Modes of mass transport in electrochemistry

Mass transport from one region in solution to another, arising from:

- **Convection** (net transport of a volume element of solution, e.g. stirring or hydrodynamics), which can be *natural* (presence of density gradient in solution) or *forced* (hydrodynamic techniques)
- **Migration**, which describes the transport of charges in solution under the effect of an electrical field (gradient of electrical potential)
- **Diffusion**, which describes the transport of a species in solution under the effect of a gradient of chemical potential (or concentration)
- *Migration* and *diffusion* arise from gradients of **electrochemical potential** $\bar{\mu}_i$

Mass transport in solution: the flux (*J*)

The presence of gradients in solution is the driving force for mass transfer, which is described in terms of a **flux, *J*,** *which operates to alleviate the magnitude of the gradients*

Nernst-Planck Equation (for linear mass transfer)

$[\text{mol cm}^{-2}\ \text{s}^{-1}] \leftarrow$

$$\boldsymbol{J_j(x)} = \underbrace{\boxed{-\boldsymbol{D_i}\frac{\partial C_i(x)}{\partial x}}}_{\textbf{Diffusion}} \underbrace{\boxed{-\frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x}}}_{\textbf{Migration}} + \underbrace{\boxed{\cancel{C_i v(x)}}}_{\textbf{Convection}}$$

Unstirred or stagnant solution approximation

The effect of gradients in electrochemical potential

- The flux is proportional to the gradient of electrochemical potential (*i = charged species*)

$$\boldsymbol{J_i} \propto \boldsymbol{\nabla \bar{\mu}_i} \qquad \boldsymbol{\nabla} = \frac{\boldsymbol{\partial}}{\boldsymbol{\partial x}}$$

Vector operator (gradient) for linear mass transfer

- The flux is equivalent to a current density (*i = charged species*)
- <u>Large concentration of supporting electrolyte:</u> the effect of migration on the electroactive species *i* can be neglected

$$\boldsymbol{J_i(x)} = -\boldsymbol{D_i}\frac{\partial C_i(x)}{\partial x} - \cancel{\frac{z_iF}{RT}D_iC_i\frac{\partial \phi(x)}{\partial x}}$$

Diffusive mass transfer: the Fick's laws

A. Fick (1829 - 1901)

Fick's laws: *Differential equations* describing the flux and the concentration gradient of a species as functions of **time (*t*)** and **position (*x*)**

Assumption: linear (1D) diffusion

Fick's 1st law

$$-J_i(x,t) = \boldsymbol{D_i}\frac{\partial C_i(x,t)}{\partial x}$$

Net diffusive mass transport of a species i, described as number of moles passing through a unit area per unit time (mol s^{-1} cm^{-2})

Diffusion coefficient

Constant term

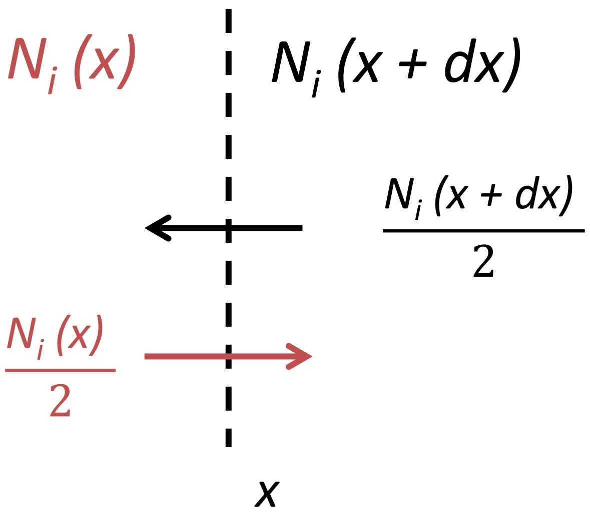
[cm^2/s]

Concentration gradient

The flux is proportional to the concentration gradient

Diffusive mass transfer: the Fick's laws

A. Fick (1829 - 1901)



Number of moles

dx = step length

$N_i(x)$

$N_i(x + dx)$

$\frac{N_i(x + dx)}{2}$

$\frac{N_i(x)}{2}$

x

$$J_i(x,t) = \frac{1}{A} \cdot \frac{\frac{N_i(x)}{2} - \frac{N_i(x+dx)}{2}}{dt} \cdot \frac{dx^2}{dx^2}$$

$$J_i(x,t) = \frac{dx^2}{2dt} \cdot \frac{N_i(x) - N_i(x+dx)}{Adx \cdot dx}$$

Concentration

$$J_i(x,t) = \boxed{\frac{dx^2}{2dt}} \cdot \frac{C_i(x) - C_i(x+dx)}{dx}$$

constant term

Diffusion coefficient D_i

1° Fick's law

Diffusive mass transfer: the Fick's laws

A. Fick (1829 - 1901)

- The **diffusion coefficient D** reflects the intrinsic tendency of a molecule to diffuse and depends on the **molecule size** (bigger molecules have typically smaller D)
- Molecular species typically have **D ≈ 10^{-6} – 10^{-5} cm^2/s**
- Determines how far a species diffuses in a certain time

$$\sqrt{\langle x^2 \rangle} = \sqrt{2Dt}$$

root-mean-square displacement at time t

- Provides an estimation for the **thickness of the diffusion layer**

How thick is a diffusion layer?

