

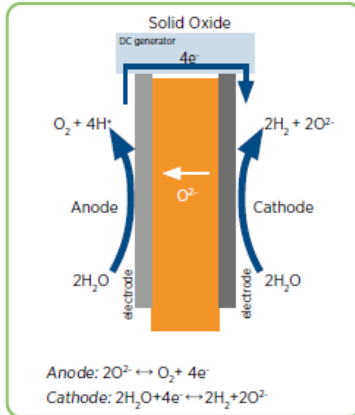
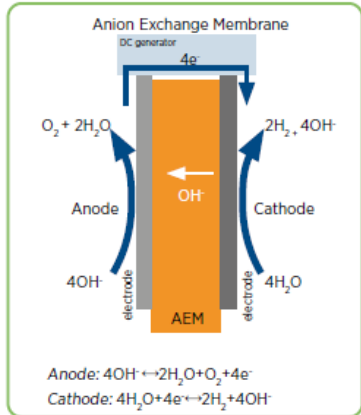
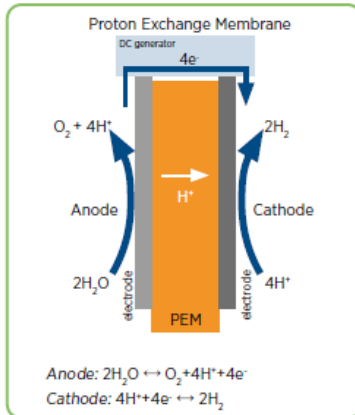
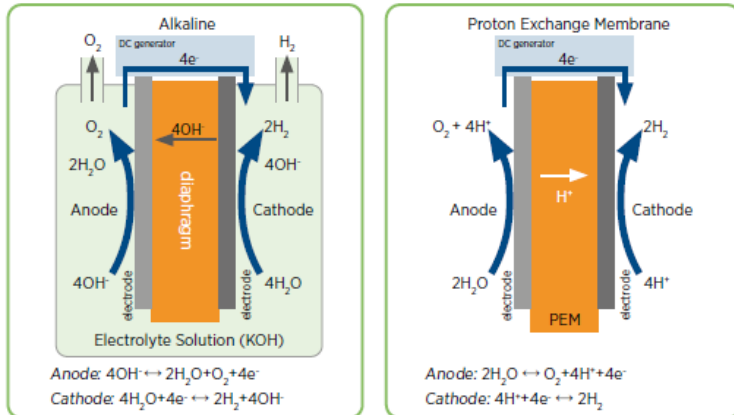
- ✓ Lectures through Zoom until mid-term exam. However, anyone who comes to the classroom may come.
- ✓ The midterm exam is scheduled for April 18th on Monday.

All Solid State Battery (전고체 배터리)

	Main compounds	Ionic conductivity	Temp. stability	Production	Humid stability
Oxide(LLZO)	Li, La, Zr, O	10^{-4} S/cm	◎	△	○
Polymer	Poly Ethylene	10^{-5} S/cm	○	◎	○
Sulfide(LGPS)	Li, P, Ge, S	10^{-3} S/cm	◎	◎	△

Electrolyzer (수전해)

Different types of commercially available electrolysis technologies.



자료: IRENA (2020)

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

	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 NaHCO ₃ 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

Fuel cell (연료전지)

Table 9.1 Types of Fuel Cells

Fuel-cell type	Main application	Operating temperature [°C]	Comments
Direct methanol	Portable power	25–90	Uses same membrane as PEM FC
Proton-exchange membrane (PEMFC) 고분자 전해질	Automotive, buses portable	60–90	Tolerant to carbon dioxide in air Requires precious metal catalysts Rapid start-up and shutdown
Alkaline (AFC)	Space	80–100	Requires pure hydrogen and oxygen Nonprecious metal catalysts possible
Phosphoric acid (PAFC) 인산형	Stationary, combined heat and power	180–220	Operates on reformed fuels Long life Some cogeneration possible
Molten carbonate (MCFC)	Stationary, combined heat and power	600–650	High efficiency Good cogeneration
Solid oxide (SOFC) 고체산화물	Stationary, combined heat and power	650–1000	High efficiency High temperature limits materials available and makes thermal cycles challenging

Electrode structures & configurations

1. Porous electrodes
2. Three-phase electrodes
3. Electrodes with flow



Electrode in electrochemical systems

✓ 3-D structures (rather than planar electrodes)

- to increase the reaction area per volume
- to provide storage volume for solid reactants
- to support dispersed catalysts
- to establish a so-called three-phase boundary
- to efficiently evolve gases

✓ Examples of porous electrode

- electrochemical double-layer capacitors (ch.11): capacitance is proportional to the surface area
- the positive electrode of the lead-acid battery (ch.7, 8): need a large interfacial area
- the cathode of a phosphoric acid fuel cell (ch. 9): three phases (gas, liquid. Solid) needed

Porous electrode terminology

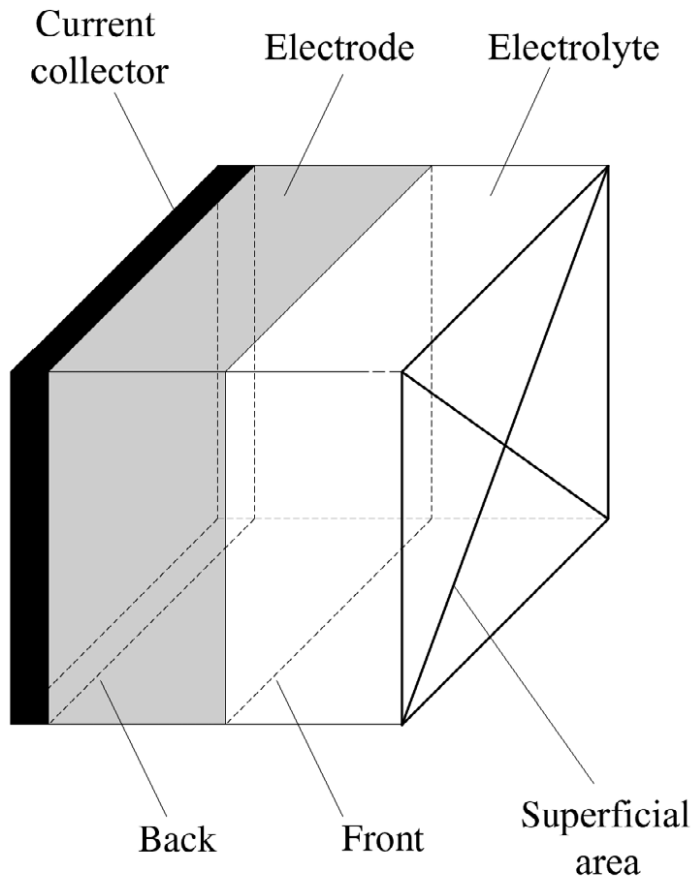


Figure 5.16 Porous electrode terminology.

