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: capacitance is proportional to the surface area
-the positive electrode of the lead-acid battery: need a large interfacial area
-the cathode of a phosphoric acid fuel cell: three phases (gas, liquid. Solid) needed
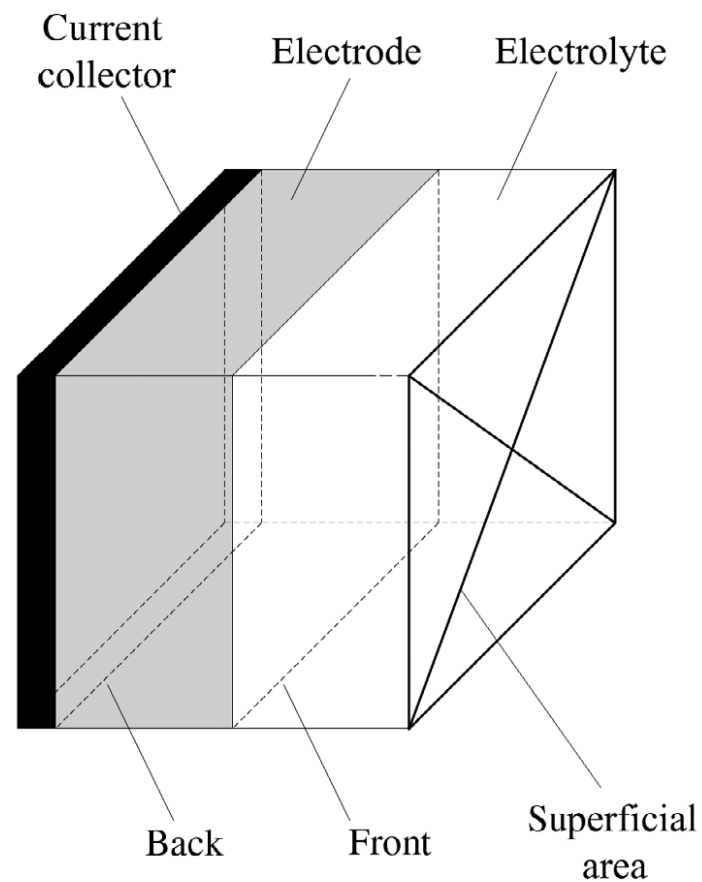
Porous electrode terminology

Figure 5.16   Porous electrode terminology.

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 cm² internal surface area of each pore → 25,000 cm² (= 2.5 m²) total pore surface area

→ 250 times greater than the flat area of original electrode
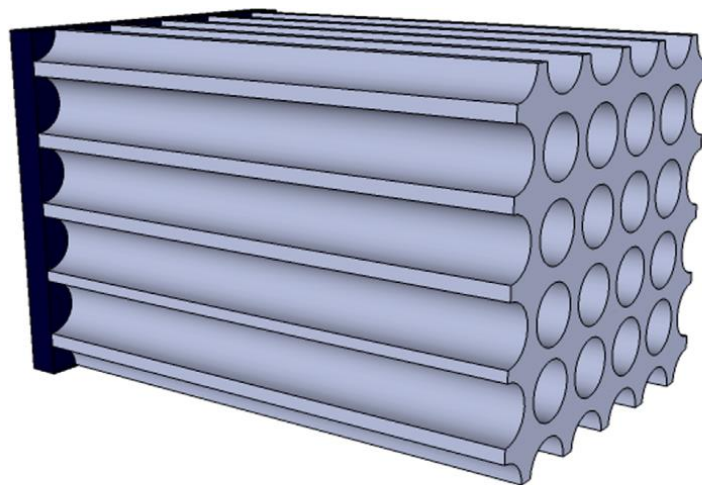

Figure 5.1   Straight pores of an idealized porous electrode.

