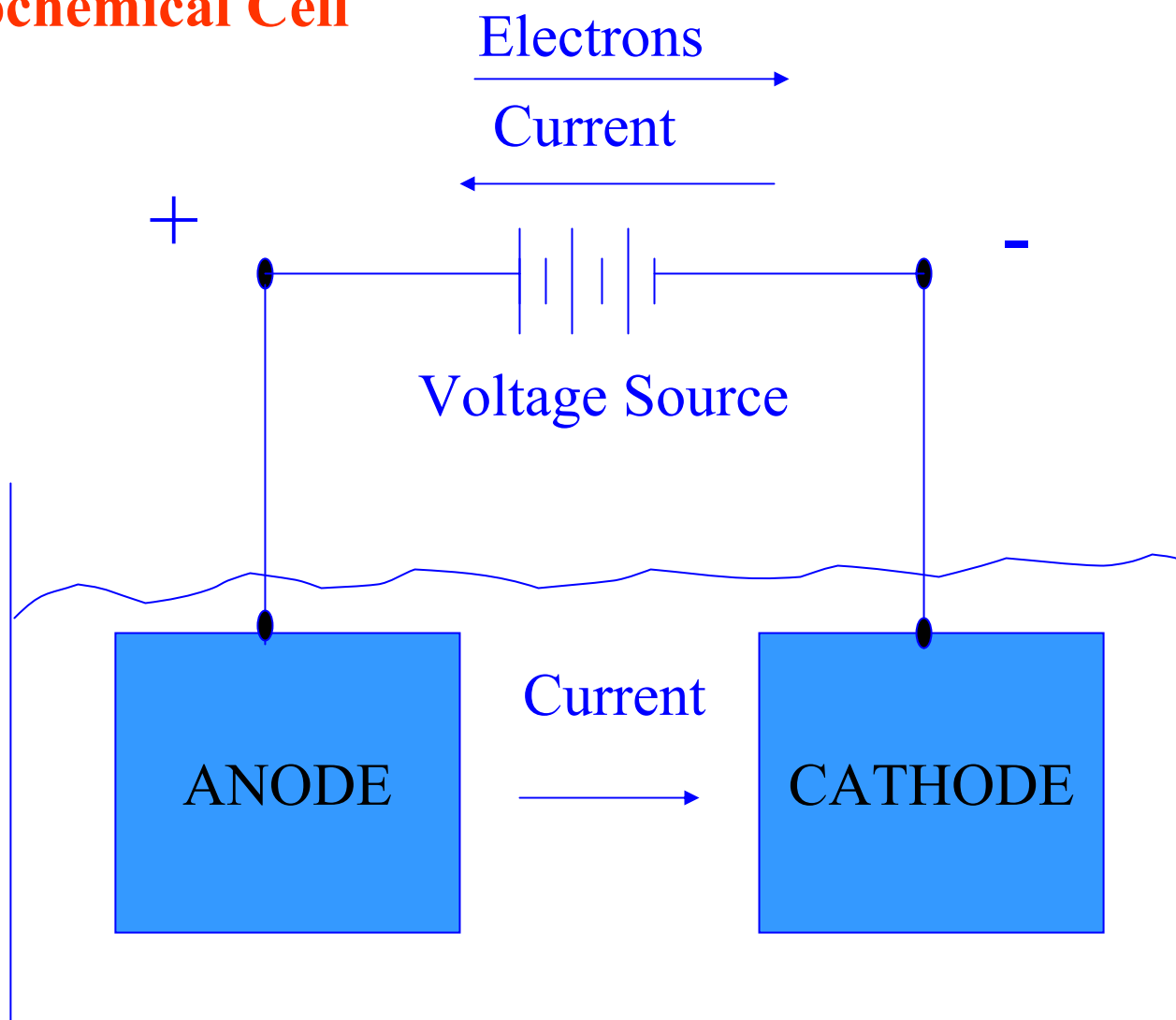
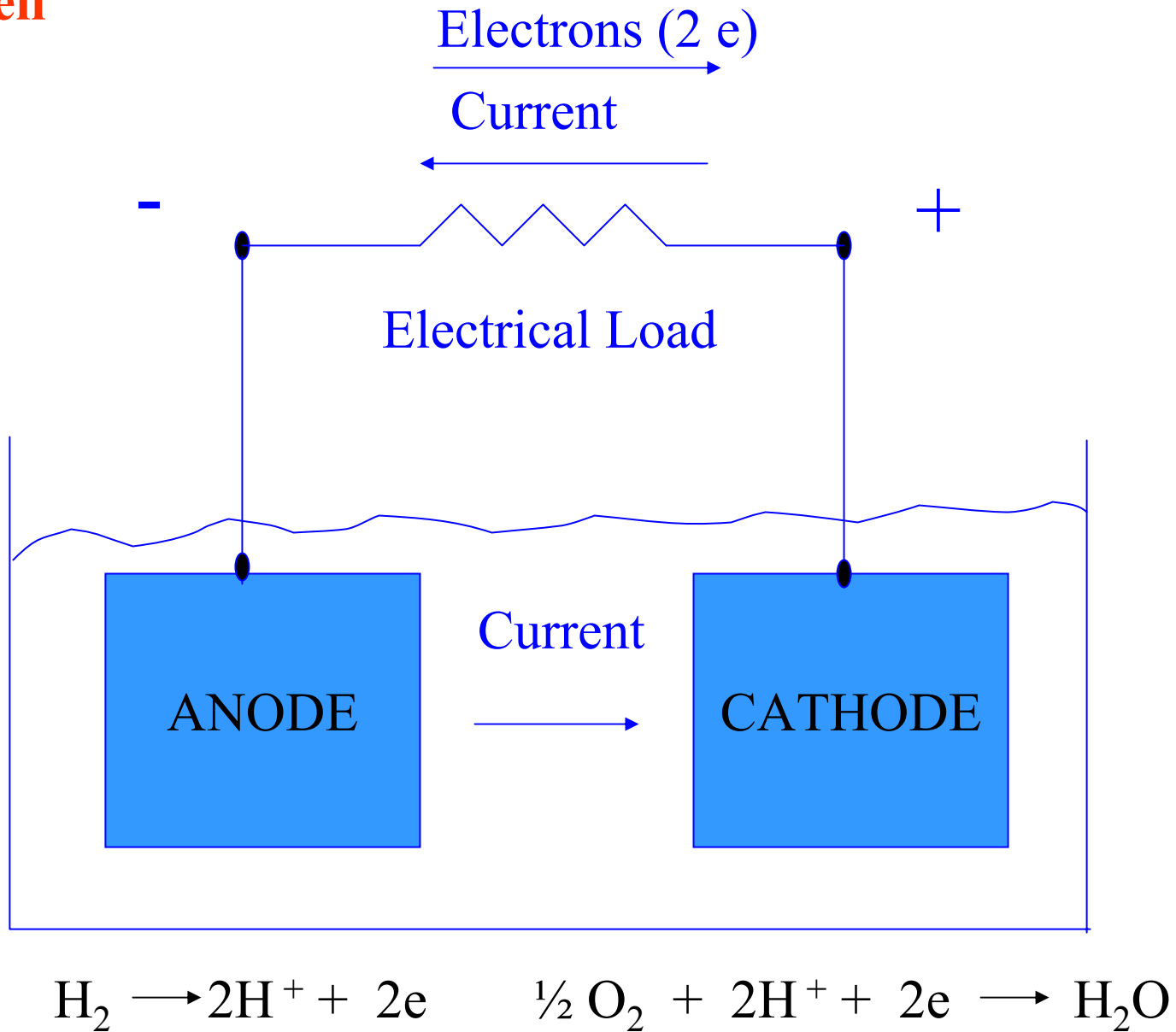


Basic Concepts in Electrochemistry

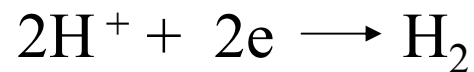
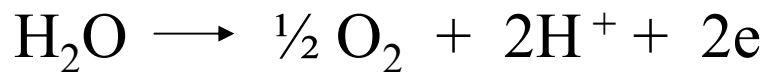
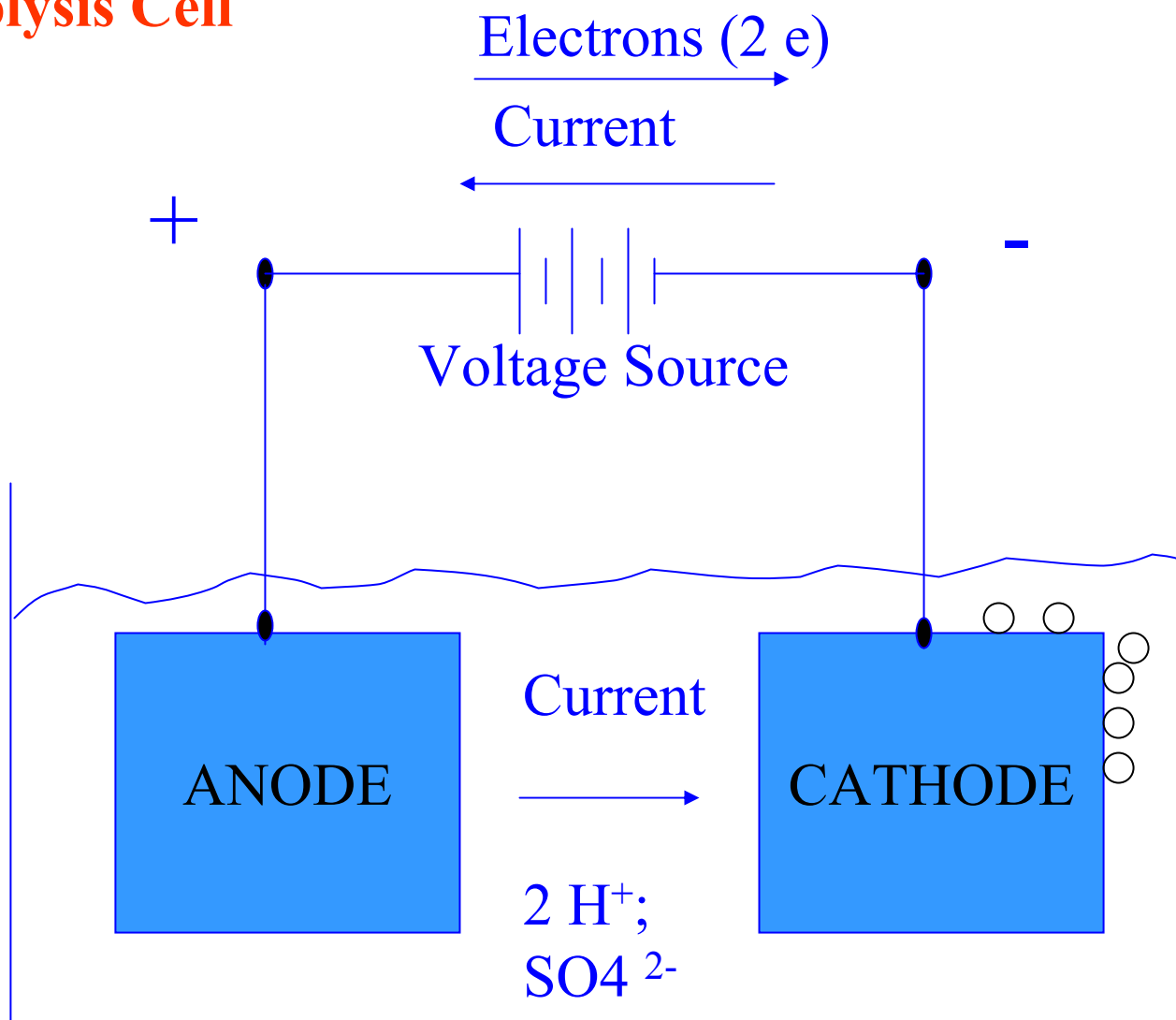
Electrochemical Cell



Fuel Cell



Electrolysis Cell



What is electrochemistry?

Electrochemistry is defined as the branch of chemistry that examines the phenomena resulting from combined chemical and electrical effects.