-**Porosity**: the empty or void portion of the electrode

-**Superficial area**: the area of a plane cutting through the electrode normal to the direction of superficial current

-**Specific interfacial area**: the actual physical surface area of electrode in contact with the electrolyte divided by the volume of the electrode (m^{-1})

Mathematical description of porous electrodes

- ✓ Assume straight cylindrical pores in an electrically conductive matrix
- to increase surface area in a given electrode volume
- assume 10 x 10 cm, 1 mm thick, 10 μm diameter each pore, 2.5 μm minimum distance between pores
- 64 million pores in 10 x 10 cm, 0.0004 cm^2 internal surface area of each pore → 25,000 cm^2 (= 2.5 m^2) total pore surface area
- 250 times greater than the flat area of original electrode

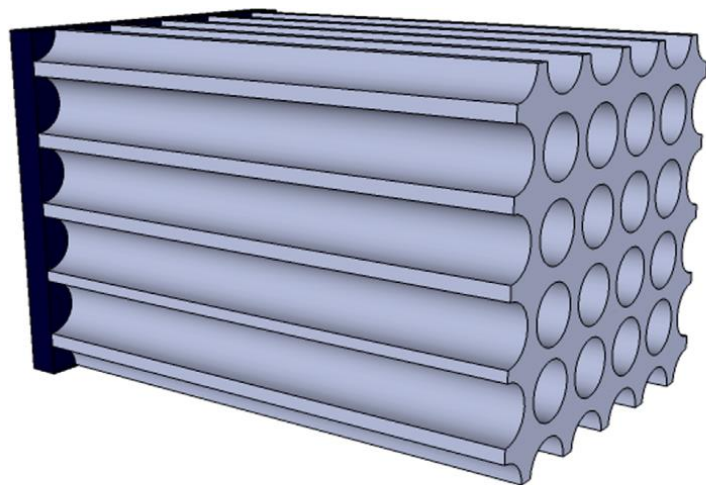


Figure 5.1 Straight pores of an idealized porous electrode.

✓ Porous electrode theory

-1-D approach in textbook (3-D is beyond the scope of this lecture)

→ $x = 0$ at the back of the porous electrode (in contact with the current collector), $x = L$ at the other side of the electrode (L is thickness)

-current density and potential at the electrode (solid phase): i_1, ϕ_1

-current density and potential in the electrolyte (liquid phase): i_2, ϕ_2

$i_1 = I/A$ at $x = 0$, $i_2 = I/A$ at $x = L$, where I/A is the specified current density

In between $x=0$ & $x=L$, the current is split btwn the solid and liquid phases

(**A: superficial area**, $10\text{cm} \times 10\text{cm} = 100\text{cm}^2 = 0.01\text{m}^2$), $i_1 + i_2 = I/A$

Volumetric charge generation rate = ai_n

i_n : the current density normal to **actual surface** (A/m^2)

a: the surface area per volume or specific interfacial area (m^{-1})

→ volumetric charge generation rate: unit of $\text{A}\cdot\text{m}^{-3}$ or $\text{C}\cdot\text{m}^{-3}\text{s}^{-1}$

For Fig.5.1, **a** = combined surface area / superficial volume

$$= 2.5 \text{ m}^2 / (0.1 \text{ m} \times 0.1 \text{ m} \times 0.001 \text{ m}) = 250,000 \text{ m}^{-1}$$

charge balance for the current in solution(i_2) & solid phase(i_1):

$$ai_n = -\nabla \cdot i_1 = \nabla \cdot i_2, \quad \nabla \cdot i_1 + \nabla \cdot i_2 = 0$$

material balance for the species in solution:

rate of accumulation of species i , accumulation = in-out + generation

$$\partial c_i / \partial t = -\nabla \cdot N_i + R_i$$

c_i : concentration in the electrolyte \rightarrow in porous electrode, $c_i \varepsilon$, where ε is the volume fraction of the electrolyte (porosity)

the flux, N_i , is the superficial molar flux (Nernst-Planck equation, \mathcal{J})

R_i : the generation rate

material balance for porous electrodes:

$$\partial \varepsilon c_i / \partial t = -\nabla \cdot N_i + R_i$$

$$R_i = a j_n$$

where j_n is the species reaction rate at the surface in moles/(s·m)

From Faraday's law, $j_i = -(s_i/nF)j_n$

where s_i is the stoichiometric coefficient for species i (positive or negative (negative for anodic reaction))

$$\partial \varepsilon c_i / \partial t = -\nabla \cdot N_i - a(s_i/nF)j_n = -\nabla \cdot N_i - (s_i/nF)\nabla \cdot i_2 ,$$

Nernst-Planck equation, $N_i = -\varepsilon D_i \nabla c_i - \varepsilon z_i u_i F c_i \nabla \phi + \varepsilon c_i v_i$

Characterization of porous electrodes

- Porosity (ϵ) or void volume fraction : the empty space of the electrode available to the electrolyte (or gas phase) \rightarrow most important feature of any porous media

$$\epsilon = (\text{total volume} - \text{volume occupied by solid phase}) / \text{total volume}$$

- Specific interfacial area (a) : unit, m^{-1}

$$a = \text{interfacial area} / \text{superficial volume}$$

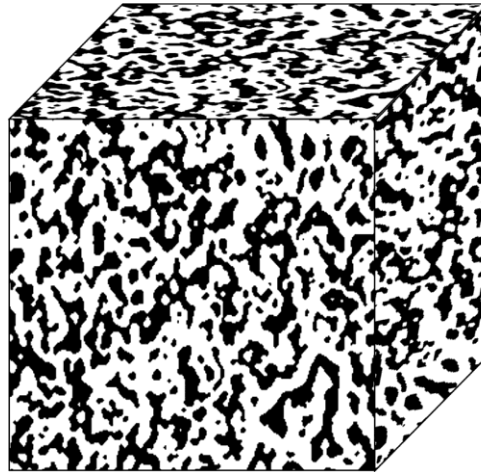


Figure 5.2 Typical porous electrode.

