

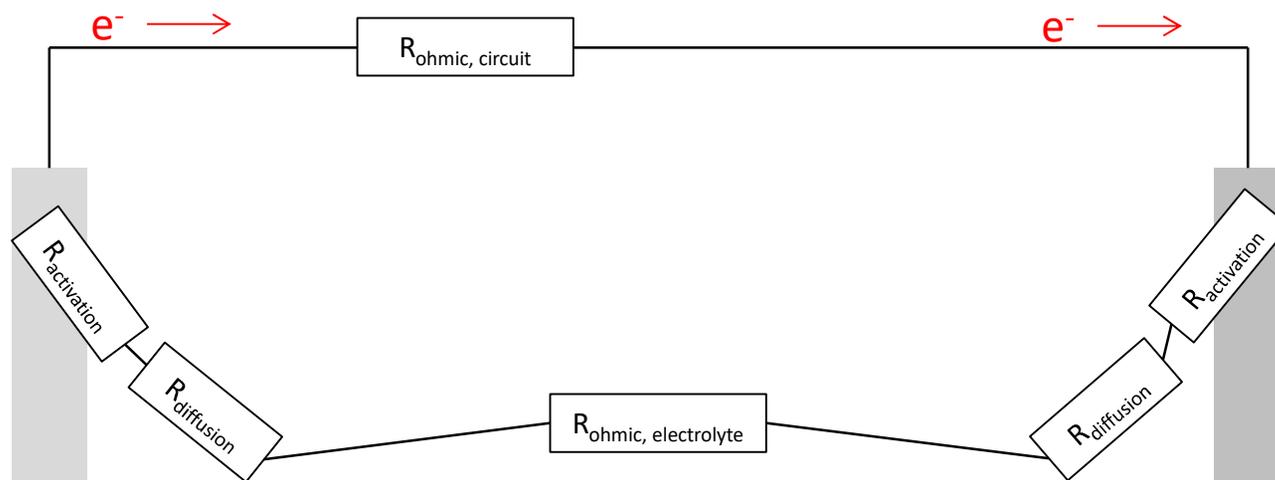
Microbial electrochemical technologies – fundamental aspects and methods of analysis

