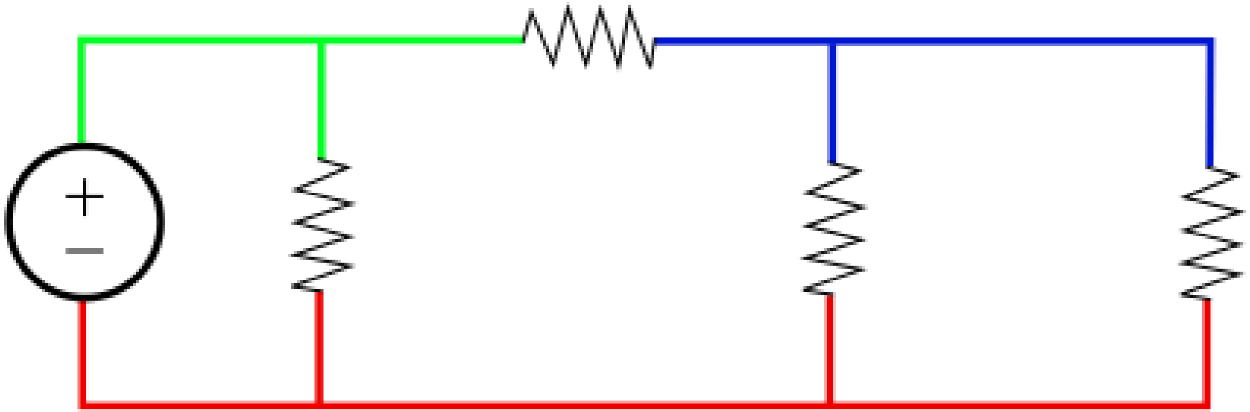
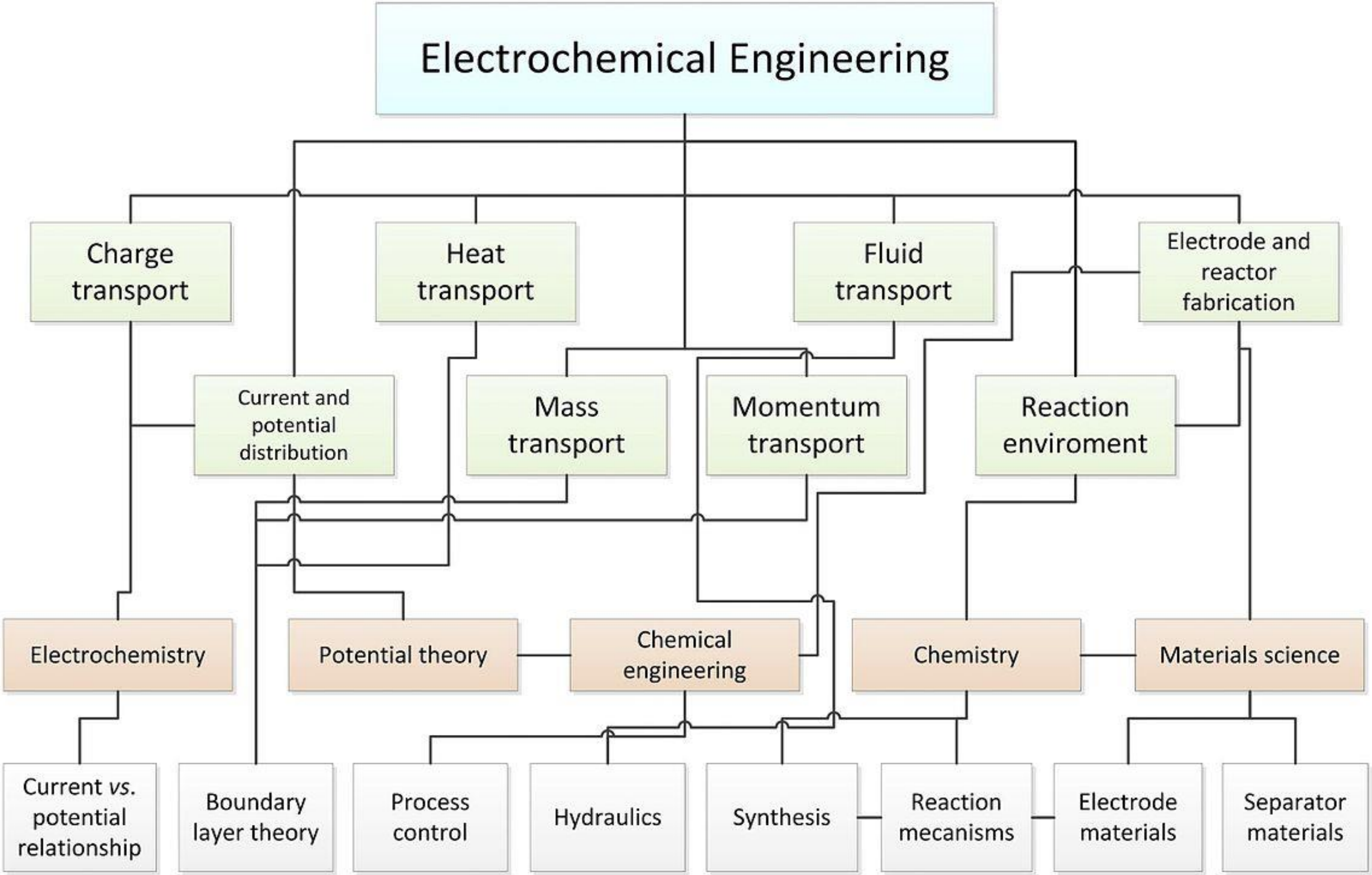
CHAPTER (3)

THORY OF DESIGN AND OPERATION OF ELECTROCHEMICAL REACTORS



Introduction to Electrochemical Engineering (ECE)

- **ECE** combines the study of heterogeneous charge transfer at electrode/electrolyte interphases with the development of practical materials and processes. Fundamental considerations include electrode materials and the kinetics of redox species.
- The development of the technology involves the study of the electrochemical reactors, their mass transport conditions, hydrodynamics, geometry and components as well as the evaluation of its overall performance in terms of reaction conversion and energy efficiency.
- **ECE** requires knowledge several areas particularly chemical engineering, chemistry (particularly electrochemistry), engineering and solution thermodynamics, materials engineering and corrosion, among others.
- **Figure (3.1)** illustrate various aspects and specialties involved in ECE.