Diffusive mass transfer: the Fick's laws

Fick's 2nd law

$$\frac{\partial C_i(x,t)}{\partial t} = \boldsymbol{D_i}\left(\frac{\partial^2 C_i(x,t)}{\partial x^2}\right)$$

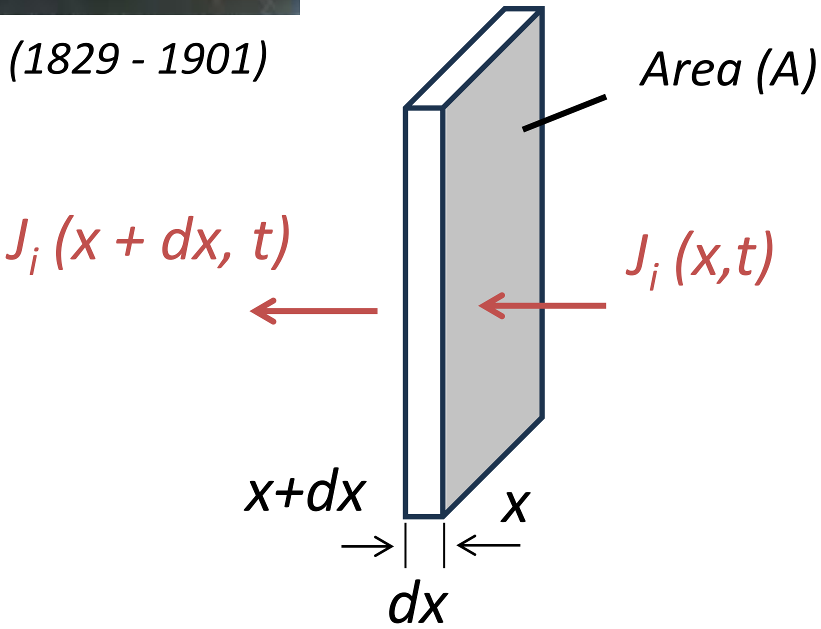
Gradient of concentration of the species i with ***time***

A. Fick (1829 - 1901)

$$\frac{\partial C_i(x,t)}{\partial t} = \frac{J_i(x,t) - J_i(x+dx,t)}{dx}$$

$$J_i(x+dx,t) = J_i(x,t) + \left(\frac{\partial J_i(x,t)}{\partial x}\right) dx$$

$$\frac{\partial C_i(x,t)}{\partial t} = -\left(\frac{\partial J_i(x,t)}{\partial x}\right)$$



from Fick's 1st law…

$$\frac{\partial C_i(x,t)}{\partial t} = \left(\frac{\partial}{\partial x}\right)\left[D_i\left(\frac{\partial C_i(x,t)}{\partial x}\right)\right]$$

Diffusive mass transfer: the Fick's laws

$$\frac{\partial C_i(x,t)}{\partial t} = D_i\left(\frac{\partial^2 C_i(x,t)}{\partial x^2}\right)$$

Linear diffusion equation

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i$$

General Fick's 2nd law for ***any geometry***

Laplacian operator

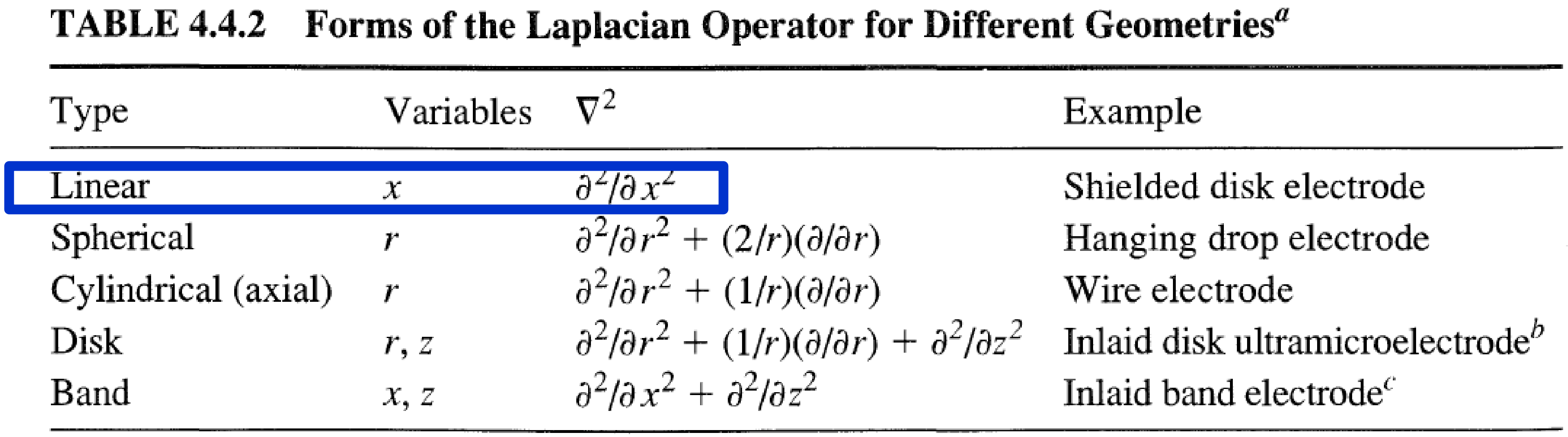


TABLE 4.4.2 Forms of the Laplacian Operator for Different Geometries[a]

Type	Variables	∇^2	Example
Linear	x	$\partial^2/\partial x^2$	Shielded disk electrode
Spherical	r	$\partial^2/\partial r^2 + (2/r)(\partial/\partial r)$	Hanging drop electrode
Cylindrical (axial)	r	$\partial^2/\partial r^2 + (1/r)(\partial/\partial r)$	Wire electrode
Disk	r, z	$\partial^2/\partial r^2 + (1/r)(\partial/\partial r) + \partial^2/\partial z^2$	Inlaid disk ultramicroelectrode[b]
Band	x, z	$\partial^2/\partial x^2 + \partial^2/\partial z^2$	Inlaid band electrode[c]

Bard & Faulkner, Electrochemical Methods, 2nd Ed, 2001

The electrochemical problem

Purely diffusive electroactive species $Ox + ne^- \rightleftharpoons Red$

$$J_{Ox}(0,t) = -J_{Red}(0,t)$$

$$\boldsymbol{-J_{Ox}(0,t) = \frac{i}{nFA} = D_{Ox}\left(\frac{\partial C_{Ox}(x,t)}{\partial x}\right)_{x=0}}$$