Week 3 – Kinetics

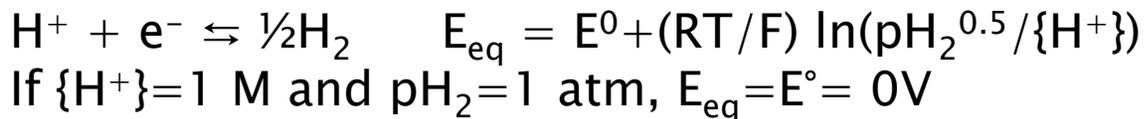
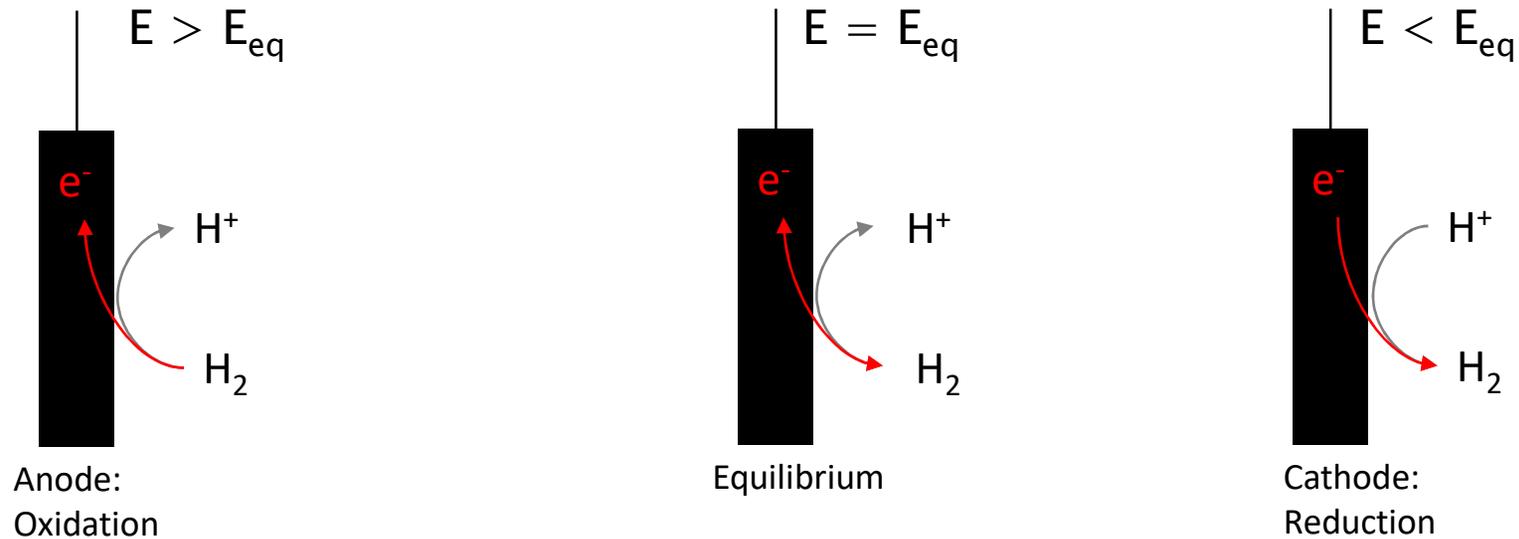
- Activation energy and catalysts
- Electrode reaction kinetics
- Deriving the current-overpotential equation
- Tafel plots

Before we start...

- **Remember activation losses**
 - A cause of potential losses in electrochemical reactors
 - Has to do with the slowness of charge transfer between the electrode and the electrolyte, **i.e. kinetics**

