40%, Final Exam 40%, Homeworks & Attendance 20 %

LECTURE ROOM & TIME: Rm #302-720, 12:30-13:45 Mon. & Wed.

OFFICE HOUR: Rm #302-729, 14:00-17:00 Mon. & Wed.

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Universitas Indonesia (국립 인도네시아 대학교)



ASIAN GAMES 2018



Why this coursework?

Electric vehicle spec. (battery)

Power 90 kW

Energy density 140 Wh/kg, Power density 250 W/kg

Battery weight 300 kg

Efficiency 7 km/kWh

280 km driving distance

Fuel cell vehicle

Power 113 kW (153 HP)

Power density 3 kW/l, 2kW/kg, FC weight 56 kg

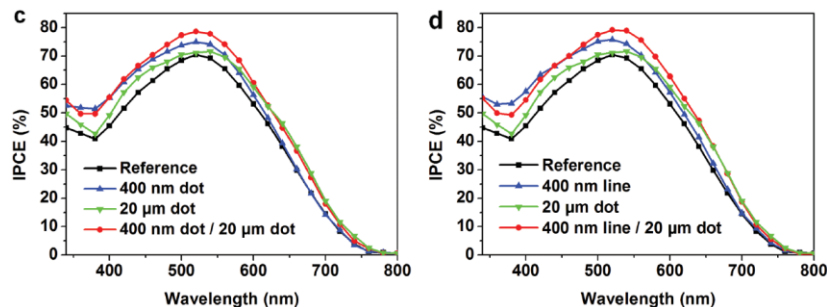
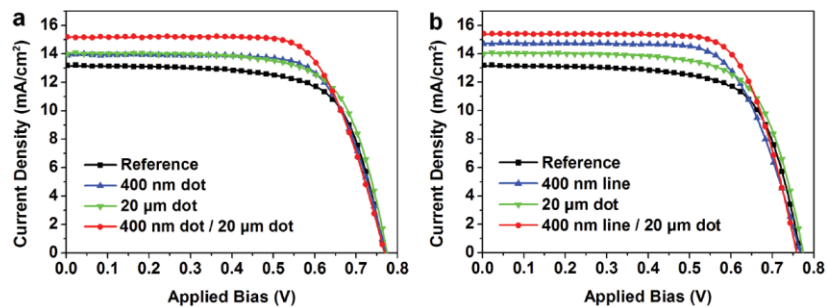
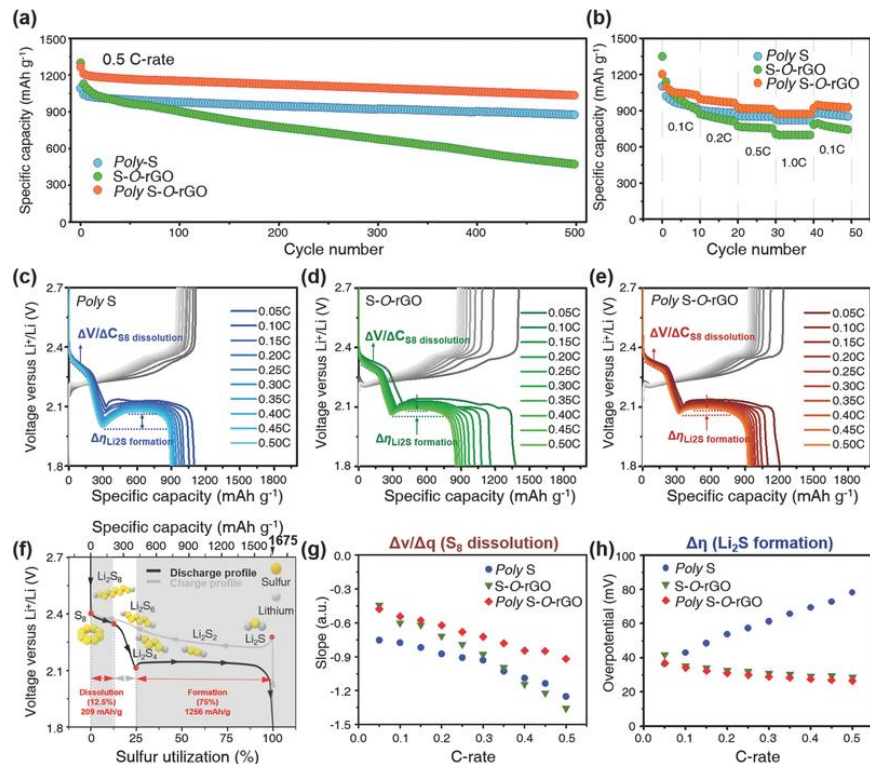
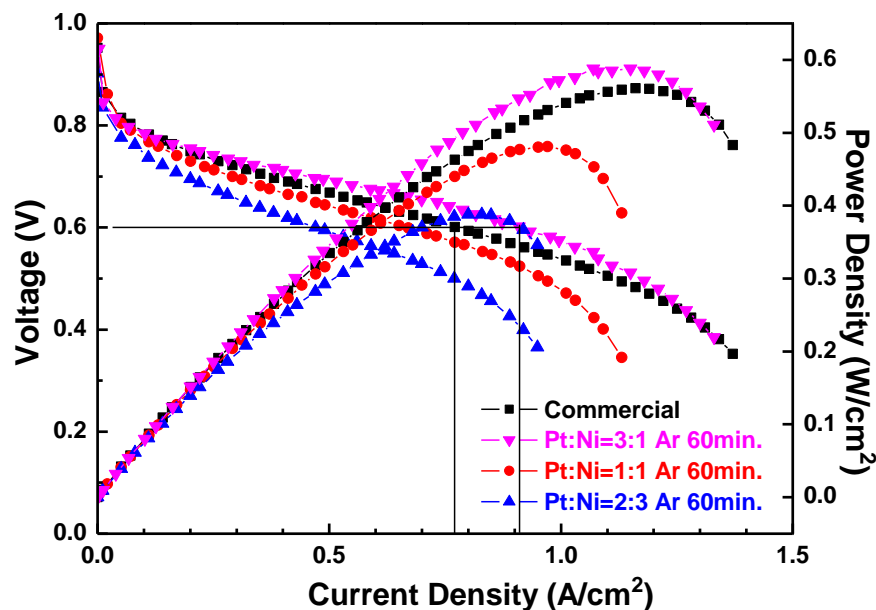
Efficiency 6 km/kWh