- For a single sphere of radius r , $a = 4\pi r^2 / (4/3\pi r^3) = 3/r$
- Smaller pore $\rightarrow a \uparrow$

$$a = (\text{number of spheres})4\pi r^2 / \text{volume} =$$

$$\{ [V(1-\varepsilon) / (4/3\pi r^3)] 4\pi r^2 \} / V = 3(1 - \varepsilon)/r$$

- Characteristic pore size (r_p)

$$r_p = \text{cross section available for transport} / \text{wetted perimeter}$$

$$= \text{volume available for transport} / \text{wetted surface}$$

$$= (\text{volume of voids} / \text{bed volume}) / (\text{wetted surface} / \text{bed volume})$$

$$= \varepsilon / a = [\varepsilon / (1 - \varepsilon)](r/3)$$

- smaller void volume \rightarrow pore diameter \downarrow ,
- larger porosity \rightarrow pore diameter \uparrow

- A typical porous electrode has a distribution of pore sizes rather than the single pore size
- Pore size distribution : measured with Hg-intrusion porosimetry
 - larger pores are easier to fill than small ones
 - Hg volume vs. pressure to pore diameter
- Primary pore volume : the volume inside the individual particles
- Secondary pore volume : the volume between particles

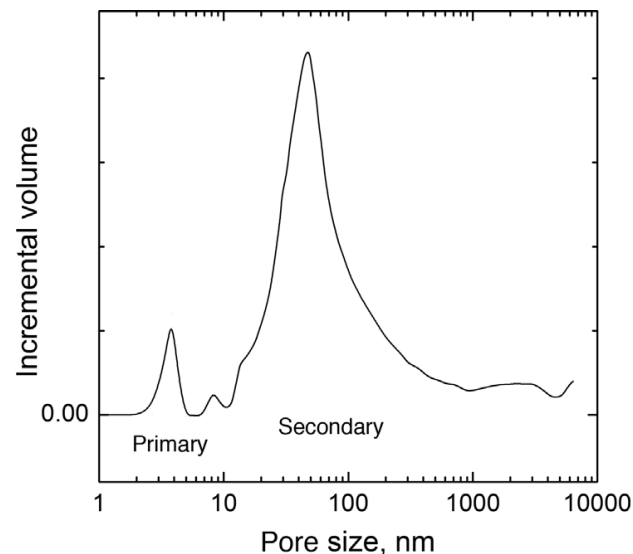


Illustration 5.1

Figure 5.3 Bimodal distribution of pore sizes for a hypothetical electrode containing metal catalyst on carbon.

Impact of porous electrode on transport

- Effective transport properties in porous structure
 - (i) cross-sectional area available for transport is reduced by the presence of the solid phase,
 - (ii) effective area = (superficial area) x (porosity) → the path length for transport is increased
- Tortuosity (τ) : a tortuous path → τ : as high as 6~20, typical 2~3 for many applications

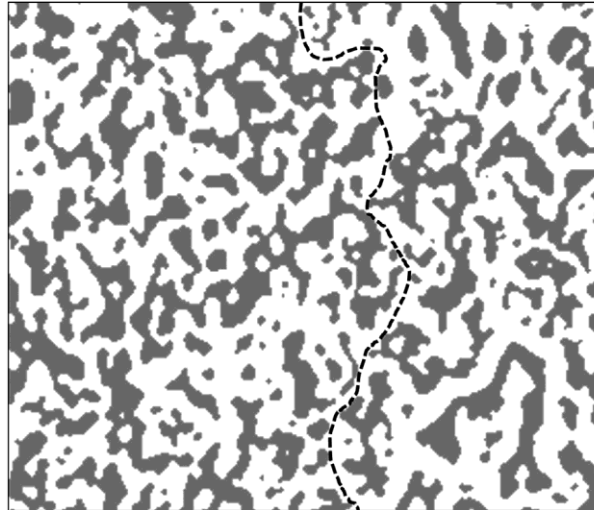


Figure 5.4 Tortuous path through porous media.

- Tortuosity(τ), porosity(ϵ), conductivity in pore media & bulk(κ_{eff} , κ_{bulk})

$$\kappa_{\text{eff}} = \kappa_{\text{bulk}}(\epsilon/\tau)$$

- Higher tortuosity \rightarrow lower effective conductivity
- Bruggeman relationship

$$\kappa_{\text{eff}} = \kappa_{\text{bulk}}\epsilon^{1.5}$$

- A similar expression for **diffusivity and mobility**

Illustration 5.2

Current distribution of porous electrodes

- In the porous electrode,
 - κ_{eff} : the conductivity of the electrolyte
 - σ_{eff} : the conductivity of the solid
 - $K_r \equiv \kappa/\sigma$
 - v^2 : the ratio of the ohmic and the kinetic resistances (eq. (5.31))

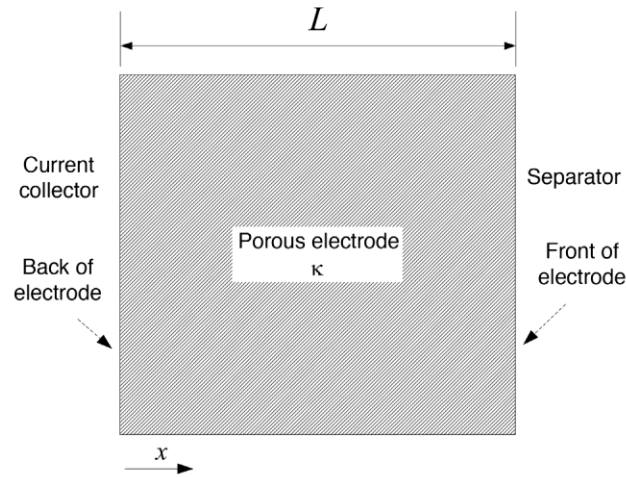


Figure 5.5 One-dimensional porous electrode showing front and back of the electrode.

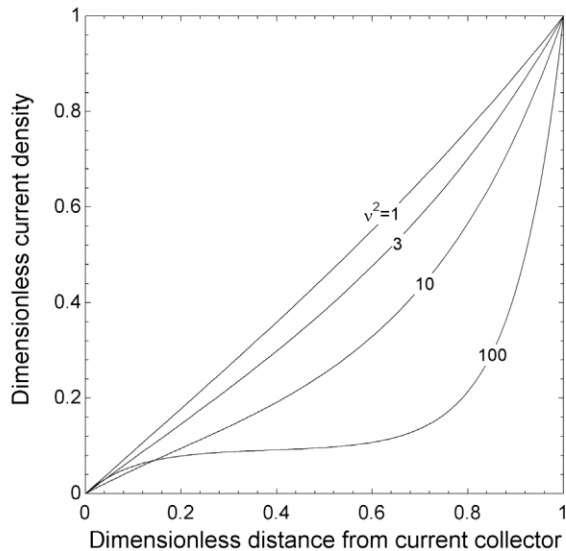
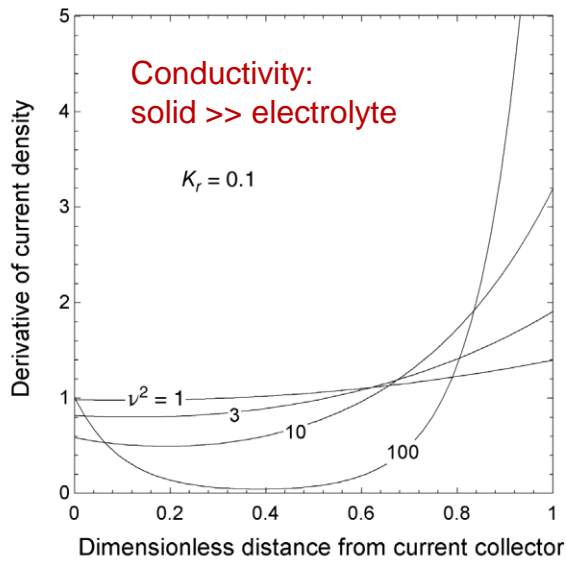


Figure 5.6 Dimensionless current density and its derivative across the electrode. The back of the electrode is at $z=0$, the front is at $z=1$, adjacent to the electrolyte. $K_r = 0.1$.