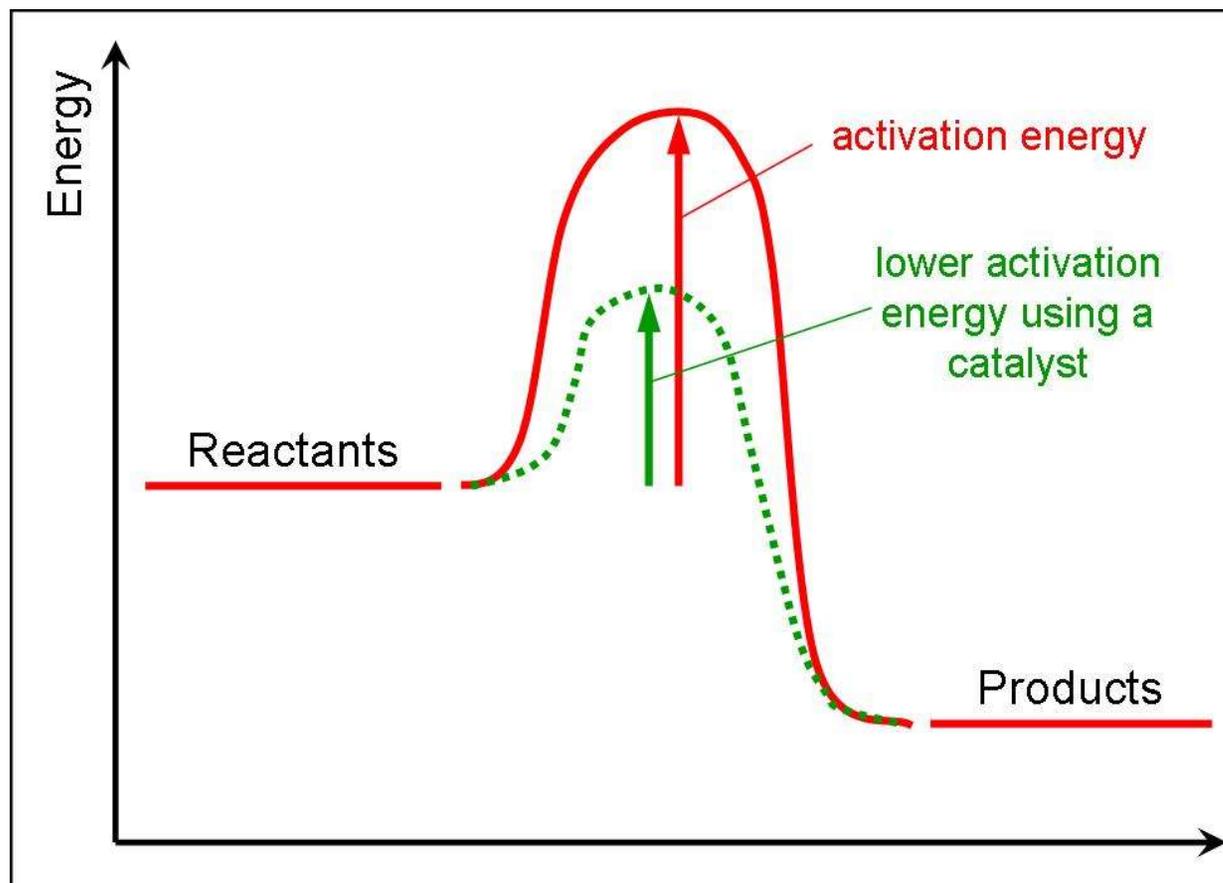


Electrode reaction kinetics



At E_{eq} oxidation and reduction reaction rates are the same, no net current
 If we raise $E_{electrode} \rightarrow$ anodic current is flowing
 If we lower $E_{electrode} \rightarrow$ cathodic current is flowing

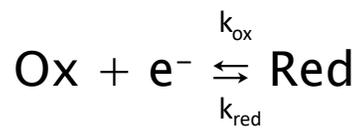
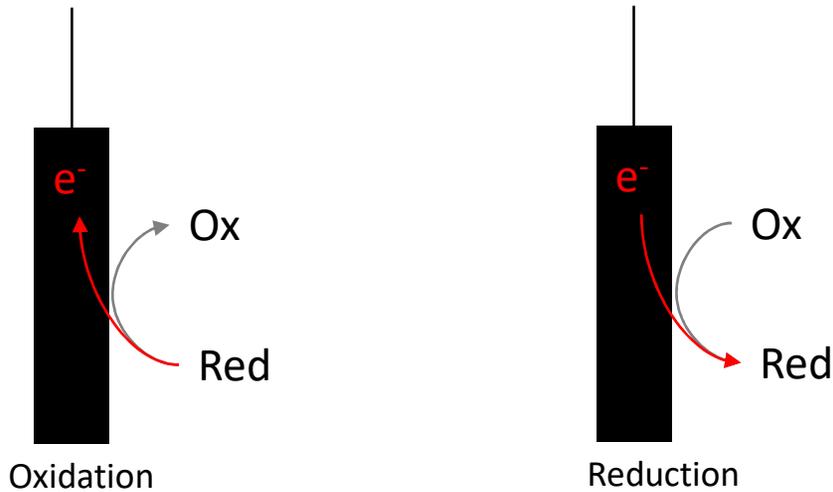
Activation energy and effect of catalysts