Electrochemical Engineering

Charge transport

Heat transport

Fluid transport

Electrode and reactor fabrication

Current and potential distribution

Mass transport

Momentum transport

Reaction enviroment

Electrochemistry

Potential theory

Chemical engineering

Chemistry

Materials science

Current *vs.* potential relationship

Boundary layer theory

Process control

Hydraulics

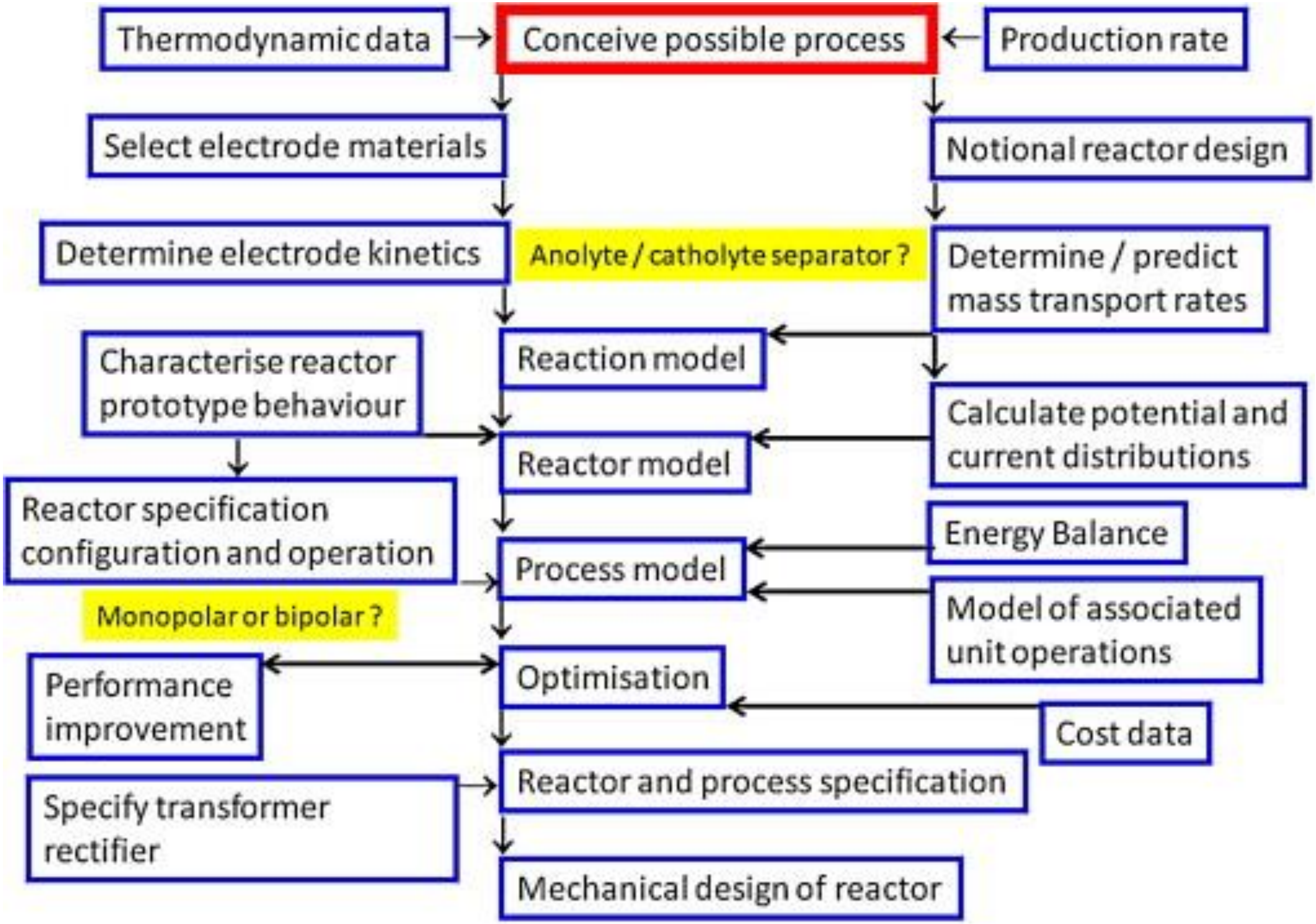
Synthesis

Reaction mecanisms

Electrode materials

Separator materials

Relationship between electrochemical engineering and other disciplines.
After F.C. Walsh, 1993.



Thermodynamic data

Conceive possible process

Production rate

Select electrode materials

Notional reactor design

Determine electrode kinetics

Anolyte / catholyte separator ?

Determine / predict mass transport rates

Reaction model

Characterise reactor prototype behaviour

Calculate potential and current distributions

Reactor model

Reactor specification configuration and operation

Energy Balance

Process model

Model of associated unit operations

Monopolar or bipolar ?

Performance improvement

Optimisation

Cost data

Reactor and process specification

Specify transformer rectifier

Mechanical design of reactor

Electrochemical Cell Configurations

- Different electrochemical cells and have been developed for various applications in the past.
- An electrochemical reactor may be composed of one or more interconnected electrochemical cells.
- According to the criteria of high mass-transfer coefficient and/or large specific electrode area, these cells or reactors can be classified as:

1. Cells with relatively small electrode area but improved mass transport to increase mass-transfer coefficient by setting the electrodes in motion or by applying turbulence promoters. Examples are:
    - the pump cell, and
    - cells with vibrating electrodes or electrolytes.

Electrochemical Cell/Reactor Configurations

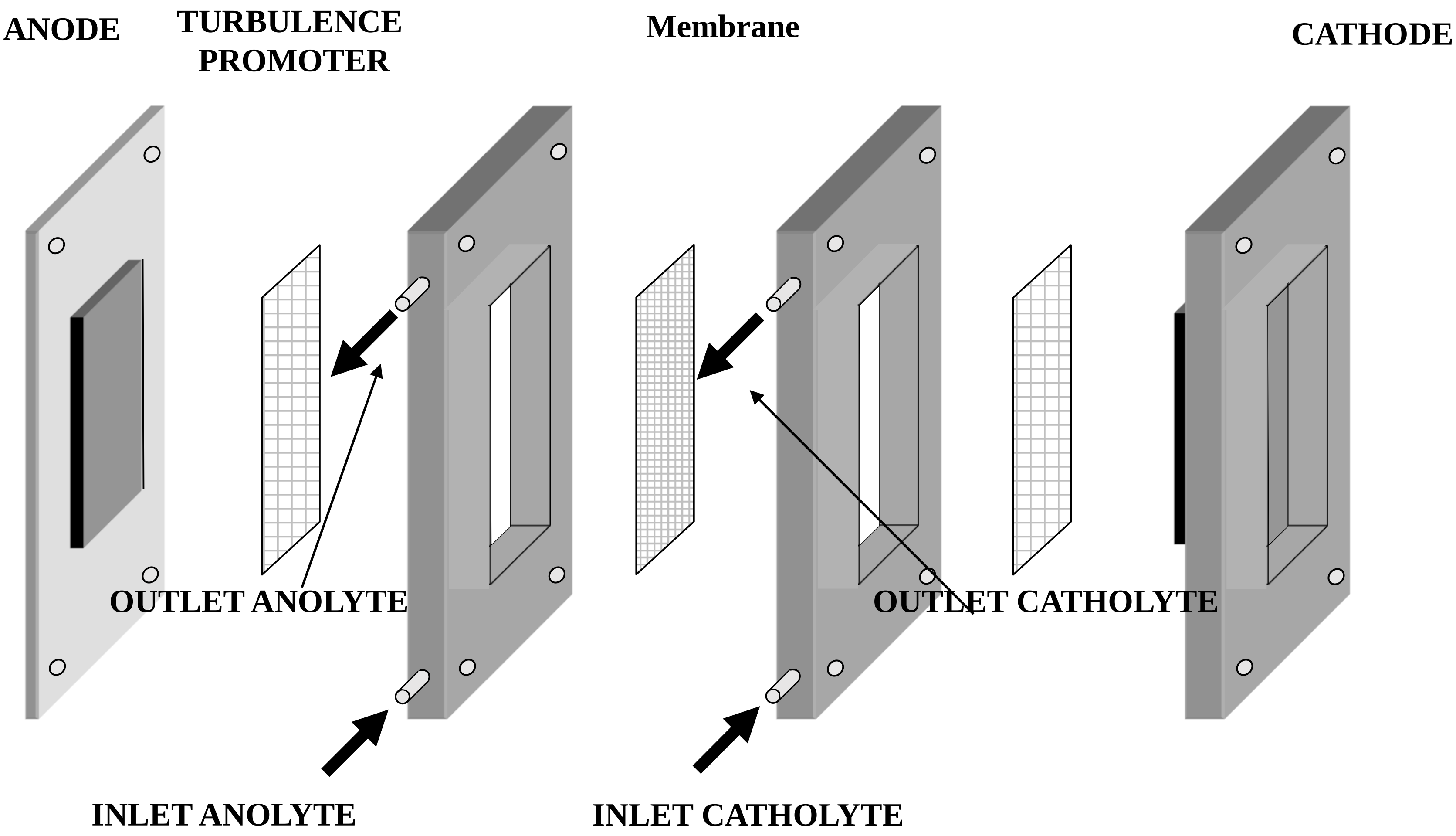
2. Cells with enlarged electrode area in a small cell volume are found in:

- the multiple-cathode cell,
- the extended surface electrolysis (ESE) cell, and
- the capillary gap cell.

3. Cells with three-dimensional electrodes providing enlarged specific electrode area and improved mass transport due to the specific fluid dynamics inside the three dimensional structure include:

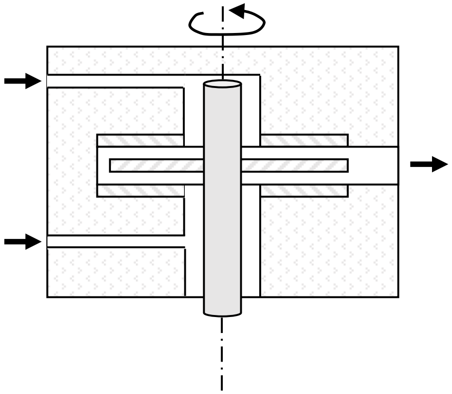
- the porous flow-through cell,
- **the fixed-bed (or packed-bed) cell**,
- **the fluidized-bed cell**, and
- the rolling tube cell.