~460 km driving distance

(5 kg H₂ in tank (87 kg))

cf. Gasoline engine: **~800 km, 60~70 liter tank, 12 km/liter**

I-V Curves in Fuel Cell, Battery, Solar Cell

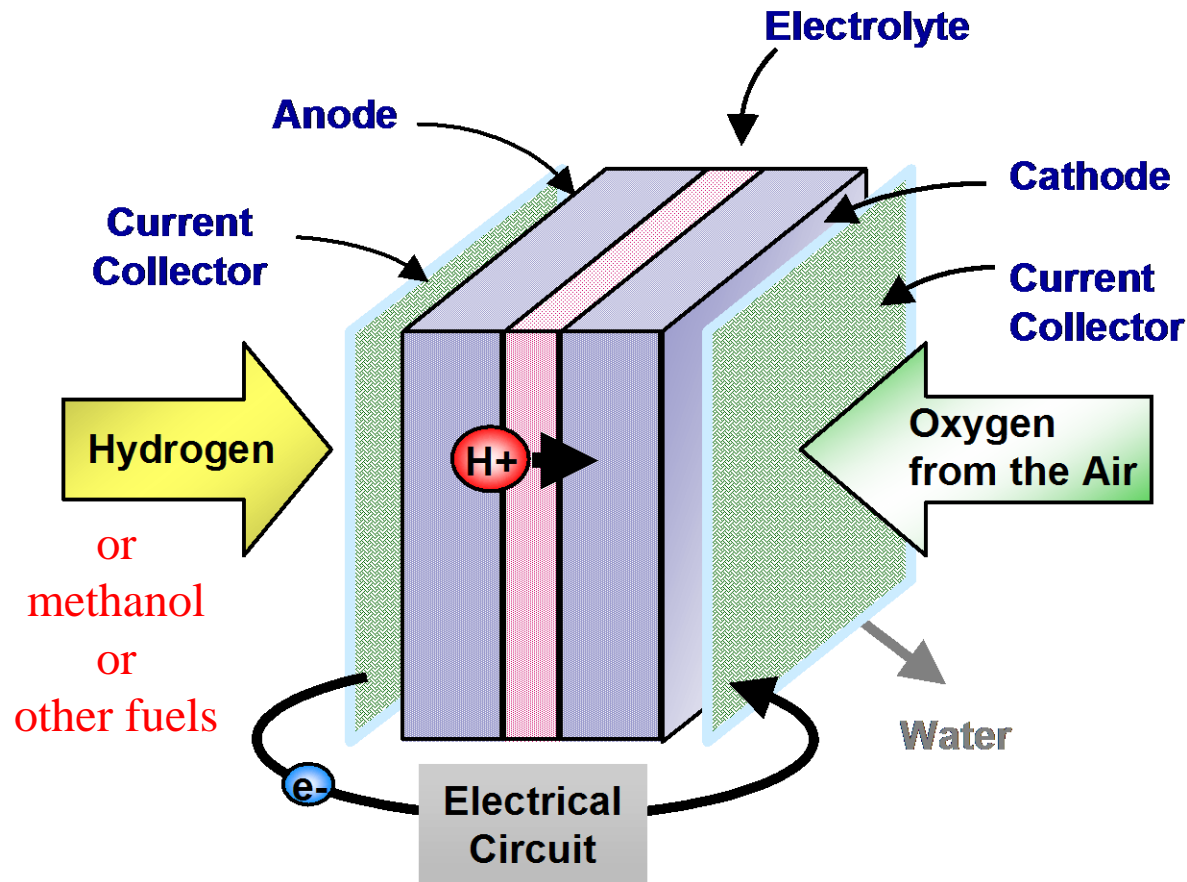


1. Fuel Cell: Electrochemical Principles (Mench, ch. 2)

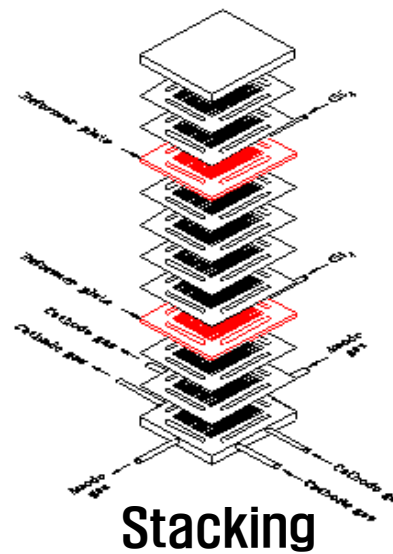
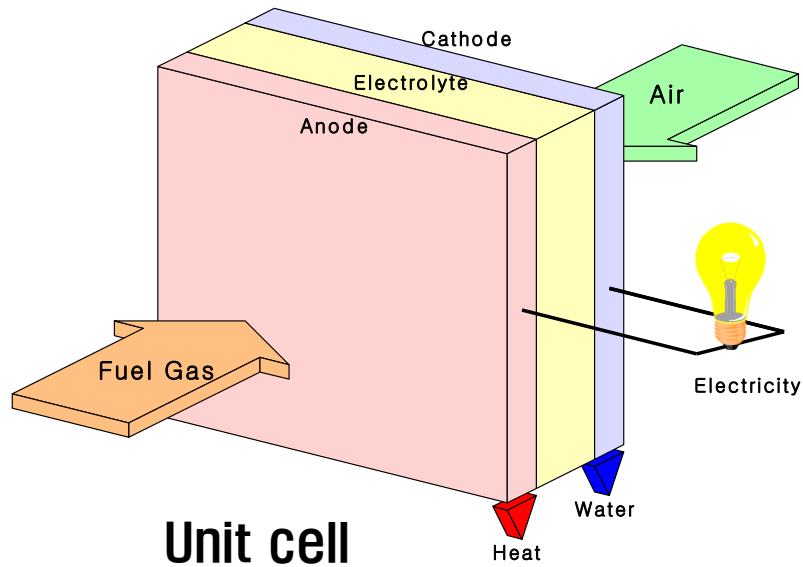
1. Electrochemical vs. chemical reactions
2. Electrochemical reaction
3. Scientific units, constants, and basic laws
4. Faraday's laws: consumption and production of species
5. Measures of reactant utilization efficiency
6. The generic fuel cell

Fuel cell

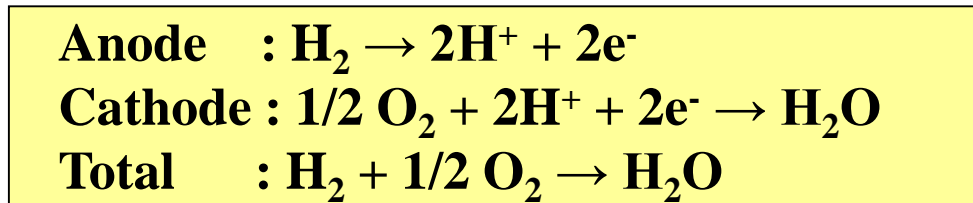
an electrochemical cell which can continuously convert the chemical energy of a fuel and an oxidant to electrical energy