Small v^2 : kinetic resistance controlled \rightarrow uniform current distribution

large v^2 : ohmic resistance controlled \rightarrow non-uniform current distribution

$K_r \rightarrow 0$; electrolyte limited

$K_r \rightarrow \infty$; solid limited

Typically $\sigma \gg \kappa$

Illustration 5.3

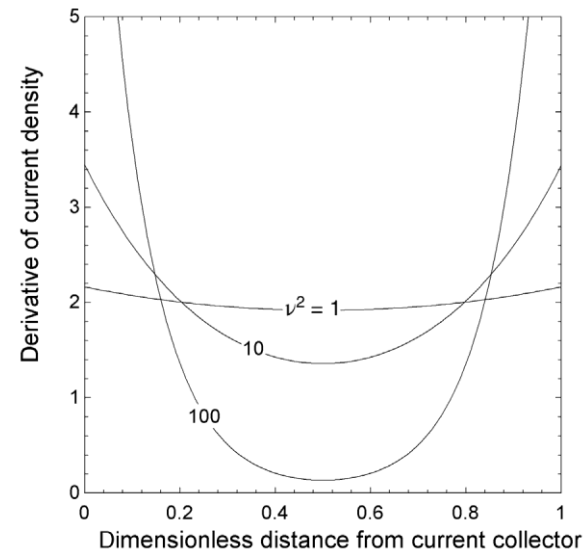


Figure 5.7 Current distribution with equal electronic and ionic conductivity.

The internal resistance of a porous electrode (eq. (5.42))

large v^2 : ohmic resistance controlled \rightarrow non-uniform current distribution

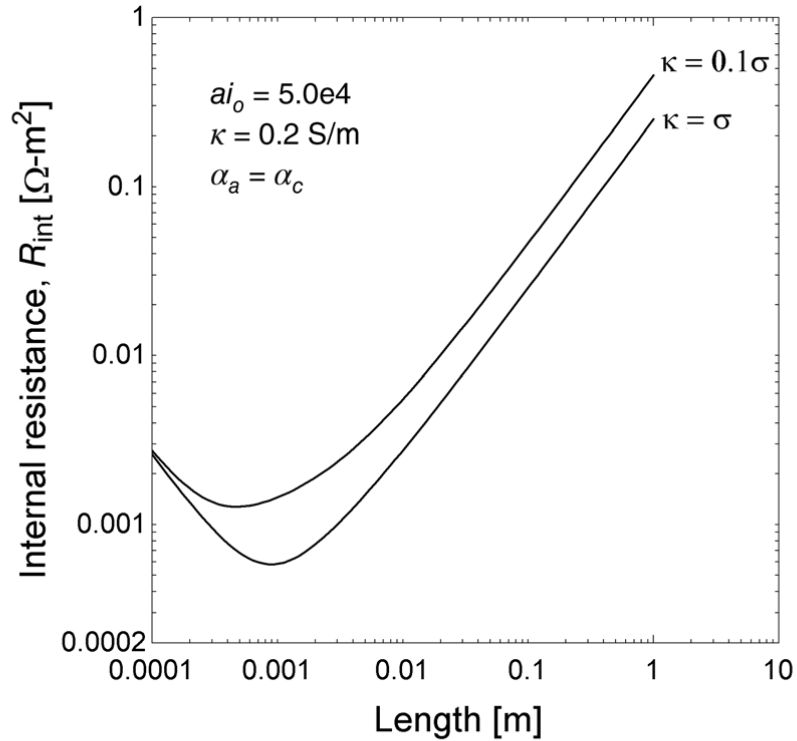
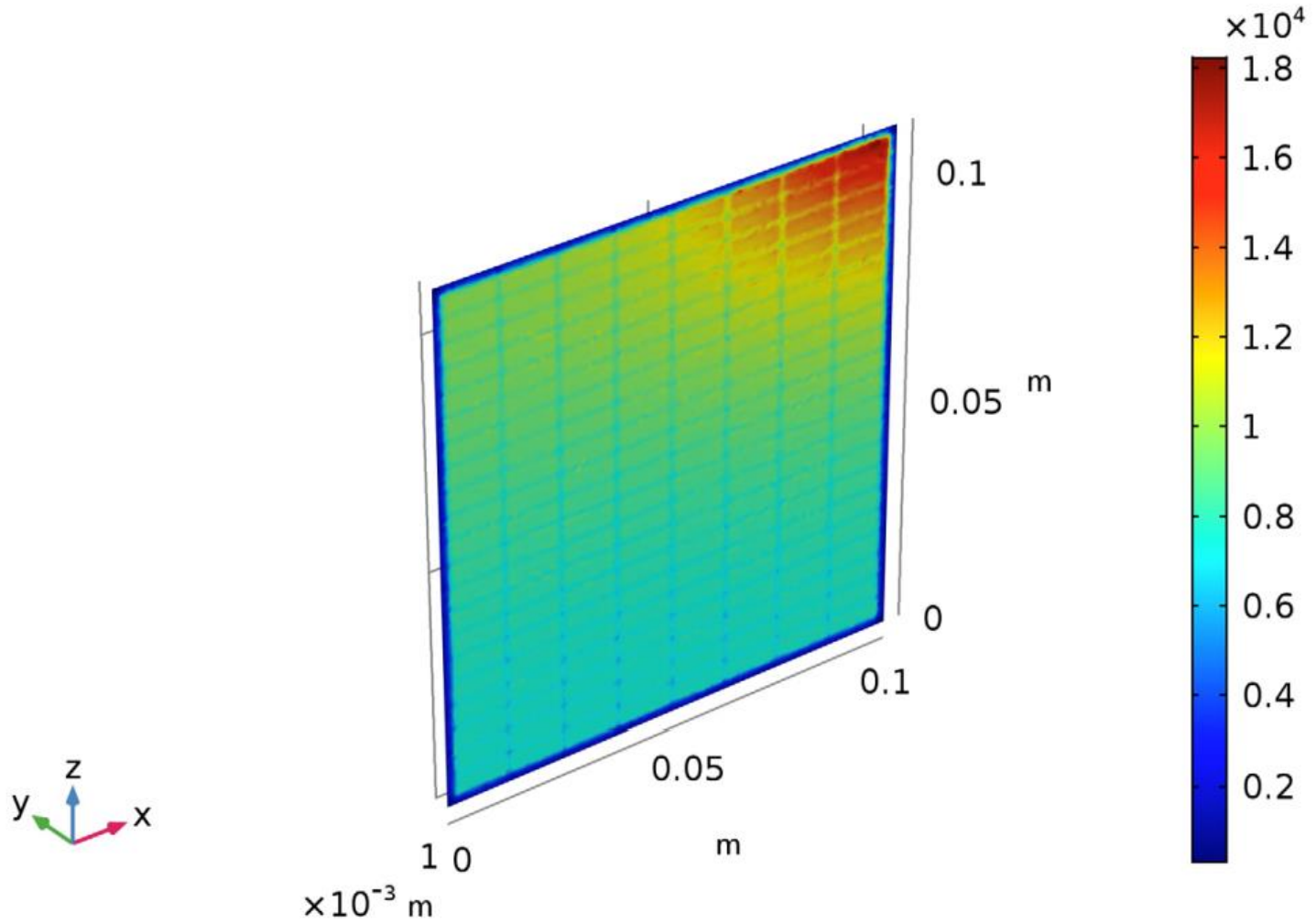