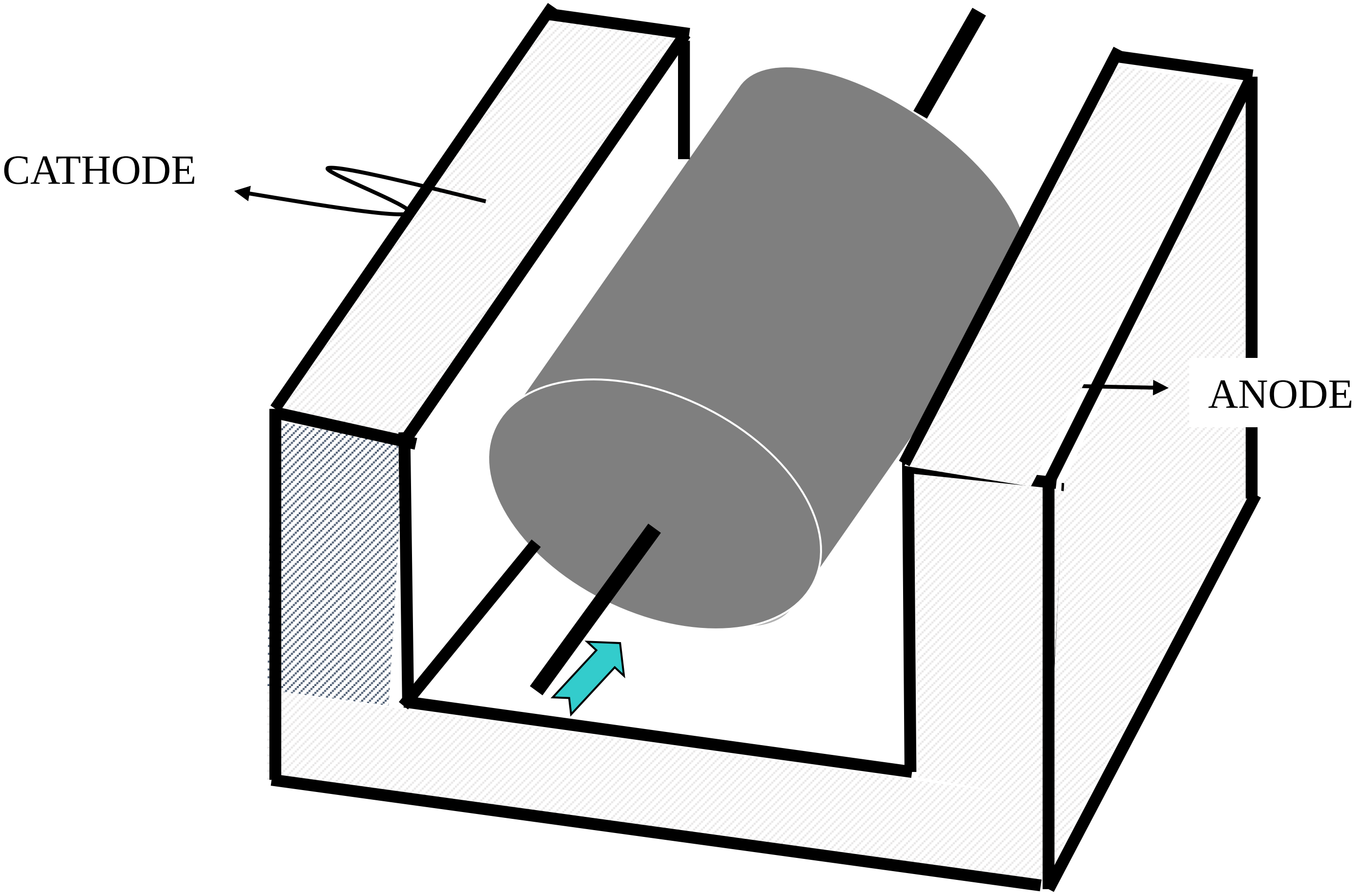
SINGLE FLOW CELL



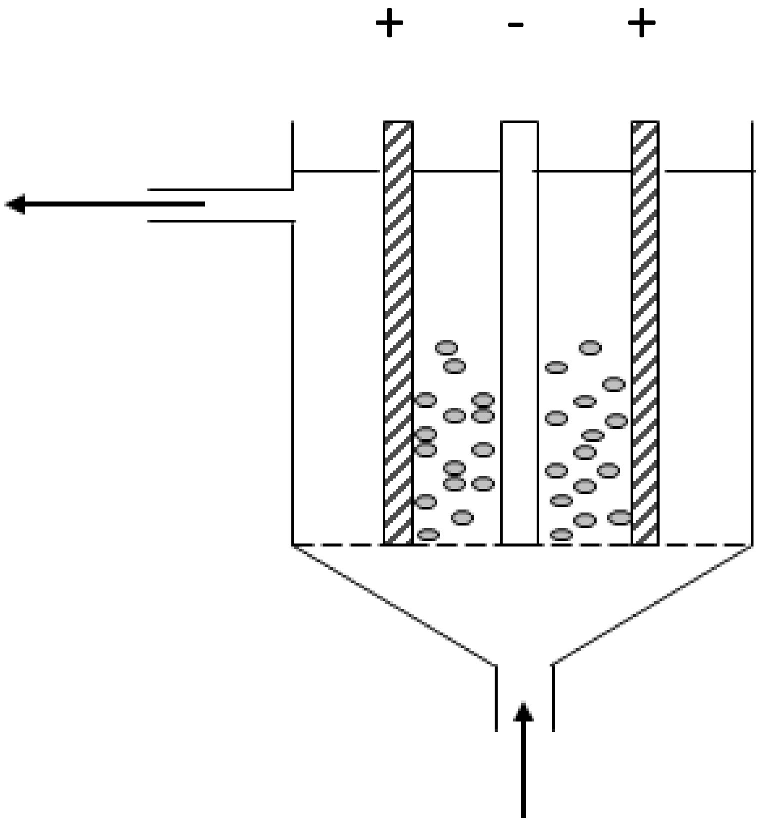
Example: Hydrogen Fuel cells

Rotating electrode cell

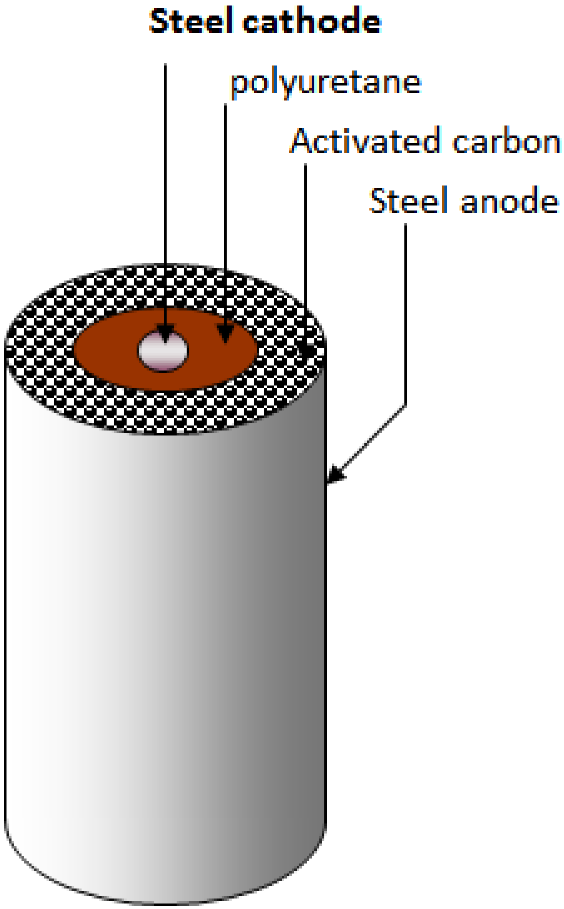




OTHER CELLS



Packed bed cell



Cell with continuous regeneration of the adsorbent

Electrochemical Cell/Reactor Configurations

Design and arrangement aspects of EC Cells/Reactors:

1. Size, shape and material of construction
2. Electrode area, shape and material of construction
3. Separators such as membranes
4. Means of electroactive ions transport
5. Connection of cathodes and anodes
6. Potential distribution
7. Arrangement that reflects the needs of desired application, e.g., high currents and space utilization in industrial electrolysis.
8. Accessibility and ease of treatment for growing or dissolving electrodes (e.g. metal deposition processes).

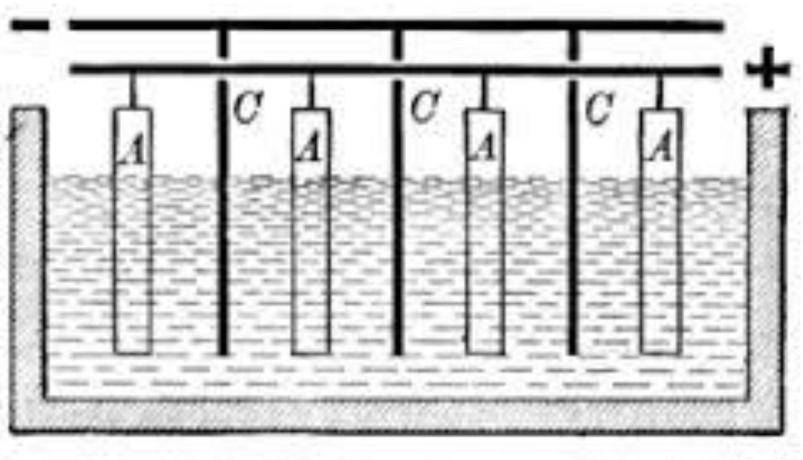
Industrial Electrochemical Reactors:

- The following types of electrochemical reactors are most common in industry:

1. Tank-type
   - Parallel-plate reactor (Figures 3.2a).
   - Cylindrical electrodes / Cylindrical tank reactor (Figures 3.2b).
2. Fixed-bed reactor, and
3. Fluidized-bed reactor (Figures 3.3 and 3.4).

- The first type reactor is composed of a series of vertical parallel cathodes and anodes arranged alternatively in a rectangular container called the **"tank".**
- Each cathode and anode combination forms a **"cell"**; so that the tank contains a number of cells arranged in parallel.
- All cathodes are connected to a common conductor called the "negative bus bar".
- Similarly, anodes are connected to a common "positive bus bar".