Principle of fuel cell



Stack



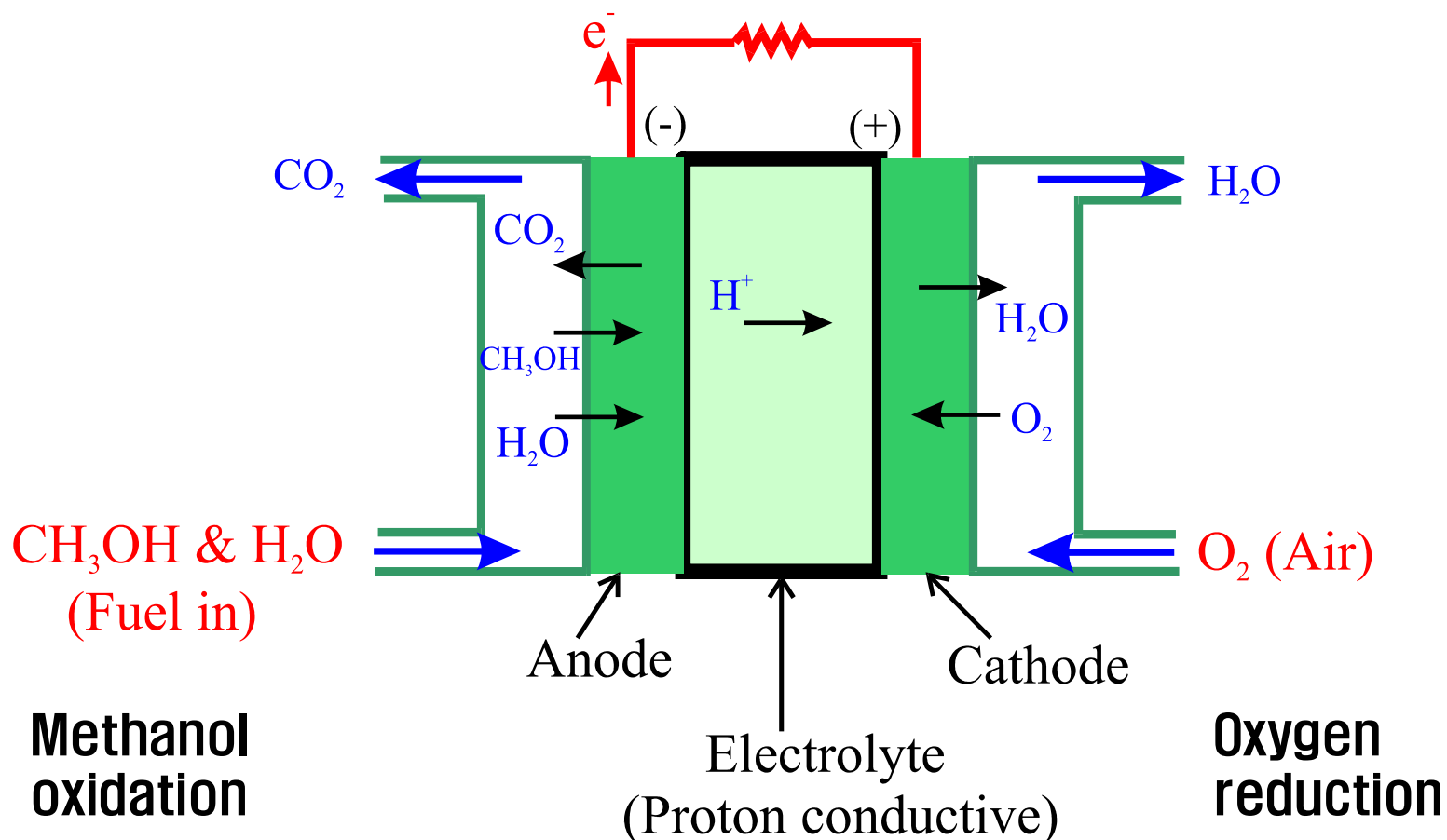
Fuel cell station

Fuel cell : hydrogen + oxygen [air] \rightarrow water + electric energy

Respiration : glucose + oxygen (air) \rightarrow carbon dioxide+ water + energy

Organic fuel cells

Direct Methanol Fuel Cell (DMFC)



Liquid fuels: formic acid, ethanol, glucose, nitrogen compounds...

Integrated roles in fuel cell

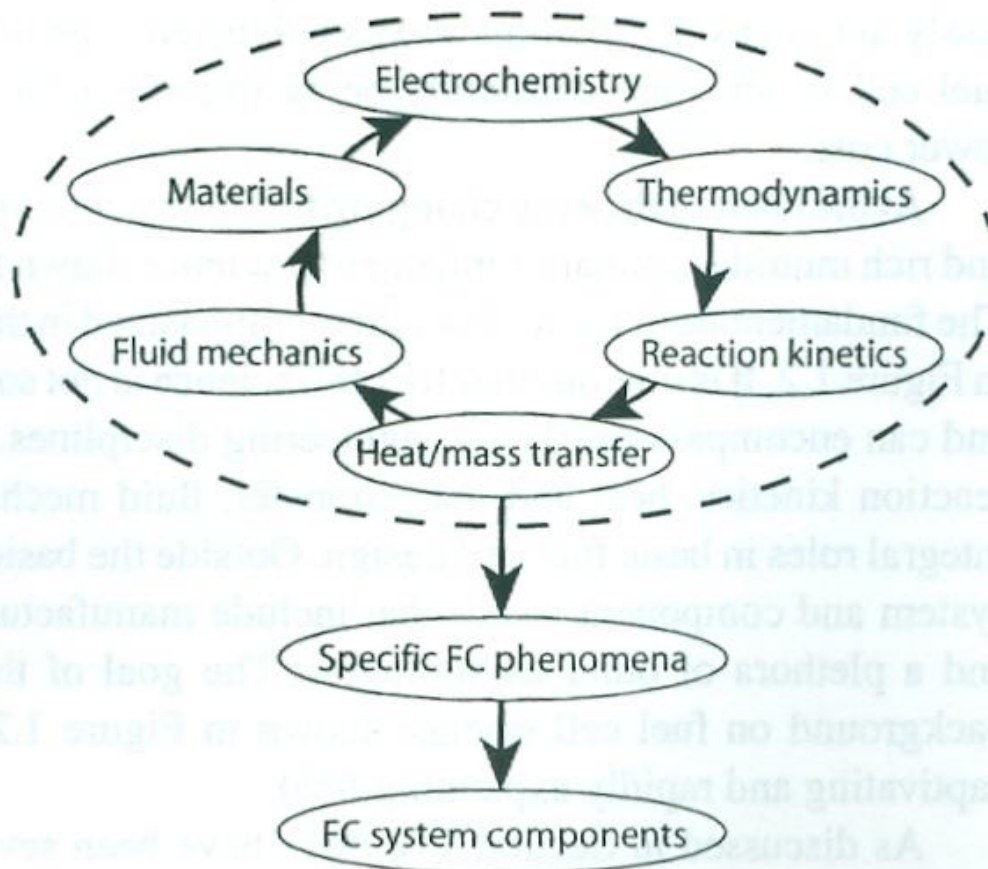


Figure 1.2 Major engineering disciplines involved in fundamental fuel cell science.

1. Electrochemical vs. chemical reactions

-Heat engine: limited thermal efficiency by the Carnot cycle

$$\eta_{\text{th,Carnot}} = 1 - (T_{\text{L}}/T_{\text{H}})$$

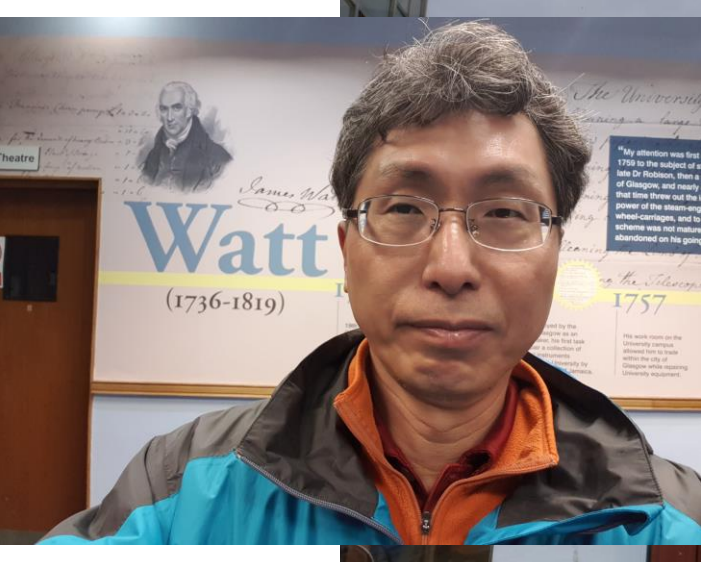
T_{H} : max. temp. of the heat engine(K), T_{L} : ejection T of the engine

e.g. heat engine operated at 400°C (673K) & eject heat at 50°C (323K) \rightarrow efficiency?