Types of processes

- This field covers:

- **Electrolytic processes:**

Reactions in which chemical changes occur on the passage of an electrical current

- **Galvanic or Voltaic processes:**

Chemical reactions that result in the production of electrical energy

Electrochemical cell

An electrochemical cell typically consists of:

- Two electronic conductors (also called electrodes)
- An ionic conductor (called an electrolyte)

Modes of charge transport

Charge transport in the electrodes occurs via the motion of electrons (or holes),

Charge transport in the electrolyte occurs via the motion of ions (positive and negative)

Reactions – half cell and overall

At each electrode, an electrochemical reaction occurs. This reaction is called a half cell reaction (since there are two electrodes in a typical cell at which reactions occur)

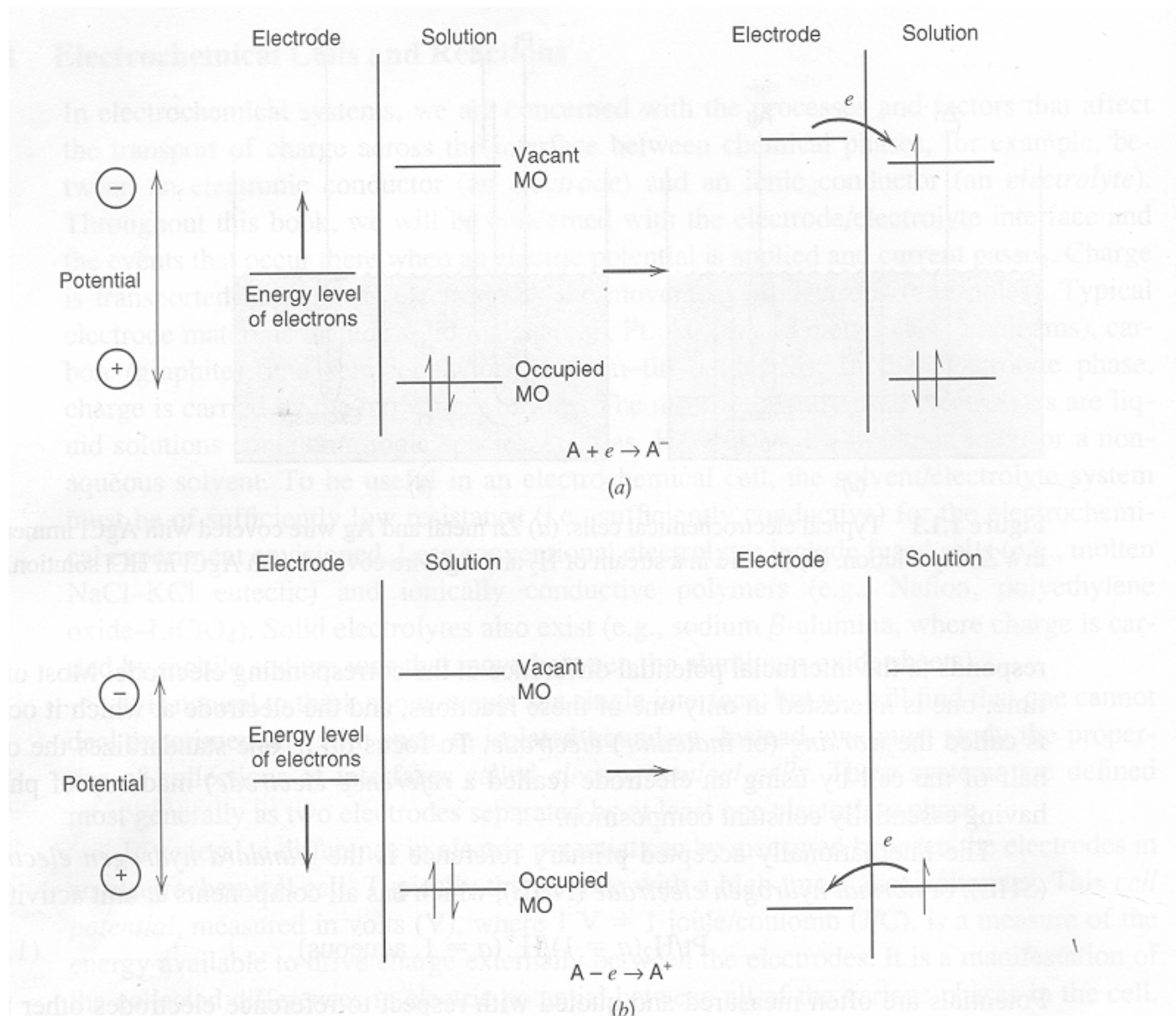
The overall chemical reaction of the cell is given by combining the two individual half cell reactions

Half cell reaction types

- There are two fundamental types of half cell reactions:
 - Oxidation reactions
 - Reduction reactions

A reaction is classified as oxidation or reduction depending on the direction of electron transfer

Oxidation and reduction energetics



Oxidation

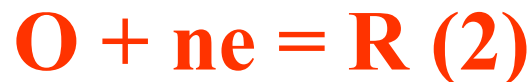
- Involves the loss of an electron
- Involves the transfer of electrons from the species to the electrode



Oxidation is an energetic process, and occurs when the energy of the electrode dips below the highest occupied molecular orbital of the compound – see figure part b

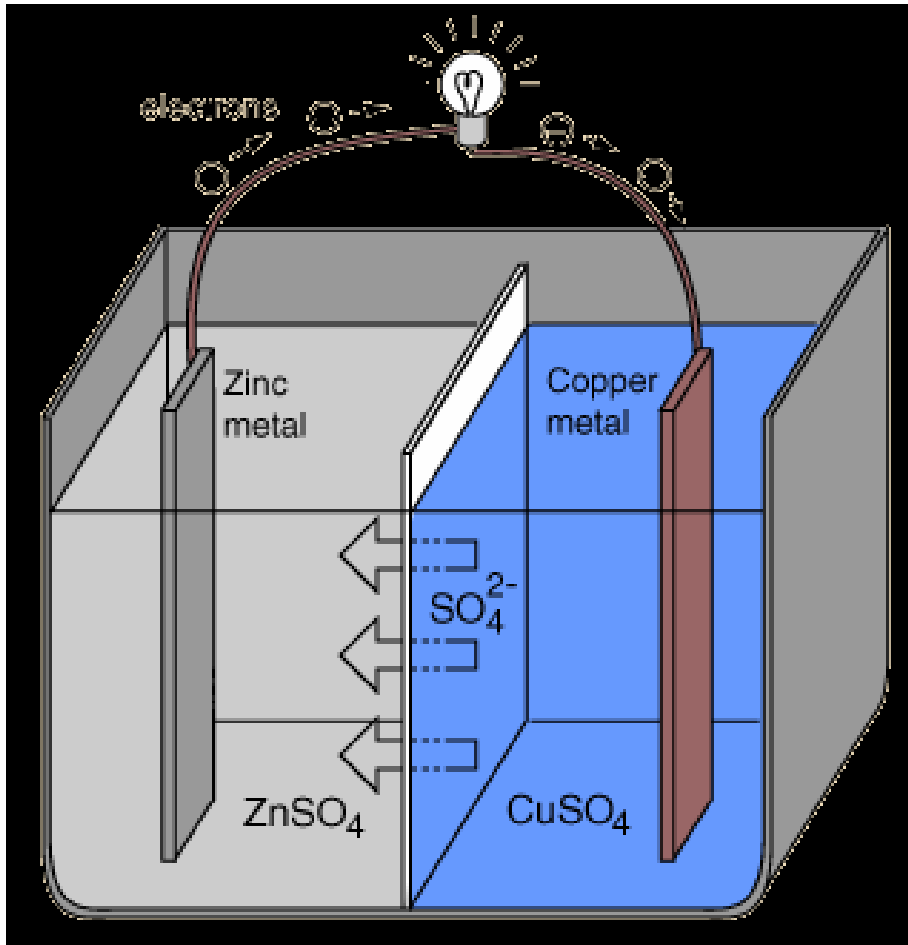
Reduction

- Involves the gain of an electron
- Involves the transfer of electrons from the electrode to the species



Reduction is also an energetic process, and occurs when the energy of the electrode increases above the lowest vacant molecular orbital of the compound – see figure part a

Example of electrochemical cell



Zinc and copper metals placed in a solution of their respective sulfates, and separated by a semi permeable membrane

Reactions

- Zinc metal gets oxidized - goes into solution:



- Copper ions in solution – reduced; copper metal - deposited on the copper electrode



- Electrons for reduction obtained from the zinc electrode - external wire
- Sulfate ions [reaction (4)] migrate through the membrane, - react with the zinc ions [from (3)] - zinc sulfate

Convention

- Electrode at which the oxidation reaction occurs is called the **anode**
- Electrode at which the reduction reaction occurs is called the **cathode**

Thus in the above example, the zinc electrode was the anode and the copper electrode was the cathode

Working and counter electrodes

The electrode at which the reaction of interest occurs is called **the working electrode**

The electrode at which the other (coupled) reaction occurs is called **the counter electrode**

A third electrode, called the reference electrode may also be used

What gets oxidized?

- In previous example:
 - Zn was oxidized
 - Cu was reduced

For a given set of two reversible redox reactions, Thermodynamics predicts which reaction proceeds as an oxidation and which proceeds as a reduction

Electrode potential

The electrode potential for a reaction is derived directly from the free energy change for that reaction

$$\Delta G = - NFE$$

The standard oxidation potential is equal in magnitude, but opposite in sign to the std. reduction potential

Competing reactions

- For a set of 2 competing reactions:

The reaction with the lower standard reduction potential gets oxidized - the other reaction proceeds as a reduction



Thus, in the above example, Zn is oxidized, and Cu is reduced

Rationale

$$\Delta G_{\text{cell}} = -NFE_{\text{cell}}$$

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

For a feasible reaction: E_{cell} must be positive (so that ΔG_{cell} is negative – recall thermodynamic criterion for feasibility)

Therefore:

$$E_{\text{cathode}} - E_{\text{anode}} > 0 \text{ or}$$

$$E_{\text{cathode}} > E_{\text{anode}}$$

- Since oxidation occurs at the anode – the species with the lower reduction potential will get oxidized
- This is to ensure that ΔG_{cell} is negative
- This is why Zn got oxidized (and Cu reduced) in the above example.
- In this case: $E_{\text{cell}} = 1.102$.
- If the reverse were to occur, E_{cell} would be: -1.102 , leading to a positive ΔG_{cell}

Sources of E°_{red} values

Comprehensive listings of E°_{red} values for most half cell reactions are available in:

- The Lange's Handbook of chemistry**
- The CRC Handbook of chemistry and physics**

Faraday's law

Relationship between the quantity of current (charge) passed through a system, and the quantity of (electro) chemical change that occurs due to the passage of the current

Mathematical statement

$$m = M I t / n F \quad (5)$$

m - mass of substance

M - molecular weight of the substance

I - current passed (A)

t - time for which the current is passed
(s)

n - number of electrons transferred

F - Faraday constant (96475 C / eqv)

Key concept

The amount of chemical change is proportional to the amount of current passed

Faraday's second law

Restatement of the first law for a fixed quantity of charge passing through the system

Faradaic processes

All processes that obey Faraday's law are termed faradaic processes

All these processes involve electron transfer at an electrode / electrolyte interface

These reactions are also called electron / charge transfer reactions

Electrodes at which these processes occur are called charge transfer electrodes

Nonfaradaic processes

Sometimes changes exist in the electrode / electrolyte interface without charge transfer taking place

These changes are due to processes such as adsorption and desorption

Such processes are called nonfaradaic processes

**No electrons flow through the electrode /
electrolyte interface during nonfaradaic
processes**

**However, transient external currents can
be generated by nonfaradaic processes**

More on nonfaradaic processes

Faradaic processes interest us the most!

Therefore, care must be taken to ensure that the effects of the nonfaradaic processes are understood and quantified.

Some examples of nonfaradaic processes are discussed in the following slides

Ideally polarized electrodes

An electrode at which there is no charge transfer across the electrode / electrolyte interface over all potential ranges is called an ideally polarized electrode (IPE)

Examples of IPEs

None exist that can cover the entire potential range in solution

A mercury electrode in contact with deaerated KCl behaves as an IPE over a potential range of $\sim 2V$

Other electrodes are ideally polarized over much smaller ranges

Behaviour of an IPE

Recall – no charge transfer possible at IPE /
electrolyte interface

The behaviour of such an interface when the
potential across the electrode is changed
resembles that of a plain capacitor

An IPE follows the standard capacitor
equation

Mathematical treatment

$$Q = C_d E \text{ (6) – capacitor equation}$$

Q - charge stored in coulombs (C)

C_d - capacitance in farads (F)

E - potential across the capacitor /IPE (V)

When voltage is applied across an IPE, the “electrical double layer” is charged until eqn. 6 is obeyed

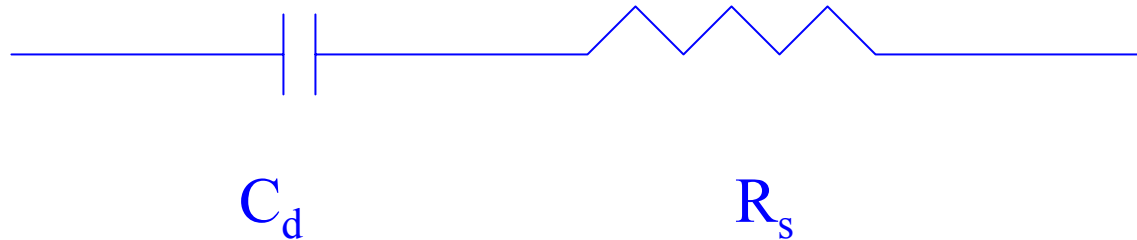
During charging a charging current flows through the system

Significance of charging currents

- Contributes to total current measured
- Cannot be ignored— especially for low faradaic currents – may exceed faradaic currents in such cases

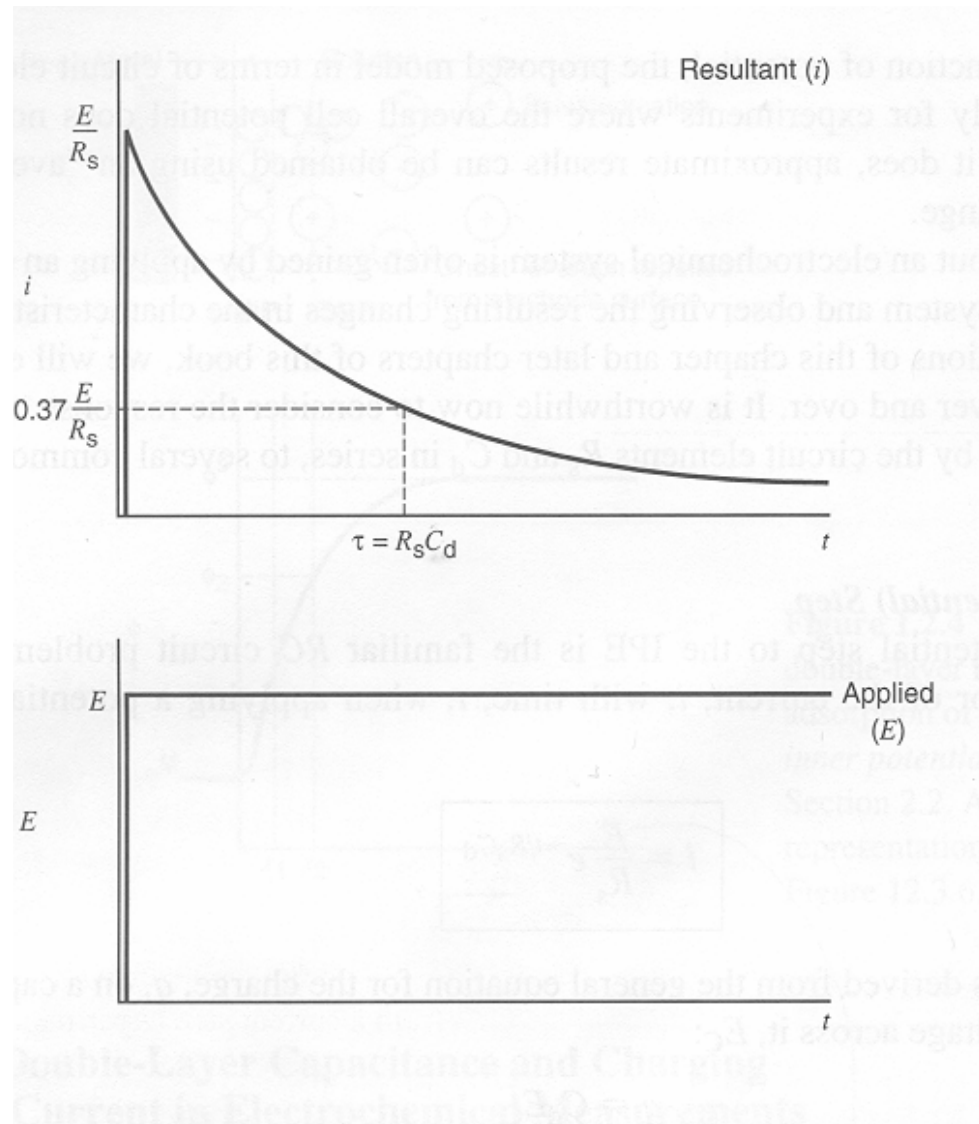
To better understand the effect of charging, we need to examine mathematically the responses of an IPE to various electrochemical stimuli