Figure 5.8 Internal resistance of an electrode assuming linear kinetics.

Surface: -cd.nll (A/m²)



COMSOL

Gas-liquid interface in porous electrodes

- Porous electrode → capillary action or capillarity
→ surface tension(γ) causes the fluid to rise in the capillary
- Contact angle : $\theta < 90^\circ$ (hydrophilic or wetting, concave meniscus)
 $\theta > 90^\circ$ (hydrophobic or non-wetting, convex meniscus)

$$h = 2\gamma \cos\theta / \rho g r$$

- Capillary pressure (p_c), $p_c \equiv p_{nw} - p_w = 2\gamma \cos\theta / r$

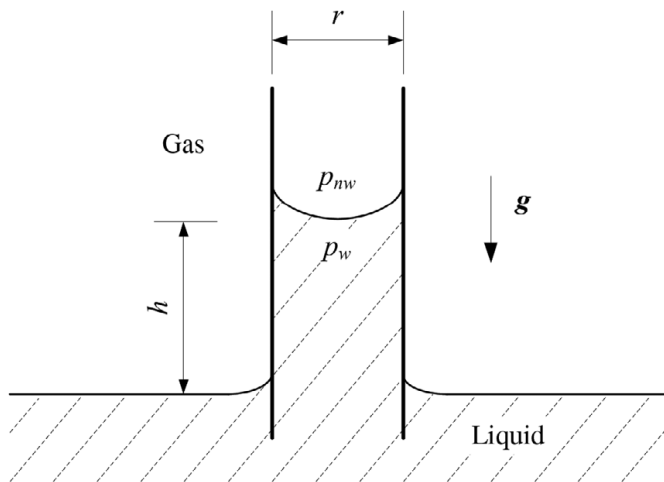
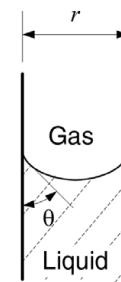
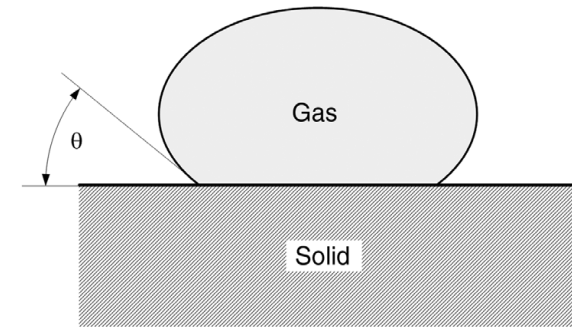


Figure 5.9 Capillary rise in a small tube.



(a)



(b)

Figure 5.10 (a) Contact angle associated with capillary rise. (b) Contact angle for gas bubble attached to solid surface.

참고: Capillary rise

- Force balance at the top of the meniscus

Total wetting force = gravitational force of the water column

$$2\pi r \gamma \cos \theta = (\rho - \rho_0) (\pi r^2 h) g = \Delta\rho (\pi r^2 h) g$$

ρ = density of the liquid

ρ_0 = density of the air

$$h = 2\gamma \cos \theta / \Delta\rho g r$$

Another view

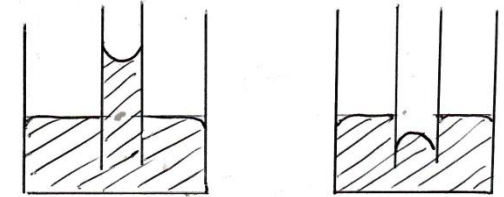
pressure difference between the points Q and Q_0 : $\Delta P = \rho_0 g h$

pressure difference between the points P and P_0 : $\Delta P = -2\gamma/R + \rho g h$

The two ΔP 's should be the same. $r = R \cos \theta$

$$2\gamma/R = \Delta\rho g h \rightarrow h = 2\gamma \cos \theta / \Delta\rho g r$$

More accurately, $h' = h + r/3$

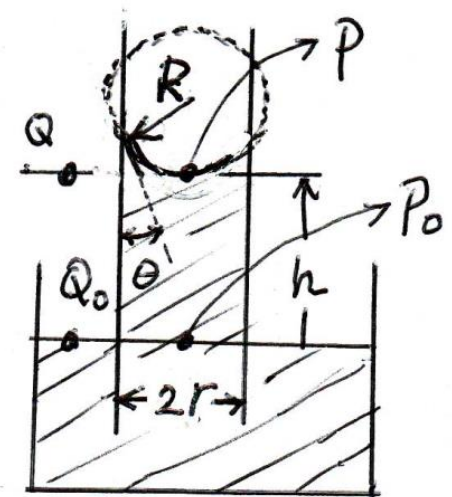


capillary
rise

$$\gamma_c > \gamma_l$$

capillary
depression

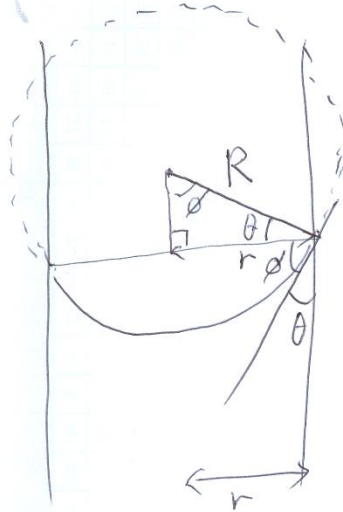
$$\gamma_c < \gamma_l$$



$$\Delta p = \frac{2\gamma}{r}$$

$r \downarrow \rightarrow \Delta p \uparrow$ (large P_i (internal pressure))