Concentration profile *at the electrode surface*

$$\frac{i}{FA} = -\sum_i n_i \cdot J_i(0,t) = \sum_i n_i \cdot D_i \left[\frac{\partial C_i(x,t)}{\partial x}\right]_{x=0}$$

Electrochemical problem

Solving the mass-transfer equations (diffusion) → *Relationship describing the* ***concentrations*** *of the species as functions of the variables* ***x*** *and* ***t***

How to solve partial differential equations?

$$\frac{\partial C(x,t)}{\partial t} = D\left(\frac{\partial^2 C(x,t)}{\partial x^2}\right)$$

Partial differential equation (PDE)

- Concentration of the species are **functions of both distance (*x*) and time (*t*)**
- *Ordinary differential equations (ODEs)* contain derivatives of functions of a single variable only
- PDEs are often characterized by **multiple solutions**
- *The specific solution of a PDE requires the definition of the* ***boundary conditions*** *for each species involved in the redox process*
- Different boundary conditions usually lead to different solutions of PDE

The boundary conditions

1. Initial conditions *(concentration profile at **t = 0**)*

$$\boldsymbol{C_{Ox}(x,0) = f(x)}$$

Es. $C_{Ox}(x,0) = C^*_{Ox}$ $\qquad C_{Red}(x,0) = 0$

2. Semi-infinite boundary conditions *(approximation related to the volume of the cell reactors compared to the size of the diffusion layer)*

$$\lim_{x\to\infty} C_{Ox}(x,t) = C^*_{Ox} \qquad \lim_{x\to\infty} C_{Red}(x,t) = 0$$

electrochemical cells are usually (not always!) much bigger than the diffusion layer

3. Electrode surface boundary conditions *(related to the concentrations of the species (or their gradients) at the electrode surface, **x = 0**)*

This condition is ***specific for the particular electrochemical experiment considered***

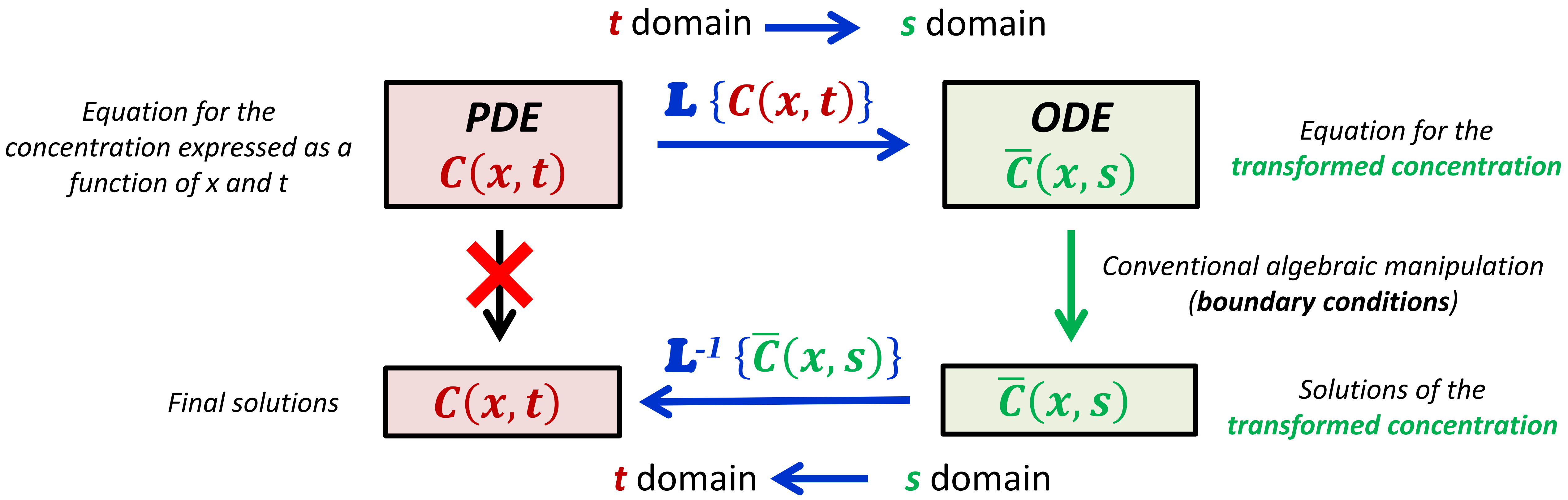
Potential-controlled experiments

$$C_{Ox}(0,t) = f(E) \qquad \frac{C_{Ox}(0,t)}{C_{Red}(0,t)} = f(E)$$

The Laplace transformation

$$\mathbf{L}\{F(t)\} = \bar{F}(s) \equiv \int_0^\infty e^{-st} F(t)\,dt$$

Laplace transformation is a mathematical tool, enabling a conversion of the problem into a domain where simpler mathematical manipulation is possible