✓ 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,
in between x = 0 and x = L, the current is split between the solid and liquid phases (superficial area, e.a. 10 cm x 10 cm), $i_1 + i_2$ = 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 Am^{-3} or C·m^{-3}s^{-1}

For Fig.5.1, a = combined surface area / superficial volume
         = 2.5 m^2 / (0.1 m x 0.1 m x 0.001 m) = 250,000 m^{-1}

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

Characterization of porous electrodes

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

$$\varepsilon = \text{(total volume – volume occupied by solid phase) / total volume}$$

- Specific interfacial area (a) : unit, m^{-1}
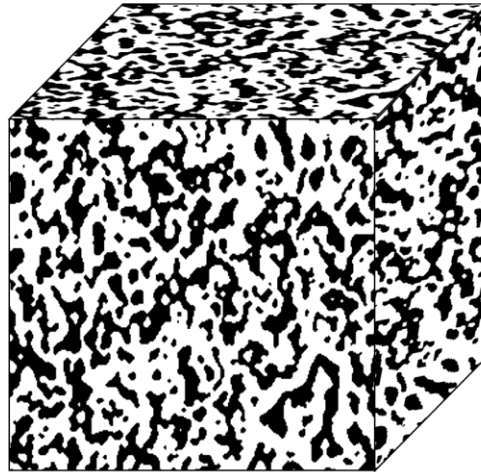
$$a = \text{interfacial area / superficial volume}$$

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 → a↑

    a = (number of spheres)$4\pi r^2$ / 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 = cross section available for transport / wetted perimeter
      = volume available for transport / wetted surface

      = (volume of voids / bed volume) / (wetted surface / bed volume)
      = $\varepsilon / a = [\varepsilon / (1 - \varepsilon)](r/3)$

- smaller void volume → pore diameter↓,
  larger porosity → pore diameter↑

- 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
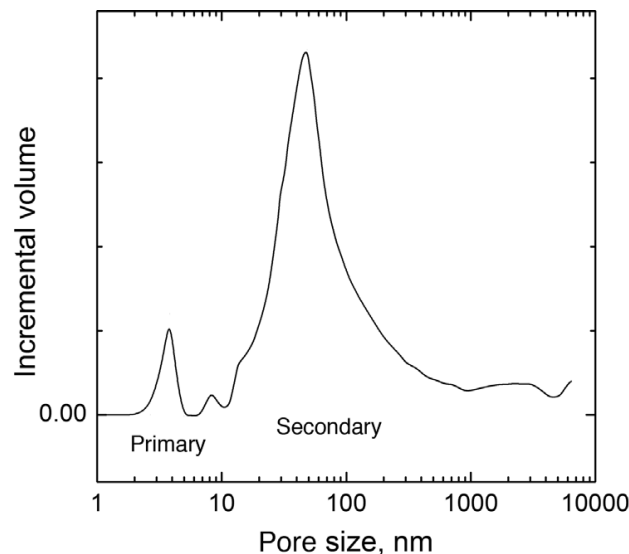- Secondary pore volume : the volume between particles

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
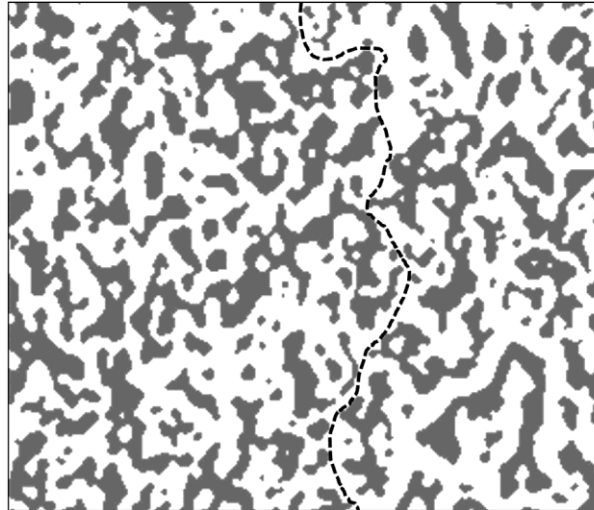   many applications

Figure 5.4 Tortuous path through porous media.