\rightarrow liquid \uparrow (liquid rise) \rightarrow = hydrostatic pressure
to decrease total free energy



$$R \cos \theta = r$$

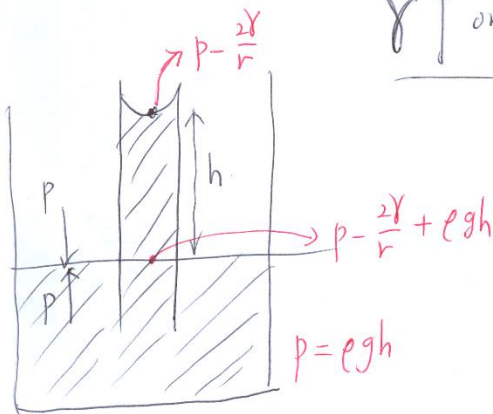
$$R = \frac{r}{\cos \theta}$$

$$\Delta \rho g h = \frac{2\gamma}{R} = \frac{2\gamma}{r} \cos \theta$$

$\Delta \rho$: density difference between
liquid and gas pressure

if $\theta = 0 \rightarrow \gamma = \frac{1}{2} r h \Delta \rho g$

$\gamma \uparrow$ or $r \downarrow \Rightarrow h \uparrow$

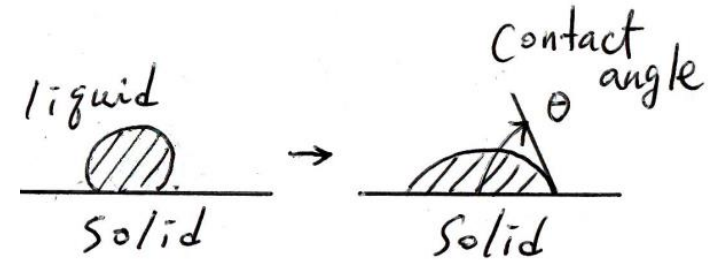


참고: Capillary rise and depression

- Wetting

$\theta = 0^\circ$: complete wetting

$\theta = 180^\circ$: complete dewetting



- Wetting occurs to minimize the total free energy which includes the surface and **interfacial** free energies

- Force balance at the interface

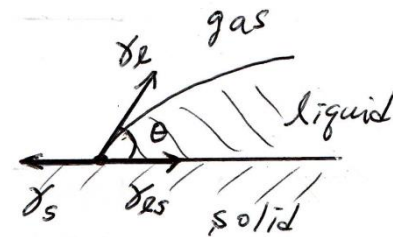
- Criteria for wetting

When the interface area is increased by dA ,

$$\begin{aligned} dG &= \gamma_{ls} dA + \gamma_l \cos \theta dA - \gamma_s dA \\ &= (\gamma_{ls} + \gamma_l \cos \theta - \gamma_s) dA = x dA \end{aligned}$$

If $x < 0 \rightarrow$ wetting occurs, and

If $x > 0 \rightarrow$ dewetting occurs.



$$\gamma_l \cos \theta + \gamma_{ls} = \gamma_s$$

There is a certain contact angle for which $x = 0$: equilibrium contact angle

- Hydrophilic materials will have a positive capillary pressure and naturally wick up the fluid → hydrophobic materials will have a negative capillary pressure and pressure must be applied to wet the material
- Saturation level (S_i) : fluid fill the void volume
(e.g. electrolyte in fuel cell electrode)

$$S_i = \text{volume filled by phase } i / \text{void volume}$$

→ S_i depends on surface tension, contact angle, pore size distribution

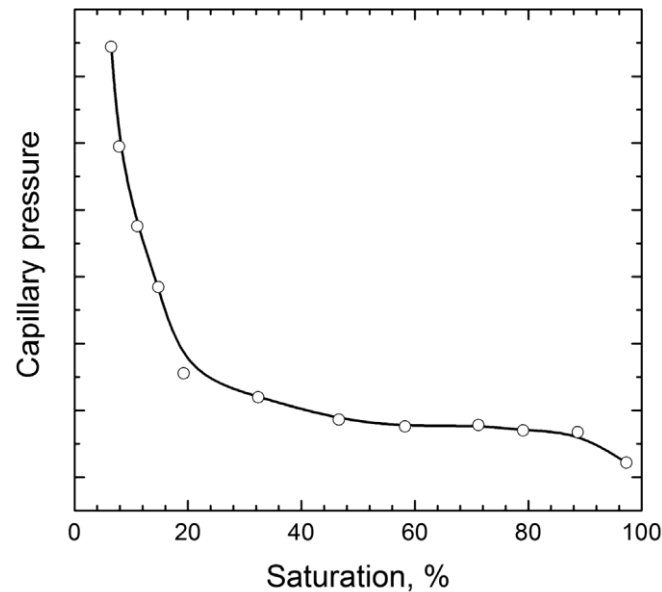
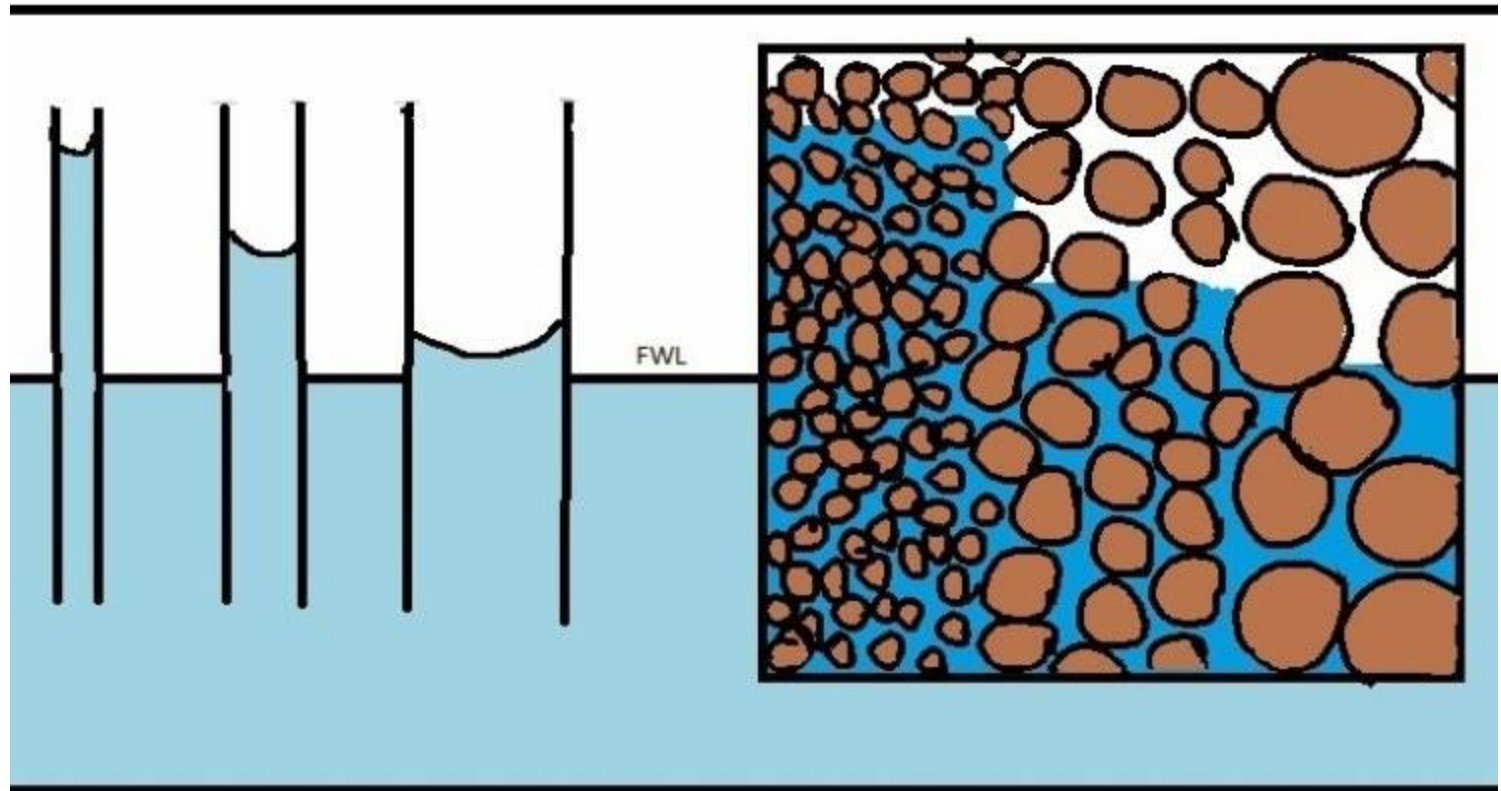


