



EMA4303/5305
Electrochemical Engineering
Lecture 03
Electrochemical Kinetics

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Electrochemical Kinetics

□ Electrochemical kinetics

“**Electrochemical kinetics is a field of electrochemistry studying the rate of electrochemical processes.** Due to electrochemical phenomena unfolding at the interface between an electrode and an electrolyte, there are accompanying phenomena to electrochemical reactions which contribute to the overall reaction rate.” (Wikipedia)

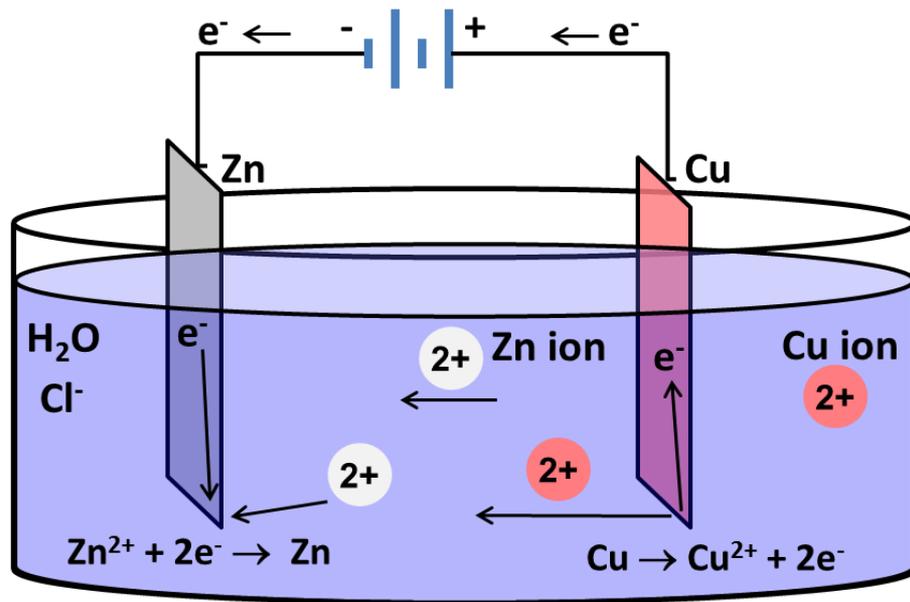
“The main goal of the electrochemical kinetics is to find **a relationship between the electrode overpotential and current density** due to an applied potential.” (S. N. Lvov)

□ Main contents of this lecture

- Overpotential (η)
- Charge transfer overpotential
 - **Butler-Volmer equation**
 - Tafel equation
- Mass transfer overpotential

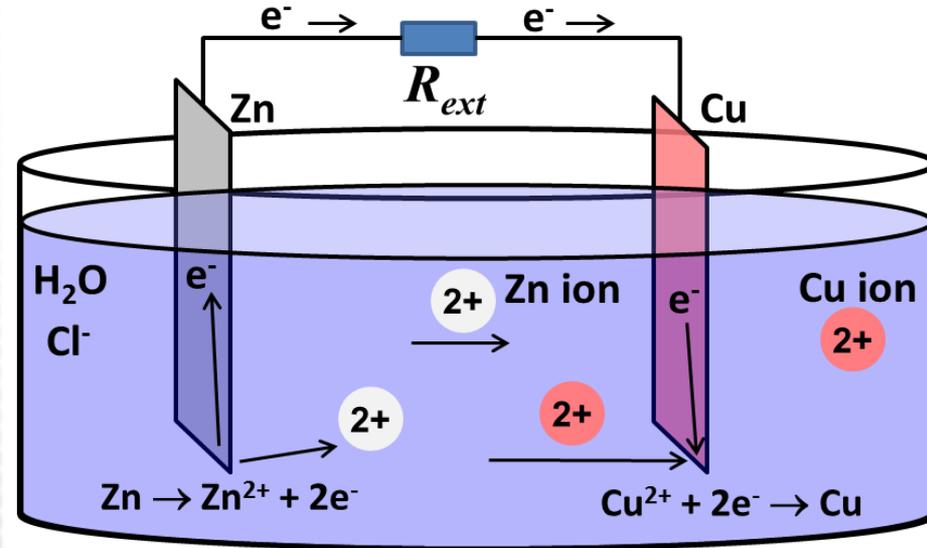


Cell Potential in Different Modes



Electrolytic cell (EC)

$$E_{\text{Applied}} = E_{\text{EQ}} + IR_{\text{int}}$$



Galvanic cell (GC)