-Heat engine: operation temperature $\uparrow \rightarrow$ efficiency \uparrow

-Electrochemical engine: not subject to Carnot limitations

Glasgow, UK (Aug. 19–24, 2018)



Watt



Kelvin



Adam Smith

2. Electrochemical reaction

Basic reaction circuit

Current: motion of charged species and can be in the form of anions (e.g. O^{2-}), cations (e.g. H^+), or electrons

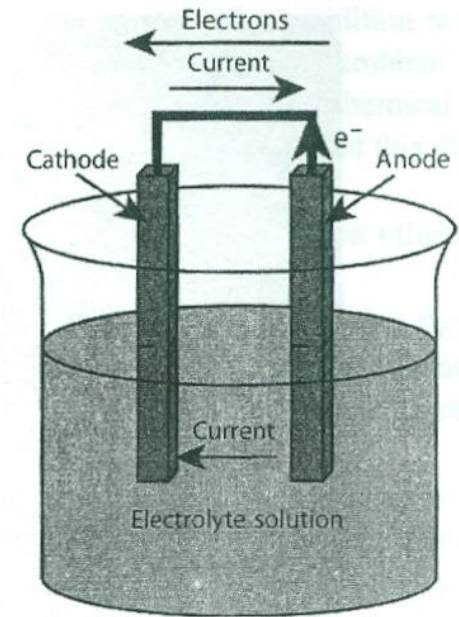


Figure 2.2 Basic reaction circuit.

- Anode: oxidation \rightarrow loss of e^- \rightarrow increase in the valence state
- Cathode: reduction \rightarrow consume e^- \rightarrow reducing the valence state
- Electrolyte: to conduct ions from one electrode to the other & to prevent e^- short-circuiting between the electrodes \rightarrow liquid or solid
- External connection

(1) Global vs. elementary reaction

-Overall H₂-O₂ fuel cell reaction: $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$ $E_0 = 1.229 \text{ V}$

-In acidic electrolyte

anode: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ $E_0 = 0.000 \text{ V}$

cathode: $1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$ $E_0 = 1.229 \text{ V}$

Total: $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$ $E_0 = 1.229 \text{ V}$

-In alkaline electrolyte

anode: $\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$ $E_0 = -0.828 \text{ V}$

cathode: $1/2\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$ $E_0 = 0.401 \text{ V}$

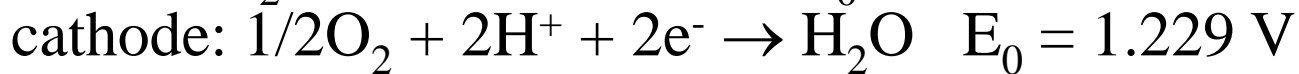
Total: $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$ $E_0 = 1.229 \text{ V}$

-Hydrogen oxidation reaction(HOR): not single step \rightarrow
elementary steps

-Oxygen reduction reaction(ORR): reaction steps still unknown

(2) Conservation of charge

Fuel cell



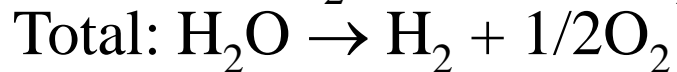
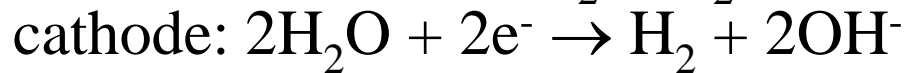
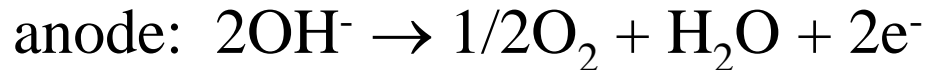
-Chemical energy of electrochemical reaction \rightarrow products $<$ reactants \rightarrow thermodynamically favorable \rightarrow reaction generate current (a flow of electrons or ions) \rightarrow “galvanic”

cf. thermodynamics can not determine the rate of reaction (electrochemical kinetics)

-Fuel cell, battery, corrosion \rightarrow “galvanic” electrochemical reactions

cf. “electrolytic” electrochemical reactions require energy input to occur → electrochemical energy consuming reaction
→ chemical energy of electrochemical rxn: products > reactants

e.g., water electrolysis (HER(hydrogen evolution rxn) & OER)
gold plating, Al production



(3) Summary

- (i) Current is the flow of charge species through the electrolyte(ions) and through the external circuit(electrons)
- (ii) Current is defined as the flow of positive charge and is thus movement in a direction opposite to the electron flow
- (iii) For both galvanic and electrolytic rxns, electrons are conducted from the anode, through the external circuit, and to cathode
- (iv) For both galvanic and electrolytic rxns, oxidation occurs at the anode and reduction occurs at the cathode
- (v) The sign of the electrode depends on type of cell. For a galvanic rxn, reduction occurs at a higher voltage potential than oxidation and thus the cathode is designated as the positive electrode. For an electrolytic cell, the opposite is true and the anode is the positive electrode. In a rechargeable car battery, the cathode is the positive(+).

3. Scientific units, constants, basic laws

(1) Elemental charge, current, voltage, resistance

(i) Current (I): rate of the flow of charged species

Total charge passed = q (C, Coulomb) = $\int (dc/dt)dt = \int Idt$

I: A (ampere) unit

1 C = 6.28×10^{18} electrons passed = 1 A · s

(charge on a single electron = 1.6×10^{-19} C)

1 A = 1 C/s, 6.28×10^{18} charges moving in one second

1 Ah = (C/s) · h · 3600 s/h = 3600 C

(cf. total energy, 1 Wh = 1 J/s · h · 3600s/h = 3600 J)

(ii) Voltage

Volt (V): a measure of the potential to do electrical work

Electrical work is done when current flows through a resistance

$$1 \text{ V} = 1 \text{ J/C}$$

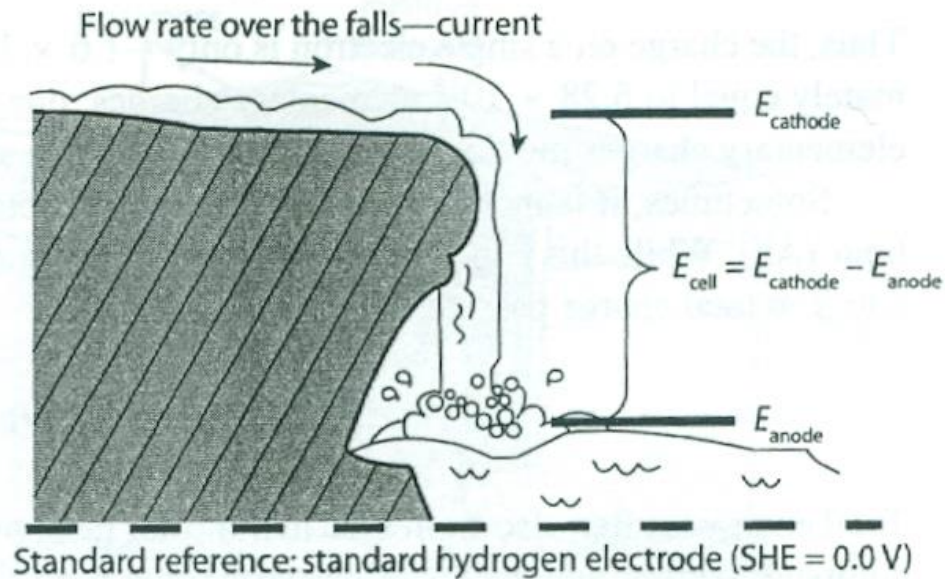


Figure 2.6 Waterfall analogy to voltage potential. E represents the voltage potential.