Model representation of an IPE



The IPE system can be represented as a capacitance (C_d) in series with the electrolyte resistance (R_s)

Application of a potential step



Input

A potential step is applied – i.e. the potential is raised from an initial value to a higher value, and held at the higher value

See previous fig. , bottom graph

Result of potential step application

- The double layer is charged

$$Q = C_d E \quad (6)$$

NOTE:

The applied voltage must equal the sum of the voltage drops across the resistor (E_r) and capacitor (E_c), we have

$$\mathbf{E} = \mathbf{E}_r + \mathbf{E}_c \quad (7)$$

Applying Ohm's law,

$$\mathbf{E}_r = \mathbf{I} \mathbf{R}_s \quad (8)$$

from (6),

$$\mathbf{E}_c = \mathbf{Q}/\mathbf{C}_d \quad (9)$$

Therefore:

$$\mathbf{E} = \mathbf{I}\mathbf{R}_s + \mathbf{Q}/\mathbf{C}_d \quad (10)$$

By definition, current is the rate of flow of charge

Therefore:

$$I = dQ/dt \text{ (11)}$$

Equation 10 can be rewritten as:

$$I = dQ/dt = -Q/R_s C_d + E/R_s$$

Solution

Initial condition: that the capacitor is initially uncharged ($Q = 0$ at $t = 0$)

solution of eqn. 2 is:

$$Q = E C_d [1 - e^{(-t/R_s C_d)}] \quad (13)$$

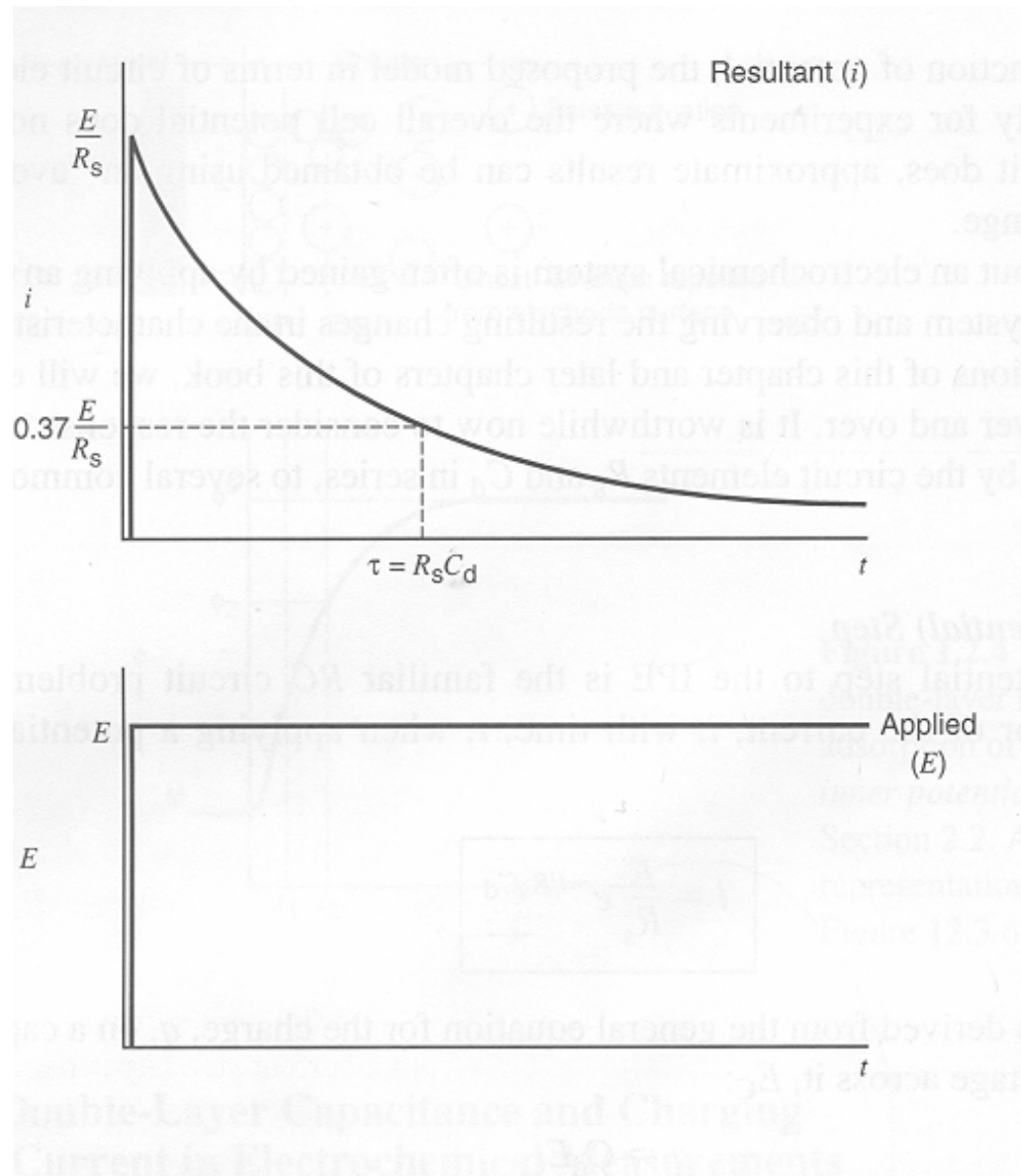
Time dependence of charging current

Differentiating eqn. 13 w.r.t. time, we get:

$$I = (E/R_s) * e^{(-t/R_s C_d)} \quad (14)$$

Equation 14 describes the time dependence of the charging current in response to a potential step – also see following figure, top graph

Graphical representation



Practical significance

Product of R_s and C_d has units of time – called time constant (τ)

For typical values of R_s and C_d , the charging current dies down to an insignificant level in a few hundred microseconds

Any faradaic current must be measured after this time period to avoid the influence of the charging current

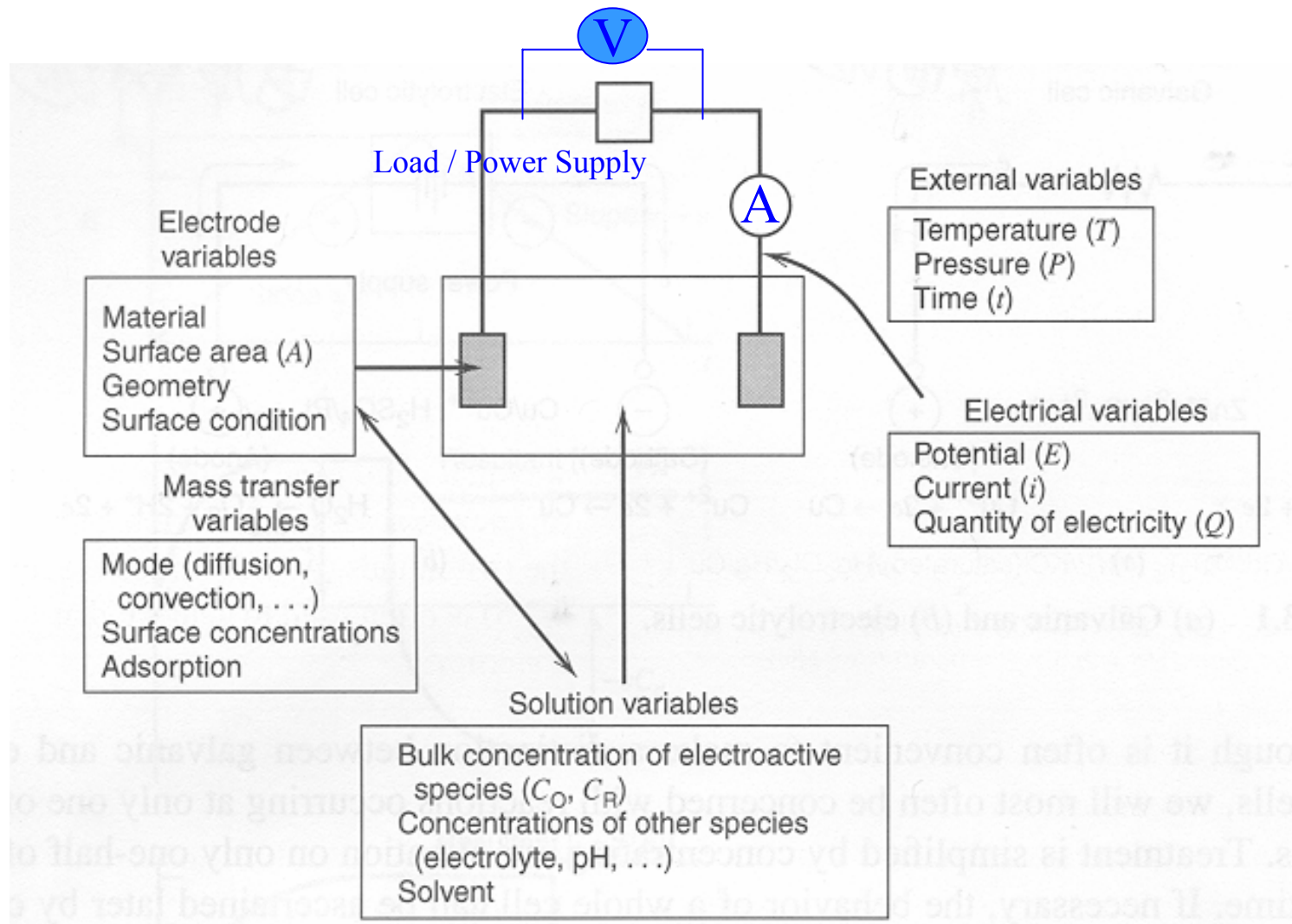
Back to faradaic processes

Investigation of electrochemical behaviour

**Involves holding certain variables constant
while observing the trends in others**

Typical variable shown in diagram

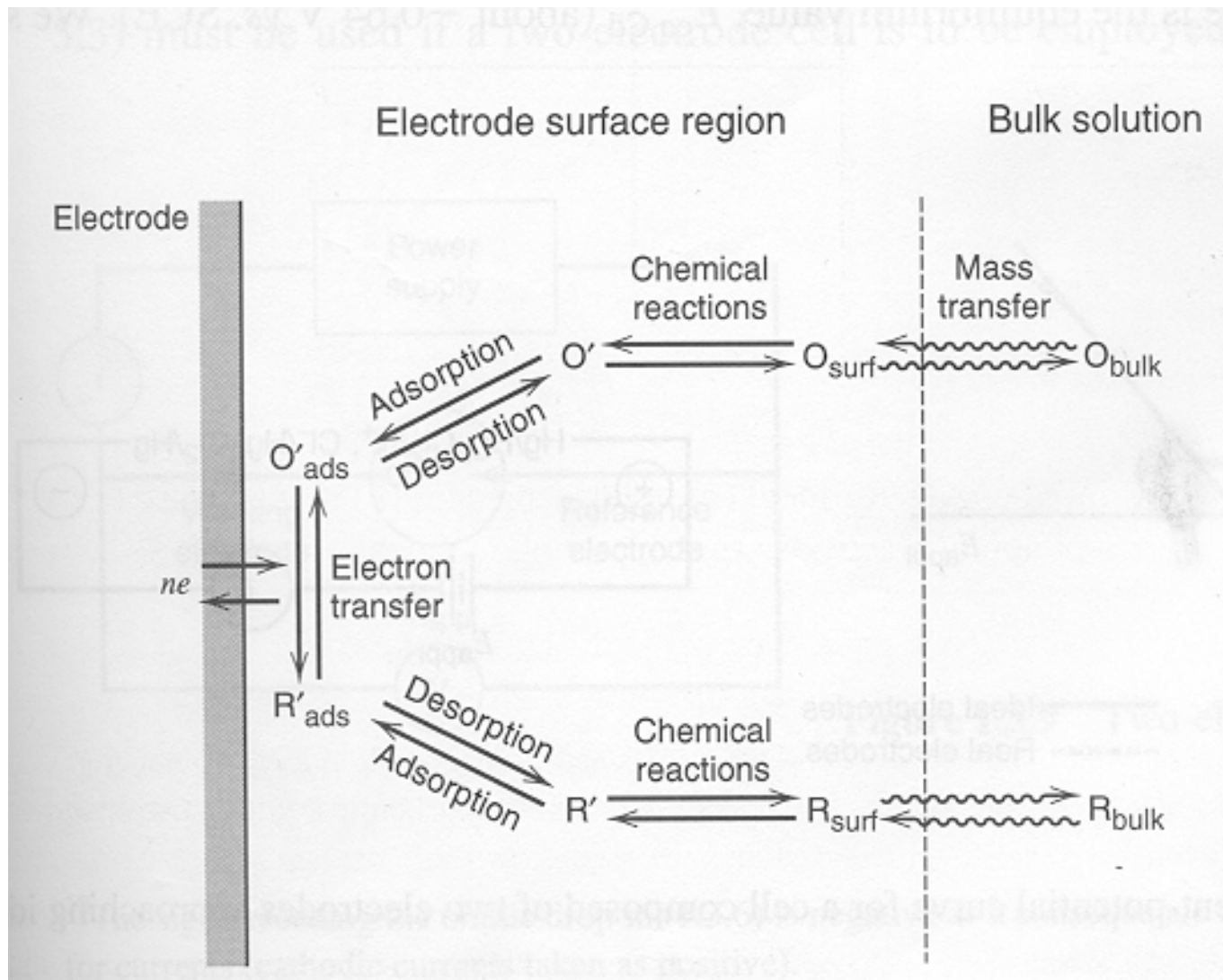
Variables to be considered



Main aspects of interest

- From a fuel cell point of view, the main aspects of interest are:
 - Electrochemical kinetics
 - Ionic and electronic resistances
 - a. In electrolyte
 - b. In electrodes
 - Mass transport through the electrodes