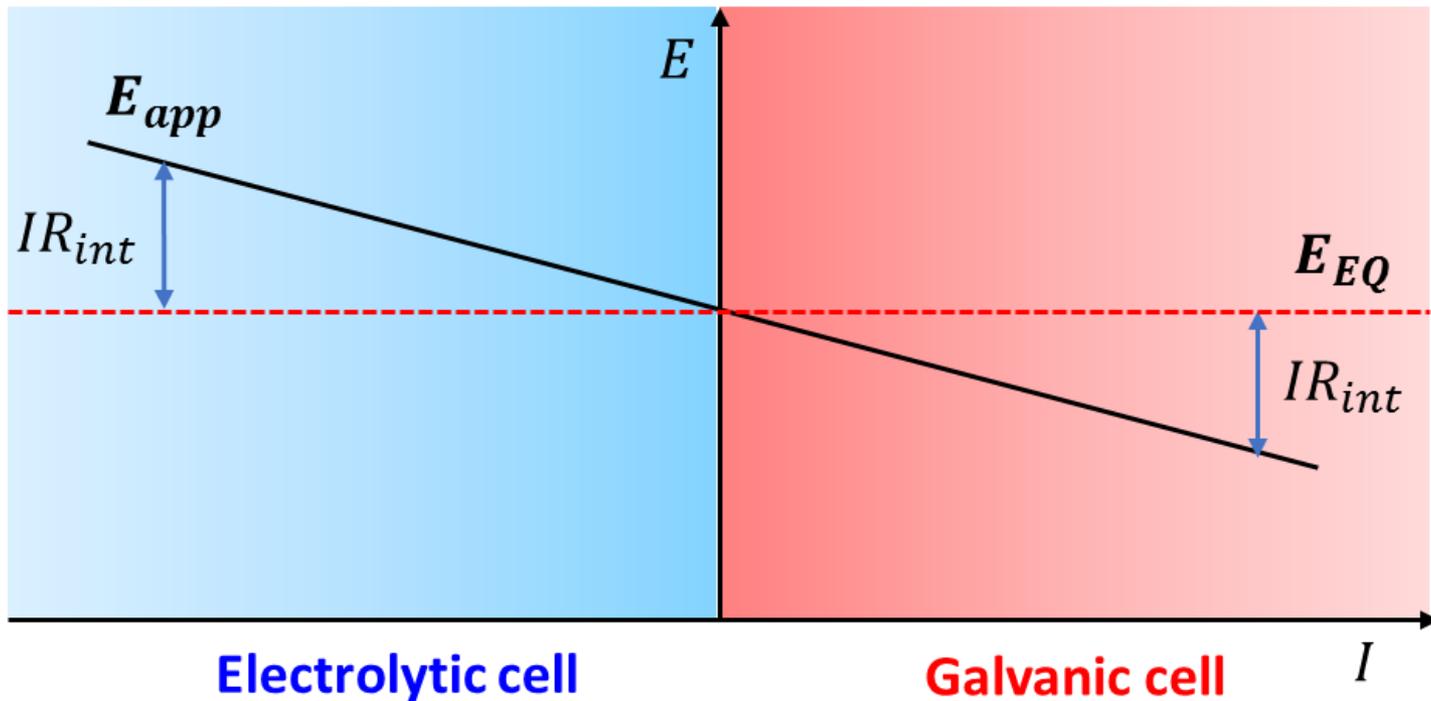
$$E_{\text{EQ}} = I (R_{\text{ext}} + R_{\text{int}})$$

$$E_{\text{ext}} = E_{\text{EQ}} - IR_{\text{int}} = IR_{\text{ext}}$$



Cell Potential-Current Dependence

- R_{int} represents the total internal resistance of the cell, which is usually not zero, in most cases. Therefore, the difference between cell equilibrium potential and apparent potential is proportional to the current passing through the cell.



Cell potential-current dependences



Overpotential (η)

□ Overpotential for a single electrode

- The difference between the actual potential (measured) for an electrode, E , and the equilibrium potential for that electrode, E_{EQ} , is called the overpotential of that electrode, $\eta = E - E_{EQ}$, which could be either positive or negative, depending on the direction of the half (cell) reaction.

□ Difference between cell equilibrium potential and external potential

- The total difference between cell equilibrium potential and actual cell potential, is due to the cell internal resistance R_{int} :

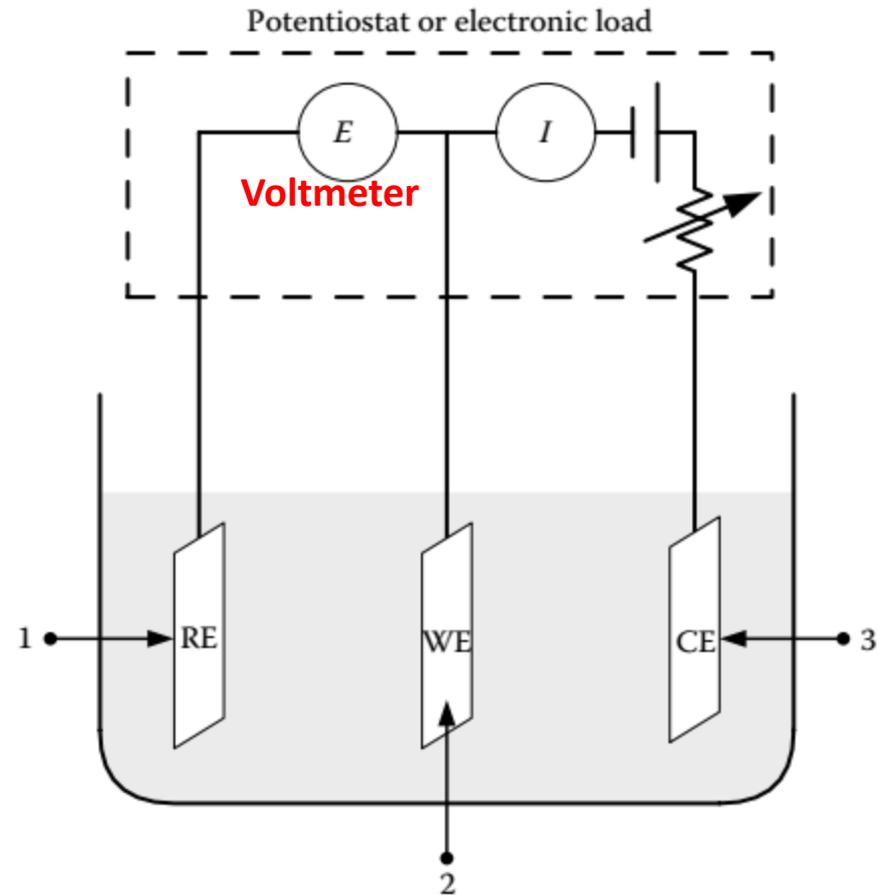
$$\Delta E_{GC} = E_{EQ} - E_{ext} = IR_{int} = \eta_{Electrodes} + IR_{\Omega}$$

$$\Delta E_{EC} = E_{App} - E_{EQ} = IR_{int} = \eta_{Electrodes} + IR_{\Omega}$$