t domain → s domain

Equation for the concentration expressed as a function of x and t

PDE

$C(x,t)$

$\mathbf{L}\,\{C(x,t)\}$

ODE

$\bar{C}(x,s)$

Equation for the ***transformed concentration***

*Conventional algebraic manipulation (**boundary conditions**)*

$\mathbf{L}^{-1}\,\{\bar{C}(x,s)\}$

Final solutions

$C(x,t)$

$\bar{C}(x,s)$

Solutions of the ***transformed concentration***

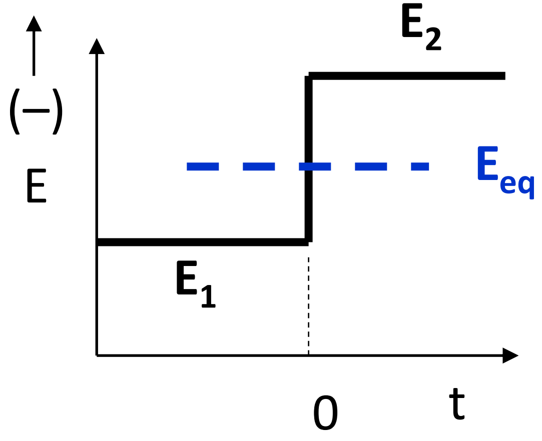
t domain ← s domain

Step-potential experiment

Constant applied potential E (potentiostatic) experiment

Current (*i*) measured as a function of time or E

$$Ox + e^- \longrightarrow Red$$

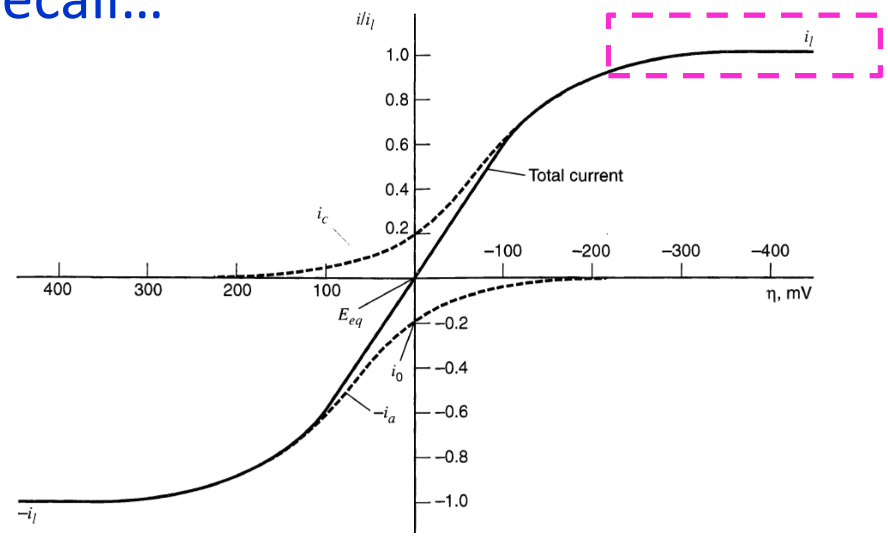


$E_2 << E_{eq}$

$\eta << 0$

...Recall...

Mass-transfer limited current region
(η << 0)



Bard & Faulkner, 2nd Ed., Wiley, 2001

Objective: find out expressions describing the **concentration profile (C(x,t))** of the electroactive species and the **current vs. time**

Step-potential experiment

- Planar electrode
- Unstirred solution
- Only diffusive mass transport (linear diffusion)
- **Initial condition** $C_{Ox}(x,0) = C^*_{Ox}$ for *t = 0*
- ***Microelectrode*** (reaction volume is assumed to be so high and the area of the electrode so small that the current flowing does not significantly affect the bulk concentration of the electroactive species)
- **Semi-infinite condition** $\lim_{x \to \infty} C_{Ox}(x,t) = C^*_{Ox}$
- **Surface concentration condition** (*very large η*, diffusion-limited current regardless of the ET kinetics)

3rd boundary condition
(specific step-E experiment)

$$\boxed{C_{Ox}(0,t) = 0}$$ for *t > 0*

Solving the differential equation

$$\frac{\partial C_{Ox}(x,t)}{\partial t} = D_{Ox}\left(\frac{\partial^2 C_{Ox}(x,t)}{\partial x^2}\right)$$

$$\xrightarrow{\mathcal{L}}$$

$$\int_0^\infty e^{-st}\left[D_{Ox}\left(\frac{\partial^2 C_{Ox}(x,t)}{\partial x^2}\right)\right]dt = D_{Ox}\frac{\partial^2}{\partial x^2}\underbrace{\int_0^\infty e^{-st}C_{Ox}(x,t)dt}_{\boldsymbol{\bar{C}_{Ox}(x,s)}} =$$

$$= D_{Ox}\frac{\partial^2 \bar{C}_{Ox}(x,\boldsymbol{s})}{\partial x^2}$$

Solving the differential equation

$$\frac{\partial C_{Ox}(x,t)}{\partial t} = D_{Ox}\left(\frac{\partial^2 C_{Ox}(x,t)}{\partial x^2}\right)$$

$\mathcal{L}$

$$\int_0^\infty e^{-st}\frac{\partial C_{Ox}(x,t)}{\partial t}dt = \left[e^{-st}C_{Ox}(x,t)\right]_0^\infty - \int_0^\infty C_{Ox}(x,t)(-se^{-st})dt$$

Integration by parts

$$= \underbrace{-C_{Ox}(x,0)}_{\boldsymbol{C^*_{Ox}}} + s\underbrace{\int_0^\infty C_{Ox}(x,t)(e^{-st})dt}_{\boldsymbol{\bar{C}_{Ox}(x,s)}}$$

$$\int_a^b g(x)f'(x)dx = [g(x)f(x)]_a^b - \int_a^b f(x)g'(x)dx$$

Intial boundary condition

Solving the differential equation

$$-C^*_{Ox} + s\bar{\boldsymbol{C}}_{\boldsymbol{Ox}}(\boldsymbol{x},\boldsymbol{s}) = D_{Ox}\left(\frac{\partial^2 \bar{\boldsymbol{C}}_{\boldsymbol{Ox}}(\boldsymbol{x},\boldsymbol{s})}{\partial x^2}\right)$$

$$\frac{\partial^2 \bar{\boldsymbol{C}}_{\boldsymbol{Ox}}(\boldsymbol{x},\boldsymbol{s})}{\partial x^2} - \frac{s}{D_{Ox}}\bar{\boldsymbol{C}}_{\boldsymbol{Ox}}(\boldsymbol{x},\boldsymbol{s}) + \frac{C^*_{Ox}}{D_{Ox}} = 0$$

2^{nd} order ordinary differential equation (ODE)

$$\bar{\boldsymbol{C}}_{\boldsymbol{Ox}}(\boldsymbol{x},\boldsymbol{s}) = \frac{C^*_{Ox}}{s} + A'(s)e^{\left[-\sqrt{\frac{s}{D_{Ox}}}x\right]} + B'(s)e^{\left[\sqrt{\frac{s}{D_{Ox}}}x\right]}$$

General solution

Constants

which values???