These processes are illustrated in the following schematic



Current

Current may be written as the rate of change of charge:

$$I = dQ/dt \text{ (15)}$$

The number of moles (N) participating in an n electron electrochemical reaction is given by

$$N = Q/nF \text{ (16)}$$

Reaction rate

- The electrochemical reaction rate can be written as:

$$\text{Rate (mol/s)} = dN/dt$$

From 16,

$$\text{Rate} = (1/nF) dQ/dt$$

From 15,

$$\text{Rate} = I/nF \quad (17)$$

Thus the current is a direct measure of the rate of electrochemical reaction

Reaction flux

- Sometimes, it is convenient to express quantities as a flux:
- Dividing the rate (17) by the active area of the electrode (A , cm^2), we get:

$$\text{Flux (J, mol/cm}^2\cdot\text{s)} = I/nFA$$

- Replacing I/A by i (current density A/cm^2), we get:

$$\text{Flux (J, mol/cm}^2\cdot\text{s)} = I/nFA = i/nF \quad (18)$$

Polarization and overpotential

- Faradaic reactions – have an equilibrium potential - based upon reaction free energy
- On passing faradaic current - the potential shifts from this equilibrium potential
- This shift is termed polarization
- Extent of shift - measured by the overpotential (η)

$$\eta = E - E_{\text{eq}}, \quad (19)$$

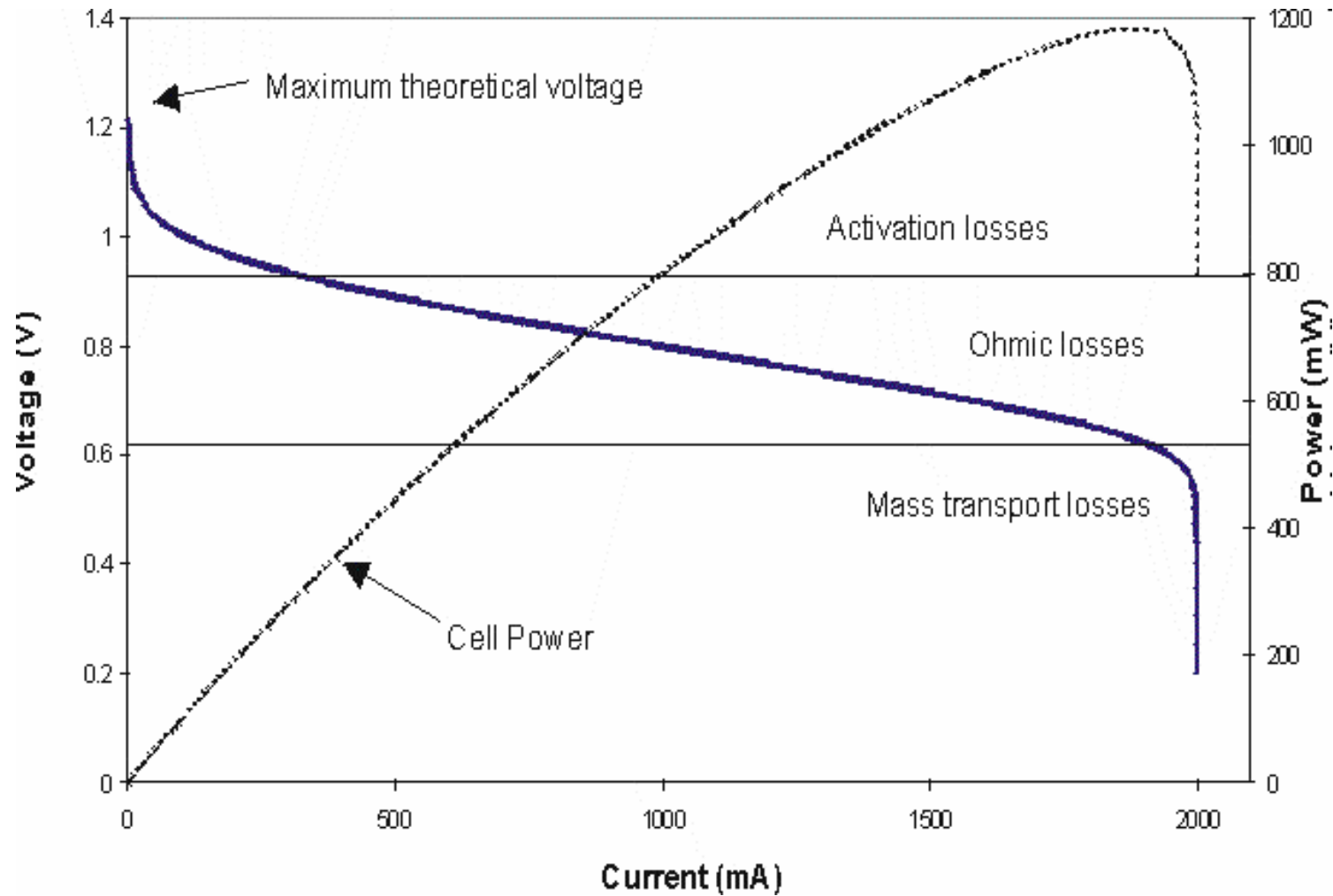
Polarization curves

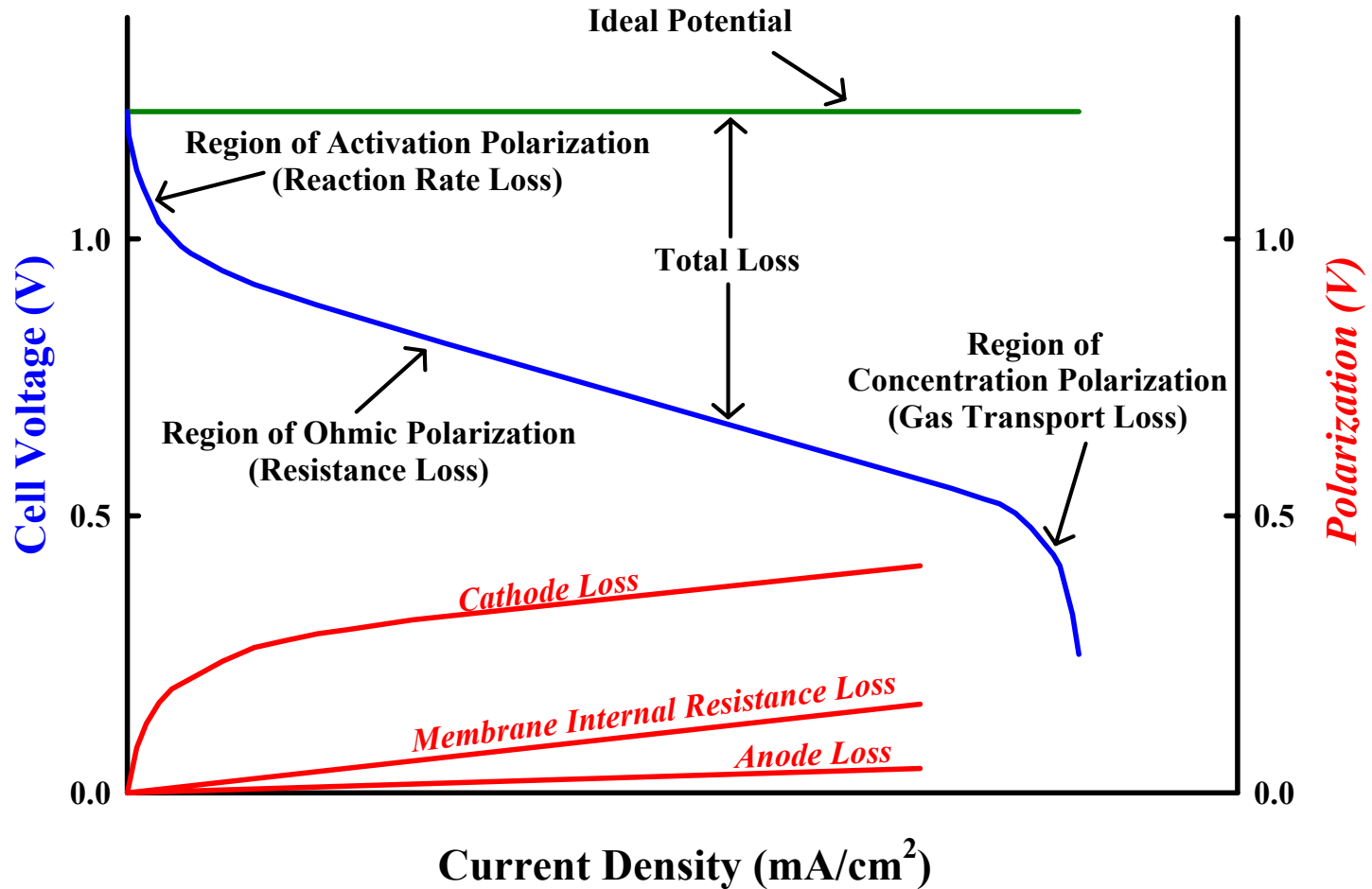
Information about the faradaic reaction is gained by determining current as a function of potential or vice versa.

The resulting curves (see following figure) are called polarization curves (or V-I curves or E-I curves).

Obtaining such curves is a critical part of fuel cell research.

Typical fuel cell polarization curve





Resistance in electrochemical cells

Types of resistance

- Electronic resistance – due to electronic current through electrodes and external circuit – can be minimized by using electron conducting materials
- Ionic resistance - due to ionic current through electrolyte – needs to be considered seriously as it leads to losses

Ion transport

- At the anode - excess of positive ions – build up of positive charge
- At the cathode – excess of negative ions - build up of negative charge
- Buildup of ionic charge - released by the ion transport
- Positive ions move from anode to cathode and vice versa

Transport numbers

The fractions of current carried by the positive and negative ions are given by their transport numbers

$t_+ + t_-$ respectively

Each mole of current passed corresponds to 1 mole of electrochemical change at each electrode.

Therefore the amount of ions transported in the electrolyte also equals 1 mol. Thus:

$$t_+ + t_- = 1 \quad (20).$$

For multiple species

More generally,

$$\Sigma t_i = 1 \quad (21)$$

This equation is valid when more than one type of ion is in solution.

The transport numbers of ions are determined by the conductance (L) of the electrolyte

Conductance and conductivity

- The conductance of an electrolyte is given by:

$$L = \kappa A / l \quad (22)$$

A - active area of contact

l - length (thickness) of electrolyte matrix

κ – conductivity - intrinsic property of the electrolyte

Conductance has units of Seimens (S), and conductivity of S/cm

Conductivity

The conductivity of the electrolyte has a contribution from every ion in solution

- Conductivity is proportional to:
 - concentration of the ion (C)
 - charge of ion (z)
 - a property that determines its migration velocity – also called mobility

Mobility

Mobility is defined as the limiting velocity of the ion in an electric field of unit strength

Now, force exerted by an electric field of strength E is given by:

$$F = eE \cdot z \quad (23)$$

Where e is the electronic charge

Opposing force

- An opposing force exists due to frictional drag.
- This is represented by the Stokes equation:

$$F_{\text{opp}} = 6\Pi r v \quad (24)$$

ν - viscosity of the solution

r - ionic radius

v - velocity of the ion in solution

Terminal velocity of ion

When the forces exactly counterbalance each other, the ion attains a steady state velocity called the terminal velocity

This terminal velocity is termed the mobility (u) when the electric field strength is unity:

$$u = z e / 6\pi\eta r \quad (25)$$

Back to conductivity

- With the above expression for mobility, we write the following expression for κ

$$\kappa = F \sum z_i u_i C_i \quad (26)$$

- Now recall – transport no. (t) - contribution made by each individual ion to the total current carried in solution.

Expression for transport no.