Electrical power, $P_e = IV = IE_{\text{cell}}$

Standard potential, SHE: arbitrarily assigned to 0 V

Standard electrochemical reduction potential

Oxidation potential:
simply opposite sign

Table 2.1 Partial Electrochemical Reduction Potential Series at 298°C

Half Reaction	Voltage E° (V)
$\text{Ag}_{\text{aq}}^+ + \text{e}^- \rightarrow \text{Ag}_{\text{s}}$	+0.799
$\text{AgBr}_{\text{s}} + \text{e}^- \rightarrow \text{Ag}_{\text{s}} + \text{Br}_{\text{aq}}^-$	+0.095
$\text{AgCl}_{\text{s}} + \text{e}^- \rightarrow \text{Ag}_{\text{s}} + \text{Cl}_{\text{aq}}^-$	+0.222
$\text{HClO}_{\text{aq}} + \text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{Cl}_{2,\text{g}} + \text{H}_2\text{O}_{\text{l}}$	+1.63
$\text{Cu}_{\text{aq}}^{2+} + 2\text{e}^- \rightarrow \text{Cu}_{\text{s}}$	+0.337
$\text{Fe}_{\text{aq}}^{2+} + 2\text{e}^- \rightarrow \text{Fe}_{\text{s}}$	-0.440
$\text{Fe}_{\text{aq}}^{3+} + 3\text{e}^- \rightarrow \text{Fe}_{\text{s}}$	+0.771
$2\text{H}_{\text{aq}}^+ + 2\text{e}^- \rightarrow \text{H}_{2,\text{g}}$	0.000
$2\text{H}_2\text{O}_{\text{l}} + 2\text{e}^- \rightarrow \text{H}_{2,\text{g}} + 2\text{OH}_{\text{aq}}^-$	-0.830
$\text{HO}_{2,\text{aq}}^- + \text{H}_2\text{O}_{\text{l}} + 2\text{e}^- \rightarrow 3\text{OH}_{\text{aq}}^-$	+0.880
$\text{H}_2\text{O}_{2,\text{aq}} + 2\text{H}_{\text{aq}}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}_{\text{l}}$	+1.776
$\text{K}_{\text{aq}}^+ + \text{e}^- \rightarrow \text{K}_{\text{s}}$	-2.925
$\text{Li}_{\text{aq}}^+ + \text{e}^- \rightarrow \text{Li}_{\text{s}}$	-3.05
$\text{Mg}_{\text{aq}}^{2+} + 2\text{e}^- \rightarrow \text{Mg}_{\text{s}}$	-2.37
$\text{N}_{2,\text{g}} + 4\text{H}_2\text{O}_{\text{l}} + 4\text{e}^- \rightarrow 4\text{OH}_{\text{aq}}^- + \text{N}_2\text{H}_{4,\text{aq}}$	-1.16
$\text{N}_{2,\text{g}} + 5\text{H}_{\text{aq}}^+ + 4\text{e}^- \rightarrow \text{N}_2\text{H}_{5,\text{aq}}^-$	-0.23
$\text{NO}_{3,\text{aq}}^- + 4\text{H}_{\text{aq}}^+ + 3\text{e}^- \rightarrow \text{NO}_{\text{g}} + 2\text{H}_2\text{O}_{\text{l}}$	+0.96
$\text{Na}_{\text{aq}}^+ + \text{e}^- \rightarrow \text{Na}_{\text{s}}$	-2.71
$\text{Ni}_{\text{aq}}^{2+} + 2\text{e}^- \rightarrow \text{Ni}_{\text{s}}$	-0.28
$\text{Zn}_{\text{aq}}^{2+} + 2\text{e}^- \rightarrow \text{Zn}_{\text{s}}$	-0.76
$\text{O}_{2,\text{g}} + 4\text{H}_{\text{aq}}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}_{\text{l}}$	+1.23
$\text{O}_{2,\text{g}} + 2\text{H}_{\text{aq}}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_{2,\text{aq}}$	+0.68
$\text{O}_{2,\text{g}} + 2\text{H}_2\text{O}_{\text{l}} + 4\text{e}^- \rightarrow 4\text{OH}_{\text{aq}}^-$	+0.40
$\text{O}_{3,\text{g}} + 2\text{H}_{\text{aq}}^+ + 2\text{e}^- \rightarrow \text{O}_{2,\text{g}} + \text{H}_2\text{O}_{\text{l}}$	+2.07
$\text{S}_{\text{s}} + 2\text{H}_{\text{aq}}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{S}_{\text{g}}$	+0.141
$\text{H}_2\text{SO}_{3,\text{aq}} + 4\text{H}_{\text{aq}}^+ + 4\text{e}^- \rightarrow \text{S}_{\text{(s)}} + 3\text{H}_2\text{O}_{\text{l}}$	+0.450
$\text{HSO}_{4,\text{aq}}^- + 4\text{H}_{\text{aq}}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{SO}_{3,\text{aq}} + \text{H}_2\text{O}_{\text{l}}$	+0.170

Source: From [5].

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

If E_{cell} positive \rightarrow “galvanic”

If E_{cell} negative \rightarrow minimum applied voltage required to initiate the electrolytic rxn

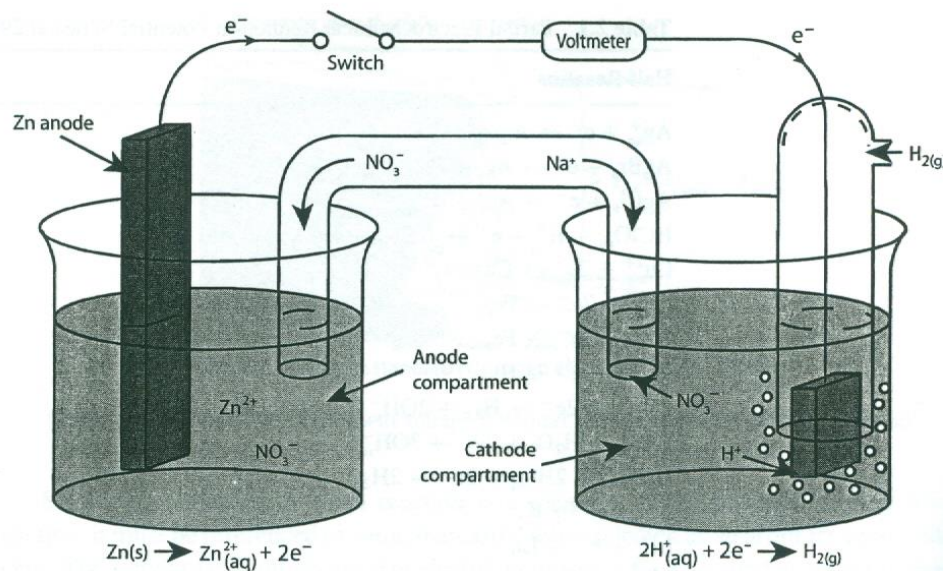


Figure 2.7 The SHE used to reference a zinc oxidation reaction. (Adapted from Ref. [5].)