Illustration 5.4

Figure 5.11 Fill as a function of capillary pressure.



Three-phase electrodes

- Example of three-phase electrode : the cathode of low temperature in fuel cell → gas, liquid, solid in contact

Oxygen reduction reaction : $4\text{H}^+ + 4\text{e}^- + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

→ proton in the electrolyte, electron in solid phase, oxygen in gas phase, water in gas or liquid phase

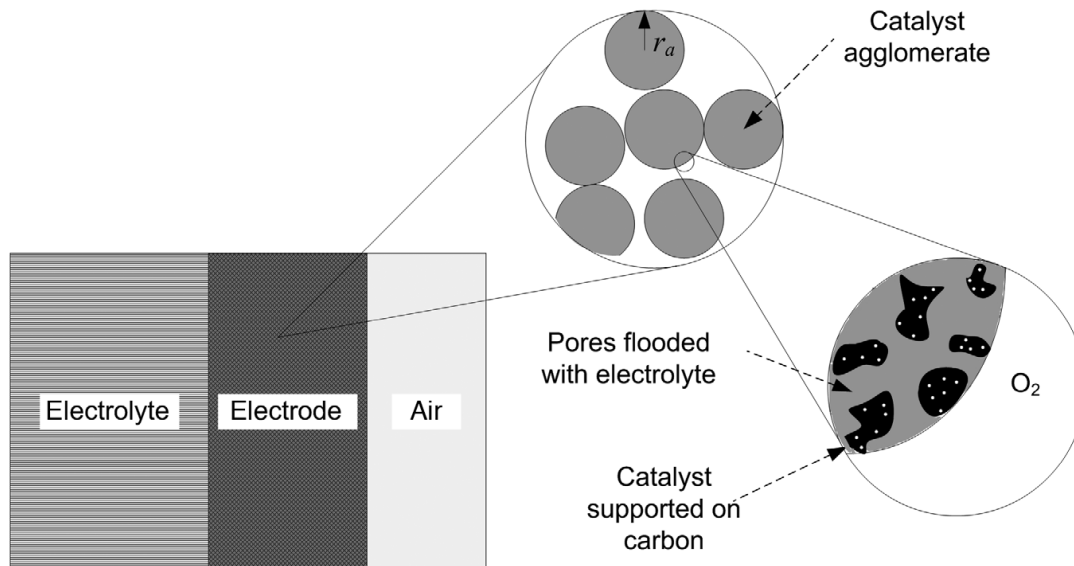
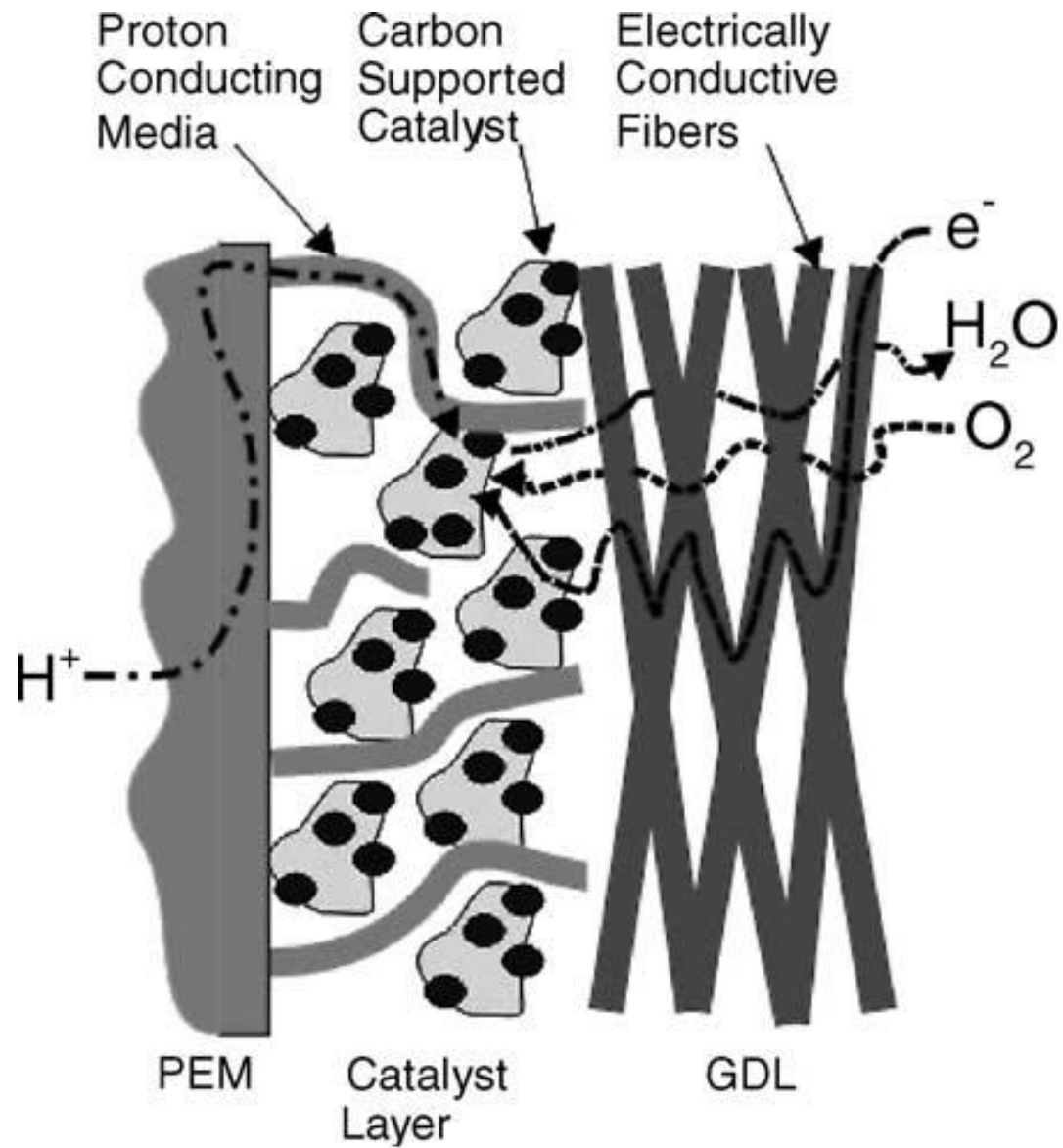