- In a **galvanic cell**, as $E_{ext} < E_{EQ}$, less energy is converted to outside electrical work (i.e., $E_{ext}Q$) than would be predicted under equilibrium condition, i.e., $E_{EQ}Q$
- In an **electrolytic cell**, as $E_{app} > E_{EQ}$, the amount of electrical energy provided $E_{App}Q$ is higher than what is actually stored as chemical energy, $E_{EQ}Q$.
- For an electrochemical cell, the total electrode overpotential consists of contributions from both the anode and the cathode, the contribution for an individual electrode cannot be separated without using a third electrode, or reference electrode

Measurement of Overpotential for A Single Electrode

- The over-potential for an electrode that is passing a current (**working electrode, WE**) cannot, in general, be determined by measurement with respect to the other current-carrying electrode (**counter electrode, CE**) in an electrochemical cell. A third electrode needs to be introduced into the cell as the **reference electrode (RE)**.
- The measured potential difference between the WE and RE allows the determination of the potential of WE with respect to the RE. If the potential difference under equilibrium is also measured, the “overpotential” for the WE under a given current could be obtained as a function of current.
- To avoid any overpotential contribution from the RE, no significant current must pass through RE, which can be achieved with a **high impedance voltmeter**.



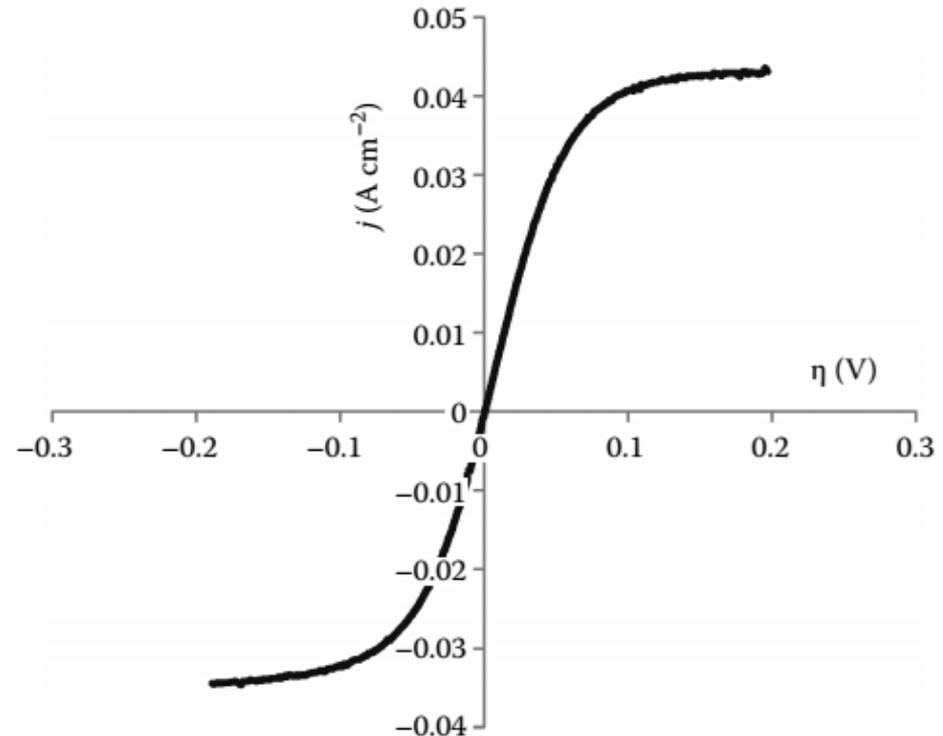
Three-electrode electrochemical cell

S. Lvov, CRC Press (2015). ISBN: 978-1-4665-8285-9



Polarization Curve of A Single Electrode

- Plot of current density (j) versus electrode overpotential (η) measure with above three-electrode cell is called the **polarization curve**.
- **Anodic polarization** (E is more positive than E_{EQ}) is related to the oxidation electrode (or half (cell)) reaction and **cathodic polarization** (E is more negative than E_{EQ}) related to the reduction reaction.
- **The current-potential can be highly nonlinear**. A limiting value for the current density is shown.



Polarization curve of a single $\text{Cu}^{2+}(\text{aq}, 0.1 \text{ mol/kg}) / \text{Cu}^{+}(\text{aq}, 0.1 \text{ mol/kg})$ redox electrode taken at ambient temperature and pressure with $\text{HCl}(\text{aq})$ concentration of 8 mol/kg

S. Lvov, CRC Press (2015). ISBN: 978-1-4665-8285-9



Main Contributions to Overpotential

❑ Charge (electron) transfer overpotential

- At low current, the rate of change of electrode potential with current is associated with the limiting rate of electron transfer across the electrode-solution interface, and is termed as **charge (electron) transfer overpotential**.

