# Complex Electrodes:

## Model of Narrow Platinated Channel

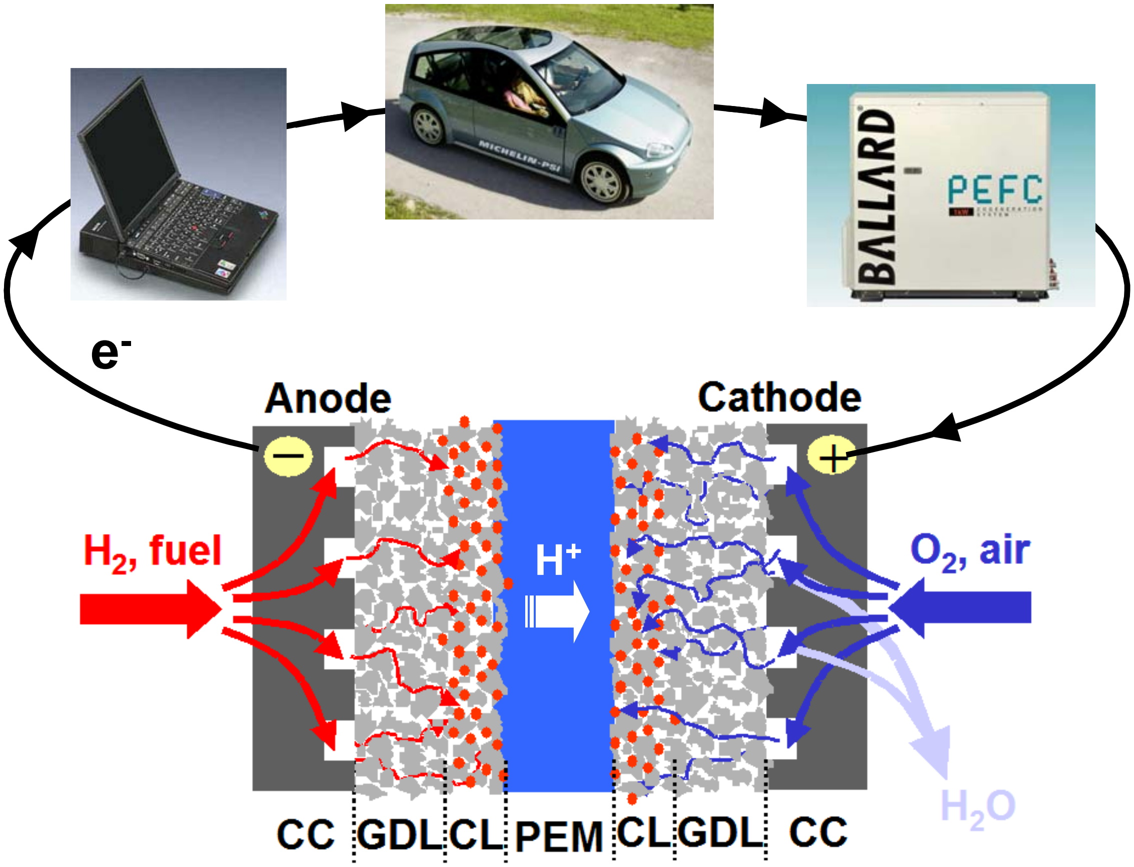
**Let's consider a stationary problem involving the interplay of**

**charge transfer kinetics**

**vs.**

**reactant diffusion**

**Fuel cell: const. supply of reactants – stationary operation.**



**Anode** : $H_2 \rightarrow 2H^+ + 2e^-$

**Cathode** : $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$

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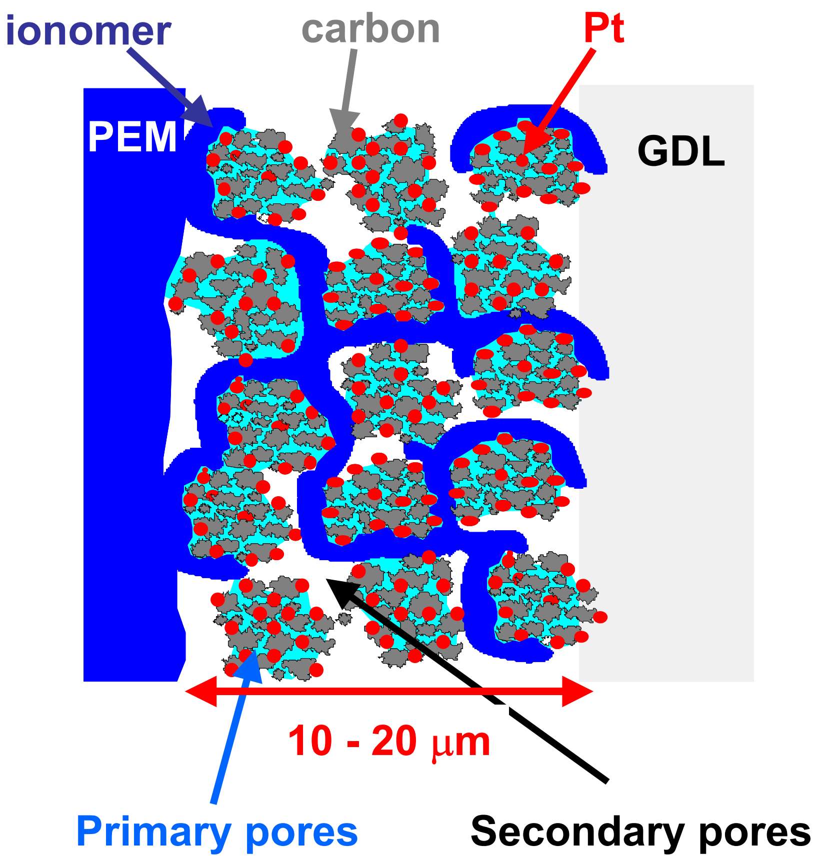
**Total** : $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

## Let's focus on the cathode… (Why?)



- Pt nanoparticles on porous carbon substrate for
  - high specific activity
  - high surface area of catalyst
  - real-to-apparent surface area ratio (heterogeneity factor) : $\xi = A^{\text{real}} / A^{\text{apparent}}$
  - cost is an essential factor – Pt utilization!