Industrial Electrochemical Reactors



bus bar

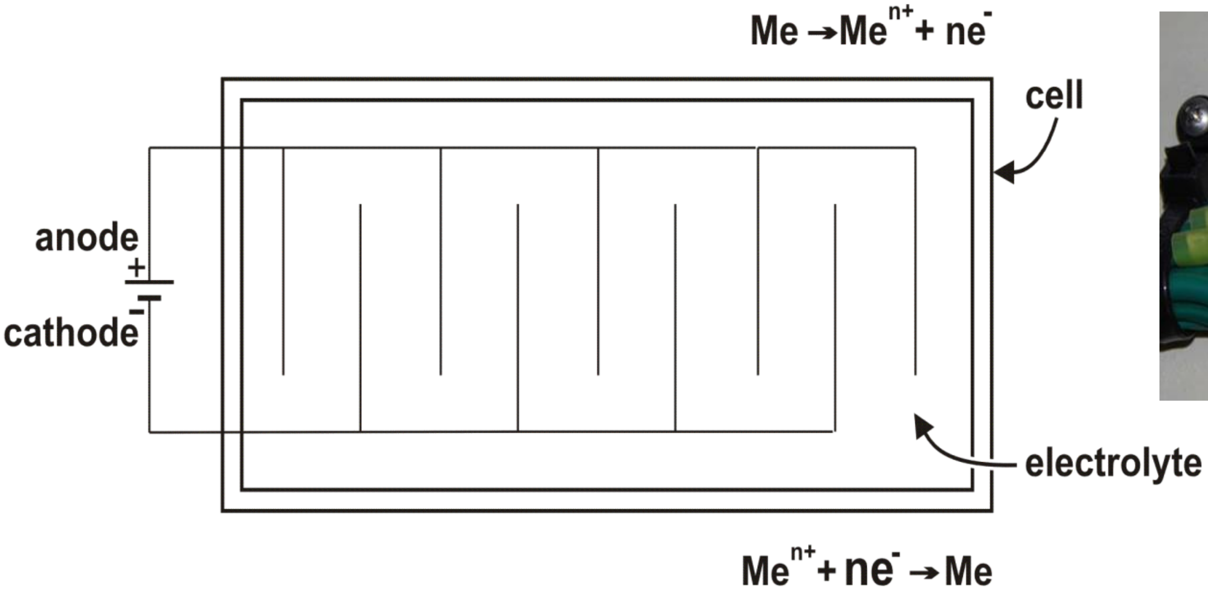


Figure (3.2a): **Parallel-Plate Tank-Type EC Reactor**

Industrial Electrochemical Reactors

- Other tank-type reactors:

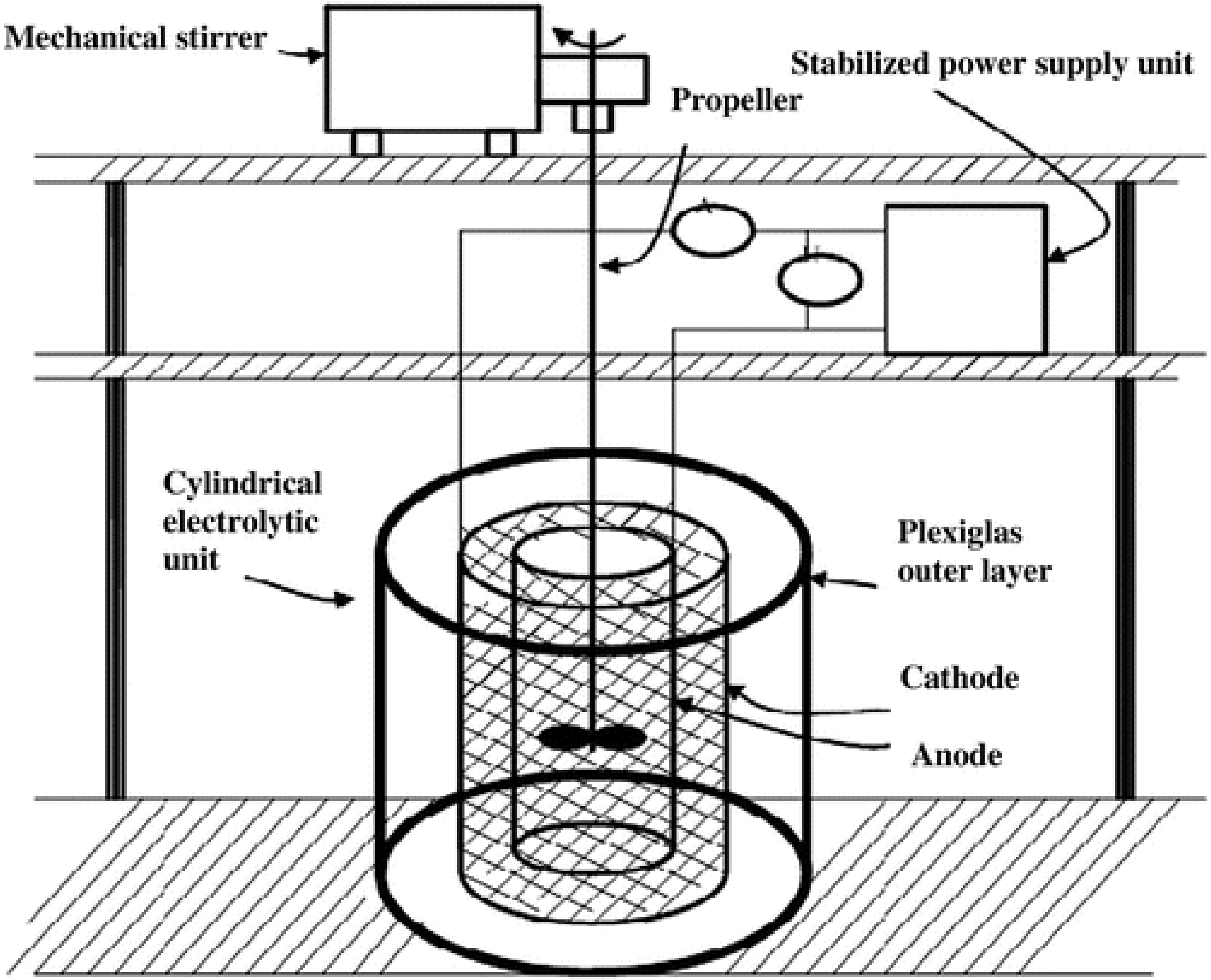


Figure (3.2b): **Cylindrical Electrodes Tank-Type EC Reactor**

Industrial Electrochemical Reactors

- Fixed-bed or Fluidized-bed electrochemical reactors are generally similar in structure.
    - In each of them, the working electrode is composed of a bed of metallic particles supported on a porous distributor.
    - The electrolyte is allowed to pass through the bed.
- For catalytic reactions, fixed-bed reactors are very common in the chemical industry due to their high conversion rate per catalyst weight.
- In case of fluidized beds, relatively high electrolyte flow rates are used to fluidize the bed while in case of packed beds; relatively low electrolyte flow rates are used.
- Fluidized-bed reactors give better contact between surfaces, high surface area and better heat and mass transfer than in the case of and packed-bed reactors and thus efficient utilization of catalysts.