❑ Mass transfer overpotential

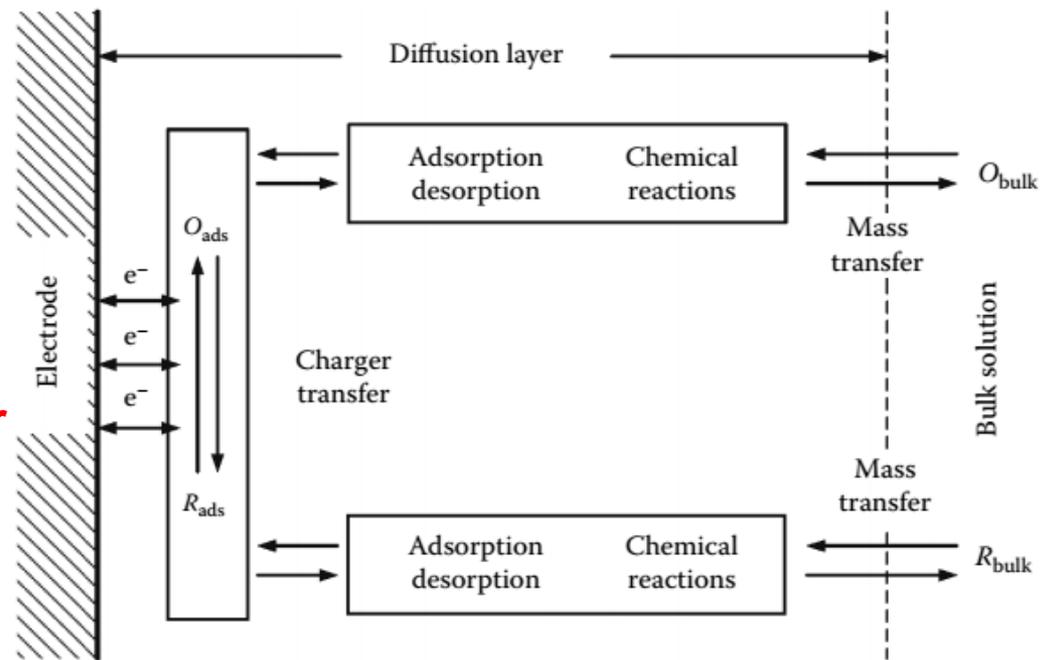
- At higher current densities, the electron transfer rate is usually no longer limiting, instead, limitations arise through delivering reactants to the electrochemical reaction interface or transporting products to the bulk solution (**mass transfer overpotential**).

❑ Others

- Chemical reactions
- Adsorption/desorption

The total overpotential of a single electrode is the sum of all contributions:

$$\eta = \sum \eta_i$$



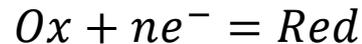
Possible processes in considering the mechanism of an electrochemical reaction

S. Lvov, CRC Press (2015). ISBN: 978-1-4665-8285-9



Charge Transfer Overpotential: Butler-Volmer Equation

For an electrochemical half-reaction:



Taking into account that the cathodic direction is from the left to right and anodic is from the right to left, an equation describing the current density, j , as a function of overpotential, η , for an elementary (one-step) electrochemical reaction can be derived:

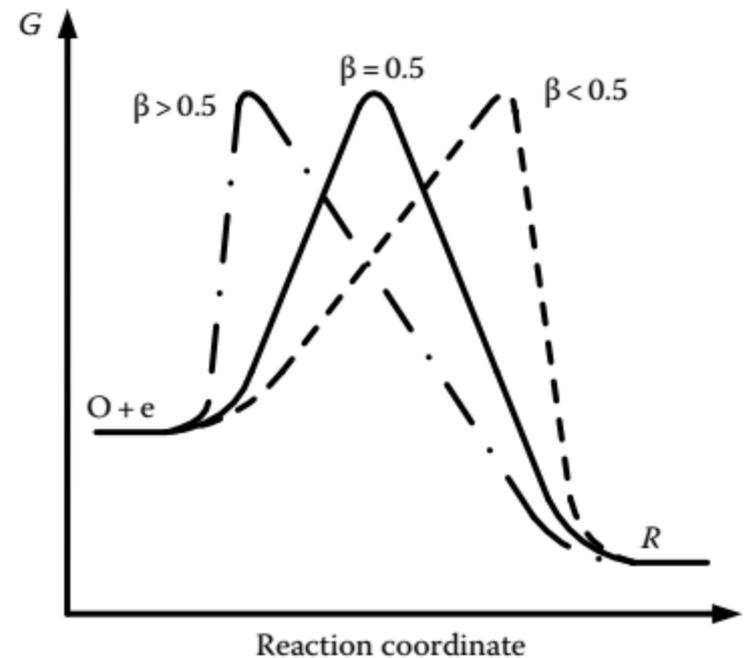
$$j = j_a + j_c = j_o \left[\exp \left\{ \frac{(1 - \beta)nF\eta}{RT} \right\} - \exp \left\{ \frac{-\beta nF\eta}{RT} \right\} \right]$$

where j_o is the exchange current density, β is the symmetry factor. This is called the **Butler-Volmer equation**, which allows expressing the current-overpotential dependence in a relatively close region to the equilibrium point ($\eta = 0$, and $j = 0$). Butler-Volmer equation is one of the most important equations in the electrochemical science and engineering and is the fundamental equation of electrode kinetics that describes the exponential relationship between the current density and the electrode potential. One of the key assumptions in deriving the equation is that the electrochemically active solution at the electrode is extensively stirred and the current is kept so low that the concentrations at the site of the electrochemical reactions (electrode surface) do not substantially differ from the bulk values.



Symmetry factor (β)

- For a reduction reaction to take place, some Gibbs energy, G , should be provided to overcome the energy barrier and reach an activated complex located on the top of the G -Reaction coordinate curve. The same approach can be used to explain the reverse oxidation reaction.
- β is an indicator of the symmetry of the Gibbs energy barrier and ranges from 0 to 1. The Gibbs energy barrier is symmetrical when $\beta = 0.5$.



Influence of symmetry factor (β) on the shape of the energy barrier of an electrochemical reduction ($Ox + e^- \rightarrow Red$) and oxidation ($Red \rightarrow Ox + e^-$) reactions.