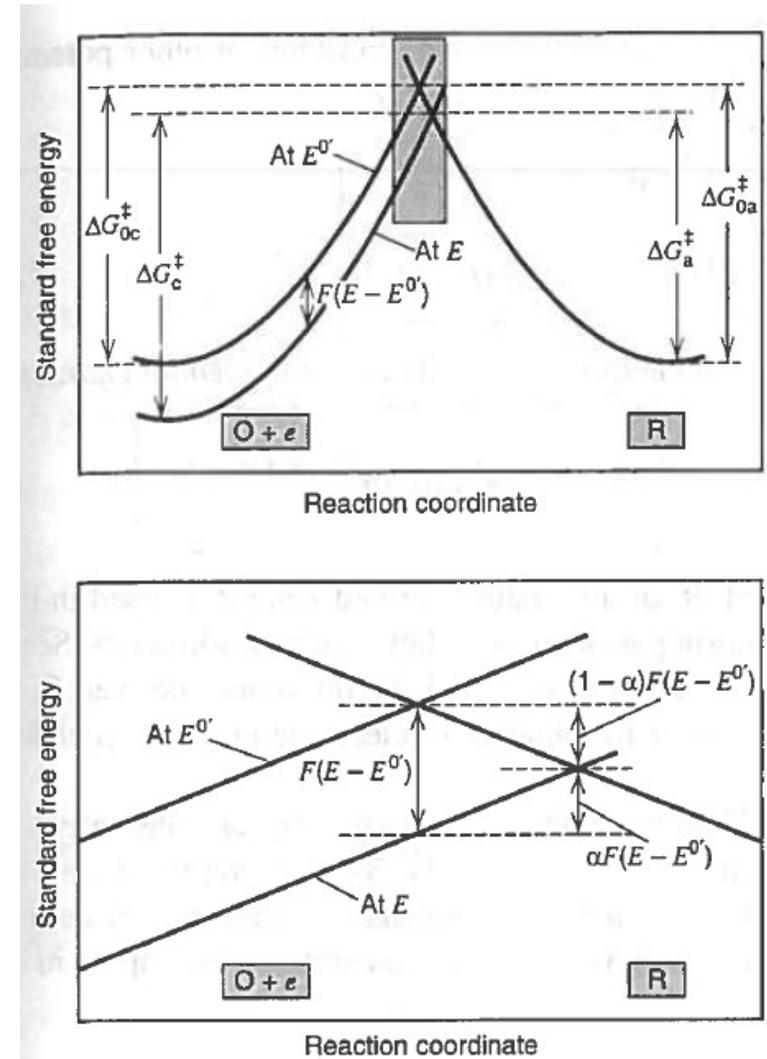
Rate of reaction described by Arrhenius equation:

$$k = A * e^{-E_a/RT}$$

Electrode reaction kinetics – deriving an expression 1



At E^0 anodic and cathodic activation energies are the same



Electrode reaction kinetics – deriving an expression 2

- If we change the electrode potential from E^0 , the anodic and cathodic activation energies will change
- $\Delta G_c = \Delta G_c^0 + \alpha F(E - E^0)$
- $\Delta G_a = \Delta G_a^0 - (1 - \alpha)F(E - E^0)$

- Insert activation energies into Arrhenius expressions:
- $k_{\text{red}} = A_{\text{red}} \exp(-\Delta G_c / RT)$
- $k_{\text{ox}} = A_{\text{ox}} \exp(-\Delta G_a / RT)$

- $k_{\text{red}} = A_{\text{red}} \exp(-\Delta G_c^0 / RT) \exp[-\alpha(F/RT)(E - E^0)]$
- $k_{\text{ox}} = A_{\text{ox}} \exp(-\Delta G_a^0 / RT) \exp[(1 - \alpha)(F/RT)(E - E^0)]$

- The first two factors describe the rate constant at equilibrium, rate of oxidation is the same as rate of reduction ($k^0 = \text{standard rate constant}$)
- $k_{\text{red}} = k^0 \exp[-\alpha(F/RT)(E - E^0)]$
- $k_{\text{ox}} = k^0 \exp[(1 - \alpha)(F/RT)(E - E^0)]$

Electrode reaction kinetics – deriving an expression 3

- $Ox + e^- \rightleftharpoons Red$
- $I_c = nFA k_{red} C_{ox}$ $(n=1 e^- \text{ in this case})$
- $I_a = nFA k_{ox} C_{red}$
- $I = I_c - I_a$