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

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

- Higher tortuosity → lower effective conductivity
- Bruggeman relationship

$$\kappa_{eff} = \kappa_{bulk}\varepsilon^{1.5}$$

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))
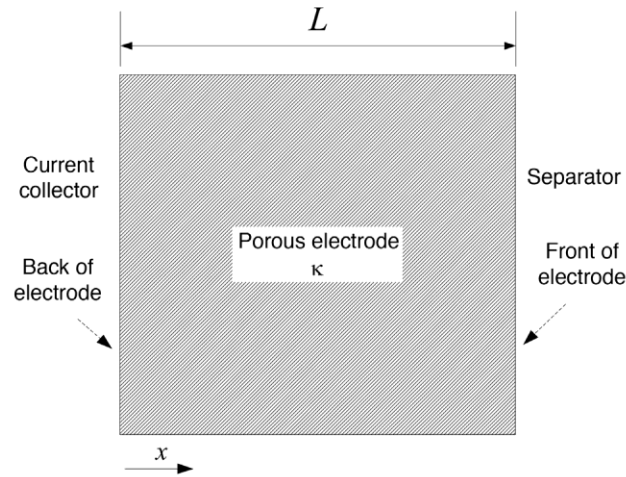
Figure 5.5 One-dimensional porous electrode showing front and back of the electrode.
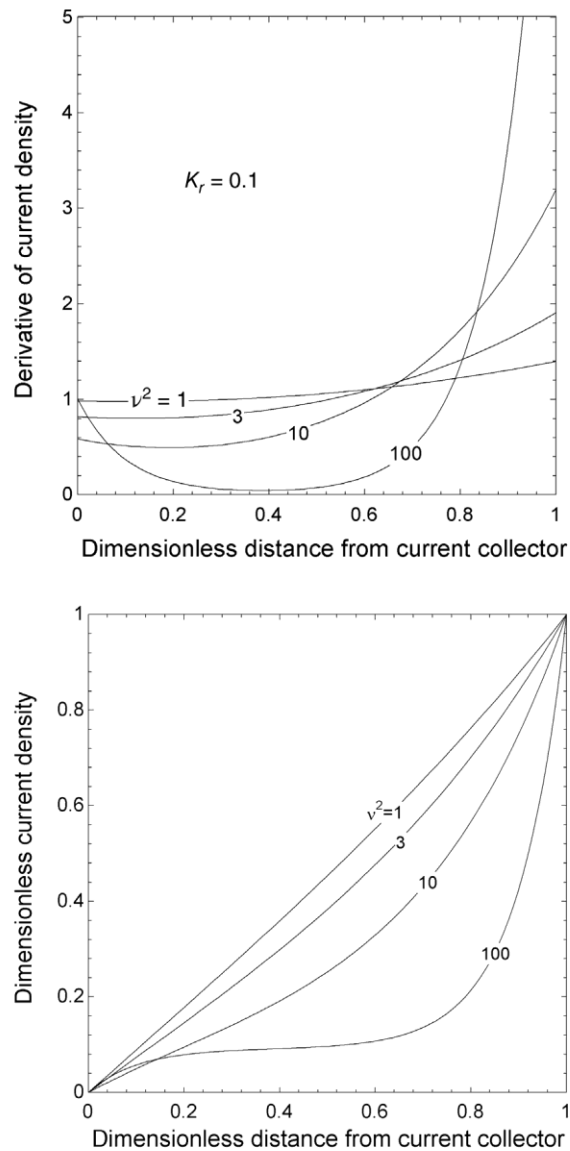
Figure 5.6 Dimensionless current density and its derivative across the electrode. The back of the electrode is a $z = 0$, the front is at $z = 1$, adjacent to the electrolyte. $Kr = 0.1$.
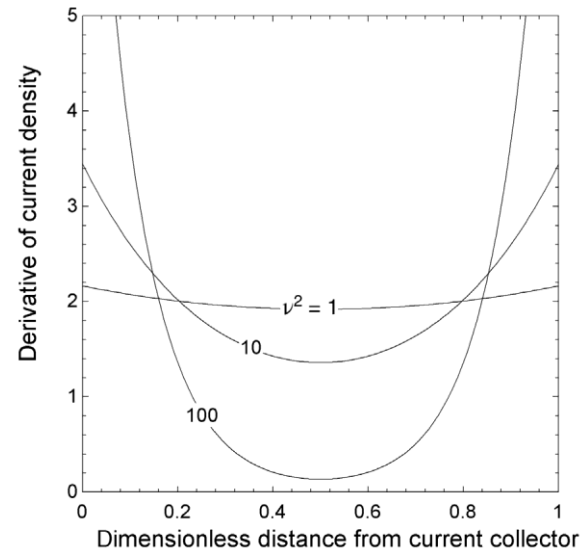
Figure 5.7 Current distribution with equal electronic and ionic conductivity.
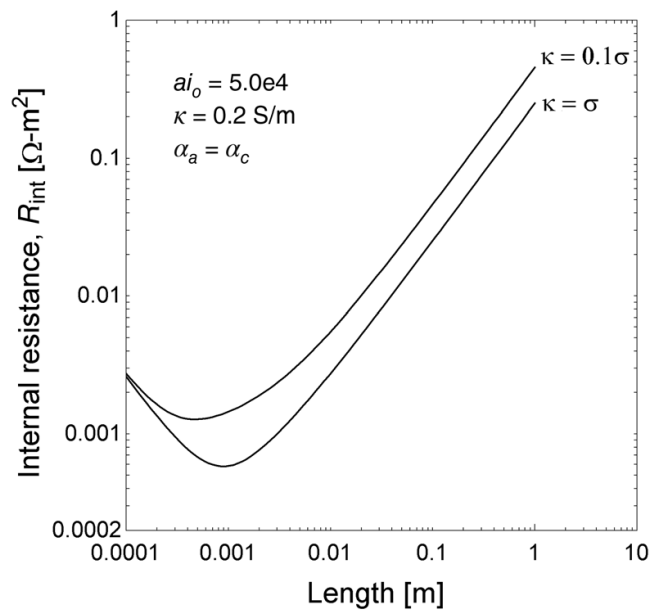
Figure 5.8 Internal resistance of an electrode assuming linear kinetics.