- ❑ 3-phase composite:
  - solid matrix (carbon and Pt)
  - proton-conductor (solid polymer electrolyte
  - micro-to-mesopores (10-100 nm)
  - partial saturation with liquid water
- ❑ practical interest and fundamental science
  - nanoparticle electrocatalysis
    (atomistic scale to single particle scale)
  - random composites (percolation theory)
  - transport and reaction in partially saturated porous media
  - nanotemplate structures

→ reactants and reaction rates: complex distributions

Of course you do not start a scientific career by considering the most complicated situations…

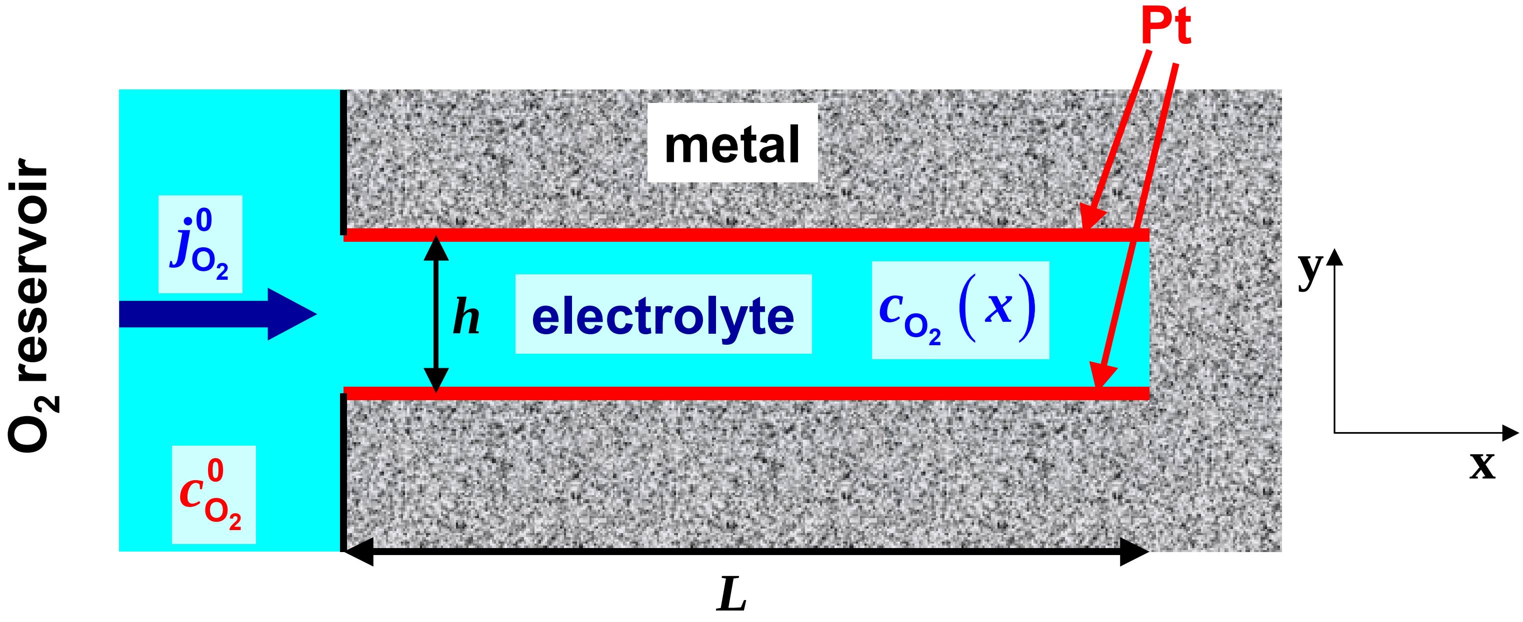
– resort to simple models and well-defined experiments!

## Model: Narrow platinated channel

**Consider oxygen reduction (cathode) as an example:**

$$\boxed{O_2 + 4H^+ + 4e^- \leftrightarrow 2\,H_2O}$$

**with** $E^0 = 1.23$ **V vs. SHE** **and** $j^{00} \sim 10^{-10}$ **A cm$^{-2}$**



**Why useful?**

**– larger effective catalyst area per electrode area**

**Channel is narrow enough ($h \ll L$):**

- **effectively a one-dimensional system**
- **only consider transport along x-direction**

## What happens?

- constant supply of $O_2$ at channel entrance
- consumption of $O_2$ in electrochemical reaction along channel walls generates electrical current
- assume high concentration and mobility of protons

  ⇒ $H^+$ uniformly distributed, abundant
- rate of reaction determined by Butler-Volmer kinetics (neglect complications in ORR as multistep process)