- Remember expressions for k coefficients
- $I = FAK^\circ(C_{ox} \exp[-\alpha(F/RT)(E-E^0)] - C_{red} \exp[(1-\alpha)(F/RT)(E-E^0)])$
- -----
- At equilibrium conditions, $I_c = I_a$ and the bulk concentrations $C_{eq,Ox}$ and $C_{eq,Red}$ are found at the electrode surfaces
- $FAK^\circ C_{eq,ox} \exp[-\alpha(F/RT)(E-E^0)] = FAK^\circ C_{eq,Red} \exp[(1-\alpha)(F/RT)(E-E^0)]$

- Rearranging the above equations yields the following, *which works out to the Nernst equation*
- $\frac{C_{eq,Ox}}{C_{eq,Red}} = e^{\frac{F}{RT}(E_{eq} - E^0)}$

- The net current is zero, but there is still a transfer of electrons to and from the electrode, this is the *exchange current*, I_0 .
- $I_0 = FAK^\circ C_{eq,ox} \exp[-\alpha(F/RT)(E-E^0)]$
- Raise both sides of the Nernst expression to $-\alpha$ and insert $\rightarrow I_0 = FAK^\circ C_{eq,ox}^{(1-\alpha)} C_{eq,Red}^{(\alpha)}$
- **The exchange current is proportional to the standard rate constant**

Electrode reaction kinetics – deriving an expression 4

- By dividing the expression for I with the expression for I_0 we get the current-overpotential equation

- $$I = I_0 \left[\frac{C_{Ox}}{C_{eq,Ox}} e^{-\alpha f \eta} - \frac{C_{Red}}{C_{eq,Red}} e^{(1-\alpha) f \eta} \right]$$

- $f = F/RT$

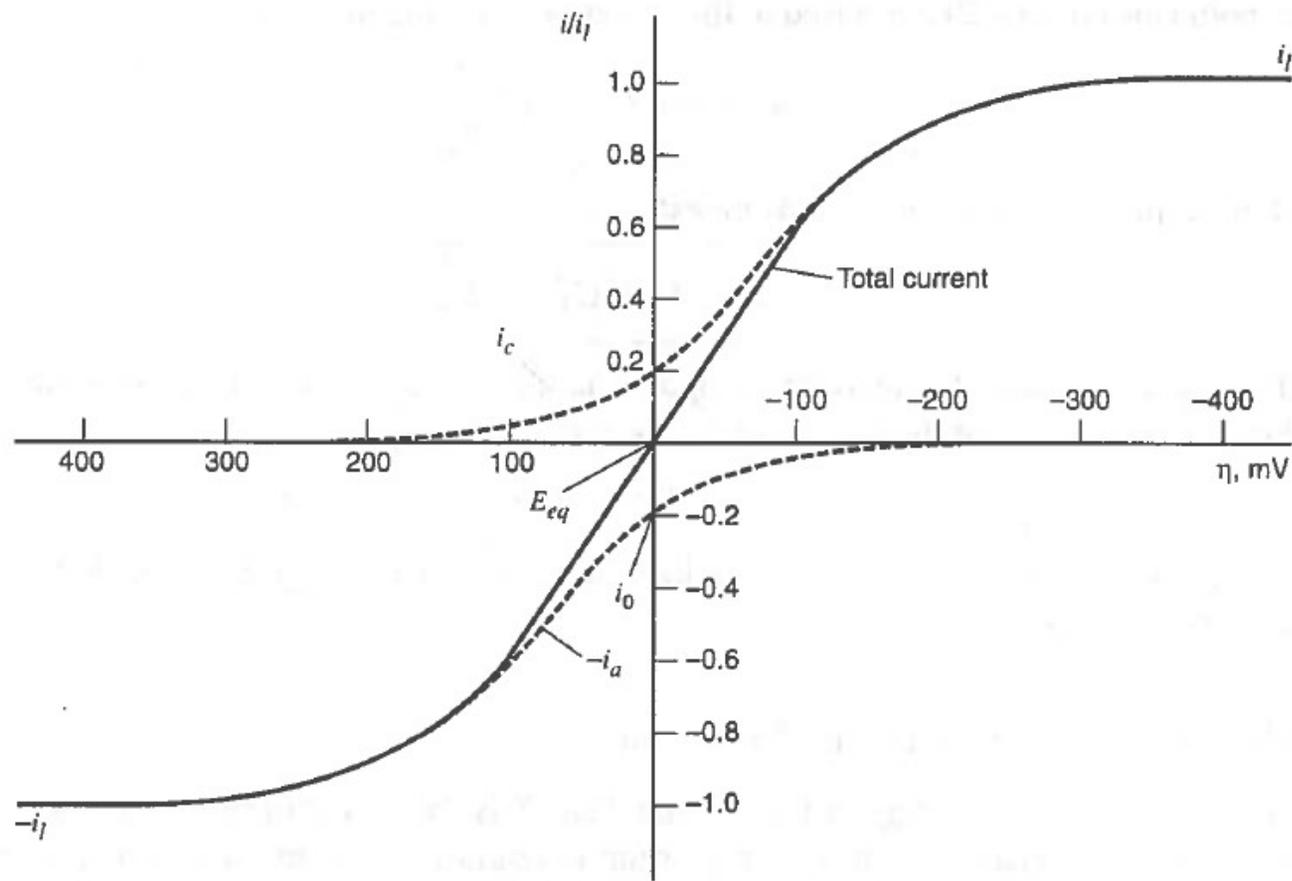
- $\eta = E - E_{eq}$ (overpotential)