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 : $\theta < 90°$ (hydrophilic or wetting, concave meniscus)
  $\theta > 90°$ (hydrophobic or non-wetting, convex meniscus)

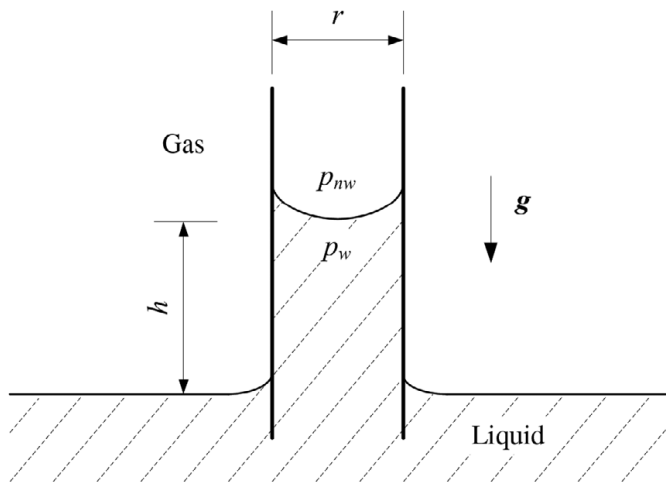$$h = 2\gamma\cos\theta / \rho g r$$

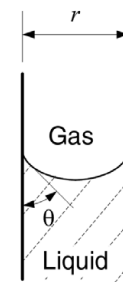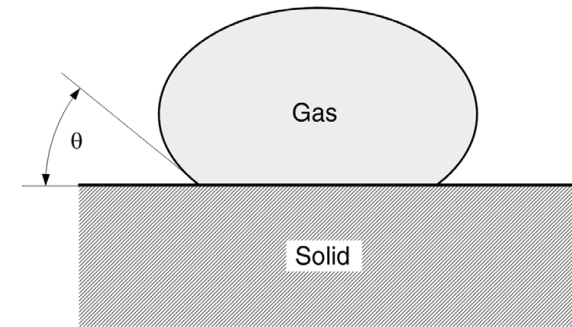- Capillary pressure (p_c), $p_c \equiv p_{nw} - p_w = 2\gamma\cos\theta / r$

Figure 5.9 Capillary rise in a small tube.