Solving the differential equation

$$\bar{\boldsymbol{C}}_{\boldsymbol{Ox}}(\boldsymbol{x},\boldsymbol{s}) = \frac{C^*_{Ox}}{s} + A'(s)e^{\left[-\sqrt{\frac{s}{D_{Ox}}}x\right]} + B'(s)e^{\left[\sqrt{\frac{s}{D_{Ox}}}x\right]}$$

$$\lim_{x\to\infty} C_{Ox}(x,t) = C^*_{Ox} \quad \xrightarrow[\textit{(use Table)}]{\boldsymbol{L}} \quad \lim_{x\to\infty} \bar{\boldsymbol{C}}_{\boldsymbol{Ox}}(\boldsymbol{x},\boldsymbol{s}) = \frac{C^*_{Ox}}{s}$$

Semi-infinite boundary condition

B'(s) *should be equal to 0*

$$\bar{\boldsymbol{C}}_{\boldsymbol{Ox}}(\boldsymbol{x},\boldsymbol{s}) = \frac{C^*_{Ox}}{s} + A'(s)e^{\left[-\sqrt{\frac{s}{D_{Ox}}}x\right]}$$

Solving the differential equation

$$\bar{C}_{Ox}(x,s) = \frac{C^*_{Ox}}{s} + A'(s)e^{\left[-\sqrt{\frac{s}{D_{Ox}}}x\right]}$$

$\boxed{C_{Ox}(0,t) = 0}$ for x = 0, $t > 0$ $\xrightarrow{\mathcal{L}}$ $\bar{C}_{Ox}(0,s) = 0$

3rd boundary condition

(surface concentration)

$$0 = \frac{C^*_{Ox}}{s} + A'(s)e^{\left[-\sqrt{\frac{s}{D_{Ox}}}x\right]}$$

x = 0

$$A'(s) = -\frac{C^*_{Ox}}{s}$$

$$\bar{C}_{Ox}(x,s) = \frac{C^*_{Ox}}{s} - \frac{C^*_{Ox}}{s}e^{\left[-\sqrt{\frac{s}{D_{Ox}}}x\right]}$$

The concentration profiles

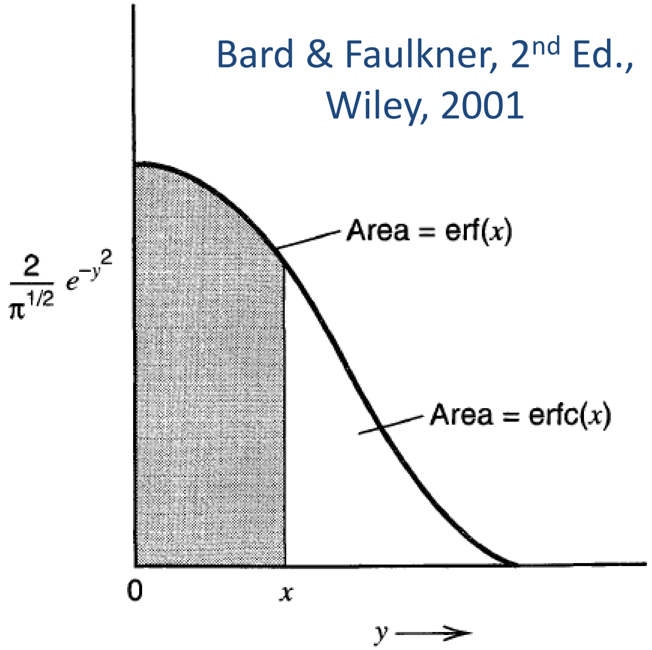
$$\bar{C}_{Ox}(x,s) = \frac{C^*_{Ox}}{s} - \frac{C^*_{Ox}}{s}\, e^{\left[-\sqrt{\frac{s}{D_{Ox}}}x\right]}$$

$$\xrightarrow[\text{(use Table)}]{\mathcal{L}^{-1}}$$

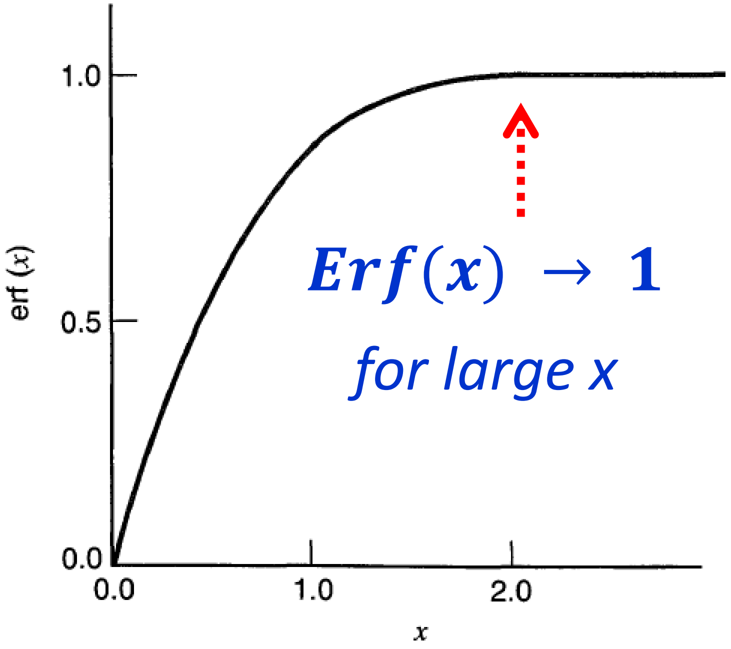
$$C_{Ox}(x,t) = C^*_{Ox}\left\{1 - erfc\left[\frac{x}{2\sqrt{D_{Ox}t}}\right]\right\}$$