The transport no. may be represented as the ratio of the contribution to conductivity made by a particular ion to the total conductivity of the solution

Thus:

$$t_i = z_i u_i C_i / \sum z_i u_i C_i \quad (27)$$

Resistance

- Resistance is defined as:

$$R = l / \kappa A \quad (28)$$

- The ionic resistance is an inherent property of the ion in motion and the electrolyte
- Effect of resistance in electrochemical cells
 - Ohm's law:

$$V = I R \quad (29 - a)$$

- R will introduce a potential drop V which will increase with current

Ohm's Law

- More appropriately Ohm's law is expressed as:

$$I = \kappa (d\Phi/dx) \text{ (29-b)}$$

where $\delta\phi(x)/\delta x$ - potential gradient

Minimizing R, IR Compensation

- R can be minimized by:
 - minimizing distance between electrodes
 - increasing area of contact (not preferred – this is governed by many other factors)
- Need to realize – some portion of R will always remain. So realistically:

$$E_{\text{measured}} = E_{\text{cathode}} - E_{\text{anode}} - IR \quad (30)$$

- If the value of R is known, one can compensate for ohmic drop – the compensated E is a closer representation of the actual E:

$$E_{\text{compensated /actual}} = E_{\text{measured}} + IR \quad (31)$$

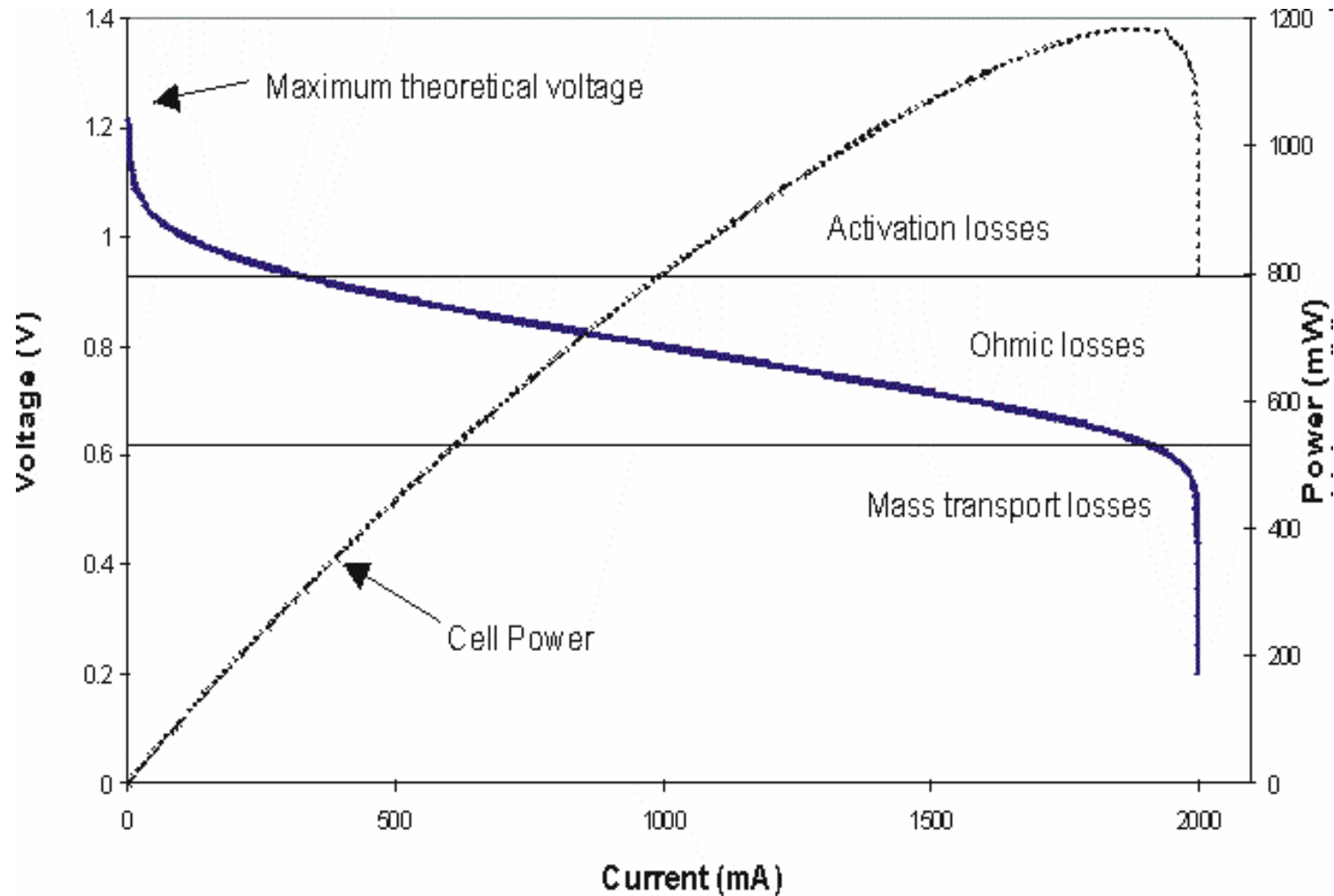
Sources of IR in the fuel cell

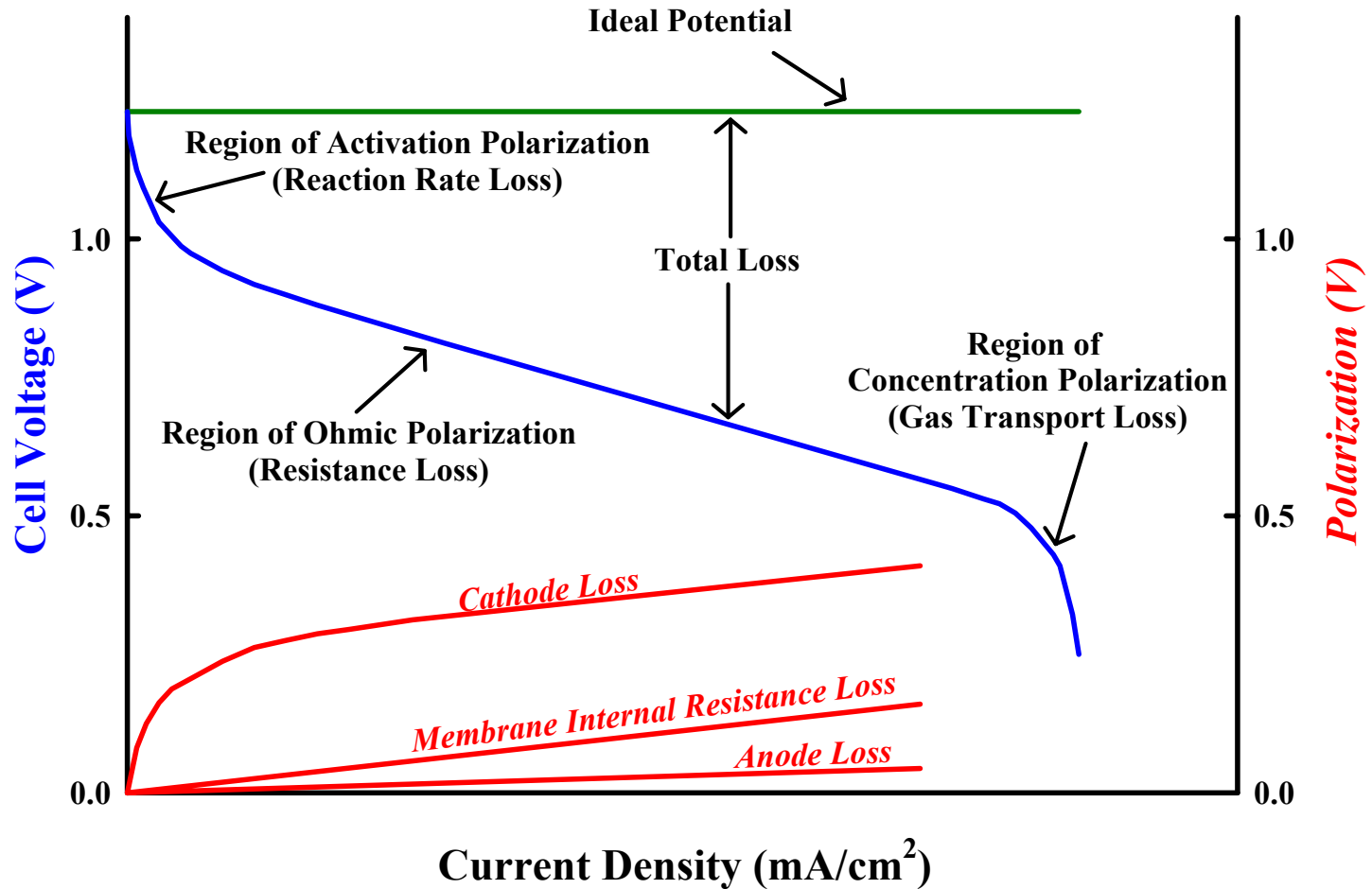
IR compensation is critical while analyzing fuel cell data for kinetic and transport parameters.

Ohmic drops occur due to IR in the electrolyte and the electrodes – the IR in the electrode should not be neglected!

IR compensation in both the electrolyte and the electrode shall be discussed in future lectures

Typical fuel cell polarization curve





Mass transport in electrochemical cells

Modes of mass transport

- There are **3 fundamental modes** of mass transport in solution. They are:
 - **Migration** – this is the motion of a charge body (such as an ion) under the influence of an electrical potential gradient
 - **Diffusion** – this is the motion of a species under the influence of a chemical potential gradient
 - **Convection** – this is hydrodynamic transport either due to density gradients (natural convection) or due to external means such as stirring (forced convection)

Governing equation

- The governing equation for mass transfer is the **Nernst–Planck equation**. For one (x) dimension (and one species):

$$J(x) = -D \left[\frac{\delta C(x)}{\delta x} \right] - \left[\frac{z F}{RT} \right] \left[D^* C \frac{\delta \phi(x)}{\delta x} \right] + C^* v(x) \quad (32)$$

J - flux in mol / cm².s

D - diffusion coefficient (cm²/s)

$\delta C(x)/\delta x$ - concentration gradient

$\delta \phi(x)/\delta x$ - potential gradient

v - velocity with which an element of solution moves in the x dimension

Current vs. flux

- Faraday's law - current produced— proportional to the number of moles of reactant in solution

$$m = M I t / n F \quad (5)$$

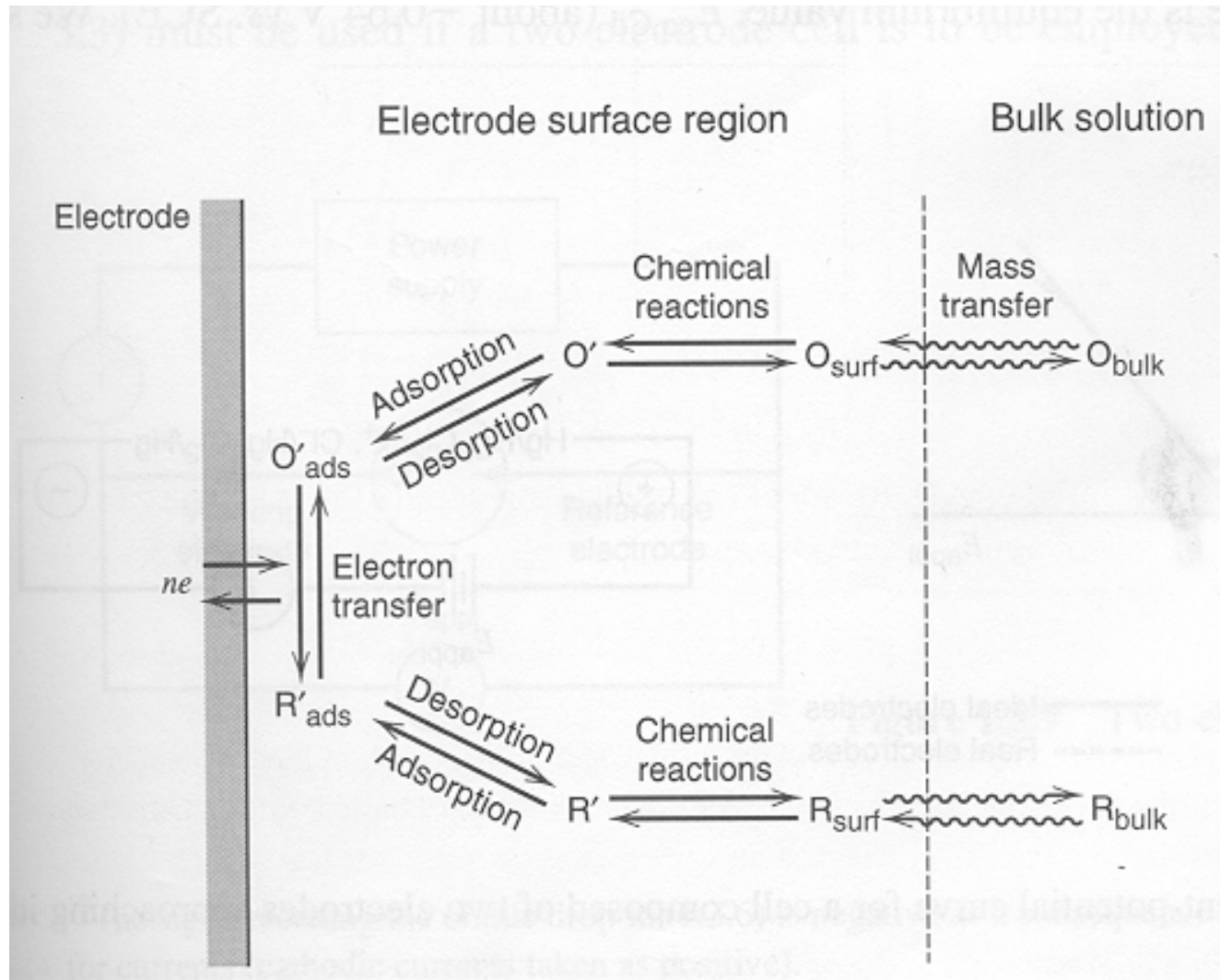
Can rewrite as:

$$I / nFA = m/MtA = N/tA = J \quad (33)$$

Where N = no. of moles

Do not confuse N with n , the no. of electrons transferred

The mass transport limit



The mass transport limit

- Recall – also see previous diagram – that reactants are consumed at the electrode
- The larger the current, the faster the rate of consumption – Faraday's law
- The reactants arrive at the electrode via transport from the bulk