S. Lvov, CRC Press (2015). ISBN: 978-1-4665-8285-9

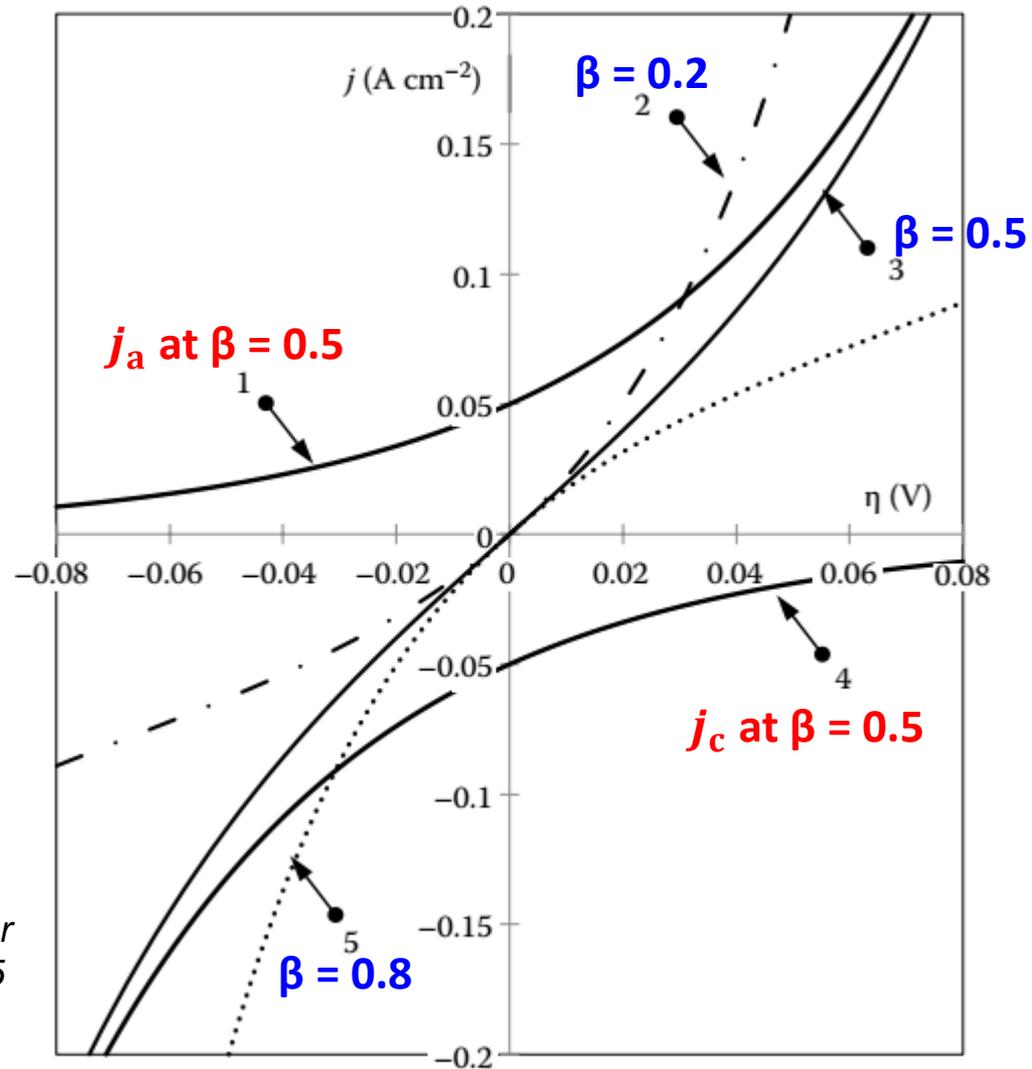


Exchange current density (j_0)

- $\beta = 0.5$, the polarization curve is symmetrical (curve #3)
- $\beta > 0.5$, the polarization curve is not symmetrical (curve #5)
- $\beta < 0.5$, the polarization curve is not symmetrical either (curve #2).
- When the electrode reaction is in a dynamic equilibrium ($\eta = 0$, and $j = 0$), the magnitude of j_a and j_c are both equal to j_0 (0.05 A/cm²).
- Larger j_0 means electrochemical reaction is intrinsically fast,
smaller j_0 means
electrochemical reaction is slow.

Current density vs. overpotential using Butler-Volmer equation to clarify its behavior plotted with j_0 of 0.05 A/cm² and temperature of 298.15 K.

S. Lvov, CRC Press (2015). ISBN: 978-1-4665-8285-9





Experimental Data on β and j_o

The amount of data on the exchange current density and symmetry factor is very limited due to experimental difficulties and insufficient studies in this area of electrochemical science and engineering.

Experimental Values of Exchange Current Density, Standard Exchange Current Density and Symmetry Coefficient

Electrode and Concentration of Aqueous Species	Aqueous Electrolyte	t (°C)	Electrode	j_o (A cm ⁻²)	j_o° (A cm ⁻²)	β
Fe ³⁺ /Fe ²⁺ (0.005 mol/L)	1 mol/L H ₂ SO ₄	25	Pt	2×10^{-3}	4×10^{-1}	0.42
K ₃ Fe(CN) ₆ /K ₄ Fe(CN) ₆ (0.02 mol/L)	0.5 mol/L K ₂ SO ₄	25	Pt	5×10^{-3}	5	0.51
Ag ⁺ /Ag (0.001 mol/L)	1 mol/L HClO ₄	25	Ag	1.5×10^{-1}	13.4	0.35
Cd ²⁺ /Cd (0.01 mol/L)	0.4 mol/L K ₂ SO ₄	25	Cd	1.5×10^{-3}	1.9×10^{-2}	0.45
Cd ²⁺ /Cd(Hg) (0.0014 mol/L)	0.5 mol/L Na ₂ SO ₄	25	Cd(Hg)	2.5×10^{-2}	4.8	0.2
Zn ²⁺ /Zn(Hg) (0.02 mol/L)	1 mol/L HClO ₄	25	Zn(Hg)	5.5×10^{-3}	0.10	0.25
Ti ⁴⁺ /Ti ³⁺ (0.001 mol/L)	1 mol/L C ₂ H ₄ O ₂	0	Pt	9×10^{-4}	0.9	0.45
H ₂ O/H ₂ , OH ⁻	1 mol/L KOH	25	Pt	10^{-3}	10^{-3}	0.5
H ⁺ /H ₂	1 mol/L H ₂ SO ₄	25	Hg	10^{-12}	10^{-12}	0.5
H ⁺ /H ₂	1 mol/L H ₂ SO ₄	25	Pt	10^{-3}	10^{-3}	0.5
H ₂ O/O ₂ , OH ⁻	1 mol/L KOH	25	Pt	10^{-6}	10^{-6}	0.7
H ⁺ , O ₂ /H ₂ O	1 mol/L H ₂ SO ₄	25	Pt	10^{-6}	10^{-6}	0.75