$$C_{Ox}(x,t) = C^*_{Ox}\,\boxed{erf\left[\frac{x}{2\sqrt{D_{Ox}t}}\right]}$$

Error function



Bard & Faulkner, 2nd Ed., Wiley, 2001



$Erf(x) \rightarrow 1$

for large x

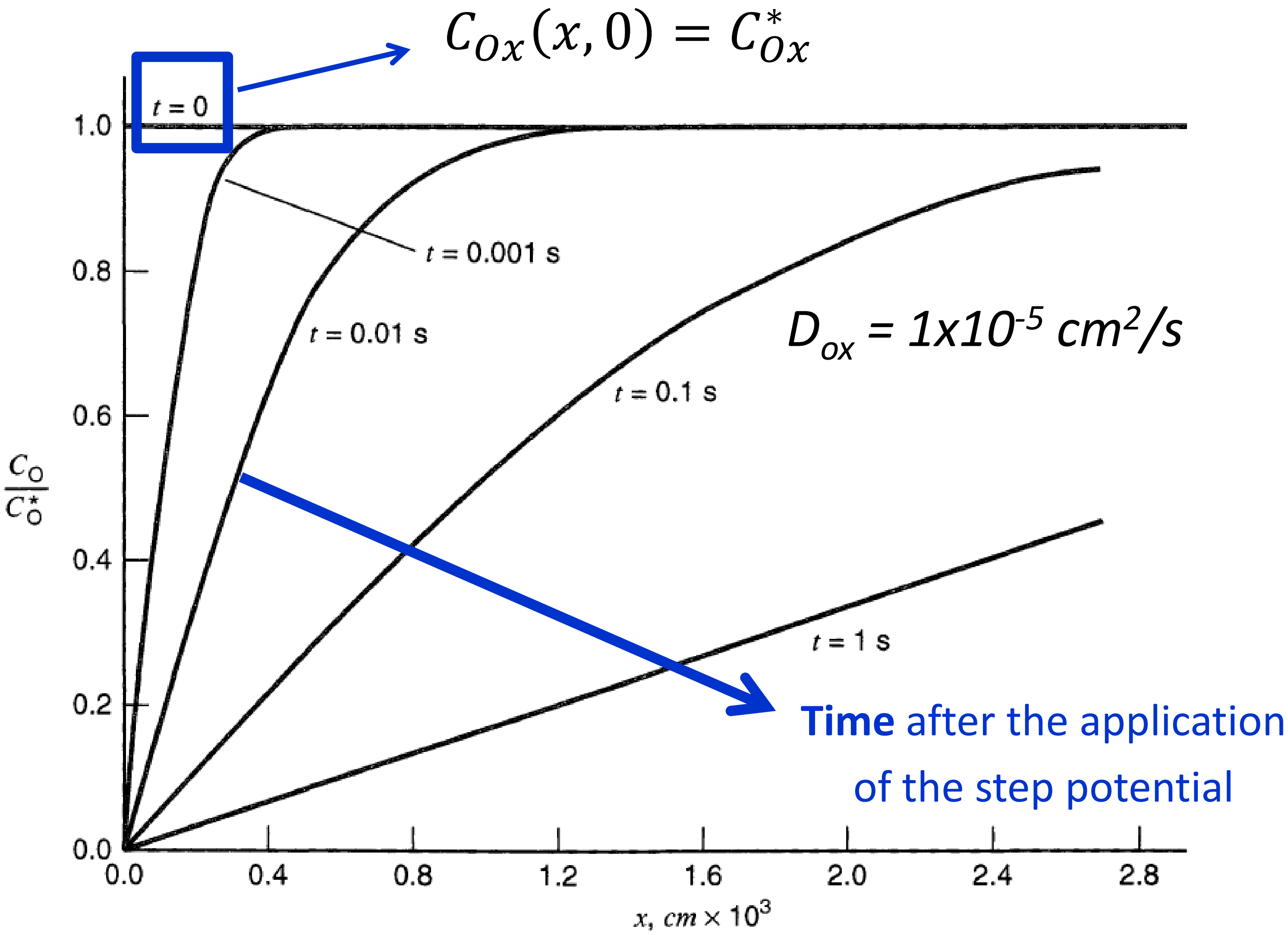
$$erf(x) \equiv \frac{2}{\pi^{1/2}}\int_0^x e^{-y^2}dy$$