Industrial Electrochemical Reactors

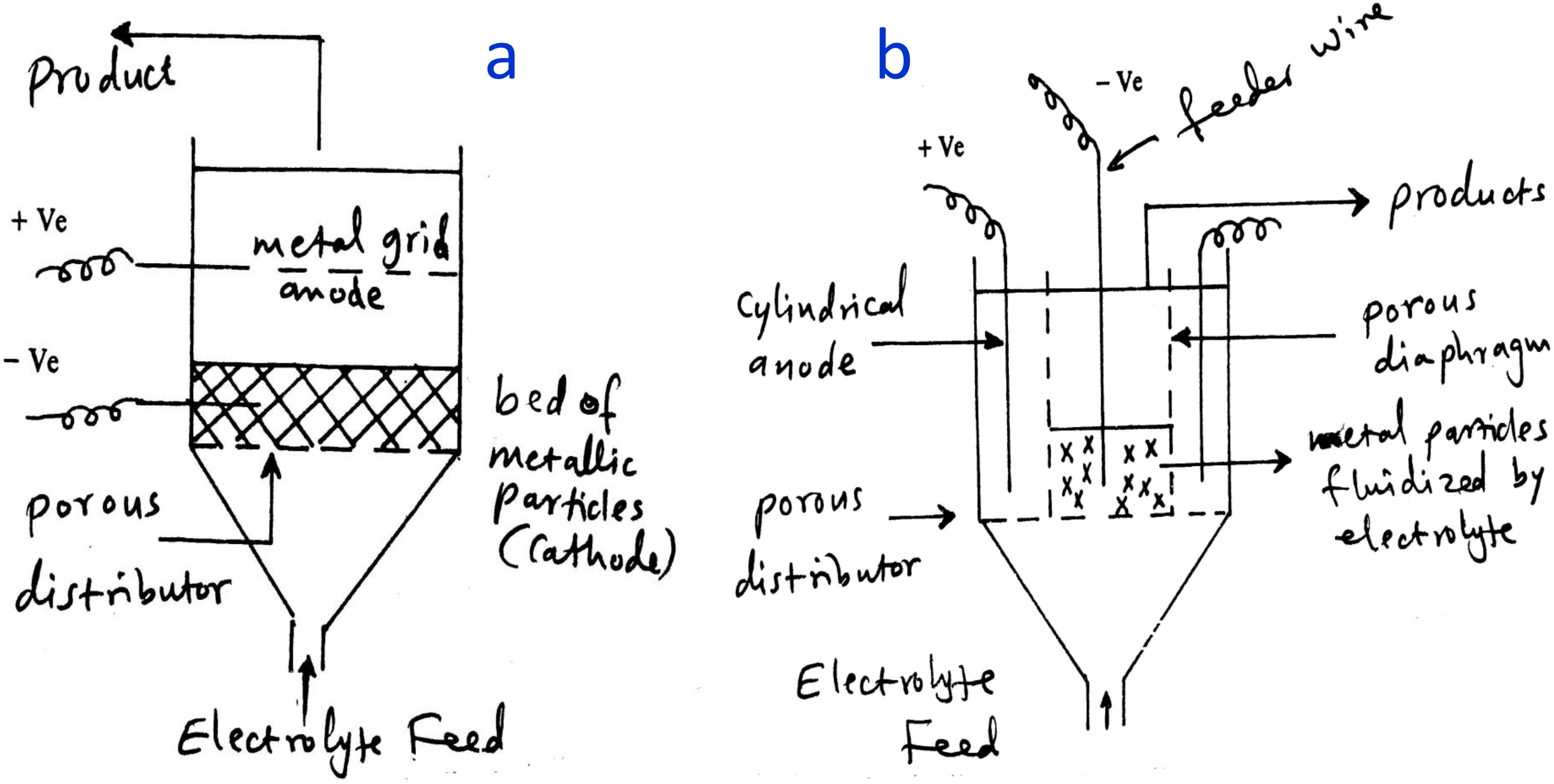
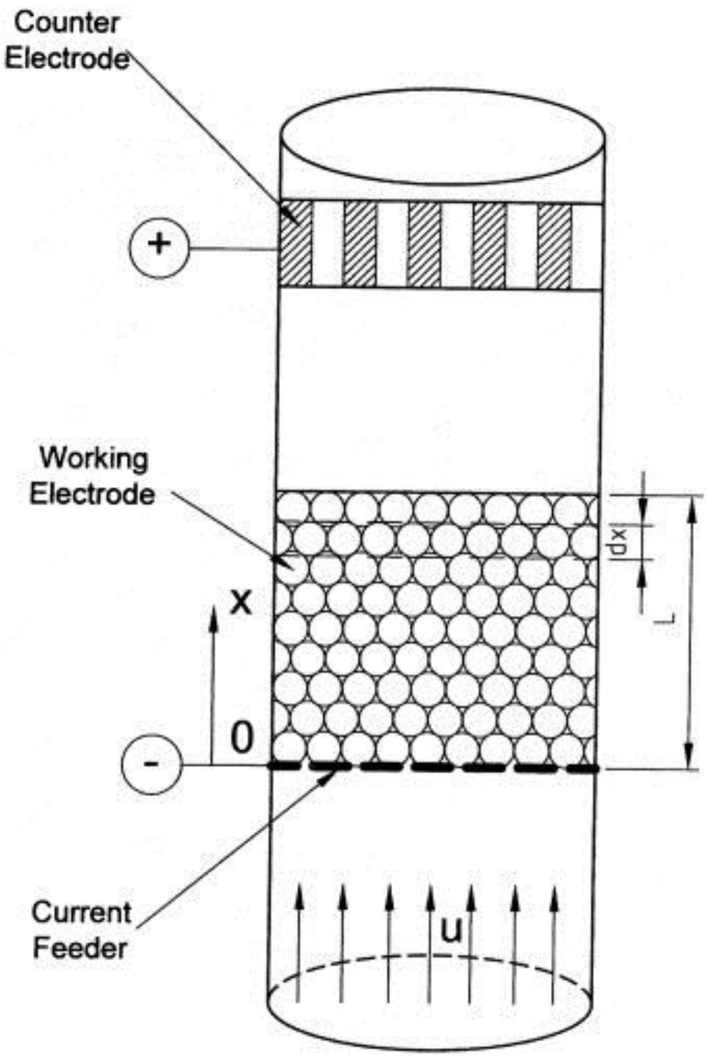
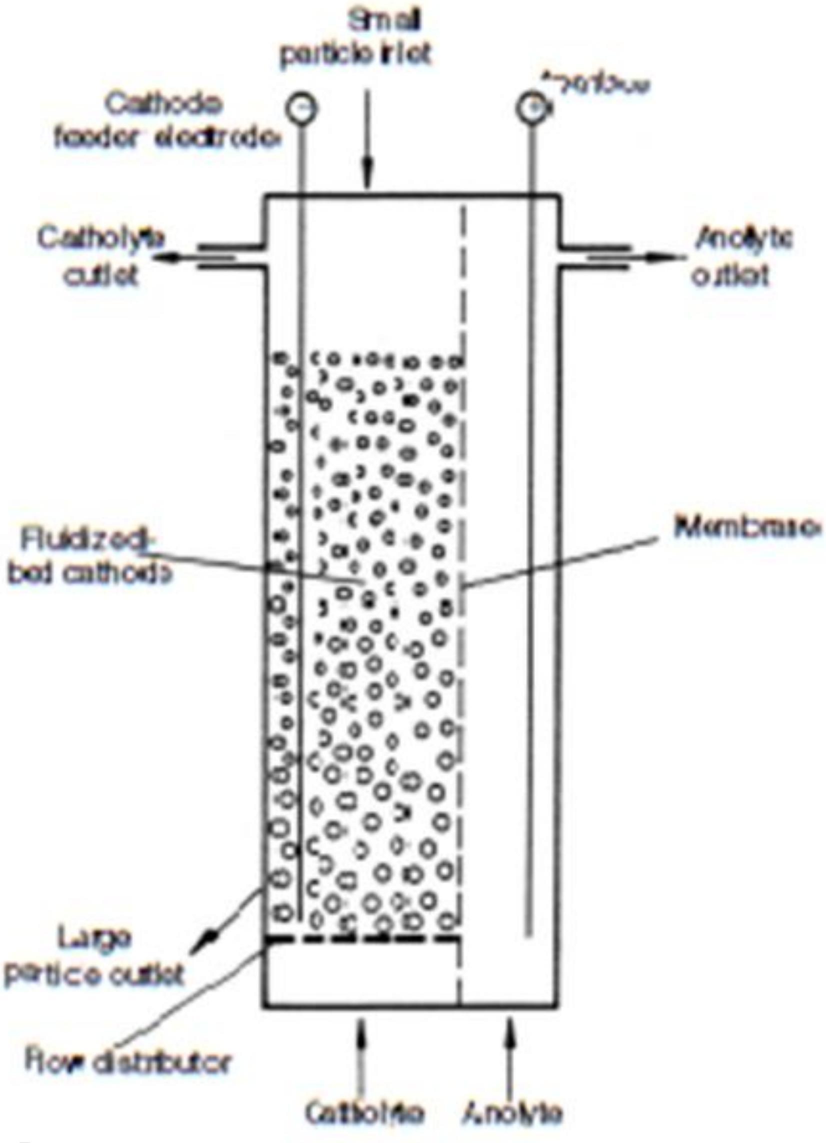


Figure (3.3): Fixed- & Fluidized-Bed EC Reactor

Industrial Electrochemical Reactors





Fluidized-bed cell

Figure (3.4):

Fixed & Fluidized-Bed Electrochemical Reactor

Industrial Electrochemical Reactors

- Packed- and Fluidized-bed electrochemical reactors have the following advantages over the parallel-plate cells:
  1. Both fixed- and fluidized-bed reactors have a very high surface area/unit volume. This means:
     - a more compact electrochemical plant for a certain capacity, that is,
     - less-floor space is needed and
     - consequently the capital costs will be less.
  2. For the same flow rate, the mass transfer coefficient in case of fixed and fluidized beds is much higher than that in the case of the parallel-plate reactor.
     - Consequently, both the limiting current and the rate of production will be higher than in the parallel-plate reactor.
- However, fixed- & fluidized-bed EC reactors are not suitable for production of metals since metals will block the pores of the bed.
  1. They are rather suitable for production of organic and inorganic chemicals (liquids and gases).
  2. Tank-type parallel plate reactor is most suitable for the production of both metals and gaseous products such as H_2 and O_2.

Advantages and Disadvantages of Electrochemical Processes

The main advantages of electrochemical processes are as follows:

- **Versatility**: Direct or indirect oxidation and reduction, phase separation, concentration or dilution, biocide functionality, applicability to a variety of media and pollutants in gases, liquids, and solids and treatment of small to large volumes from microliters up to millions of liters.

- **Energy efficiency**: Lower temperature requirements than their non electrochemical counterparts, for example, anodic destruction of organic pollutants instead of thermal incineration; power losses caused by inhomogeneous current distribution, voltage drop, and side reactions being minimized by optimization of electrode structure and cell design.

Advantages and Disadvantages of Electrochemical Processes

- **Amenability to automation:** The system inherent variables of electrochemical processes, for example, electrode potential and cell current, are particularly suitable for facilitating process automation and control.