⇒ Reaction kinetics vs. diffusive flux of $O_2$

## How significant are diffusion limitations?

- calculate diffusion limited current density

$$j_{\text{diff}} = 4FD\frac{\mathrm{d}c_{O_2}}{\mathrm{d}x}$$

- estimate maximum possible diffusion flux

$$j_{\text{diff}}^{\text{lim}} = 4FD\frac{c^0_{O_2}}{L} \sim 0.1-1\ \text{A cm}^{-2}$$

for $c^0_{O_2} \sim 0.01-0.1\ \text{M}$, $L \approx 10\ \mu\text{m}$, and $D \approx 2.55\cdot 10^{-5}\ \text{cm}^2\ \text{s}^{-1}$

## What about electrode potential $E$ ?

- Good metal conductivity

  ⇒ $E$ is uniform along channel walls

## What remains to be understood?

- Variation of reaction rate and $c_{O_2}(x)$ along x
- Relation between current density and $E$

## Butler-Volmer equation

$$j = Fk^0 \left\{ c_{red}^{s} \exp\left( \frac{\alpha F\left(E - E^0\right)}{RT} \right) - c_{ox}^{s} \exp\left( -\frac{(1-\alpha) F\left(E - E^0\right)}{RT} \right) \right\}$$

$\Rightarrow$ for appreciable current densities, $j >>> j^{00} = Fk^0$

$$\Rightarrow \qquad \frac{F\left|E - E^0\right|}{RT} >> 1$$

$$\Rightarrow \qquad \boxed{j = -Fk^0 c_{ox} \exp\left( -\frac{(1-\alpha) F\left(E - E^0\right)}{RT} \right)}$$

, where $c_{ox} = c_{O_2}$

However, now the current is distributed!

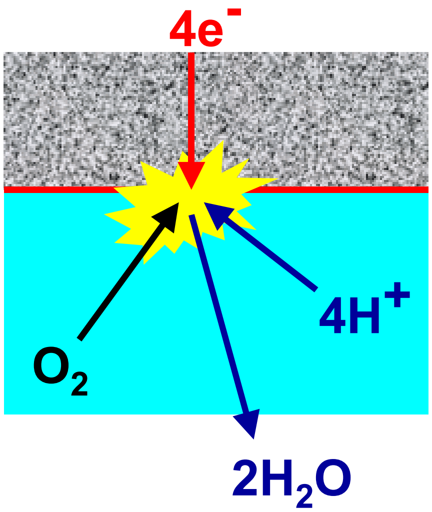
Now: Consider segment of the channel of width $\Delta x << L$

Consumption of e- in this segment due to reaction

$$\Delta j = \frac{\Delta x}{L} \left[ -Fk^0 c_{O_2}(x) \exp\left( -\frac{(1-\alpha) F\left(E - E^0\right)}{RT} \right) \right]$$

$$\Rightarrow \qquad \frac{\mathrm{d}j(x)}{\mathrm{d}x} = -\frac{Fk^0}{L} c_{O_2}(x) \exp\left( -\frac{(1-\alpha) F\left(E - E^0\right)}{RT} \right)$$

## Balance of fluxes: consider a single reaction event



**$1O_2$ molecule consumes $4e^-$**

**Current density**: rate of generation of $e^-$

## Overall: fluxes of $O_2$ and $e^-$ have to be balanced

**Oxygen flux**:

$$J_{O_2}(x) = -D\frac{\mathrm{d}c_{O_2}(x)}{\mathrm{d}x} \quad \text{(Fick's first law)}$$

convert into equivalent charge flux

$$j_{O_2}(x) = -4FD\frac{\mathrm{d}c_{O_2}(x)}{\mathrm{d}x}$$

and differentiate

$$\frac{\mathrm{d}j_{O_2}(x)}{\mathrm{d}x} = -4FD\frac{\mathrm{d}^2c_{O_2}(x)}{\mathrm{d}x^2}$$

Equate the two expressions (changes in fluxes):

$$\frac{\mathrm{d}j(x)}{\mathrm{d}x} = -\frac{Fk^0}{L}c_{O_2}(x)\exp\left(-\frac{(1-\alpha)F(E-E^0)}{RT}\right) = -4FD\frac{\mathrm{d}^2c_{O_2}(x)}{\mathrm{d}x^2} = \frac{\mathrm{d}j_{O_2}(x)}{\mathrm{d}x}$$

**Collect all constant (x-independent) factors:**

$$\frac{\mathrm{d}^2 c_{\mathrm{O}_2}(x)}{\mathrm{d}x^2} = \kappa^2 c_{\mathrm{O}_2}(x), \text{ with } \kappa^2 = \frac{k^0}{4DL}\exp\left(-\frac{(1-\alpha)F(E-E^0)}{RT}\right)$$

**where $\kappa$ is an inverse reaction penetration depth, i.e.**

$$L_\mathrm{p} = \kappa^{-1} = \sqrt{\frac{4DL}{k^0}}\exp\left(\frac{(1-\alpha)F(E-E^0)}{2RT}\right)$$

**General solution**

$$c_{\mathrm{O}_2}(x) = A\exp(\kappa x) + B\exp(-\kappa x)$$

**with boundary conditions**

$$x = 0: \; c_{\mathrm{O}_2} = c^0_{\mathrm{O}_2}, \qquad x = L: \; \frac{\mathrm{d}c_{\mathrm{O}_2}}{\mathrm{d}x} = 0$$

$$c_{\mathrm{O}_2}(x) = c^0_{\mathrm{O}_2}\frac{\cosh(\kappa(x-L))}{\cosh(\kappa L)}$$