$$erfc(x) \equiv 1 - \mathrm{erf}(x)$$

↓

Complementary function

The concentration profiles



$C_{Ox}(x,0) = C_{Ox}^*$

$D_{ox} = 1x10^{-5}\ cm^2/s$

Time after the application of the step potential

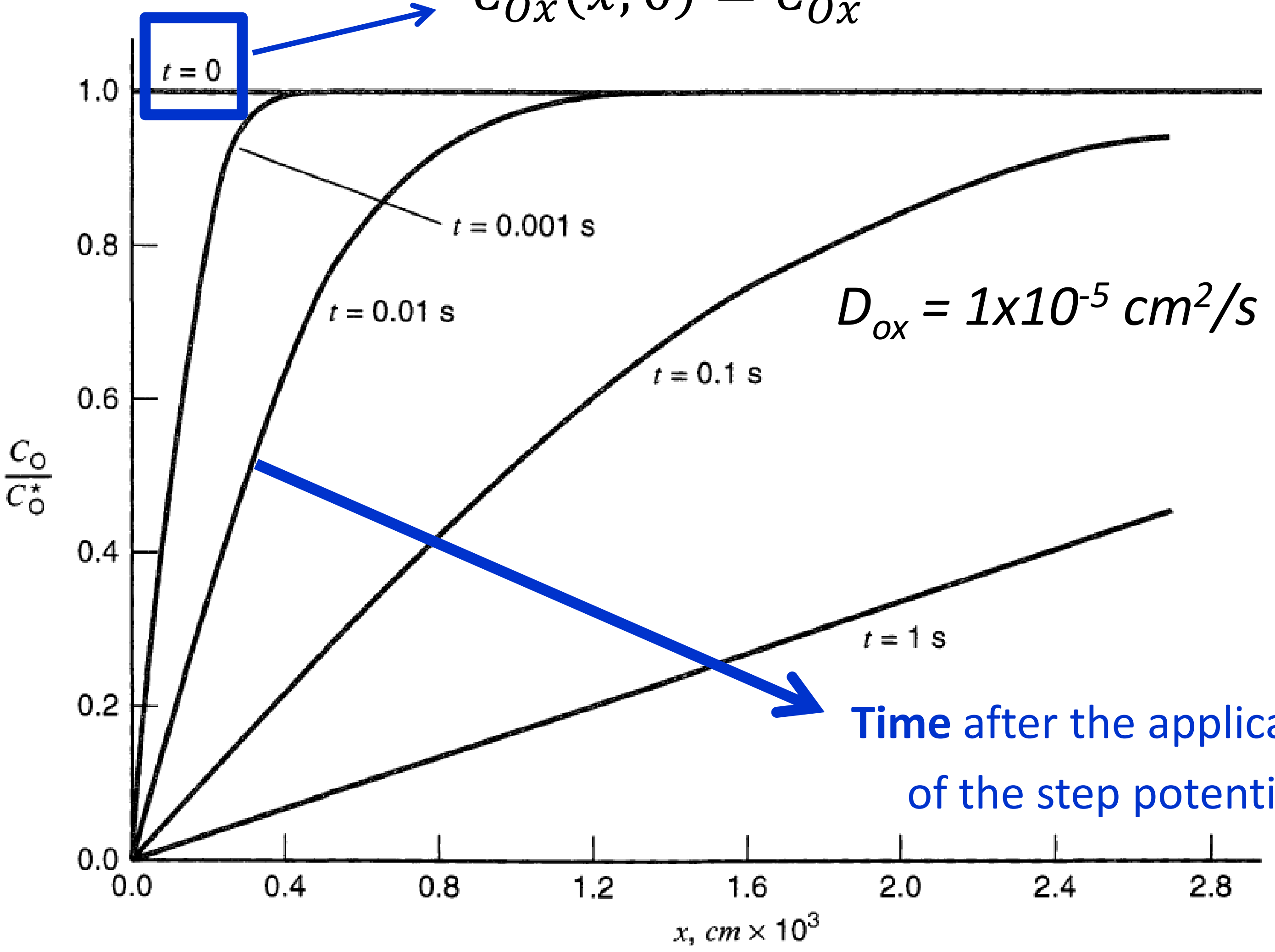
Bard & Faulkner, 2nd Ed., Wiley, 2001

$$\boldsymbol{C_{Ox}(x,t)} = C_{Ox}^*\ \boldsymbol{erf}\left[\frac{x}{2\sqrt{D_{Ox}t}}\right]$$

- **Time-dependent concentration profiles** near the electrode surface (as a function of the distance)
- Ox depletion at the surface with increasing times
- The **slope** of each concentration profile indicates the Ox **concentration gradient** $(\partial C_{Ox}(x,t)/\partial x)$ at various t

The concentration profiles

$$C_{Ox}(x,0) = C_{Ox}^{*}$$



$D_{ox} = 1x10^{-5}\ cm^2/s$

Time after the application of the step potential

Bard & Faulkner, 2nd Ed., Wiley, 2001

$$\boldsymbol{C_{Ox}(x,t)} = C_{Ox}^{*}\ \boldsymbol{erf}\left[\frac{x}{2\sqrt{D_{Ox}t}}\right]$$

- Profiles asymptotically tend to **C_{Ox}*** value

$$\frac{\partial C_{Ox}(x,t)}{\partial x} = 0 \Rightarrow C_{Ox}(x,t) = C_{Ox}^{*}$$

- Time-dependent **thickness of the diffusion layer**, which can be defined in terms of $\sqrt{\boldsymbol{D_{Ox}t}}$ (≈ $6\sqrt{D_{Ox}t}$)

The Cottrell Equation

$$-J_{Ox}(0,t) = \frac{i}{nFA} = D_{Ox}\left(\frac{\partial C_{Ox}(x,t)}{\partial x}\right)_{x=0}$$

$$\bar{C}_{Ox}(x,s) = \frac{C^*_{Ox}}{s} - \frac{C^*_{Ox}}{s}\, e^{\left[-\sqrt{\frac{s}{D_{Ox}}}x\right]}$$

$$\Big\downarrow \mathcal{L}$$

$$\frac{\bar{i}(s)}{nFA} = D_{Ox}\left(\frac{\partial \bar{C}_{Ox}(x,s)}{\partial x}\right)_{x=0} = D_{Ox}\left[-\frac{C^*_{Ox}}{s}\left(-\frac{s^{1/2}}{D_{Ox}^{1/2}}\right)e^{\left[-\sqrt{\frac{s}{D_{Ox}}}x\right]}\right]_{x=0} = D_{Ox}\left(\frac{C^*_{Ox}}{s^{1/2}D_{Ox}^{1/2}}\right)$$