S. Lvov, CRC Press (2015). ISBN: 978-1-4665-8285-9



Simplification of Butler-Volmer Equation

- At a very small overpotential ($|\eta| < 10$ mV), the exponents in the equation are small enough to expand both of them taking into account that $e^x \approx 1 + x$:

$$j = j_o \left[\exp \left\{ \frac{(1 - \beta)nF\eta}{RT} \right\} - \exp \left\{ \frac{-\beta nF\eta}{RT} \right\} \right] = j_o \left[\left\{ 1 + \frac{(1 - \beta)nF\eta}{RT} \right\} - \left\{ 1 + \frac{-\beta nF\eta}{RT} \right\} \right]$$

$$j = \frac{j_o nF\eta}{RT}$$

in which the current density is proportional to overpotential.

- When the electrode is highly cathodically polarized, $\eta \ll 0$, the first term of the equation is very small and the equation is simplified to:

$$j = -j_o \exp \left[\frac{-\beta nF\eta}{RT} \right]$$

- When the electrode is highly anodically polarized, $\eta \gg 0$, the second term of the equation is very small and the equation is simplified to:

$$j = j_o \exp \left[\frac{(1 - \beta)nF\eta}{RT} \right]$$



Tafel Equation (1)

Let us take the natural logarithm of the above two simplified B-V equations :

- When $\eta \ll 0$ (large cathodic polarization), consider only absolute value

$$|j| = j_0 \exp\left[\frac{-\beta n F \eta}{RT}\right] \quad \eta = \left[\frac{RT}{\beta n F}\right] \ln j_0 - \left[\frac{RT}{\beta n F}\right] \ln |j|$$

- When $\eta \gg 0$ (large anodic polarization),

$$j = j_0 \exp\left[\frac{(1 - \beta) n F \eta}{RT}\right] \eta = - \left[\frac{RT}{(1 - \beta) n F}\right] \ln j_0 + \left[\frac{RT}{(1 - \beta) n F}\right] \ln j$$

- Both of the above equations can be presented in a general form:

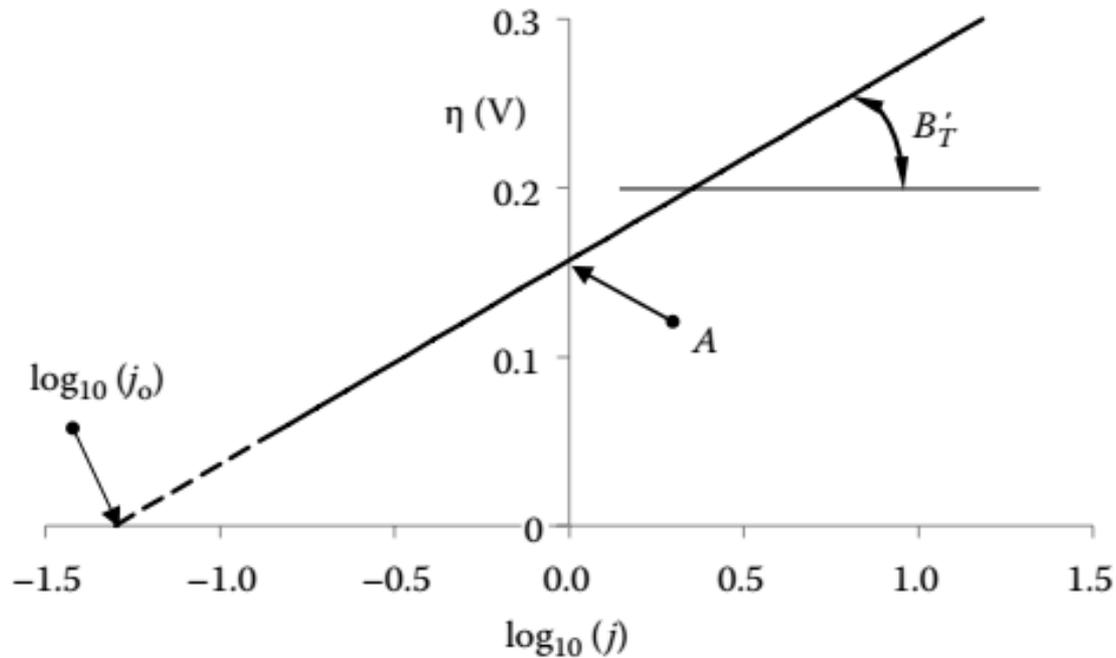
$$\eta = A_T - B_T \ln |j| = A_T - B'_T \log_{10} |j|$$

which is exactly the **Tafel equation**. The equation allows using the intercept A_T and the Tafel slope B_T or B'_T to estimate both j_0 and β . B_T and B'_T differ by a factor of 2.303.

- Note that the linear dependence between η and $\log_{10} |j|$ is applicable at overpotentials above ~30-50 mV. Therefore, the equation cannot be used at current density close to 0, where, mathematically, the overpotential will approach infinity.
- The main method to obtain the Tafel slope was taking a polarization curve by varying the electrode potential (vs. a reference electrode) and measuring the corresponding current density.



Tafel Equation (2)



An example of the Tafel plot. The current density and the exchange current density are A/cm².