**Relation between total current density $j^0$ and $E$**

$$j_0 = 4FD\left.\frac{\mathrm{d}c_{\mathrm{O}_2}}{\mathrm{d}x}\right|_{x=0}$$

**and, thus,**

$$j_0 = -\frac{4FDc^0_{\mathrm{O}_2}}{L}\kappa L\tanh(\kappa L) = -j^{\mathrm{lim}}_{\mathrm{diff}}\;\kappa L\tanh(\kappa L)$$

Before looking at graphical solutions, consider two limiting cases:

- $\kappa L = \frac{L}{L_p} << 1$:
  - large reaction penetration depth
  - rate of diffusion large compared to rate of reaction

$$\tanh(\kappa L) \approx \kappa L$$

$$j_0 = -\frac{4FDc^0_{O_2}}{L}(\kappa L)^2$$

$$j_0 = -Fk^0 c^0_{O_2} \exp\left(-\frac{(1-\alpha)F(E-E^0)}{RT}\right)$$

→ simple Tafel law retained (in limit of infinite diffusion)

Why do you gain from the channel electrode structure?

- $\kappa L = \frac{L}{L_p} >> 1$:
  - small reaction penetration depth
  - rate of reaction very large (due to large $E$) compared to rate of diffusion

$$\tanh(\kappa L) \approx 1$$

$$j_0 = -\frac{4FDc^0_{O_2}}{L}\kappa L$$

$$j_0 = -\frac{4FDc^0_{O_2}}{L}\sqrt{\frac{k^0 L}{4D}}\exp\left(-\frac{(1-\alpha)F\left(E-E^0\right)}{2RT}\right)$$

$$j_0 = -Fc^0_{O_2}\sqrt{\frac{4Dk^0}{L}}\exp\left(-\frac{(1-\alpha)F\left(E-E^0\right)}{2RT}\right)$$

**Similar dependence on potential (exponential form),**

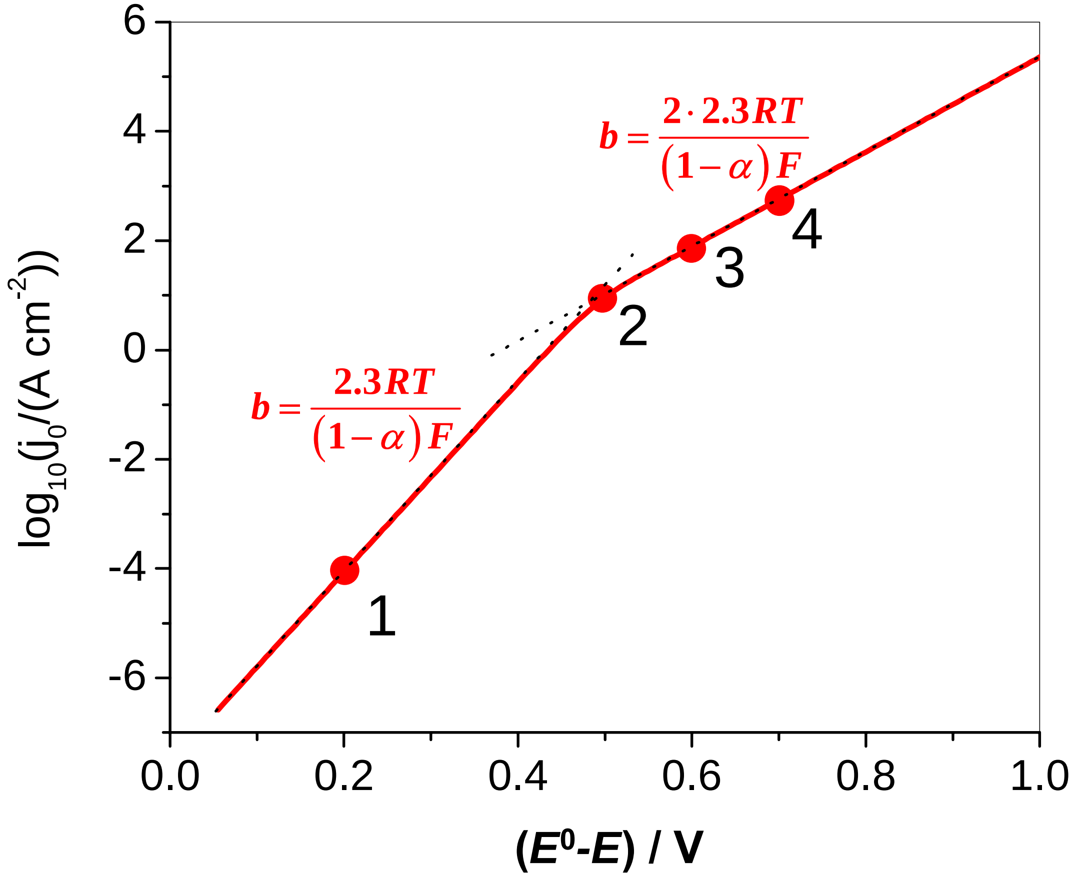
**But different Tafel-slope due to interplay of mass transport and reaction limitations.**

**Tafel-constant changes from**

$\boxed{b = \frac{2.3RT}{(1-\alpha)F} \text{ at } \kappa L << 1}$ **to** $\boxed{b' = 2b = \frac{2 \cdot 2.3 \cdot RT}{(1-\alpha)F} \text{ at } \kappa L >> 1}$

**i.e. it doubles. This is a very general signature of mass transport effects.**

## Graphical Solution



Current vs. potential (Tafel plot)