(iii) Individual electrode behavior

In a galvanic rxn, anode is lower potential compared to the cathode

e.g., fuel cell

H₂ fuel: anode (-)

air: cathode (+)

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode, red}} - E_{\text{anode, red}} \\ &= +1.23 \text{ V} - 0 \text{ V} = +1.23 \text{ V (galvanic)} \end{aligned}$$

(iv) Resistance and conductance

Electrical resistance: a measure of the potential loss associated with moving a rate of charge

Unit: ohms (Ω)

$$R = V/A = (J/C)/(C/s) = J \cdot s/C^2$$

Unit of conductance: $1/\Omega$ (mho) = siemen (S)

Resistivity (ρ): $\Omega \cdot \text{m}$

$$\rho = R \cdot A/l, \quad R = \rho(l/A) = l/(\sigma A)$$

Σ : conductivity ($(\Omega \cdot \text{m})^{-1}$)

Table 2.2 Electrical and Ionic Resistivities of Selected Materials

Electron conductors	Electron Resistivity at 293 K (Ωm)
Gold	2.44×10^{-8}
Aluminum	2.28×10^{-8}
Copper	1.7×10^{-8}
Silver	1.6×10^{-8}
Stainless steel	7.2×10^{-7}
Platinum	1.1×10^{-7}
Ruthenium	7.1×10^{-8}
Palladium	10×10^{-8}
Carbon	3.5×10^{-5a}
Water (deionized)	2.5×10^5
Polytetrafluoroethylene (Teflon)	$10^{16}-10^{17}$
Ionic Conductors	Ionic Resistivity (Ωm)
Nafion PEFC electrolyte by DuPont, fully humidified	~ 10 at 353 K
SOFC electrolyte	0.1–1 at 600–1000 K
Liquid electrolytes	Highly concentration, temperature, and ion dependent

^aDependent on direction and molecular structure.

(2) Ohm's law

$$V = IR$$

In liquid solution, Ohm's law is true only for electrolytes without ionic concentration gradients. However, Ohm's law can be considered to be true for most fuel cells

$$\text{unit } V = A \cdot \Omega \rightarrow J/C = (C/s)(Js/C^2) = J/C$$

Electrical power: the rate of work

$$P_e = IV$$

$$\text{unit } W = (C/s)(J/C) = J/s = W$$

$$P_e = IV = I \cdot IR = I^2R = (V/R) \cdot V = V^2/R$$

Example 2.1 Simple Electrical Calculations

A given circuit has a continuous 5 A DC (direct current) and an overall resistance of 10 Ω . Calculate

(a) the potential loss, in volts, to maintain steady state; (b) the electrical power dissipated as heat during operation, in watts; and (c) the total heat dissipated in 2 h.

4. Faraday's law

How much mass of a given reactant is required to produce a given amount of current? How much current is required to produce a certain amount of product? → relationship between mass and charge

Faraday constant,

$$F = 6.023 \times 10^{23} \text{ e}^-/\text{mole equivalent} / 6.242 \times 10^{18} \text{ e}^-/\text{C} = 96485 \text{ C/eq}$$

or
$$F = 96485 \text{ C/eq} / 3600 \text{ C/Ah} = 26.8 \text{ Ah/eq}$$

eq: equivalent electrons (commonly omitted)

Scaling factor n: number of electrons transferred per mole of species

$$n = \text{number of electrons} / \text{mole of species of interest} = \text{eq/mol}$$

nF : charge passed per mole of species of interest

Faraday's law

(a) For a specific charge passed, the mass of the products formed are proportional to the electrochemical equivalent weight of the products

(b) The amount of product formed or reactant consumed is directly proportional to the charge passed

Example 2.2 Faraday's Law Calculations

Consider a single hydrogen fuel cell at 4 A current output: Anode oxidation: $\text{H}_2 \rightarrow 2\text{e}^- + 2\text{H}^+$
Cathode reduction: $4\text{e}^- + 4\text{H}^+ + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ Global reaction: $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$ (a) What is the molar rate of H_2 consumed for the electrochemical reaction? (b) What is the molar rate of O_2 consumed for the electrochemical reaction? (c) What is the minimum molar flow rate of air required for the electrochemical reaction? Assume air is a mixture of 21% oxygen and 79% nitrogen by volume. (d) What is the maximum molar flow rate of air delivered for the electrochemical reaction? (e) What is the rate of water generation at the cathode in grams per hour? The molecular weight of water is 18 g/mol. (f) Can the generation rate of water be greater or less than the value predicted in part (e)?

Example 2.3 Fuel Cell Stack Calculations

Consider a 20-cell stack operating steadily in series with 100 cm^2 active area per electrode, with a current density of 0.8 A/cm^2 . The fuel cell nominal voltage is 0.6 V per plate. (a) Determine the water production in grams per hour for this stack. (b) Determine the stack voltage and electrical power output.

5. Measures of reactant utilization efficiency

Faradaic efficiency: a measure of the percent utilization of reactant in a galvanic process

$$\varepsilon_f = \frac{\textit{theoretical required rate of reactant supplied}}{\textit{actual rate of reactant supplied}}$$

≡ fuel utilization efficiency (μ_f): reactant \rightarrow fuel

$$\mu_f = \frac{\textit{theoretical required rate of fuel supplied}}{\textit{actual rate of fuel supplied}}$$

Current efficiency for an electrolytic process

$$\varepsilon_c = \frac{\textit{actual rate of species reacted or produced}}{\textit{theoretical rate of species reacted or produced}}$$

Stoichiometry(화학양론) in fuel cell: the inverse of the Faradaic efficiency

Cathodic stoichiometry

$$\lambda_c = \frac{1}{\varepsilon_{f,c}} = \frac{\text{actual rate of oxidizer delivered to cathode}}{\text{theoretical rate of oxidizer required}}$$

Anodic stoichiometry

$$\lambda_a = \frac{1}{\varepsilon_{f,a}} = \frac{\text{actual rate of fuel delivered to anode}}{\text{theoretical rate of fuel required}}$$

In fuel cell, λ_c or $\lambda_a > 1$

Example 2.4 Stoichiometry and Utilization

Consider a portable 20 cm^2 active area fuel cell operating steadily at 0.75 V , 0.6 A/cm^2 . The fuel utilization efficiency is 50% , and the cathode stoichiometry is 2.3 . The fuel cell is expected to run for three days before being recharged. The cathode operates on ambient air, and the anode runs off of compressed hydrogen gas. (a) Determine the volume of the hydrogen fuel tank required if it is stored as a compressed gas at 200 atm (20.26 MPa), 298 K . (b) How large would a pure oxygen container be if it was used to provide the oxidizer? Consider 200 atm (20.26 MPa) storage pressure and 298 K average ambient temperature.