S. Lvov, CRC Press (2015). ISBN: 978-1-4665-8285-9

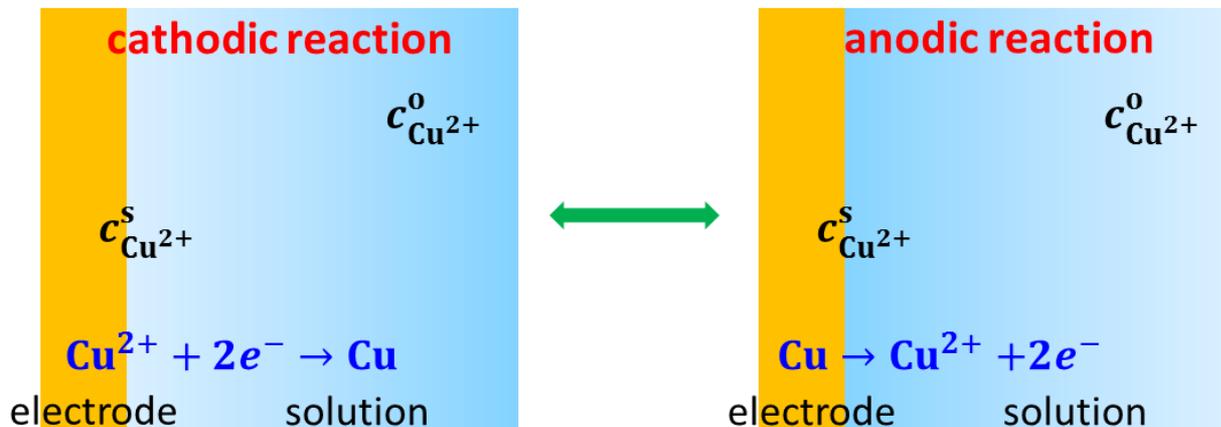


Concentration Overpotential

Once an electrochemical reaction is initiated, the concentration of those species will commonly be higher or lower at the electrode/electrolyte interface than in the bulk of solution. Roughly, the **Nernst equation** can be used to describe the overpotential due to the gradient of the concentration of the electrochemically active ions between the surface and the bulk. Let us define the concentration of the oxidized species in $Ox + ne^- \rightarrow Red$, respectively, at the surface and in bulk as c_{Ox}^s and c_{Ox}^o . Then the overpotential due to the concentration difference is

$$\eta = \frac{RT}{nF} \ln \frac{c_{Ox}^s}{c_{Ox}^o}$$

where η is positive in the anodic reaction ($c_{Ox}^s > c_{Ox}^o$) and negative in the cathodic reaction ($c_{Ox}^s < c_{Ox}^o$).





Mass Transfer Overpotential (1)

One of the case of the mass transfer overpotential is the **diffusion overpotential**. This overpotential is purely due to the Fickian diffusion. The current density, j , due to the **Fick's first law** of diffusion (one-dimensional case) is given as:

$$j = nFJ = nFD \left(\frac{\partial c}{\partial x} \right)_{x=0}$$

where D is the diffusion coefficient of the aqueous electrochemically active species, $(\partial c / \partial x)_{x=0}$ is the gradient (one-dimensional) of the species (Ox) concentration at the electrode surface ($x = 0$). Making a common approximation for $(\partial c / \partial x)_{x=0} \approx \Delta c / \delta_N$, assuming linear concentration distribution, the current density can be connected to the difference between the bulk and surface concentrations, Δc , and the Nernst diffusion layer, δ_N :

$$j \approx nFD \left[\frac{(c^s - c^0)}{\delta_N} \right]$$

The equation is applicable only in a case when **migration** can be neglected. It can be found that the current density is positive for the anodic reaction and negative for the cathodic reaction. When $c^s = 0$, the current density cannot be changed anymore and is approaching its limiting value, j_{lim} , which is defined as follows:

$$j_{\text{lim}} \approx -nFD \left[\frac{c^0}{\delta_N} \right]$$



Mass Transfer Overpotential (2)

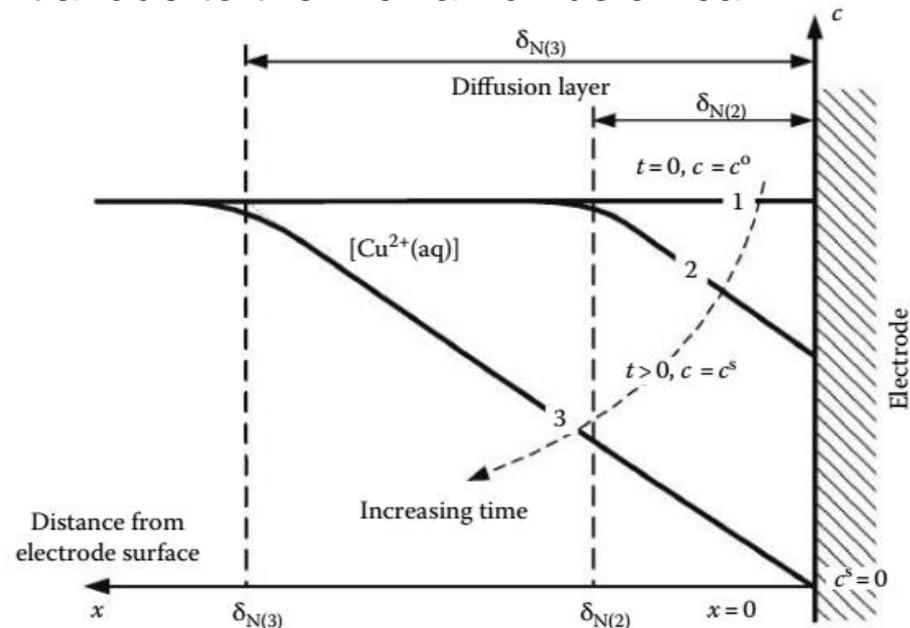
Combining the above two equations, the surface concentration can approximately be defined by the experimentally measure values of the current density and its limiting value as follows:

$$c^s = c^0 \left[1 - \left(\frac{j}{j_{lim}} \right) \right]$$

and, therefore, the mass transfer overpotential due to the Fickian diffusion can approximately be defined as follows:

$$\eta = \pm \frac{RT}{nF} \ln \left[1 - \left(\frac{j}{j_{lim}} \right) \right]$$

which is positive for the anodic reaction and negative for the cathodic reaction. The Equation allows the estimation of the **diffusion overpotential** if the limiting current density is experimentally measured.