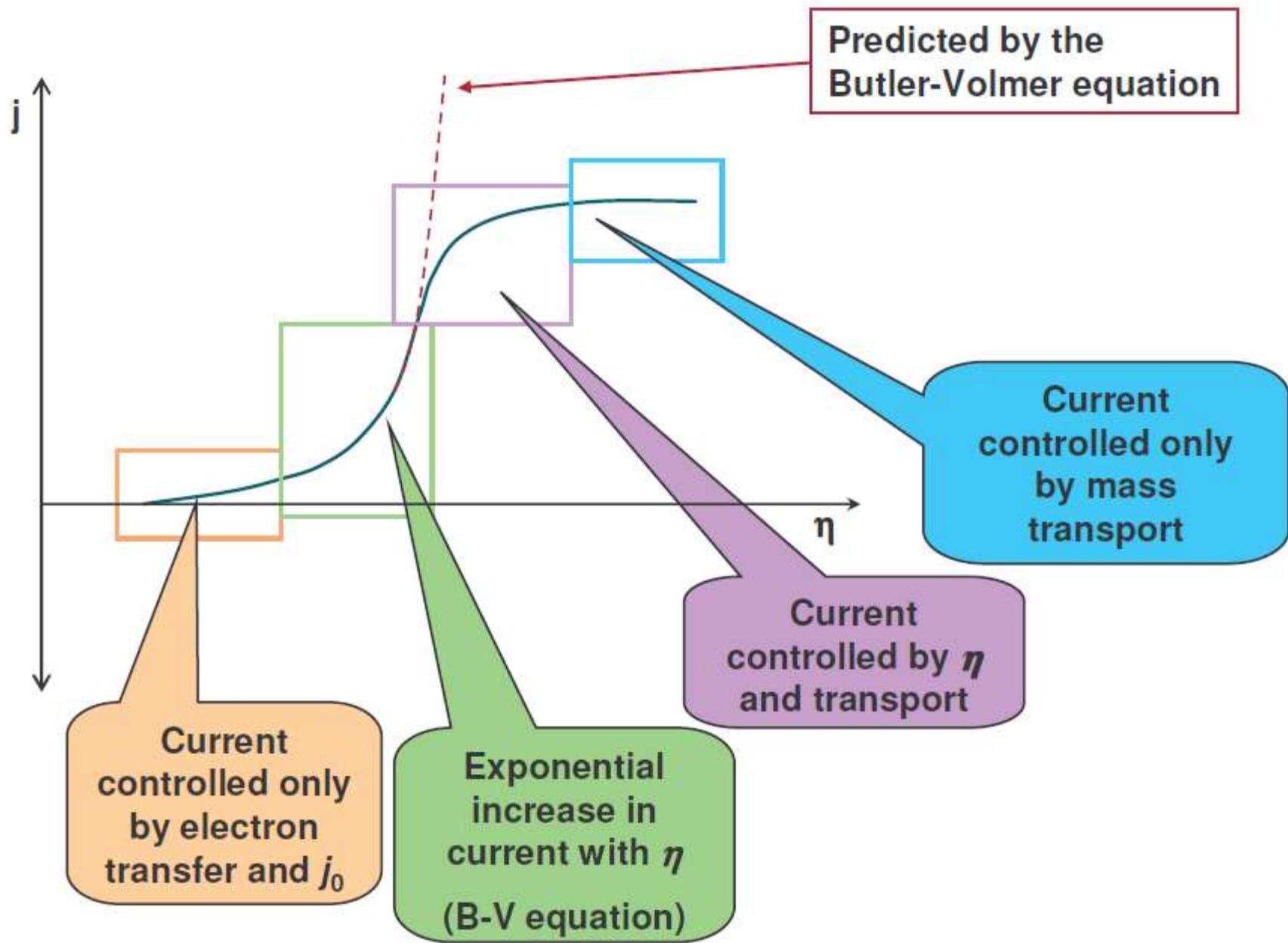
- C_{Ox} C_{Red} = Concentration near electrode surface