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

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

capillary rise

capillary depression

$\gamma_c > \gamma_l$ $\gamma_c < \gamma_l$

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. $r = R\cos\theta$

$$2\,\gamma\,/R = \Delta\rho\, g\, h \rightarrow h = 2\,\gamma\,\cos\theta\,/\,\Delta\rho\, g\, r$$
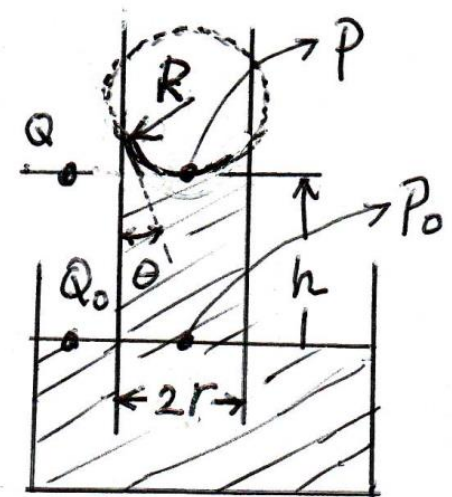
More accurately, $h' = h + r/3$
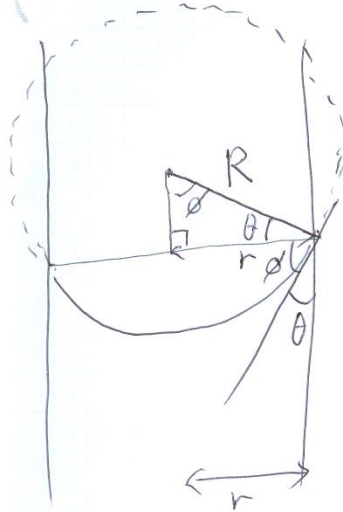
$$\Delta p = \frac{2\gamma}{r}$$

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

$\rightarrow$ liquid$\uparrow$ (liquid rise) $\rightarrow$ =hydrostatic pressure

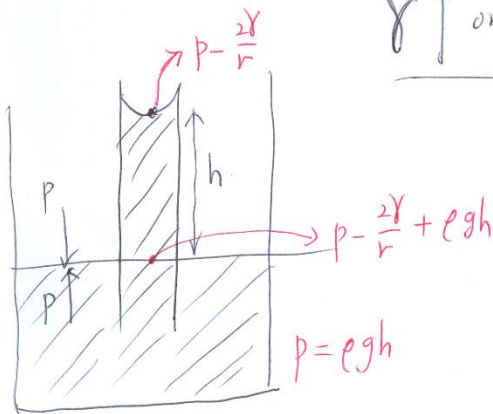to decrease total free energy

$$R\cos\theta = r$$

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

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

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

if $\theta = 0 \rightarrow \gamma = \frac{1}{2}rh\Delta\rho g$
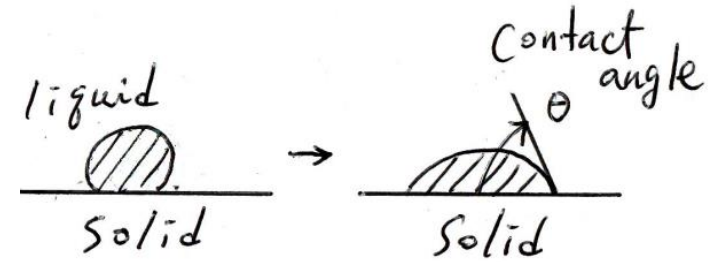
$\gamma\uparrow$ or $r\downarrow \Rightarrow h\uparrow$

$p - \frac{2\gamma}{r}$

h

$p - \frac{2\gamma}{r} + \rho gh$

$p = \rho gh$

참고: Capillary rise and depression

- ## Wetting

$\theta = 0^o$:complete wetting
$\theta = 180^o$:complete dewetting

- Wetting occurs to minimize the total free energy which includes the surface and interfacial free energies
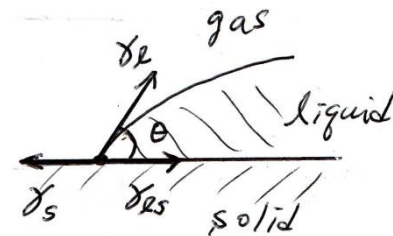
- ## Force balance at the interface

- Criteria for wetting
  When the interface area is increased by dA,

$$\gamma_\ell \cos\theta + \gamma_{\ell s} = \gamma_s$$

> $dG = \gamma_{ls}\ dA + \gamma_l \cos\theta\ dA - \gamma_s\ dA$
> $\quad = (\gamma_{ls} + \gamma_l \cos\theta - \gamma_s)\ dA = x\ dA$

If $x < 0 \rightarrow$ wetting occurs, and
If $x > 0 \rightarrow$ dewetting occurs.