- **Cost effectiveness:** Cell constructions and peripheral equipment are generally simple and, if properly designed, also inexpensive.

- Since electrochemical reactions take place at the interface of an electronic conductor (the electrode) and an ion conductor (the electrolyte), electrochemical processes are of heterogeneous nature. This implies that, despite the advantages mentioned earlier, the performance of electrochemical processes suffers from mass transport limitations and the size of the specific electrode area.

Application of Mass Transfer Theory in Reactor Design

- **For mass transfer limited processes**, it is desirable in practice to:
  1. minimize concentration polarization, and
  2. increase the limiting current in order to increase the rate of production.
- This is usually achieved by stirring the solution to decrease the diffusion layer thickness (δ) which represents the resistance to mass transfer.
- The relation between the limiting current and the degree of stirring can be deduced by dimensional analysis.
- **From Chapter (2):**

$$I = K\,(C_b - C_i) \qquad I_L = K\,.\,C_b$$

$$K = (DzF)\,/\,(t_-\,.\,\delta)$$

- If an excess of supporting electrolyte (e.g. H2SO4) is present with the electroactive ion (e.g. Cu present as CuSO4) to improve the conductivity of the electrolyte, the transfer of electroactive ion by migration becomes negligible since the ions of the supporting electrolyte carry most of the current.

Application of Mass Transfer Theory in Reactor Design

- The mass transfer coefficient, $k = D/\delta$, and assuming that **$t_- = 1$**, the limiting current density is related to the mass transfer properties of the solution by the following equation which can be used for design and operation of reactors at optimum conditions:

$$\mathbf{I_L = z.F.k\ C_b}$$

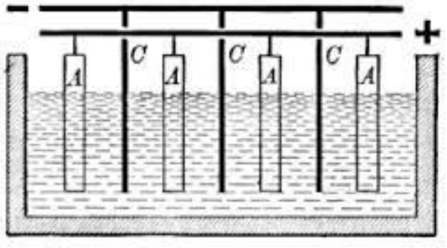
- The maximum theoretical amount of production is obtained by applying Faraday's law of electrolysis:

$$\mathbf{n_{max} = I_L.t/zF} \qquad \text{(mol units)}$$

$$\mathbf{M_{max} = M.I_L.t/zF} \qquad \text{(mass, g, units)}$$

- Mass transfer coefficient (k) can be related to other important parameters in the design and operation of the reactor by applying the dimensionless groups (numbers) of Sherwood, Reynolds, Schmidt, Grashof and Nusselt.

The Parallel-Plate Reactor



- Consider the following two cases:

  1. Natural convection: where electrolysis is conducted while the solution is static.

  2. Forced convection: where the solution is stirred by circulating the electrolyte inside the cell.

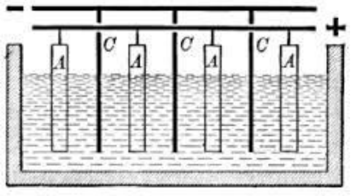
Natural Convection Mass Transfer:

- Natural Convection arises owing to the density difference at the interface and in the bulk (ρ_i is less than ρ_b).
- This is because C_i is less than C_b. This density difference results in an upward flow of the electrolyte besides the electrode.
- The flow carries a fresh supply of the electroactive ion to the electrode surface. In this case, **the mass transfer coefficient, k**, is a function of the following:

$$k = f(\rho_i, \rho_b, \mu, D, L, g)$$

where "L" is the electrode height and "g" is the acceleration of gravity.

The Parallel-Plate Reactor



- Using dimensional analysis, the mass transfer coefficient, k, can be related to the other variables using the three dimensionless groups; namely Sherwood (Sh), Schmidt (Sc) and Grashof (Gr) numbers:

$$Sh = k.\ L/D$$

$$Sc = \mu/\rho_b.\ D)$$

$$Gr = g.\ L3.\ d2\ (\rho_b - \rho_i)/(\mu 2.\ \rho_i)$$

(d = tank (reactor) diameter)

- The correlation between these dimensionless groups can be represented as:

$$Sh = a.(Gr.\ Sc)^{b}$$

where "a" and "b" are determined experimentally.

- The mass transfer equation representing natural convection at vertical electrodes was found to be:

$$Sh = 0.67\ (Gr.\ Sc)^{0.25}$$

The Parallel-Plate Reactor

Forced Convection Mass Transfer:

1) Laminar Flow: **Re < 2300: k = f (d, μ, D, L, u)**

where u = linear velocity of the circulated solution(cm.s^{-1}).

- From dimensional analysis:

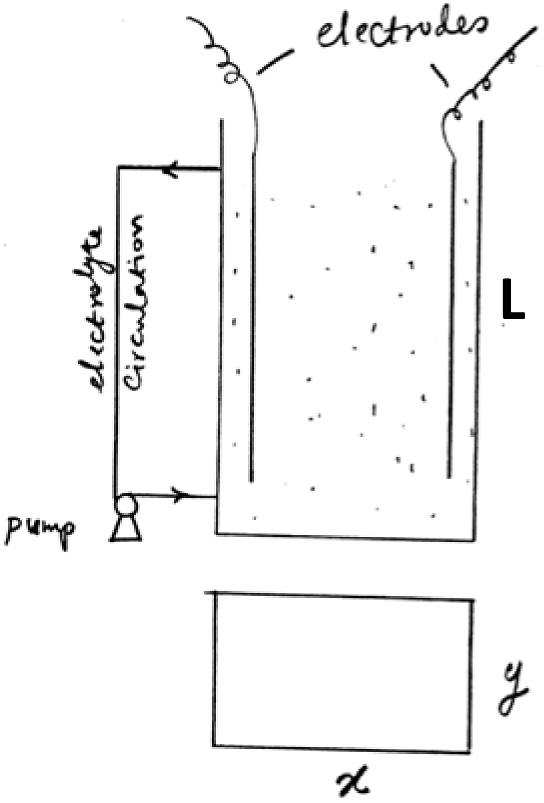
$$Sh = a.[Sc.\ Re.(de/L)]^{b}$$

where: $Re = (\rho.\ de.\ u)/\mu$

and the equivalent diameter of the cell:
de = 4x(cross sectional area)/(wetted perimeter)

The definition of the wetted perimeter is illustrated in **Figure 3.5**.

- It was found experimentally that "**a**" and "**b**" were **1.85** and **0.333**, respectively.



de = 4xy/2(x+y)

Figure (3.5)

The Parallel-Plate Reactor

2) Turbulent Flow: **Re > 2300**

From dimensional analysis:

$$Sh = a.\ Sc^{b}.\ Re^{c}$$

- It was found that the coefficients "**a**", "**b**" and "**c**" were **0.023, 0.333** and **0.8**, respectively.
- The above mass transfer correlations can be used for a given cell (electrochemical reactor) to predict the flow rate of the electrolyte required to give a desired rate of production (and the corresponding limiting current density).
- Conversely, they can be used to calculate the limiting current density and the rate of production corresponding to a given flow rate of electrolyte solution (**Figure 3.6**).

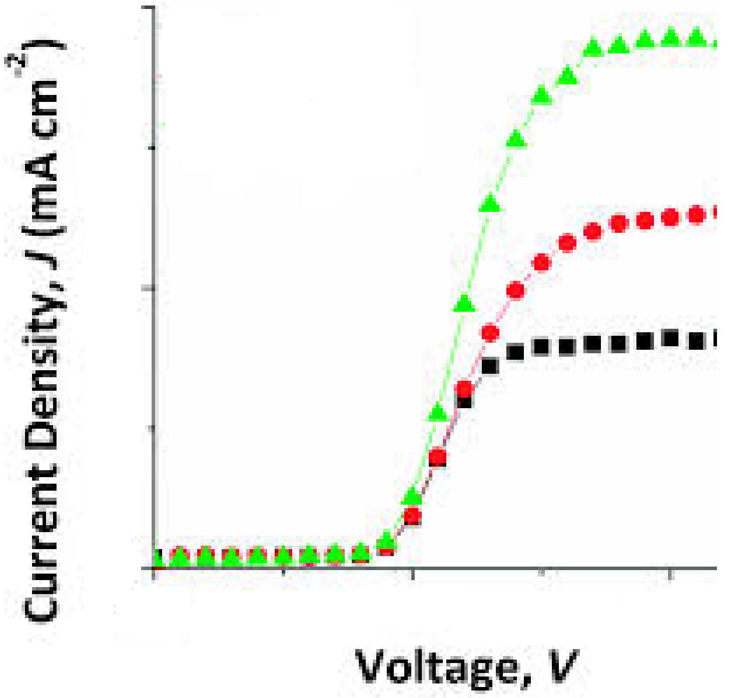


Figure (3.6): Limiting current density (IL) increases with solution flow rate

Ref. Rajesshwar and Ibanez, 1997

Fixed- & Fluidized-Bed Reactors

- The following design equations apply to this type of reactors.
- They are similar to the design equations of ordinary chemical reactors:

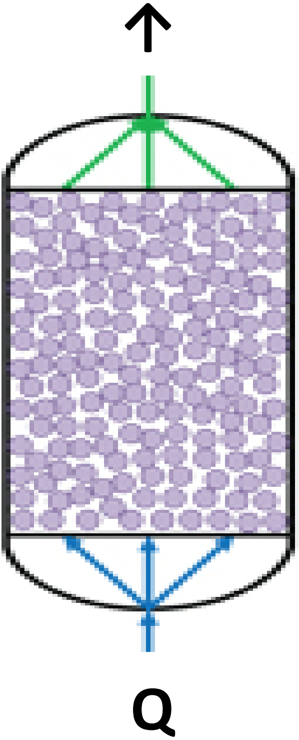
II. Fixed-Bed Reactor:

$$\mathbf{Sh = 1.52\ Re^{0.55}\ .Sc^{0.333}}$$

III. Fluidized-Bed Reactor:

$$\mathbf{Sh = \{(1-\varepsilon)/\varepsilon\}^{0.55}\ .Re^{0.55}\ .Sc^{0.333}}$$

$$\mathbf{Re = \rho.d_{pb}.u/\mu}$$



ε is the bed porosity (volume of voids/total bed volume).

d_p = particle diameter

u = linear or superficial velocity = Q/A

Q = volumetric flow rate of solution; A = cross-sectional area

(A =$\pi.d_b$^^2/4 where d_b= bed diameter

Arrangement of Cells in Electrochemical Plants

- An electrochemical plant is composed of a number of tanks connected electrically in series. Each tank contains a number of cells which are connected in parallel. Each cell consists of a cathode and an anode (**Figure 3.7-A**).
- Since cells are connected in parallel within each tank, therefore:

Cell Voltage = Tank Voltage

- Since tanks are connected in series in the plant (the current passing in each tank is the same), therefore:

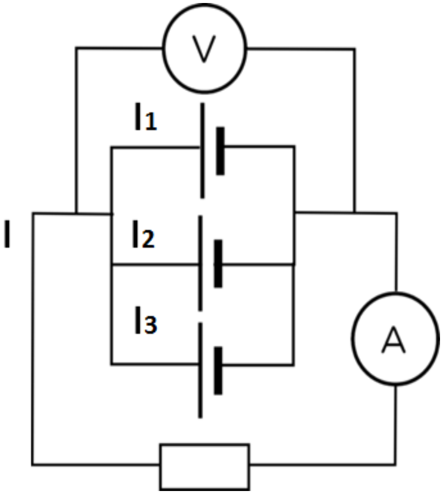
Total Plant Voltage =

(Tank Voltage) (# of Tanks)

Current / Tank = (Cell current) (# of Cells)

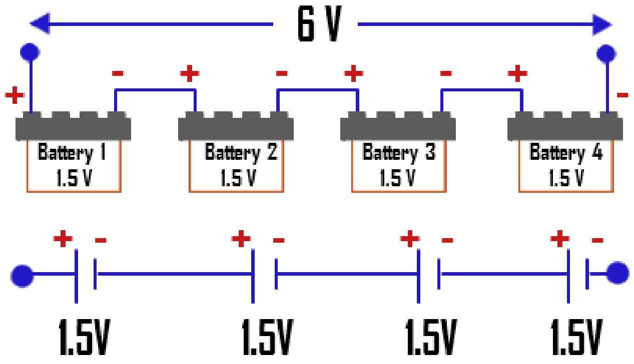
Total Rate of Production of All Tanks =

(Amount Produced/Tank) (# of Tanks)



In PARALLEL:

Same voltage, current divided

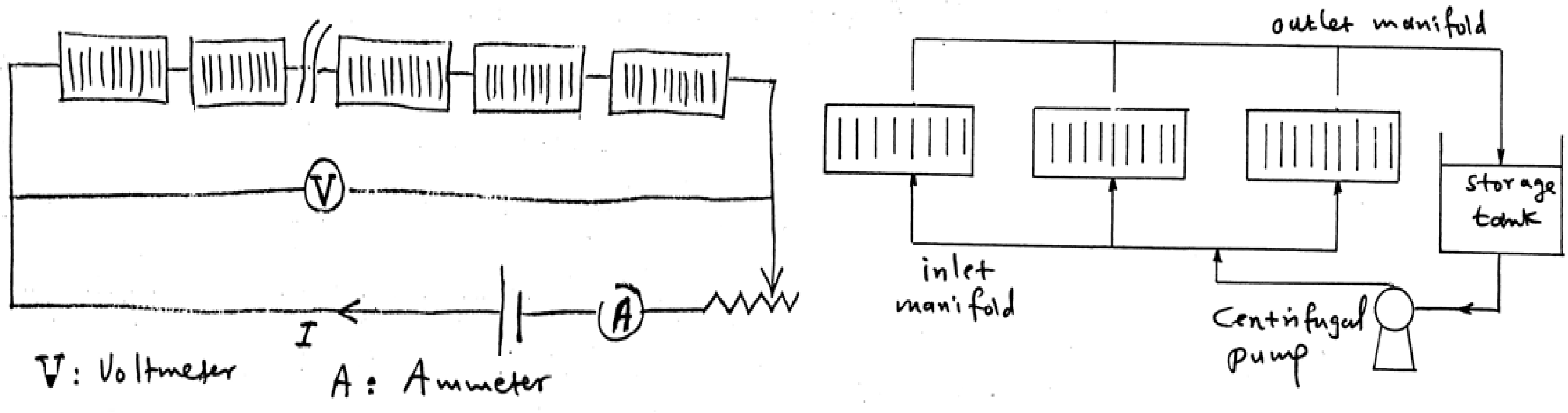


In SERIES:

Same current, voltage divided

Arrangement of Cells in Electrochemical Plants

- **Figure (3.7-B)** shows the flow cycle of the electrolyte in the plant. Circulation is usually performed by a centrifugal pump which circulates the electrolyte through the cells.
- The outlet electrolyte from the cells is collected in a storage tank where concentration, pH and temperature are automatically adjusted.

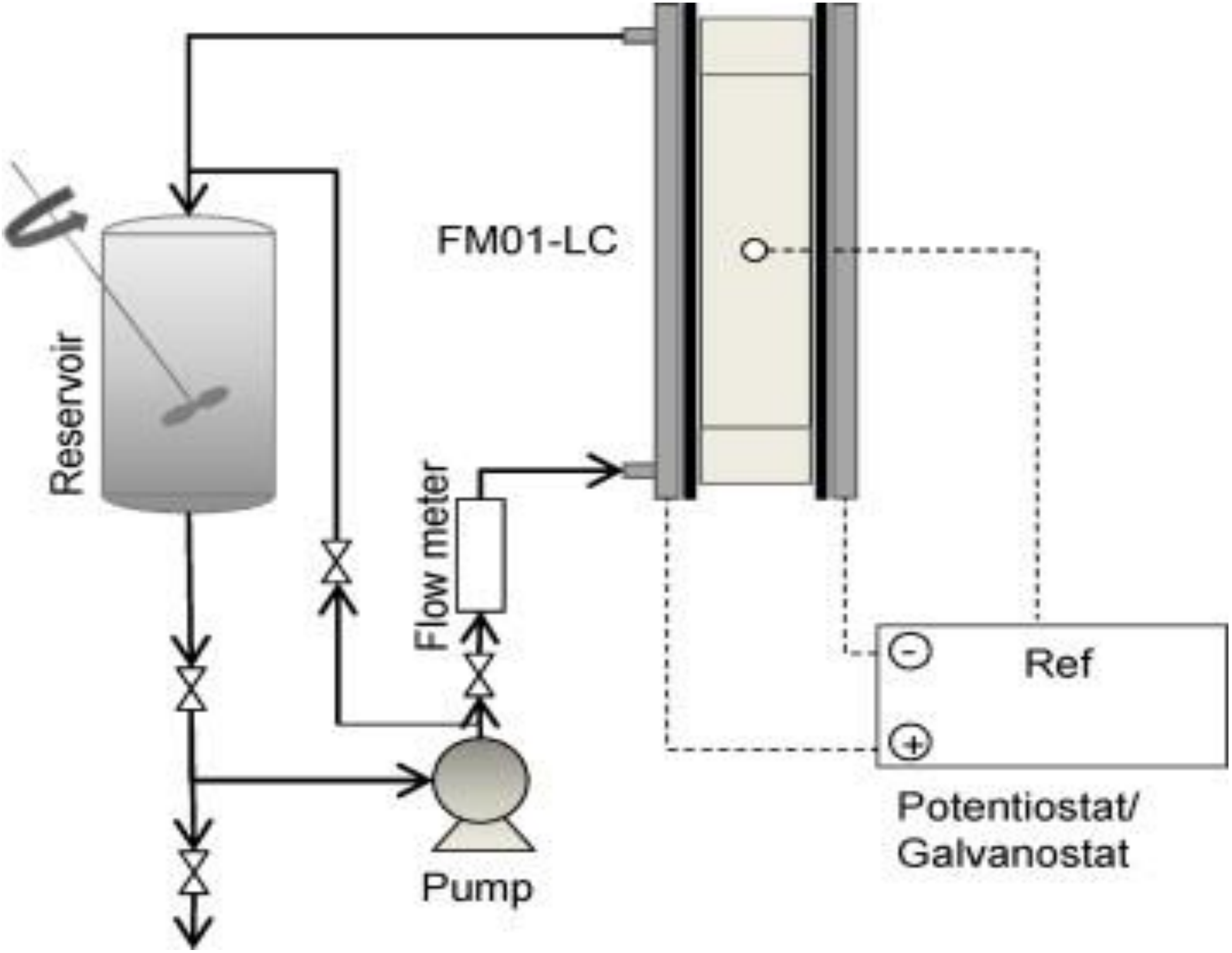


A) **B)**

Figure 3.7: Connection of Cells in EC Plants:

A) Electrical circuit B) Electrolyte recirculation cycle

Handling recirculated electrolyte in EC Cell Reactor



Selecting Optimum Operating Current Density

- In estimating the cost of a given product, the capital costs and the operating costs are usually considered.
    1. The capital costs refer to the cost of plant installation (including equipment and machines, buildings, floor space, etc.).
    2. Operating costs refer to the costs of utilities (electricity, water and fuel), labor costs, taxes, etc.