Mathematically

If maximum transport flux = reaction flux (current), the reaction is mass transport limited

$$J = I / nFA \quad (34)$$

**Reactant concentration at electrode = 0,
all reactant - immediately consumed**

**The reaction cannot proceed at a rate faster than
the mass transport limited rate**

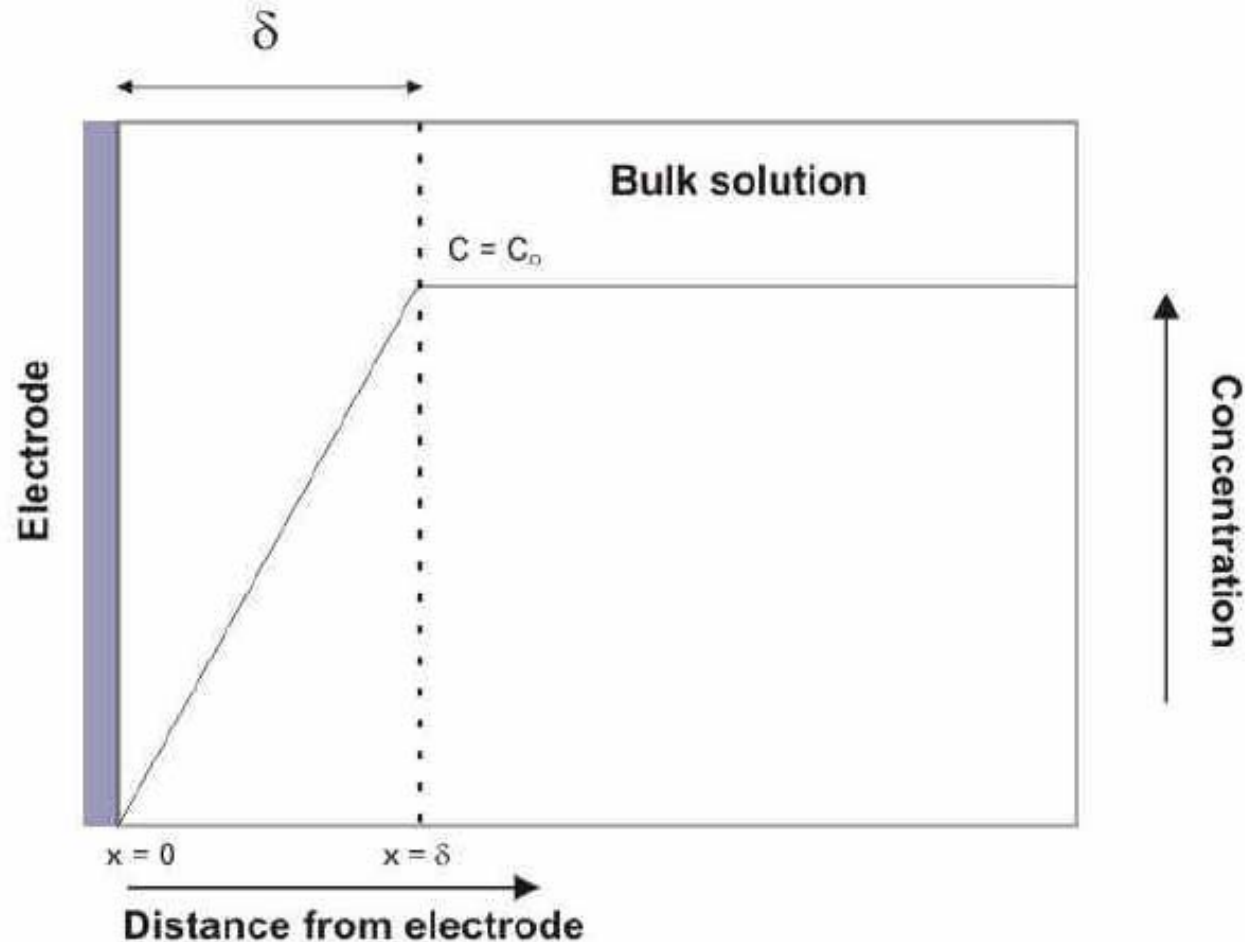
- Assume - no convective mass transport, negligible transport due to migration
- Flux at the electrode may be written as:

$$\mathbf{J} = - \mathbf{D}(\mathbf{dC/dx})_{\mathbf{x=0}} \quad (35)$$

D is the diffusion coefficient of the reactant

The Nernst diffusion layer

Thin layer that lies intermediate bounds the electrodes and the bulk)



Nernst diffusion theory

- A thin layer of electrolyte (thickness δ) in contact with the electrode surface - ion transfer controlled solely by diffusion.
- Concentration of species - maintained constant outside this layer (in the “bulk”) by convective transfer.

- Assume - linear conc. gradient in the Nernst diffusion layer
- Eqn. 35 can be rewritten as:

$$J = [D/\delta][C^* - C_{(x=0)}] \quad (36)$$

δ - thickness of the Nernst diffusion layer

C^* - bulk concentration of the reactant

The mass transfer coefficient

- Difficult to obtain precisely values of δ
- Therefore δ is grouped along with D to yield a new constant

$$k_m = D / \delta \quad (37)$$

**k_m is called the mass transfer coefficient
(units: cm/s)**

- Now:

$$\mathbf{J = I / nFA \text{ (34)}}$$

- Combining eqns. 34, 36 and 37, we have:

$$\mathbf{I/nFA = k_m [C^* - C_{(x=0)}] \text{ (38)}}$$

Current dependence on reactant concentration

The limiting current

As reaction proceeds faster- at some point all the reactant that reaches the electrode - consumed immediately

At this point $[C(x=0)]$ is zero, and the current levels off. Can be written as:

$$I_l = nFAk_m C^* \quad (39)$$

I_l is called the limiting current

- Relationship between surface and bulk concentrations – from equations 38 and 39:

$$C_{(x=0)}/C^* = [1 - (I/I_1)] \quad (40)$$

- Substituting for C^* (39),

$$C_{(x=0)} = [(I_1 - I)/(nFAk_m)] \quad (41)$$

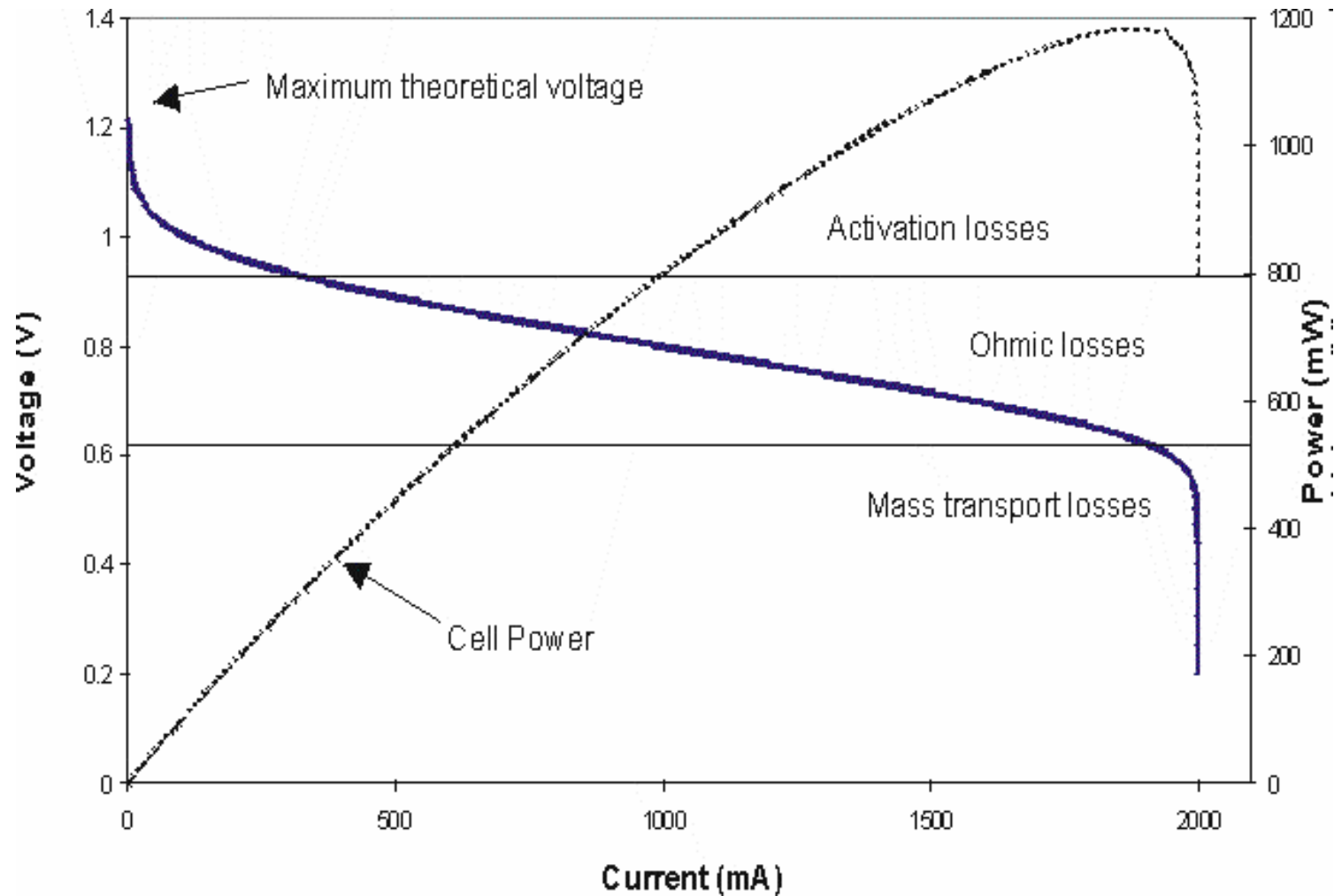
Both equations reiterate that surface concentration = 0 at the limiting current

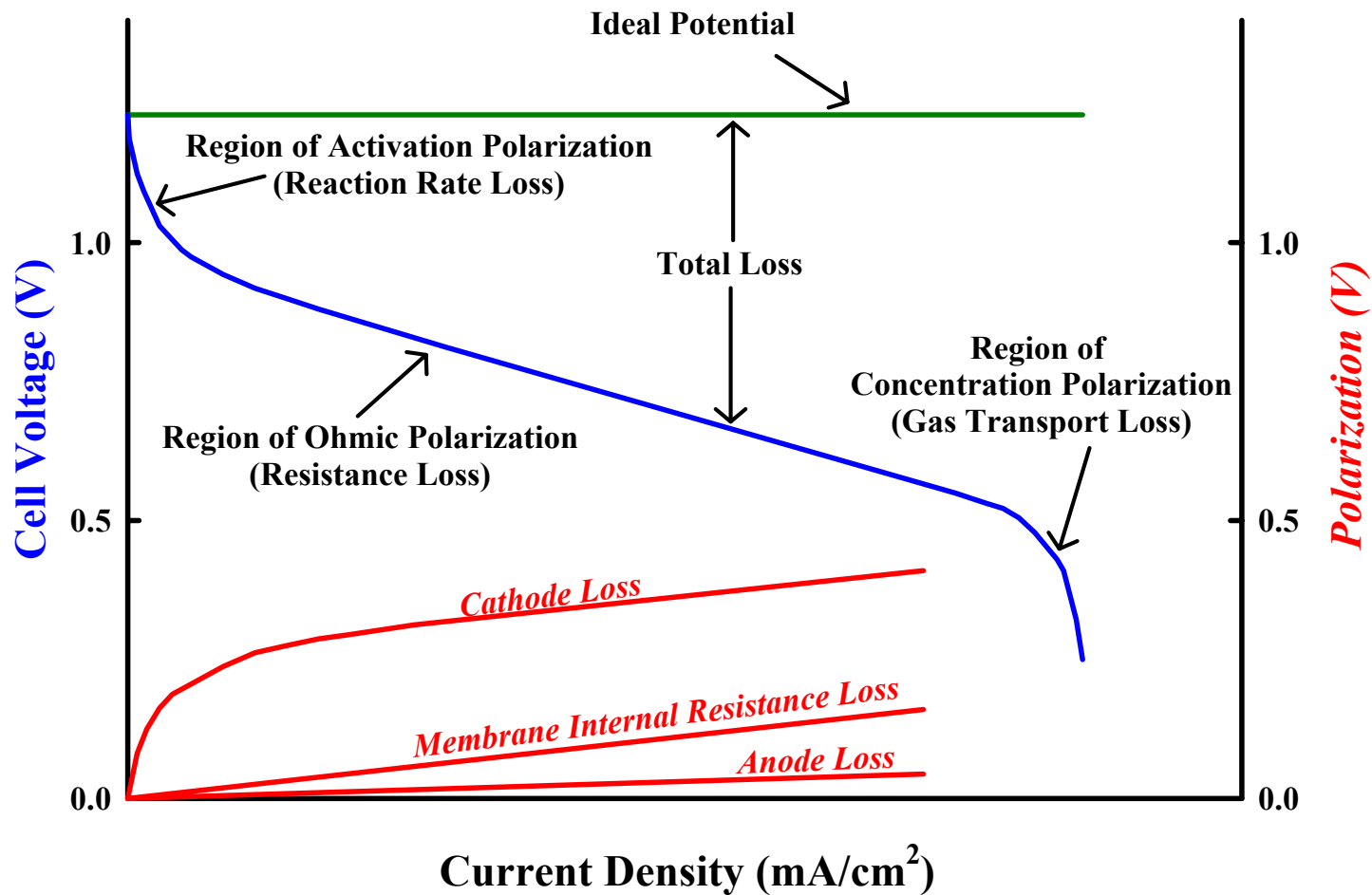
Significance of I_1

- Maximum current obtainable for given set of conditions
- Very important in fuel cell operation
- Generally, higher I_1 implies lower mass transport losses – higher efficiency