**Transition between the two limiting cases:**

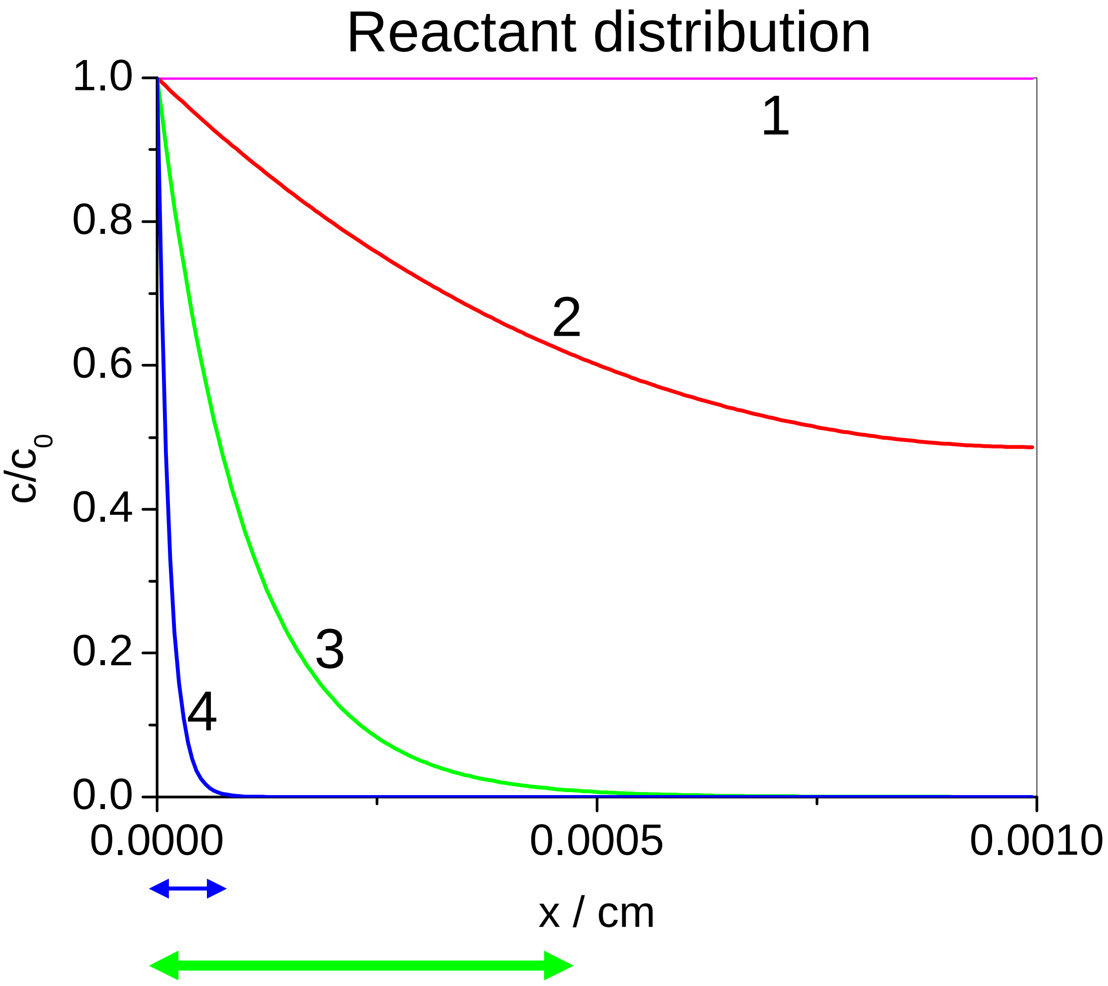
$$\kappa L = 1 \quad \Rightarrow \quad j_0^* = -j_{\text{diff}}^{\text{lim}}$$

$$L = L_{\text{p}} = \kappa^{-1} = \sqrt{\frac{4DL}{k^0}} \exp\left(\frac{(1-\alpha)F\left(E-E^0\right)}{2RT}\right)$$

$$\Rightarrow \quad E^* - E^0 = \frac{RT}{(1-\alpha)F} \ln\left(\frac{k^0 L}{4D}\right)$$

**i.e. the point $\left(j_0^*, E^*\right)$ could be used to determine $D$ and $k^0$**

# Reactant distribution along the channel



$$\delta \approx \frac{4FDc^0_{O_2}}{j_0}$$

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# Hydrodynamic Electrodes and Microelectrodes

So far:

- processes at planar electrodes
- interplay of diffusion and kinetics

In most cases:

Diffusion is most significant transport limitation. Diffusion limitations arise inevitably, since any reaction consumes reactant molecules. This consumption depletes reactant (the so-called *electroactive* species) in the vicinity of the electrode, which leads to a non-uniform distribution (see the previous notes).

Note: In principle, we would have to consider the accumulation of product species in the vicinity of the electrode as well. This would not change the basic phenomenology, i.e. the interplay between kinetics and transport would remain the same. But it would make the mathematical formalism considerably more complicated. In order to simplify things, we, thus, focus entirely on the reactant distribution, as the species being consumed.