6. The generic fuel cell

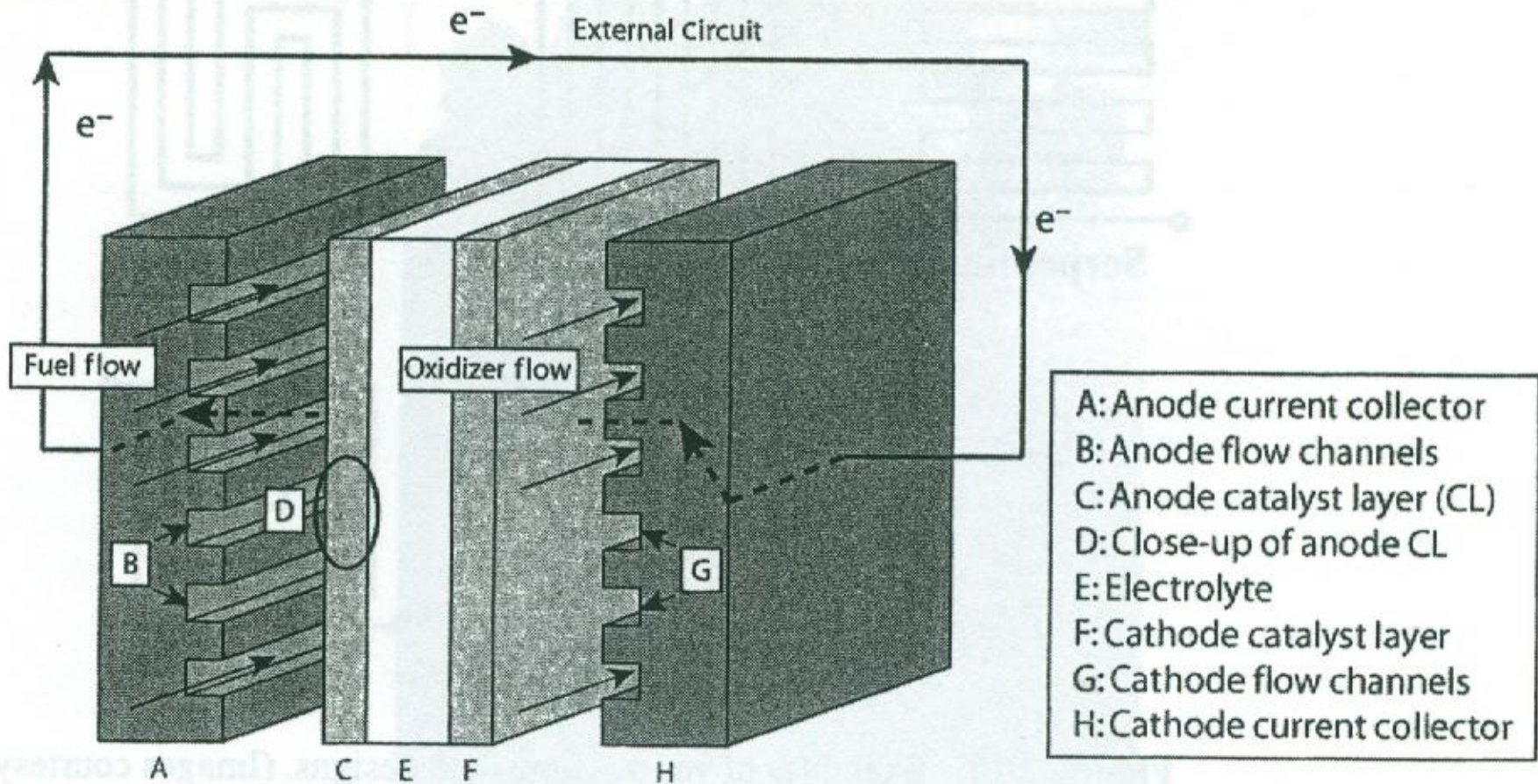


Figure 2.9 Generic fuel cell.

In fuel cell stack → anode current collector (front site) & cathodic current collector (opposite site) → “bipolar plate” or “cell interconnect”

-Functions of current collector

- (a) Conduct electrons from anode B to the external circuit or to the adjacent cathode in a stack
- (b) Deliver fuel (liquid or gas) flow through the flow channels
- (c) Provides structural integrity of stack
- (d) Dissipate waste heat generated by inefficiencies of the rxn to constant, often with a coolant flow through the current collector

-Requirements of current collector materials (graphite, doped polymers, metals, ceramics)

- (a) Lightweight, compact, highly robust
- (b) Low-cost raw material and manufacturing process

- (c) High electrical conductivity over the expected lifetime of operation
- (d) High corrosion resistance in oxidizing and reducing environments
- (e) Impermeability to fuel and oxidant flow
- (f) No disintegration of material or electrical degradation over lifetime of operation
- (g) Suitable thermal expansion properties, which is more of a concern for higher temperature fuel cells
- (h) Capable of proper sealing of reactant flow to prevent leakage → gasket used

-Anodic flow field (or fuel flow field) functions

- (a) Facilitate transport of fuel to the anode
- (b) Facilitate removal of products of reaction

-Design to optimize heat, mass transfer, current collection

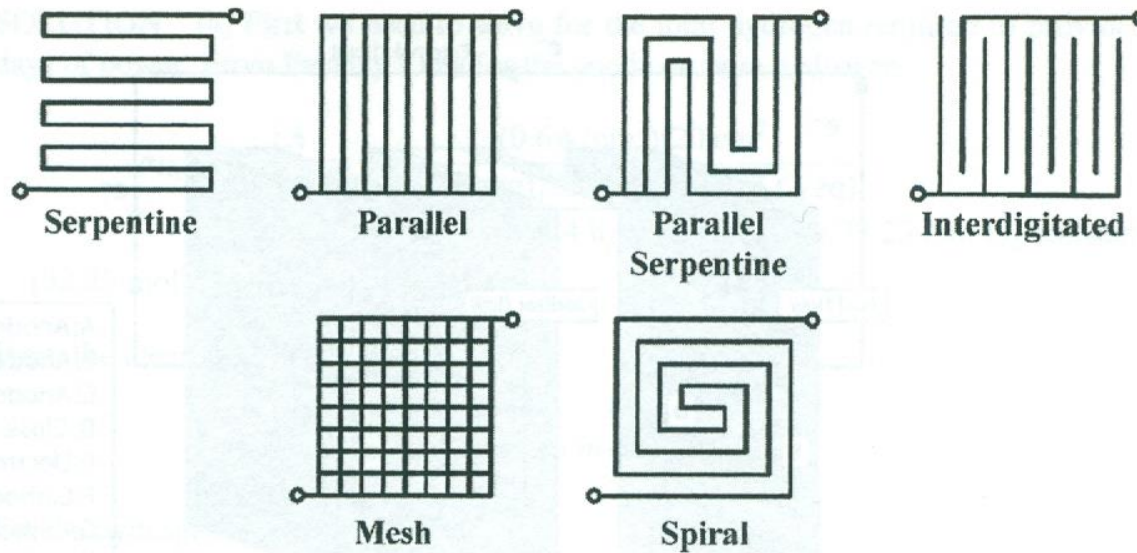


Figure 2.10 Examples of various flow field designs. (Images courtesy of Soowhan Kim.)