- $C_{eq,Ox}$ $C_{eq,Red}$ = Concentrations in bulk liquid (corresponding to E_{eq})

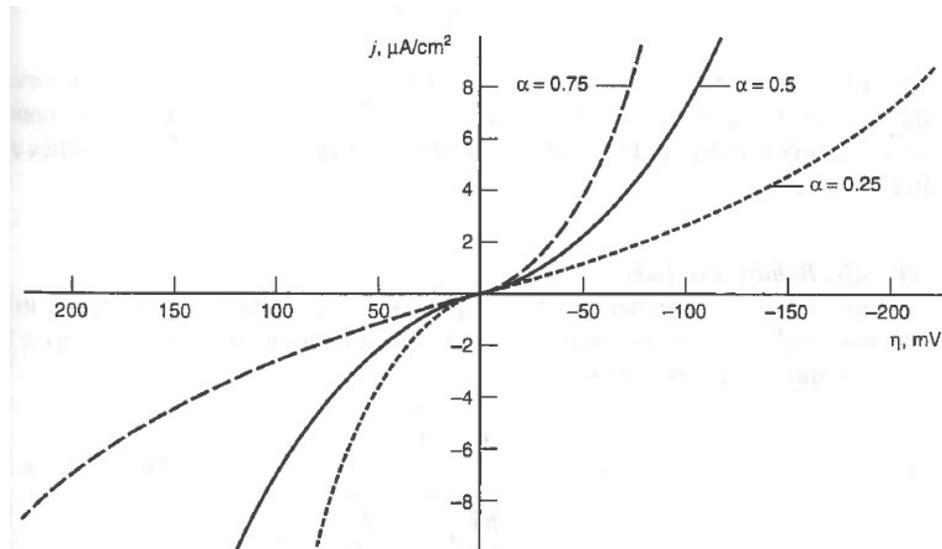
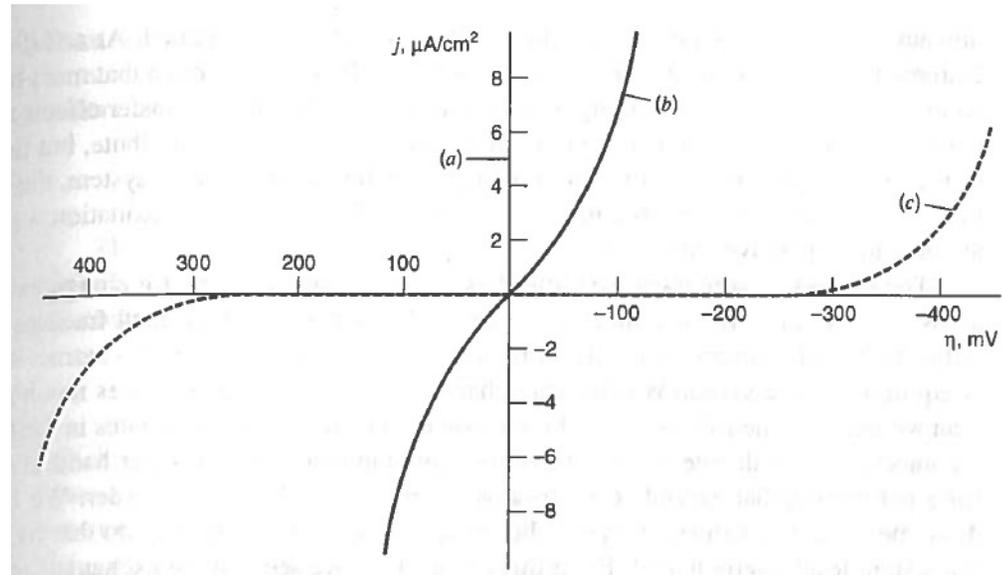
- $$I = I_0 [e^{-\alpha f \eta} - e^{(1-\alpha) f \eta}]$$
 (Simplified equation not taking diffusion limitation into account, this is called the Butler-Volmer equation)

Current-overpotential relationship





Meaning of I_0 and α

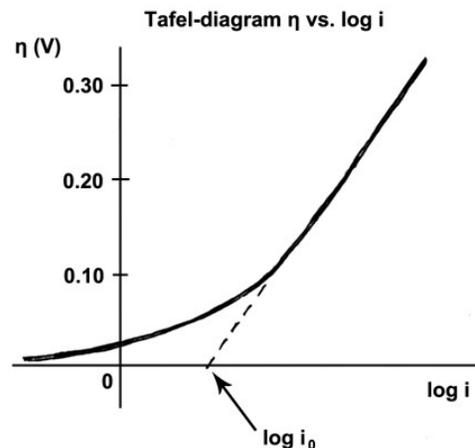


Limiting case 1 – small η

- At small x , $e^x = 1+x$
- Thus, Butler-Volmer equation simplified to
$$I = -I_0 * f * \eta$$

Limiting case 2 - Tafel equation at large η

- $I = I_0 [e^{-\alpha f \eta} - e^{(1-\alpha) f \eta}]$
- If η is very negative, $e^{-\alpha f \eta} \gg e^{(1-\alpha) f \eta}$
- $I = I_0 [e^{-\alpha f \eta}] \rightarrow \ln(I/I_0) = -\alpha f \eta$
- **$\ln(I) = \ln(I_0) - \alpha f \eta$ (Tafel equation)**
- This relationship holds when systems are not mass transfer limited



An example

- Saheb-Alam et al. (2015). Effects of storage on mixed-culture biological electrodes. *Scientific Reports*, 5:18433.

Final notes

- Current, I , is equivalent to the rate of reaction
- Usually we talk about current densities, i , which is current per unit area (A/m^2)
- The presence of a catalyst on the electrode surface will increase i by lowering the activation energy of the reaction. This can be seen as an increase in the exchange current, i_0 .