In this part, we are considering a semi-infinite system:

- Planar electrode with huge surface area
- Solution as infinite reservoir of reactant

This simple system has one characteristic length scale:

thickness of the diffusion layer (or mean free path) $\delta$

Sometimes the diffusion layer is referred to as the *"Nernst layer"*

Let's consider again: kinetic vs. diffusion limitations

- Kinetic limitations: rate constant $k^0$

  (or exchange current density $j^0 = nFk^0 {c_{\text{red}}^{\text{b}}}^{\alpha} {c_{\text{ox}}^{\text{b}}}^{1-\alpha}$)

- Diffusion limitations: diffusion constant $D$ and diffusion layer thickness $\delta$. Define a diffusion rate in the following way: $k_{\text{diff}} = \frac{D}{\delta}$

  Corresponding diffusion-limited current:

$$\boxed{j_{\text{diff}} = nFk_{\text{diff}} c_{\text{ox}}^{\text{b}} = \frac{nFDc_{\text{ox}}^{\text{b}}}{\delta}}$$

## Reversible and Irreversible Reactions

**Reactions for which $k^0 >> k_{\text{diff}}$ : reversible reactions**

**Reactions for which $k^0 << k_{\text{diff}}$ : irreversible reactions**

**[We will consider this distinction in more detail in the chapter on cyclic voltammetry.]**

**$k^0$ can vary over wide ranges (from $10^1$ cm/s for facile reactions down to $10^{-14}$ cm/s for slow reactions).**

**What determines values of $k^0$ ?**

- ❑ **electronic structure of the metal (the Fermi level)**
- ❑ **molecular structure of the solution and the**
- ❑ **LUMO for oxidized species in solution**
- ❑ **HOMO for reduced species in solution**

**In general: $k^0$ depends on the type of metal, its surface structure, the type of electrolyte and the redox species.**

**Diffusion coefficients in aqueous solution:**

- ❑ **in the range of $10^{-5}$ $cm^2/s$, small range of variation**
- ❑ **cannot be controlled in an experiment**

## Ways to control the interplay between kinetics and mass transport?

Most important variable in electrochemical experiment: **electrode potential** $E$ – control **rate of electron transfer**.

What are the other options of experimental control? Experimental techniques that allow controlling the **rate of mass transport**, i.e. $k_{\mathrm{diff}}$ .

There are two principal ways to achieve that:

- **Hydrodynamic devices** – forced convection: confine concentration variations to a thin region near the electrode surface.
- **Control the electrode geometry**: (ultra-)microelectrodes

Overall, these measures raise the rates of mass transport. **Fast rates of mass transport** make it possible to study the kinetics of **fast electron transfer reactions**.

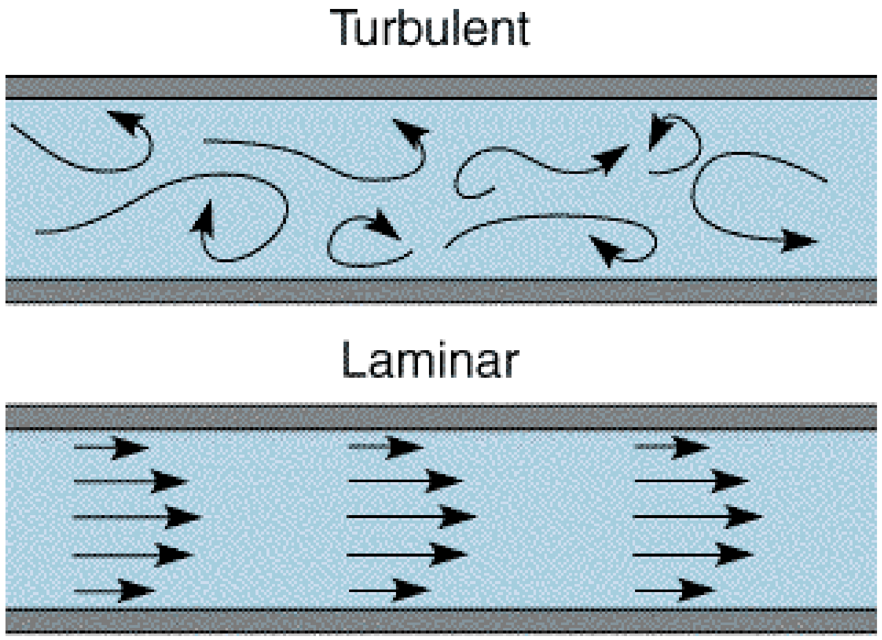
# Hydrodynamic Devices

These devices use convection to enhance and control the rate of mass transport to the electrode surface. Detectable currents are increased and the sensitivity of voltammetric measurements is enhanced.

Two approaches:

- Electrode held in fixed position, solution flowed over electrode surface by applied force, usually applied pressure gradient (e.g. wall-jet electrode)
- Electrode is designed to move which acts to mix the solution via convection.

For quantitative analysis of the electrode processes, convection must be predictable, i.e. *laminar* and not turbulent – lead to well-defined, reproducible results.