-Catalyst layer: porous, highly electrical & ionic conductive

-Functions of anode catalyst layer

(a) Enable the fuel oxidation reaction via a catalyst

(b) Conduct ions from the reaction site to the electrolyte

(c) Conduct electrons from the rxn site to the anode current collector

(d) Facilitate reactant transport & product removal to & from the catalyst locations

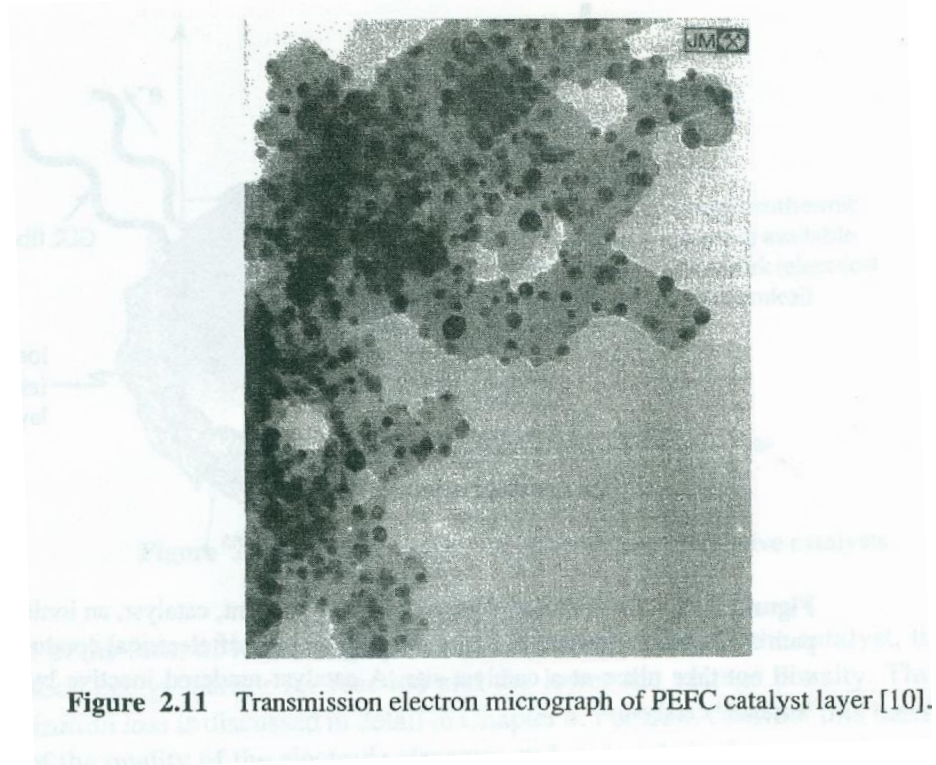
-”triple –phase boundary (TPB)”

→ reaction between

(a) open pore for the reactant

(b) The catalyst

(c) ionic conductor



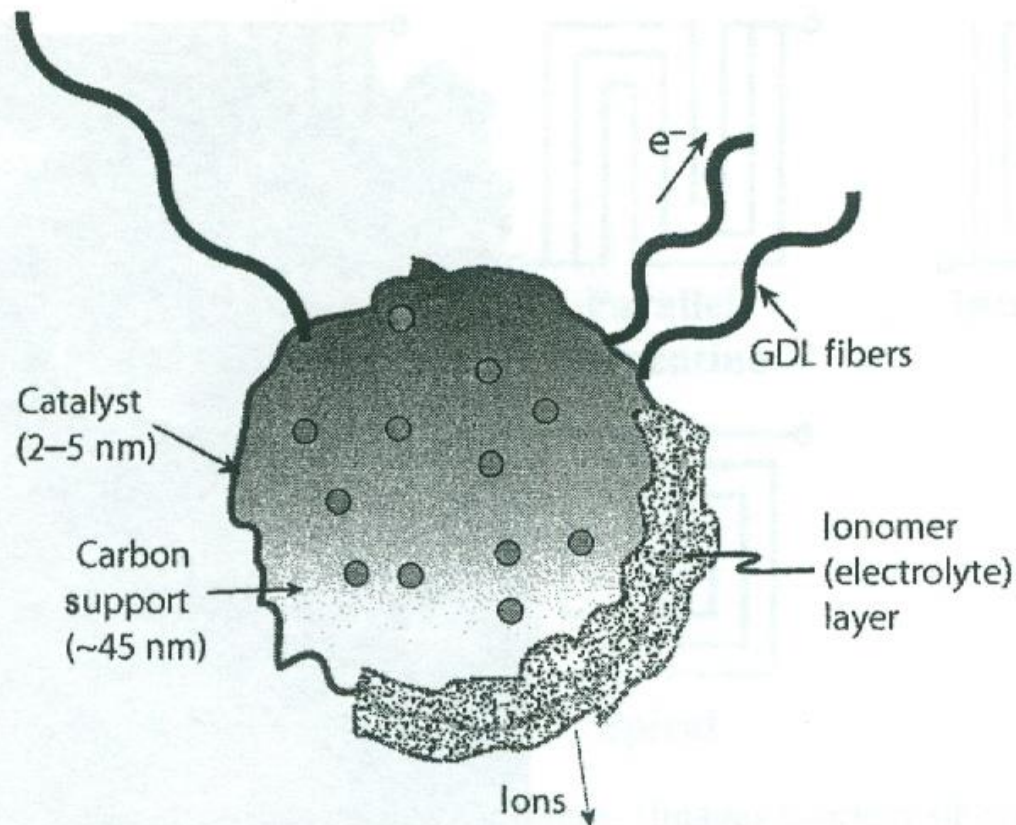


Figure 2.12 The simultaneous presence of reactant, catalyst, an ionic conductor with a continuous path to the main electrolyte, and a continuous path of electrical conductivity is needed or a reaction will not take place at a catalyst site. A catalyst rendered inactive by these situations is called an “orphan” catalyst.

-Effective catalysts

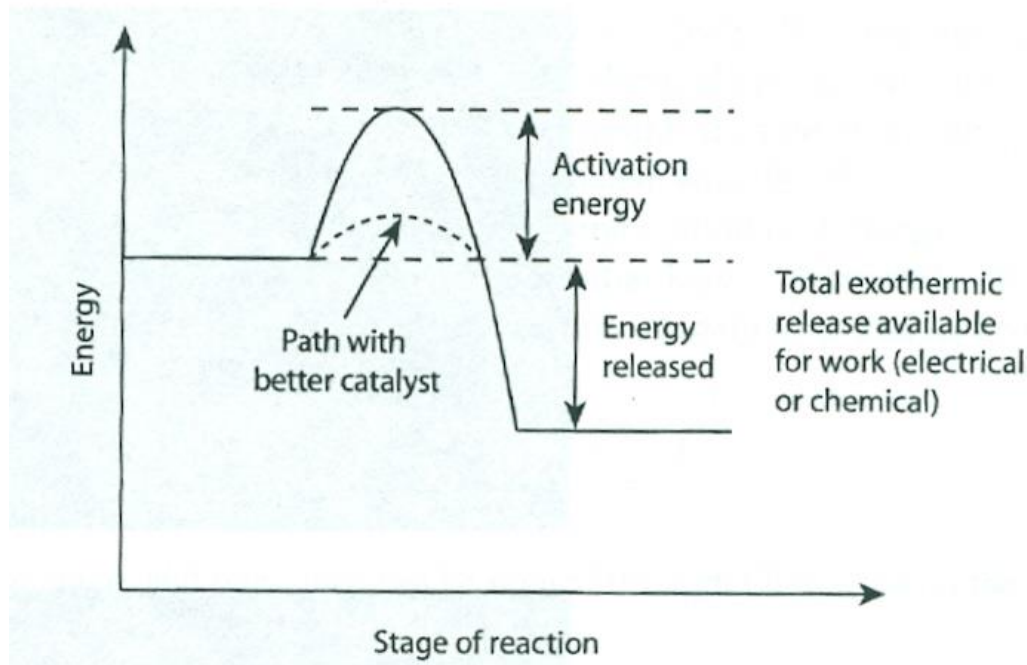


Figure 2.13 Reaction plane for effective and ineffective catalysts.

-Catalyst layer: high degree of mixed conductivity for both electrons and ions as well as a highly porous to promote reactant and product transport

Functions of electrolyte

- (a) To physically separate the reactant
- (b) To conduct the charge carrying ions from one electrode to the other
- (c) To prevent electronic conduction between the anode and cathode