- In any industry, operating conditions should be adjusted to produce the product at minimum cost.
- In electrochemical industries, the capital and the operating costs are functions of the operating current density.

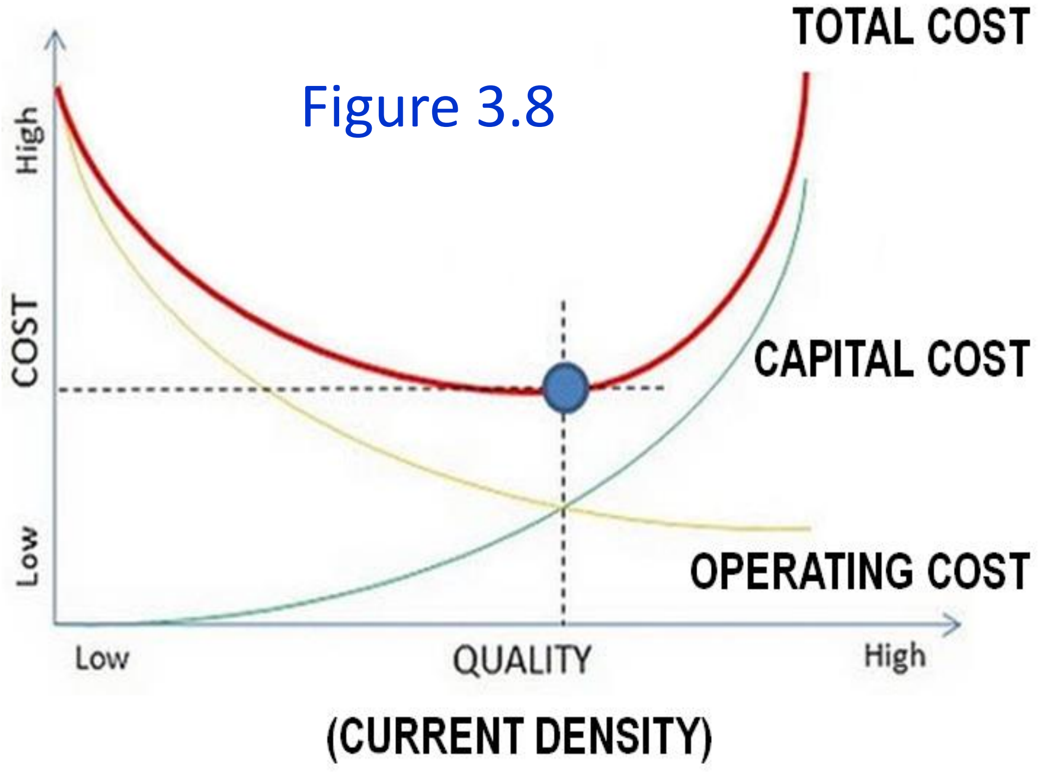
- For a given rate of production, electrochemical plants can be operated either at:
    1. high current density and low electrode area, or
    2. low current density and high electrode area.

Selecting Optimum Operating Current Density

- In the first case, energy consumption will be high (i.e., high operating costs), but the capital costs will be low because less electrode area and floor space will be needed. In the second case, energy consumption will be low (i.e., low operating costs), but the capital costs will be high because a large electrode area and a large floor space will be needed.

- Therefore, an optimum current density should be selected at which the total costs should be minimum.

- The procedure for selecting the optimum current density, known as optimization, is shown in Figure 3.8.



Heat Effects in EC Reactors: Energy Balance

- Consider a continuously operated electrochemical reactor.
- To maintain a constant reaction temperature, heat should not be allowed to accumulate inside the reactor.
- The energy balance equation can be written as:

Total Energy Input = Total Energy Output

$$\Sigma H_{Re} + E.I.t = \Sigma H_{Pr} + q$$

$$E.I.t = \Delta H_R + q$$

Where the four terms indicate enthalpy of reactants fed to the reactor, electrical energy supplied, enthalpy of products and excess energy appeared as heat. ΔH_R is the enthalpy change of the reaction.

- This heat (q) is to be removed for maintaining a constant reactor temperature.
- Some undesirable consequences of not removing this heat may be:
  - decomposition of products, and
  - water evaporation thus changing electrolyte concentration and solution properties.

Heat Effects in EC Reactors: Cooling

- Heat generated inside the electrochemical reactor should be removed to maintain a <u>constant temperature</u> for the reaction.
- There are three different ways of reactor cooling:
    1. Using a cooling jacket: This method have the disadvantage of limited efficiency for large amount of heat to be removed.
    2. Providing the reactor with a cooling coil (Figure 3.9a).
    3. Circulating the electrolyte through an external heat exchanger (Figure 3.9b).

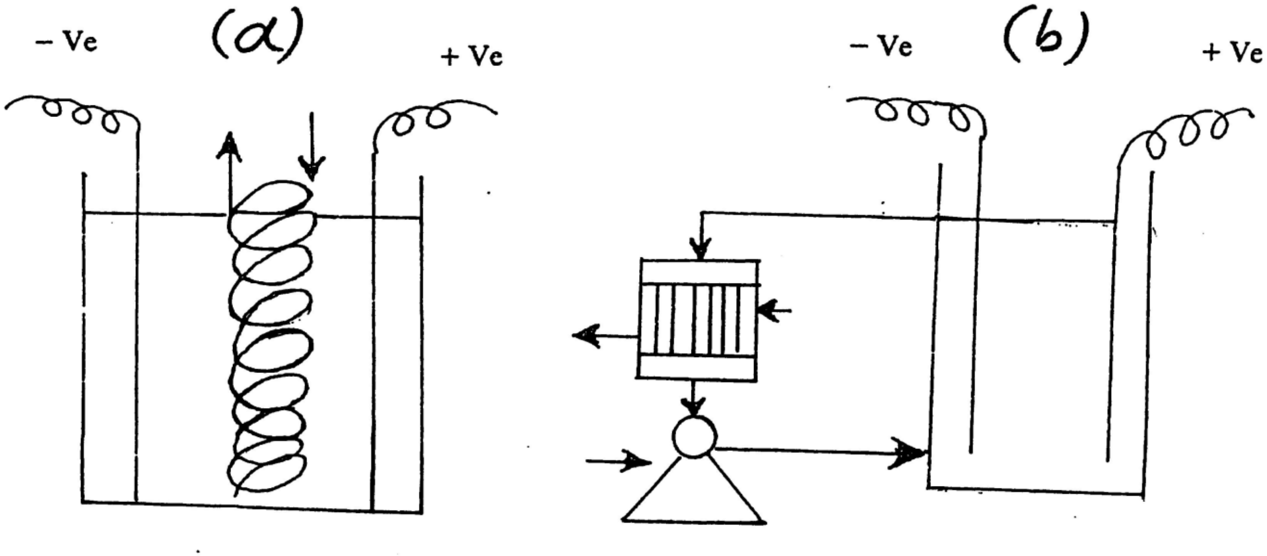


Figure 3.9

Heat Effects in EC Reactors: Heat Transfer

- In heat exchangers, heat transfer rate is expressed as follows :

$$q = U.\ A.\ \Delta T_{lm}$$

Where: q is the quantity of heat transferred in unit time,
U is the overall heat transfer coefficient,
A is the surface area available for transfer, and
ΔT_{lm} is the log mean temperature difference in the heat exchanger.

- The local heat transfer coefficient "h" can be determined from empirical correlation involving the dimensionless groups of Nusselt (Nu), Prandtl (Pr) and Reynolds (Re) numbers depending on the type of flow of electrolyte through the reactor:
- For laminar flow regime: $Nu = 1.85\ (Re.\ Pr.\ d/L)^{1/3}$
- For turbulent flow regime: $Nu = 0.023\ Re^{0.5}\ Pr^{0.33}$

$$Nu = h.L/k \qquad \& \qquad Pr = C_p\ .\mu/k$$

Where: L = length of heat transfer surface, k = thermal conductivity, C_p = heat capacity and μ = solution viscosity.