Figure 5.12 Flooded-agglomerate model.



Electrodes with flow

- Porous electrodes + fluid flow
→ two basic categories : *flow-through* and *flow-by*

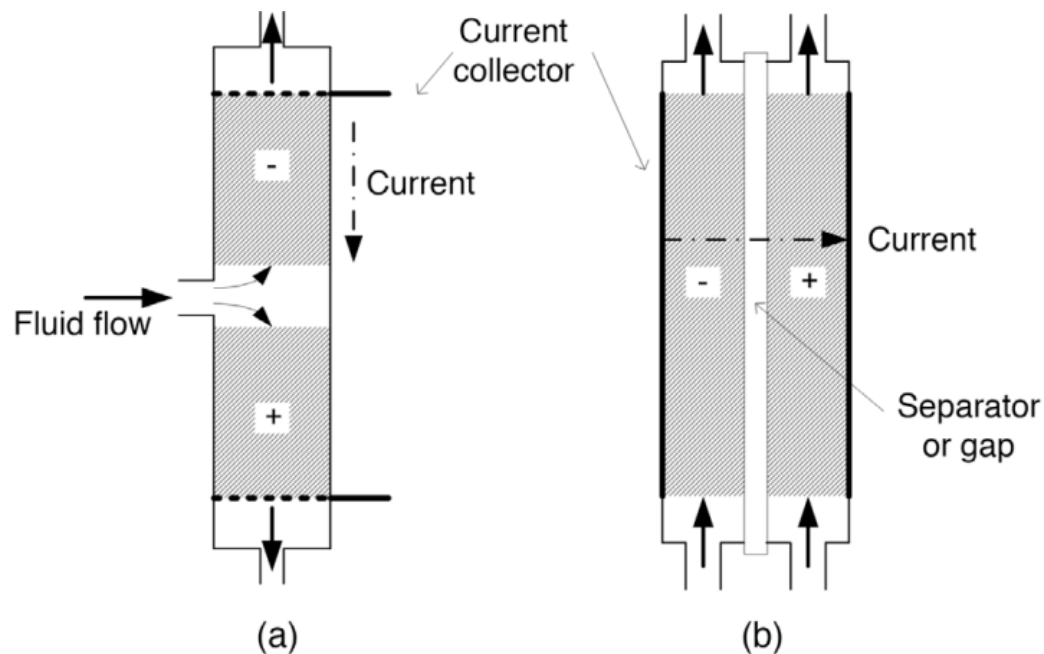


Figure 5.14 Electrode configurations for flowing systems.

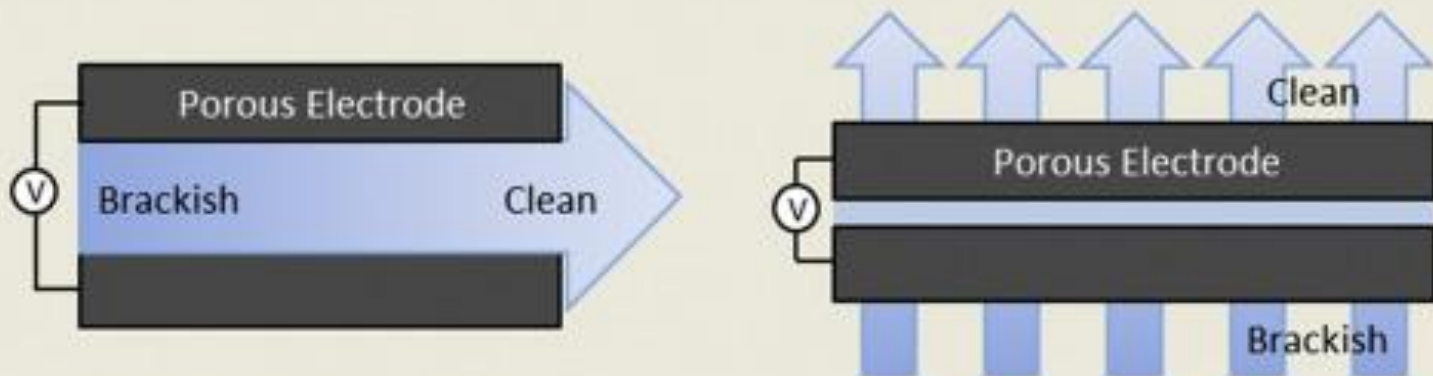
(a) Flow-through electrode. (b) Flow-by electrode.

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Flow-By vs. Flow-Through CDI



- example

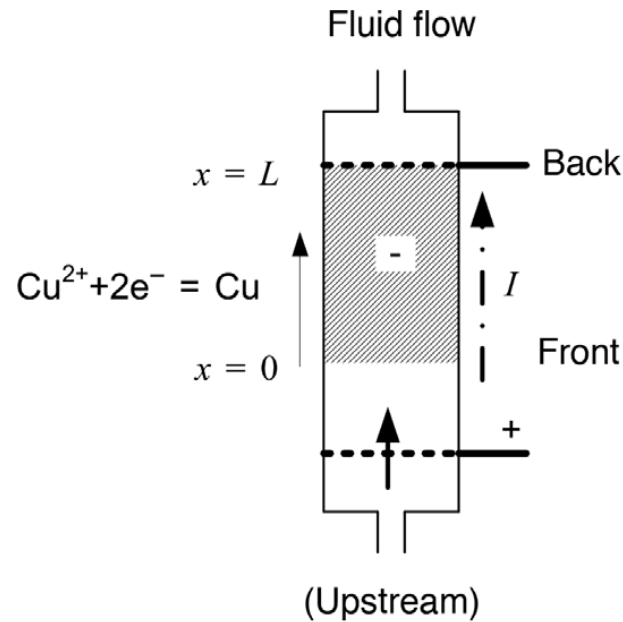


Figure 5.15 Removal of Cu^{2+} from stream.

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