Concentration gradient of $Cu^{2+}(aq)$ in the cathodic deposition of $Cu(s)$ in unstirred solutions.

S. Lvov, CRC Press (2015). ISBN: 978-1-4665-8285-9



Generalized Butler-Volmer Equation (1)

- If the mass transfer is presented by diffusion overpotential and the electron transfer is described using Butler-Volmer theory, these two approaches can be combined as follows:

$$j = j_o \left[\left(\frac{c_a^s}{c_a^0} \right) \exp \left\{ \frac{(1 - \beta)nF\eta}{RT} \right\} - \left(\frac{c_c^s}{c_c^0} \right) \exp \left\{ \frac{-\beta nF\eta}{RT} \right\} \right]$$

where the factor (c_a^s/c_a^0) of (c_c^s/c_c^0) and were introduced in front of the corresponding exponent related to the anodic and cathodic reactions, respectively. The equation can be rewritten as:

$$j = j_o \left[\left(1 - \frac{j}{j_{lim,a}} \right) \exp \left\{ \frac{(1 - \beta)nF\eta}{RT} \right\} - \left(1 - \frac{j}{j_{lim,c}} \right) \exp \left\{ \frac{-\beta nF\eta}{RT} \right\} \right]$$

which can easily be converted to:

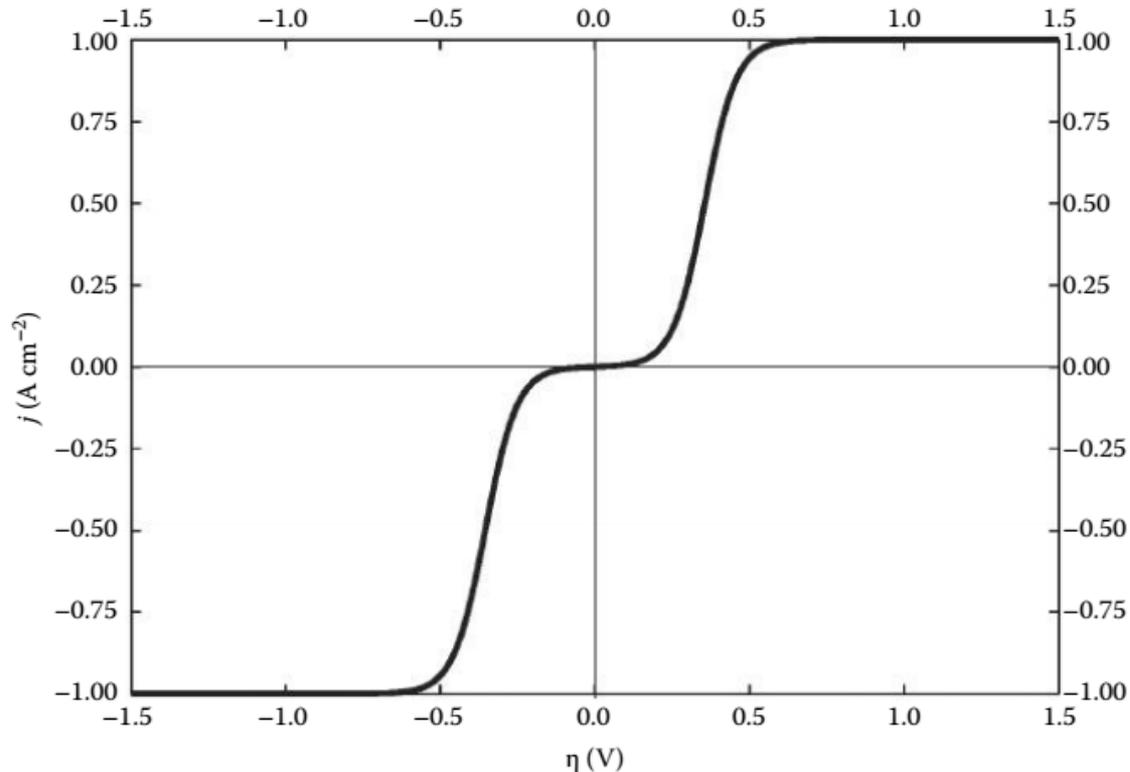
$$j = \frac{\exp \left\{ \frac{(1 - \beta)nF\eta}{RT} \right\} - \exp \left\{ \frac{-\beta nF\eta}{RT} \right\}}{\frac{1}{j_o} + \left(\frac{1}{j_{lim,a}} \right) \exp \left\{ \frac{(1 - \beta)nF\eta}{RT} \right\} - \left(\frac{1}{j_{lim,c}} \right) \exp \left\{ \frac{-\beta nF\eta}{RT} \right\}}$$

and, therefore, the current density can immediately be calculated as soon as the overpotential, η , is given, the parameters of the electrochemical reaction, β , n and j_o , $j_{lim,a}$, and $j_{lim,c}$, are provide, and the temperature, T , is specified.



Generalized Butler-Volmer Equation (2)

- When overpotential is highly negative or positive, the current density approach its limiting value to fulfill the mass transport limitation.



Current density vs. overpotential plotted using the generalized Butler-Volmer equation with following parameter: $n = 1$, $T = 298.15 \text{ K}$, $\beta = 0.5$, $j_o = 0.001 \text{ A/cm}^2$, $j_{\text{lim},a} = j_{\text{lim},c} = 1 \text{ A/cm}^2$.

S. Lvov, CRC Press (2015). ISBN: 978-1-4665-8285-9