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 = volume filled by phase I / void volume

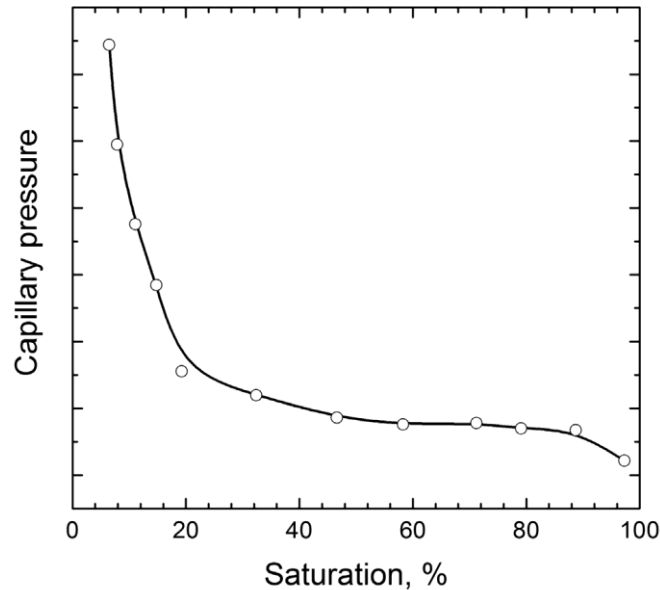→ S_i depends on surface tension, contact angle, pore size distribution

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 : $4H^+ + 4e^- + O_2 \rightarrow 2H_2O$
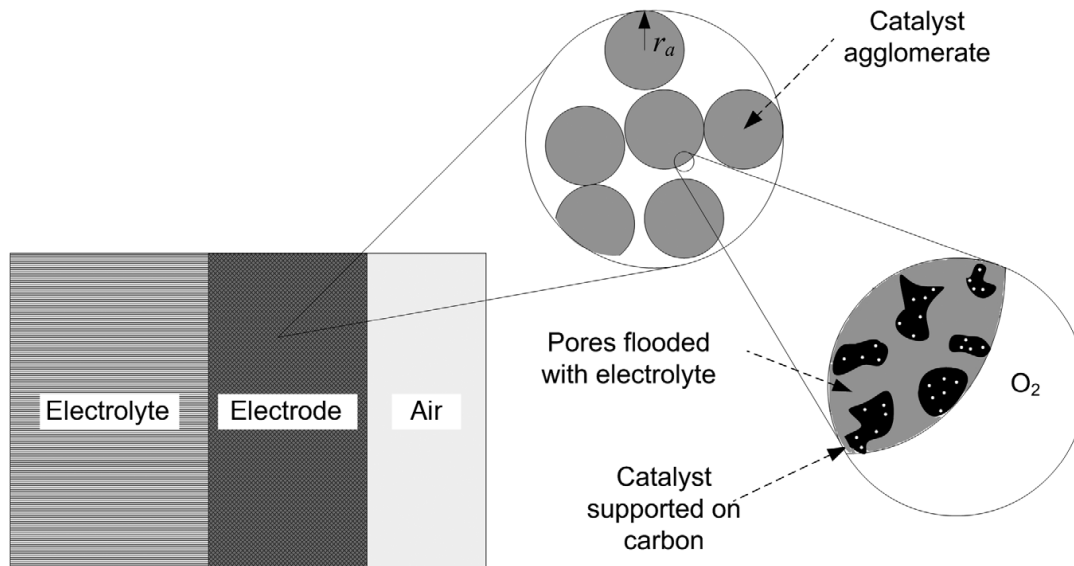   → proton in the electrolyte, electron in solid phase, oxygen in gas phase, water in gas or liquid phase

Figure 5.12   Flooded-agglomerate model.