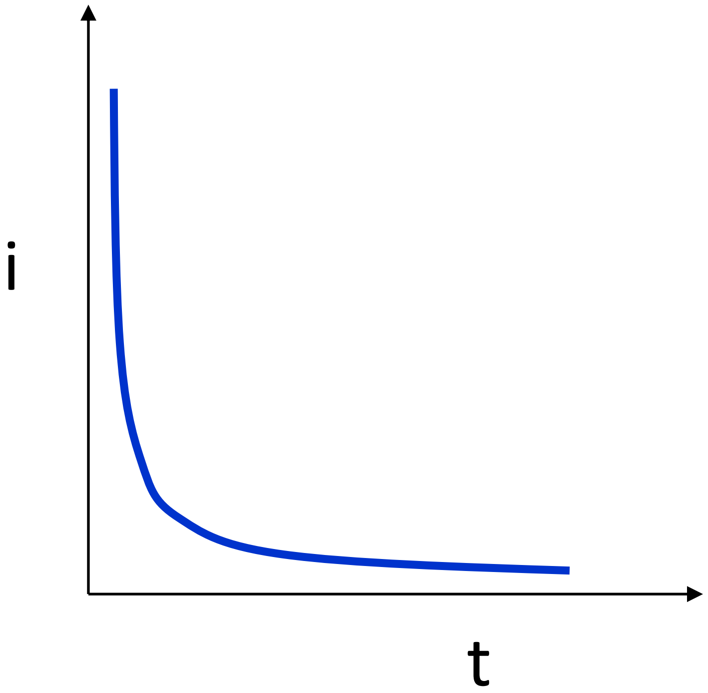
$$\bar{i}(s) = \frac{nFAD_{Ox}^{1/2}C^*_{Ox}}{s^{1/2}} \xrightarrow{\mathcal{L}^{-1}} i(t) = \frac{nFAD_{Ox}^{1/2}C^*_{Ox}}{\pi^{1/2}t^{1/2}}$$

Cottrell Equation

The Cottrell Equation

$$\boldsymbol{i}(\boldsymbol{t}) = \frac{nFAD_{Ox}^{1/2}C_{Ox}^{*}}{\pi^{1/2}\boldsymbol{t}^{\mathbf{1/2}}}$$

F. G. Cottrell
(1877 - 1948)



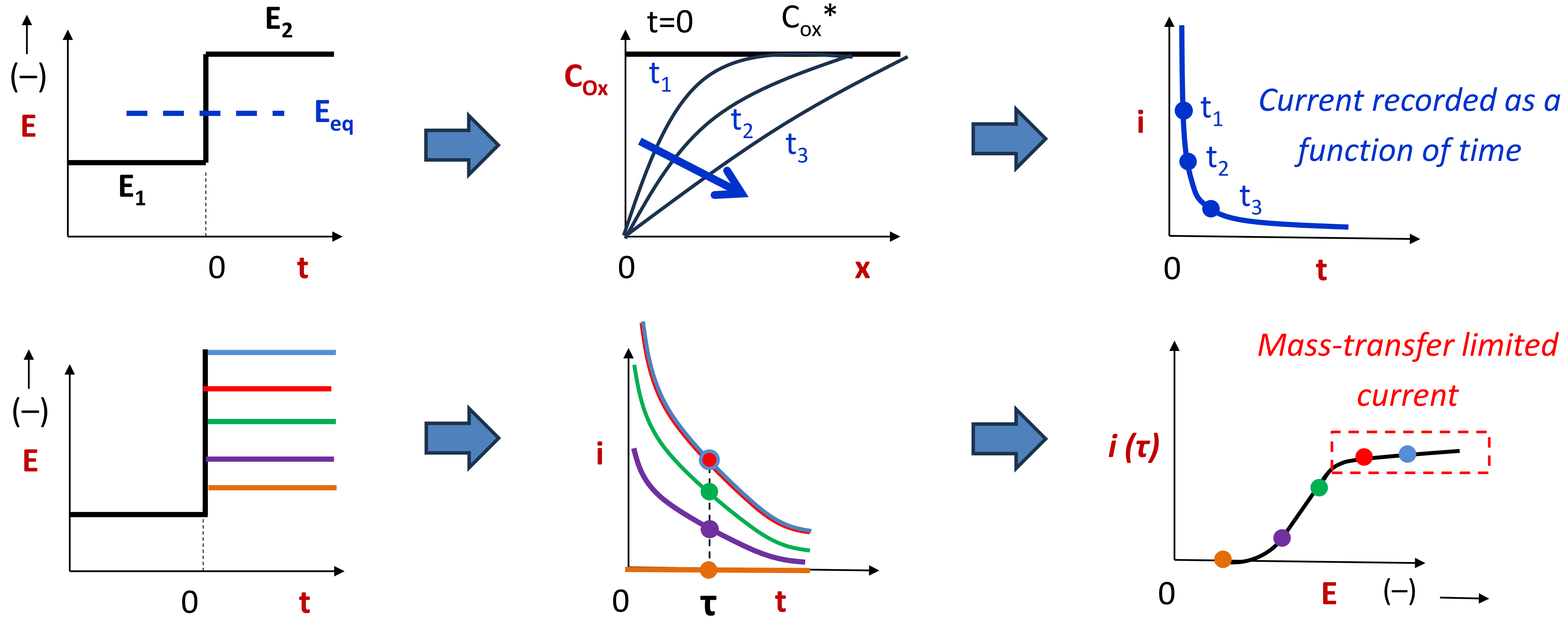
- Effect of depletion of Ox near the surface
- ***Faradaic* current inversely proportional to $\mathbf{t^{1/2}}$** (i decrease with time)
- The **linear** dependence of **i vs. $\mathbf{1/t^{1/2}}$** is **diagnostic test** for diffusion-controlled electrochemical process
- Cottrell behaviour not observed at **very short times** due to **capacitive or *non-faradaic* current** (“charging” current),

$$\boldsymbol{i_C} \propto \mathbf{1/exp}(\boldsymbol{t})$$

Chronoamperometry

$$i(t) = \frac{nFAD_{Ox}^{1/2}C_{Ox}^{*}}{\pi^{1/2}t^{1/2}}$$

Diffusion-limited current at E_2



Current recorded as a function of time

Mass-transfer limited current