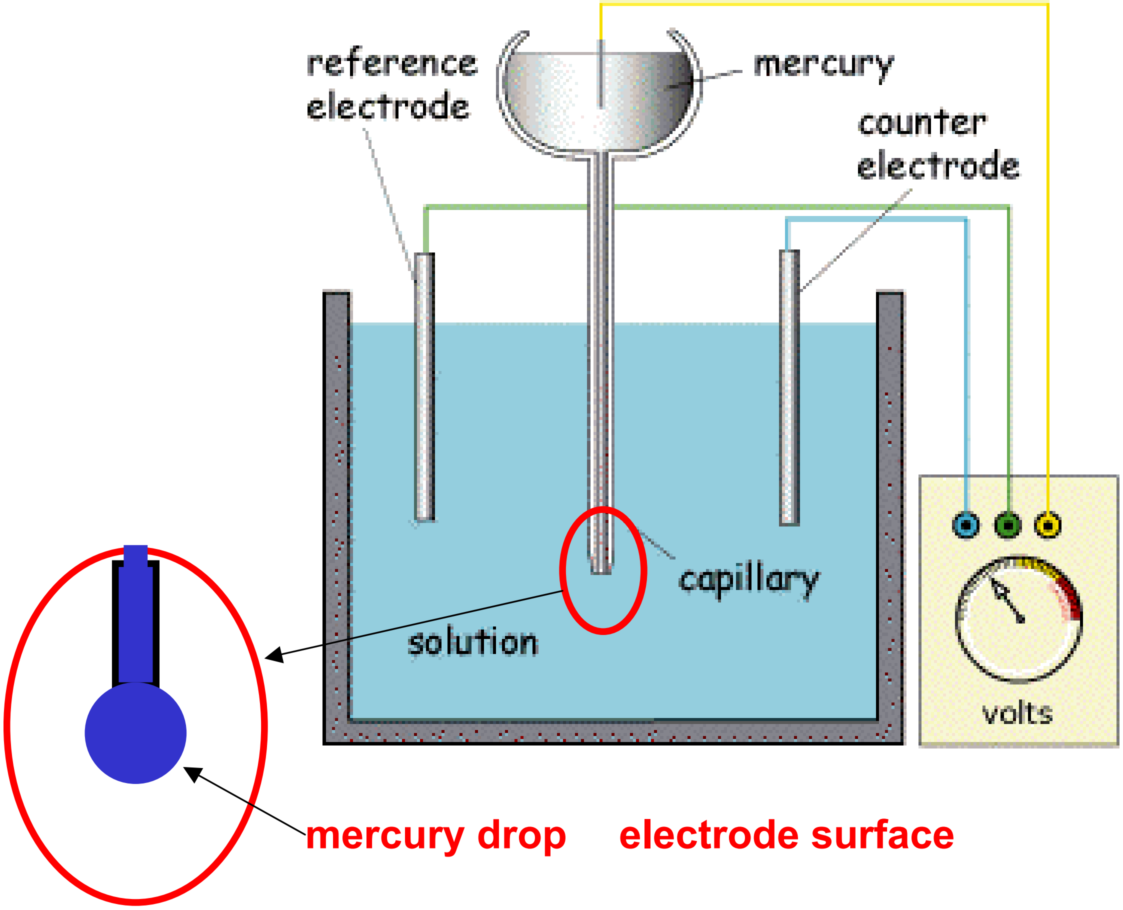


Turbulent

Laminar

## Dropping Mercury Electrode (DME)

Historically, this is the first used hydrodynamic technique. The electrochemical cell with potentiostat, working electrode (mercury), counter electrode and reference electrode is shown below.



- large reservoir of Hg connected to capillary
- Hg flows under influence of gravitation in capillary
- drop at opening of capillary grows in time until it reaches a critical size
- at this point, Hg drop detaches from tip and falls down

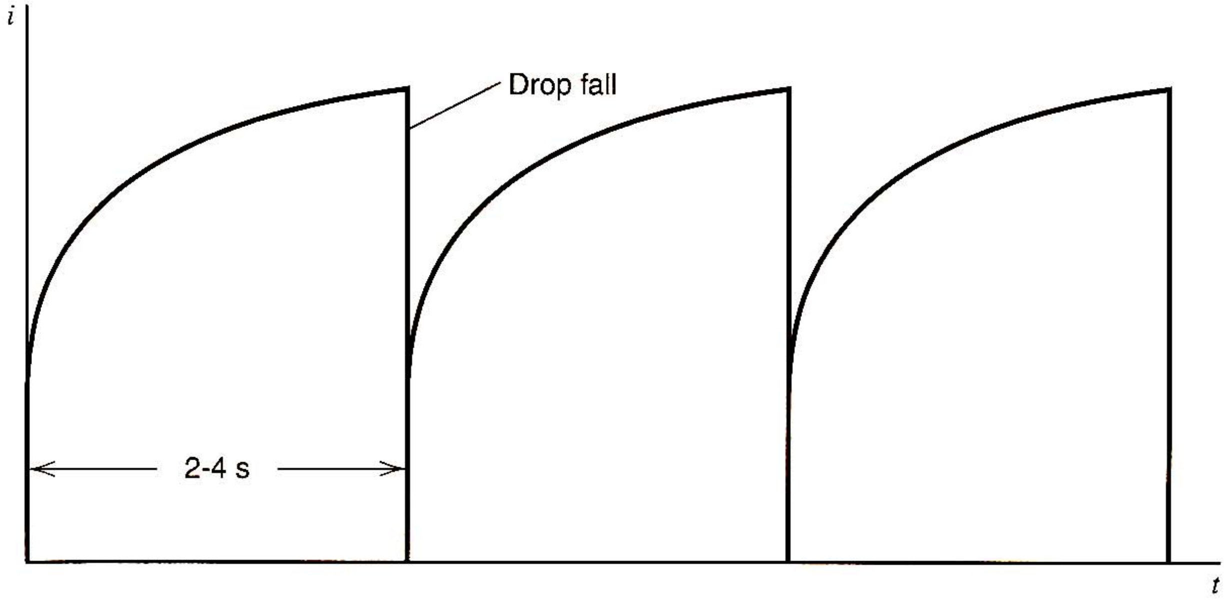
**Surface of WE** (drop surface): **refreshed in regular cycles**

Big advantage: continuous refreshing minimizes problems of electrode poisoning.

**Measured current:**

- function of surface area of the drop
- increases continuously with drop size
- when drop falls off, the current drops rapidly

The following picture shows the **cyclic current** at **DME** as function of time (in this plot: for fixed potential *E* ).