Significant research efforts devoted to enhancing I_1 in PEM systems

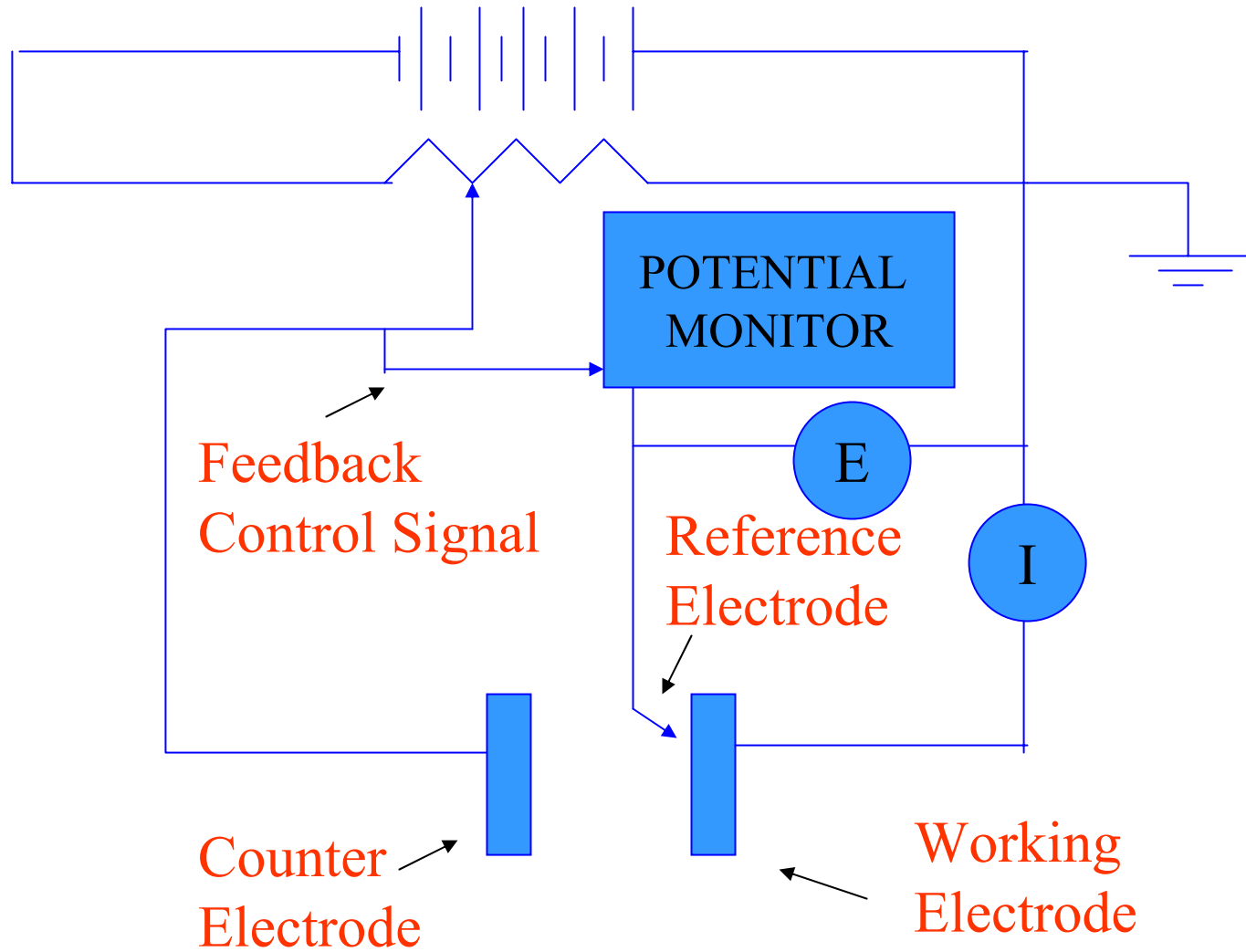
Typical fuel cell polarization curve





Common electrochemical experiments

Potentiostat



Reference electrodes - SHE

An ideal reference electrode is one that maintains a constant potential irrespective of the amount of current (if any) that is passed through it

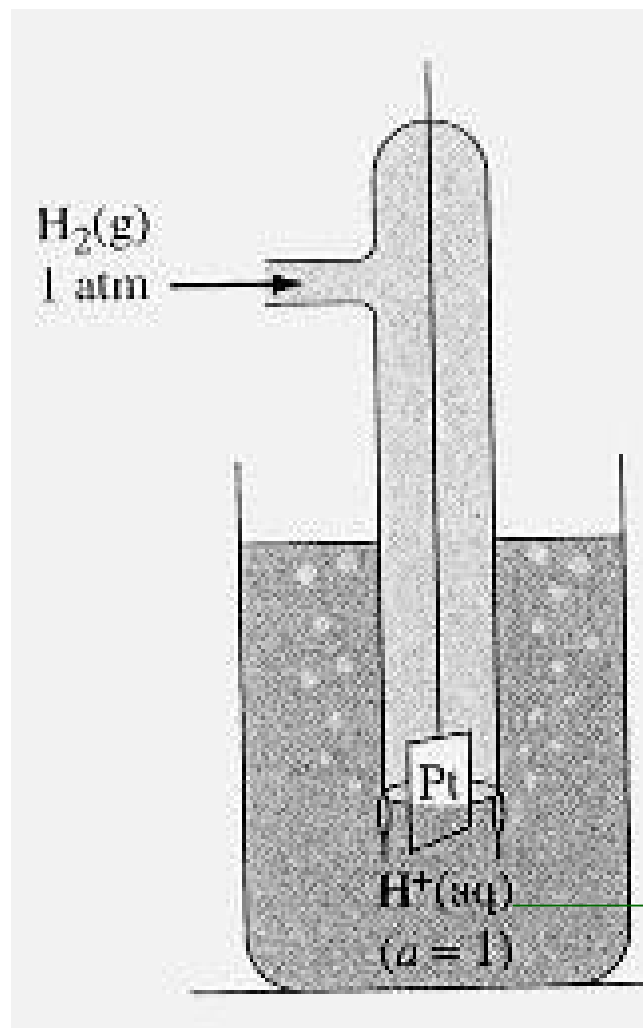
- Standard hydrogen electrode (NHE) – simplest reference electrodes
- This electrodes potential (by definition) is 0 V

- Electrode process in SHE:



- Consists of a platinum electrode immersed in a solution with a hydrogen ion concentration of 1M.
- The platinum electrode is made of a small square of platinum foil which is
- Hydrogen gas, at a pressure of 1 atmosphere, is bubbled around the electrode

SHE



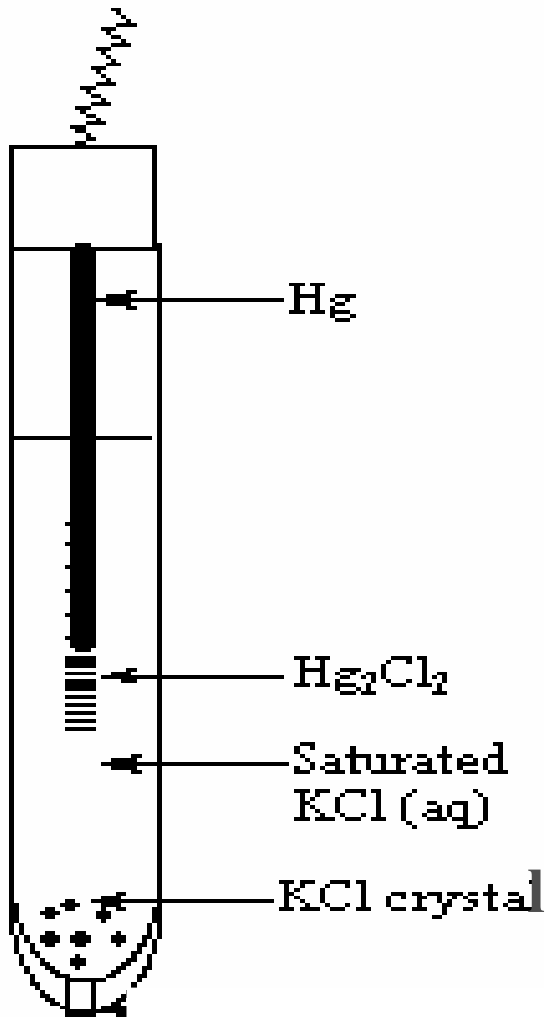
**Very difficult to
obtain unit
activity in
practice**

Other reference electrodes

- The SHE – not widely used – difficult to obtain solution of 1M activity.
- Saturated Calomel Electrode (SCE)– very popular:
 - Electrode is mercury coated with calomel (Hg_2Cl_2)
 - Electrolyte is a solution of potassium chloride and saturated calomel



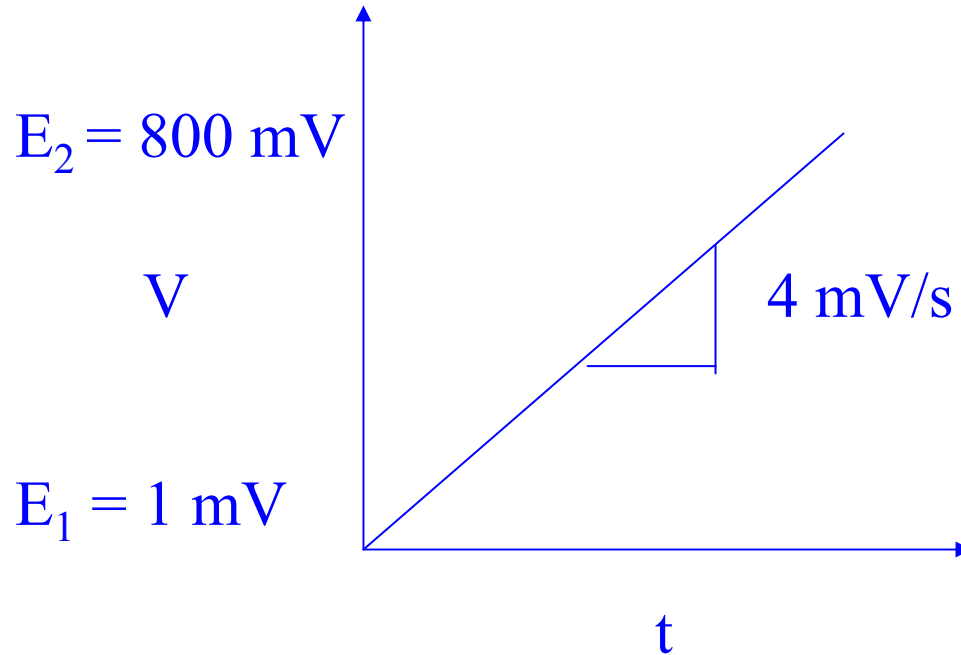
SCE



Linear Sweep Voltammetry (LSV)

- Hydrogen gas passed through counter / reference electrode (anode) nitrogen passed through cathode
- Working electrode – fuel cell cathode subjected to a potential sweep from an initial to a final voltage (typically 1 –800 mV)
- Sweep done using a potentiostat
- Fixed sweep rate – 4 mV/s
- Faradaic current monitored

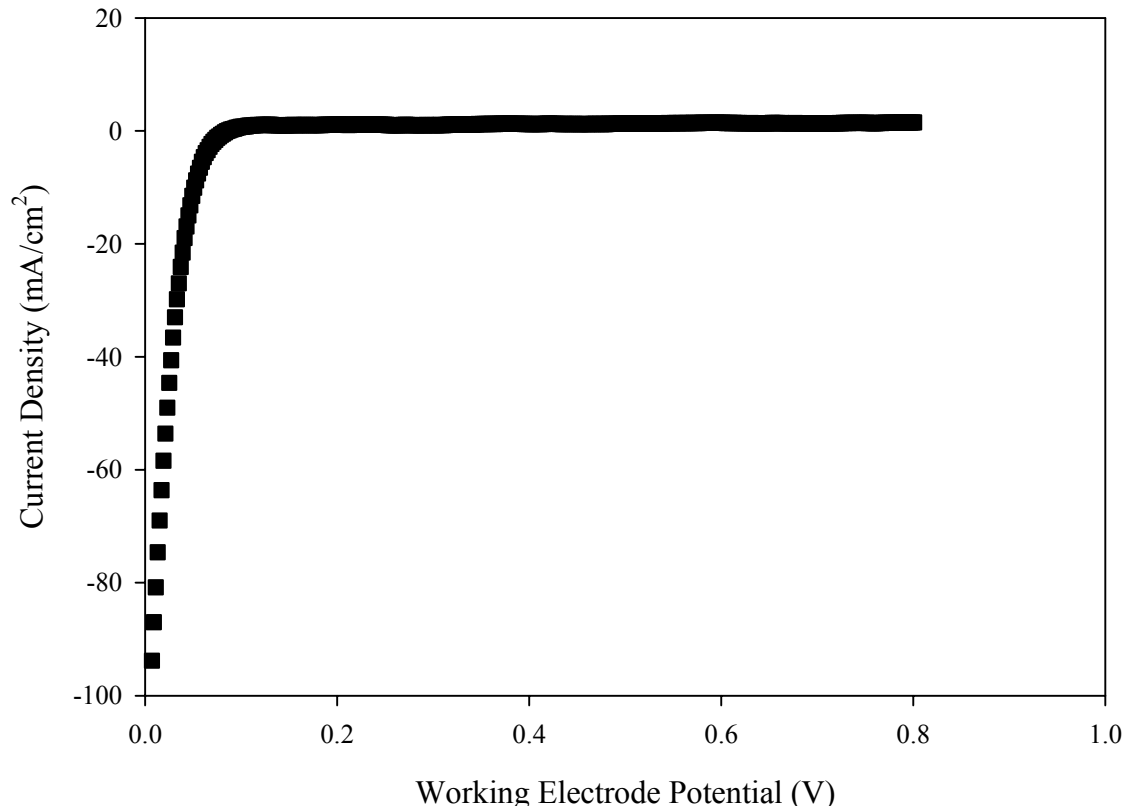
Input Function



Hydrogen – only species present – crosses over from anode to cathode through the membrane – gets oxidized at the cathode at positive potentials (above 0 V)

Output

Data obtained in a PEM fuel cell at room temperature



Response

- When the potential is 0 V
 - no net faradaic current
- When the potential exceeds 0V
 - faradaic oxidation $\text{H}_2 = \text{H}^+ + \text{e}$
- As potential moves to more positive values
 - “overpotential” / electrochemical driving force for oxidation increases
 - reaction proceeds faster until it hits the mass transport limit – since hydrogen oxidation kinetics are fast, this limit is quickly attained