Electrodes with flow

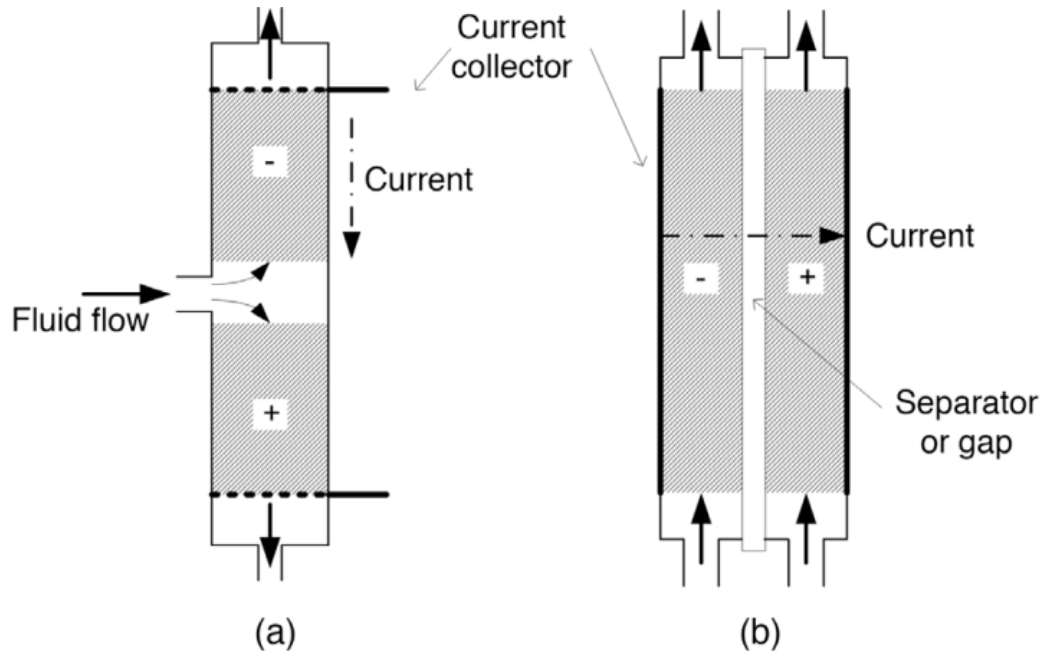- Porous electrodes + fluid flow
  → two basic categories : *flow-through* and *flow-by*

Figure 5.14 Electrode configurations for flowing systems.
(a) Flow-through electrode. (b) Flow-by electrode.

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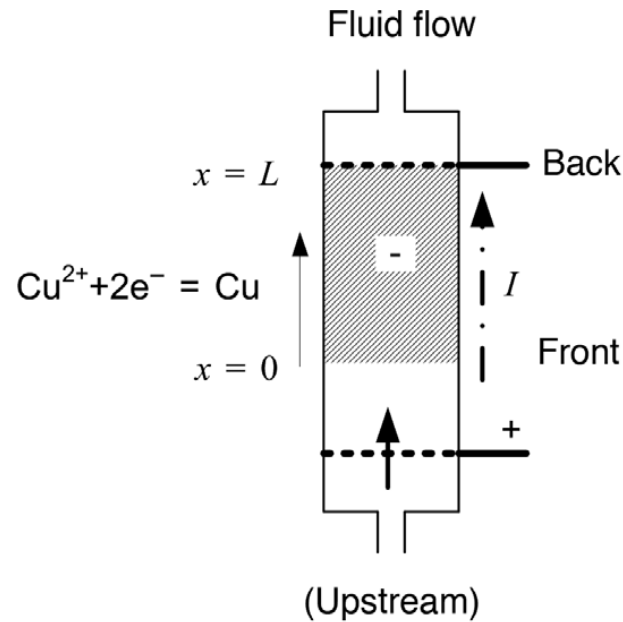
Figure 5.15 Removal of Cu^{2+} from stream.