Surface area is important property of this electrode. We, thus, have to consider *current* and NOT current densities at this electrode. Consider the limiting current due to diffusion as determined by COTTRELL-equation:

$$I_{\mathrm{L}}(t) = nFA_{\mathrm{Hg}}c_{\mathrm{ox}}^{\mathrm{b}}\sqrt{\frac{D}{\pi t}}$$

## Assumptions:

- drop is ideal sphere (simplification!), i.e. $A_{\mathrm{Hg}} = 4\pi r_0^2$, where $r_0$ is the radius
- constant mass flux $m_{\mathrm{Hg}}$ [mg s$^{-1}$] of liquid Hg in the capillary, which determines *t*-dependence of $r_0$

  $$r_0 = \left(\frac{3m_{\mathrm{Hg}}t}{4\pi\rho_{\mathrm{Hg}}}\right)^{1/3}$$

  where $\rho_{\mathrm{Hg}}$ is the density of Hg.
- effective diffusion coefficient has to be used in Cottrell equation, $D_{\mathrm{eff}} = \frac{7}{3}D$

Using all these definitions in Cottrell-equation gives the so-called ILKOVIC-equation,

$$I_{\mathrm{L}}(t) = 708nD^{1/2}c_{\mathrm{ox}}^{\mathrm{b}}m_{\mathrm{Hg}}^{2/3}t^{1/6}$$

with $I_{\mathrm{L}}$ in [A], $D$ in [cm$^2$/s], $m_{\mathrm{Hg}}$ in [mg/s], and $t$ in [s]

**DME** can be used for **voltammetric measurements**, i.e. record current as function of *E*. Historic reasons: method is called polarography; first introduced by Heyrovsky in the 1920's (Nobel prize 1959).

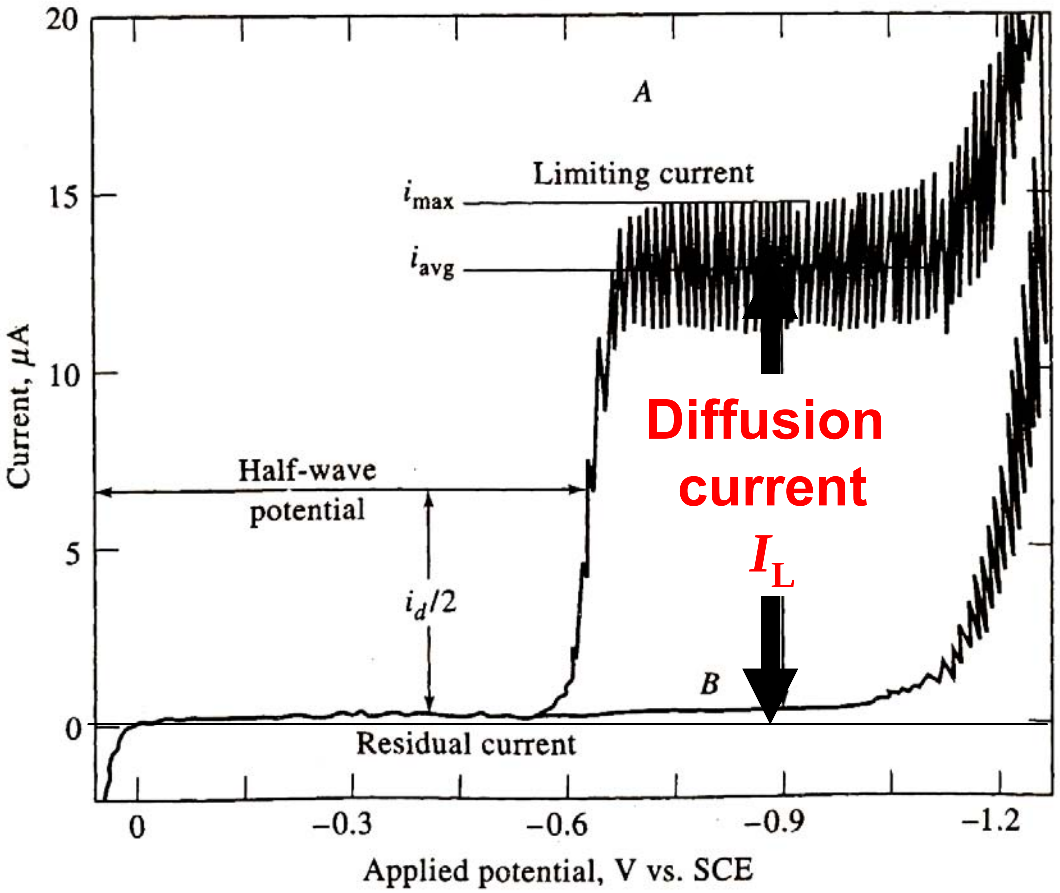
**Linear scan polarograph** (obtained by linear sweep voltammetry) for two reactions:

**Curve A**:

$Cd^{2+} + 2\,e^- + Hg \rightleftharpoons Cd(Hg)$ (reduction of Cd ions)

**Curve B**:

$2H^+ + 2\,e^- \rightleftharpoons H_2(g)$ (hydrogen evolution)



**Note: Spikes in this plot represent cycles of drop lifetime. The drop lifetime is a constant (determined by height of Hg column in reservoir and by the mass flow rate $m_{Hg}$). At large cathodic overpotentials, the current reaches a plateau. The height of this plateau is determined by the Ilkovic equation, as specified above. In principle, this electrode is operated at steady state.**