Mass transport limit

- Above a certain E, reaction becomes mass transport limited – see output figure

In the case of limiting current behaviour, the current can be converted into a reactant flux using Faraday's law

$$\mathbf{J (H_2) [mols/cm^2-s] = * i / n F}$$

Where $i = 1 \text{ mA/cm}^2$ (from voltammogram)

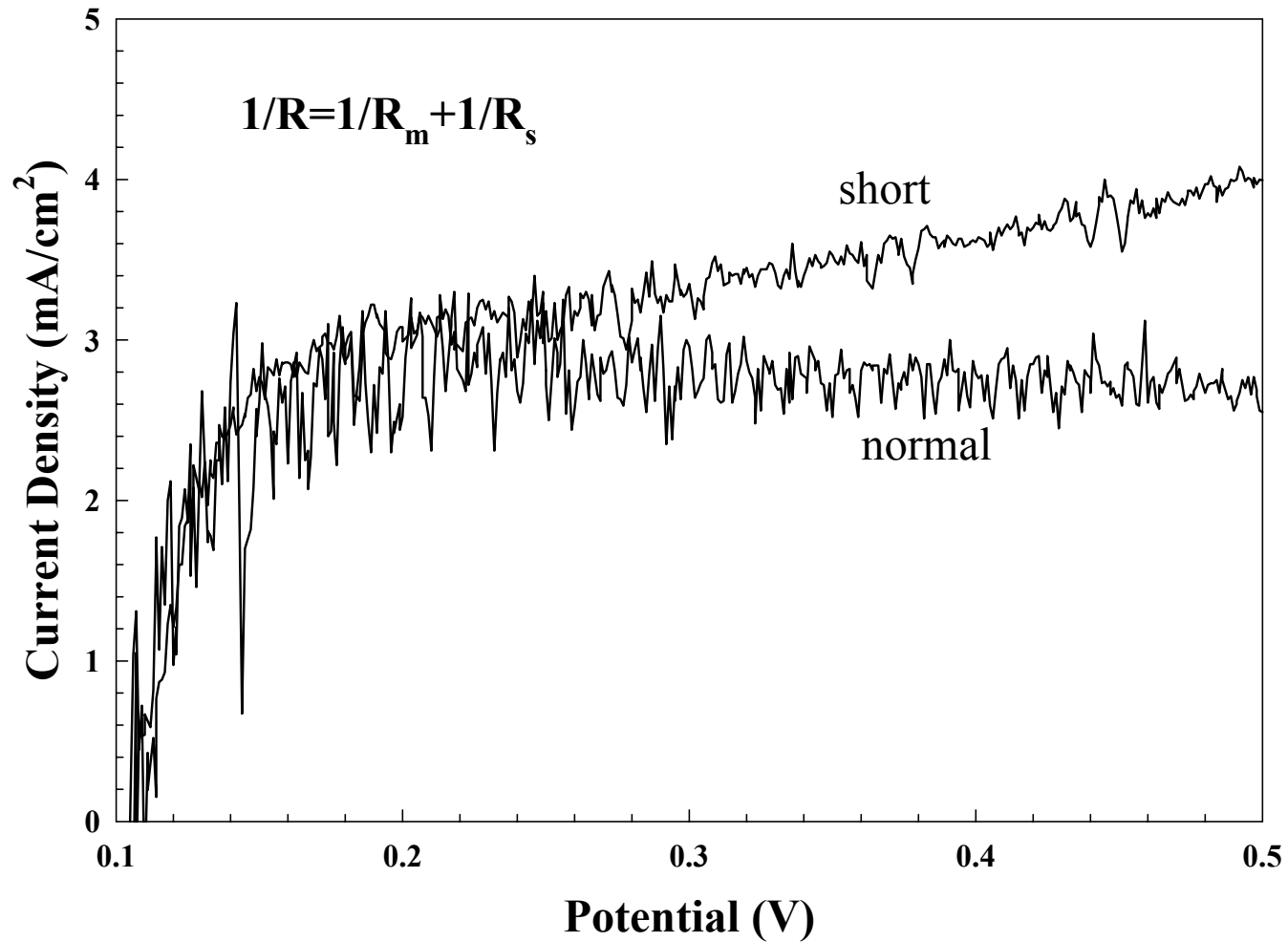
Additional details

- The experiment is typically done at a low sweep rate (1- 4 mV/s or even lower)
- This is to ensure that the Nernst diffusion layer has the time required to grow out from the electrode
- This results in “true” limiting current behaviour
- In practice, it is better to start the sweep at higher potentials to avoid effects of hydrogen evolution

The utility of LSV in fuel cell research will be further discussed in future lectures

Internal short circuit

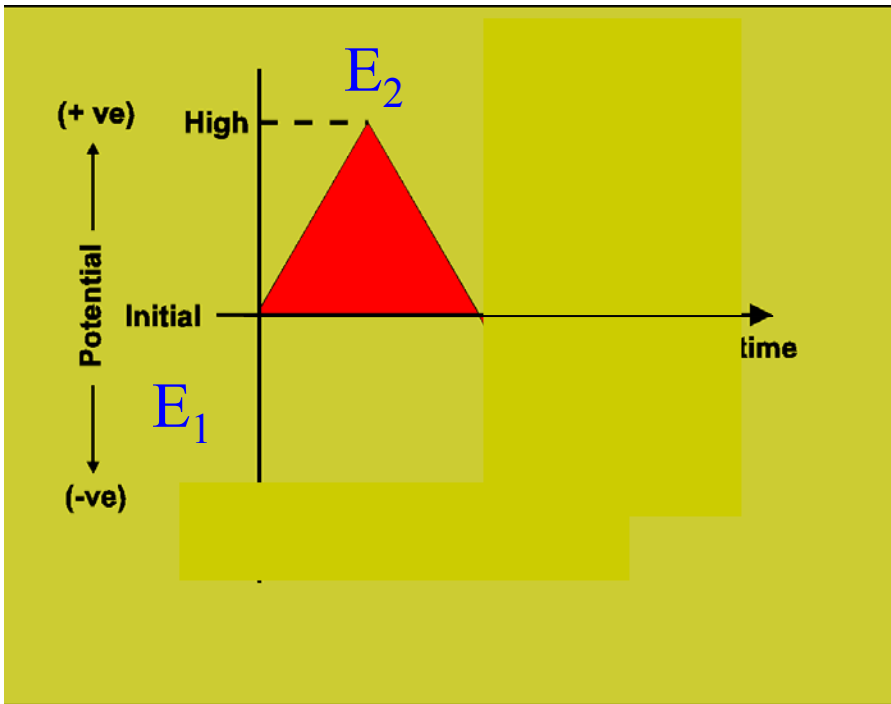
Crossover Current Density of NTPA MEAs (4 mv/s)



Cyclic voltammetry

- Potential sweep experiment (similar to LSV)
- Additional reverse sweep incorporated
- Input function:
 - start from $E = E_1$
 - sweep up to $E = E_2$
 - sweep down, back to $E = E_1$
- Done using a potentiostat
- Fixed sweep rate
- Faradaic current monitored

Typical voltammogram in electrochemical systems

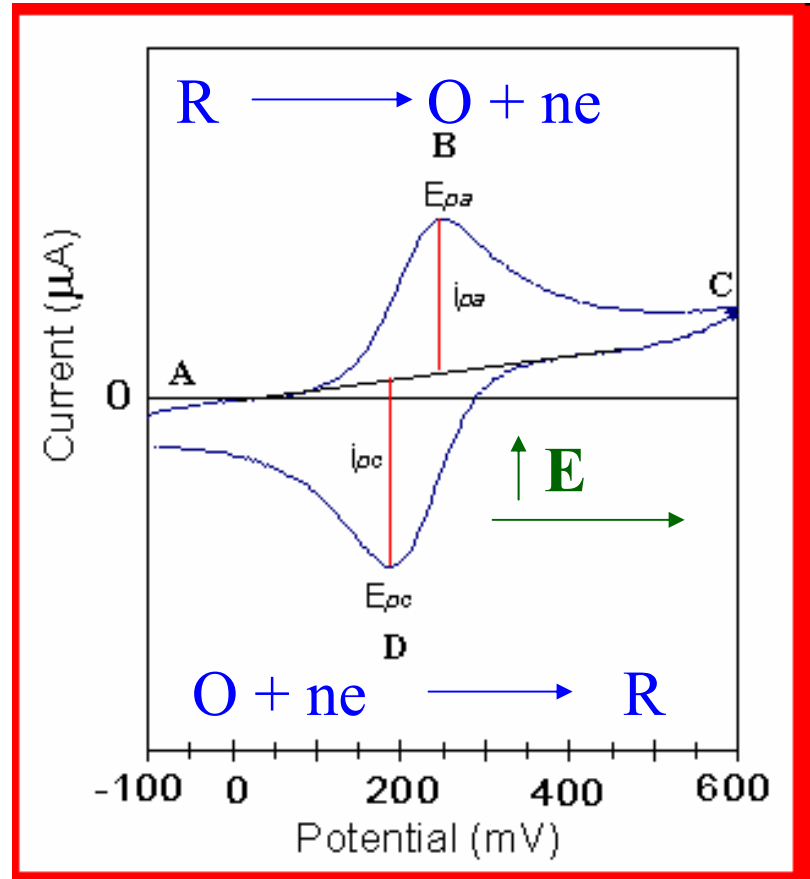


← Input

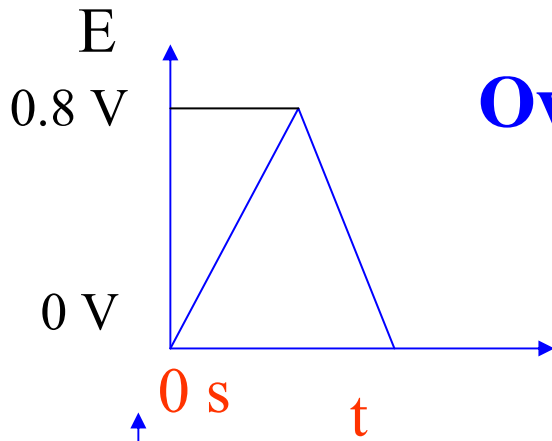
Redox Reaction :



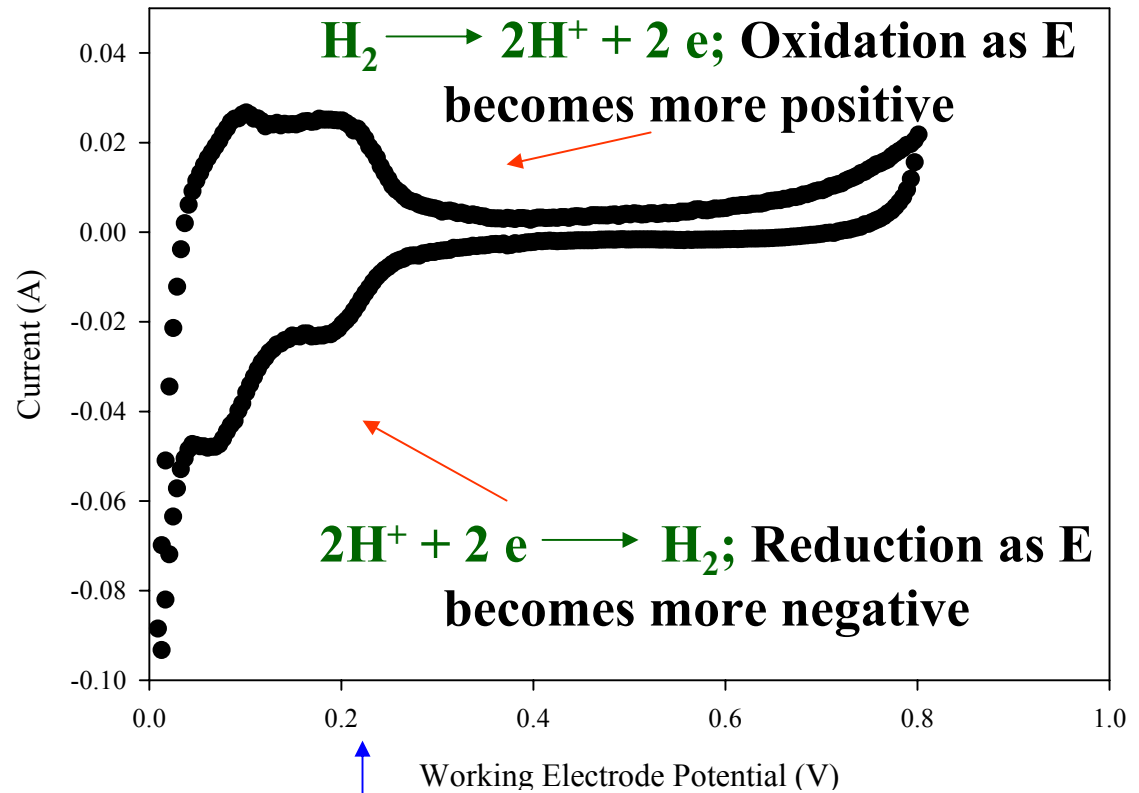
Output



Typical CV at a fuel cell cathode



Input Function



Output (Response)

Response – Fuel cell cathode CV

- Resultant current behaviour on the forward sweep - same as discussed for LSV – H_2 gets oxidized to give H^+ and electrons
- Behaviour on the reverse sweep – the opposite redox phenomenon occurs – H^+ gets reduced (gaining electrons in the process) to give H_2
- Peak symmetry – indication of reaction reversibility

Additional details

- Sweep rates (v) employed are typically higher than those in LSV ($\sim 20\text{-}30\text{mV/s}$ as opposed to $1\text{-}4\text{ mV/s}$)
- peak height scales as $v^{0.5}$
- Thus larger v – better defined peaks

**Need to ensure sweep rate is not too high -
system tends to become quasi-reversible
or irreversible**

Applications

- Studying the reversibility of reactions and redox behaviour of compounds
- Used to obtain quantitative information about the extent of reaction occurring on a surface
- In fuel cells – used to determine electrochemically active surface area of catalyst