Electrochemistry course
ACME Faculty, EHVE course
B.Sc. Studies, II year, IV semester

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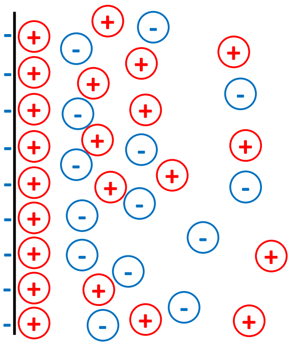
Double layer, capacitors, electrode processes kinetics

Double layer

At the electrode-electrolyte interface (assumed there are no passive layer and electrolyte decomposition products) during the cell operation center of mass of the positive charge and negative charge are separated (starting from the same point during the electroneutrality).
It means electrons are on the electrode side and cations from the electrolyte form a layer at the electrode surface. In the same time anions are moving further away, repelled by the negative charge on the electrode. Such formation is called the double layer.

Double layer



Double layer or so-called Helmholtz layer is approximated as a planar capacitor in which distance between the plates is equal to that of a distance between atoms – 0.1-nm order.

Double layer

Capacity of a capacitor: $C = \varepsilon \cdot \varepsilon_0 \cdot A/d$
where: ε – relative permittivity of a dielectric (dielectric constant);
ε_0 – permittivity of vacuum ($8.85 \cdot 10^{-12}$ F/m);
A – surface of a plate; d – dielectric layer thickness.
Traditional capacitors (*e.g.* those used in electronics) are based on electrodes separated by a dielectric (paper or glass, for instance) and accumulating electrostatic charge. Distances are expressed here in micrometers, and surface in cm^2/g.
In case of supercapacitors surface is expressed in hundreds of m^2 due to use of electrode materials with highly developed surface (of the 1000 m^2/g order).

Double layer

Supercapacitors of the **EDLC** type (electrochemical double layer capacitor) are also using the double layer as a main place for electrostatic charge storage in form of ions at the electrode surface (requires use of ions and electrode that blocks them).
Thanks to that the boundary thickness is of the order of 1 angstrom (10^{-10} m).

$C = {\sim}15 \cdot 8 \cdot 10^{-12}\ F/m \cdot 1000\ m^2 / 10^{-10}\ m = {\sim}10\ F$

Pseudo capacity

Another way to collect charge at the electrode surface is **pseudo capacity**, which bases on the redox reaction, although only of the metal ions and just at the surface. Hence, it is a normal cell, although it storages energy through the adsorption of particles at the surface only. With a proper ratio between surface and volume (proper specific surface development) both the amount of the stored charge and the rate of its charging/discharging is close to the real capacity, hence the name.

Double layer effect on electrode kinetics

At the electrode surface, as it was shown in a previous model, ions can be found. Depending on their size (ionic radius) and charge distribution in space (anions can have its distribution uneven and closer to the electrode), a mean distance between their resulting charge can vary. If they are adsorbed (permanently bounded to the surface) at the surface, then they are not solvated (direct ion-electrode contact removes solvation layers). Ions at the surface, contrary to those deep in the electrolyte, are subject to the asymmetrical interactions, thus their energy reserve is bigger.

Surface tension

Surface tension is an energy per unit of surface required to develop (increase) this surface (through deformation, stretching, *etc.*). It results from the different energy of ions/molecules at the surface compared to energy of particles deep in the solution. Attempt to change the interface surface requires "opposing" against that energy difference.

Wetting angle

Wetting angle depends on surface tension at the phase boundary. Thus, it depends on molecules of both sides. Wetting angle may concern both liquid-solid and gas-solid boundaries. Wetting angle also depends on electrode polarization, which can be used in industrial processes like degreasing.

Wetting angle

Unfortunately, lack of a proper wetting also has its consequences for electrode processes. One of the most important is gas bubbles generation process at the electrode surface (gas generation), thanks to which electrolyte has severed access to the surface. It blocks further operation of the cell. Proper wetting would cause small bubbles formation and their fast detachment from the electrode surface. Thus, the strong polarization (large potential difference) causes lower wetting angle. Thanks to that, gas bubbles are smaller and they are detaching faster.

Overpotential – wetting angle

Formation of a gas bubble is a good example of overpotential importance (gas forms due to the electrode reactions). Such overpotential is quite high – the best proof of it is lead-acid battery in which water is not decomposing (although small amount actually is). If not for the overpotential, water should decompose to hydrogen below 0 V and the Pb/Pb^{2+} potential is -0.126 V vs SHE. Overpotential of the hydrogen bubble formation (nucleation) at the lead plate is ca. 0.4 V (thus, in order for bubbles to form, potential has to be below -0.4 V vs SHE).

Electrode processes kinetics

Unidirectional (irreversible) course of the electrode processes can be obtained through the enforcement of the current flow (from the external source). Measure of the electrode process rate is a current density, thus the ratio between current and electrode surface ([A·s=C], thus amount of the charge is a current density x surface x time).

Electrode processes kinetics

Electrode process steps:

- Mass transport toward electrode
- Reaction with an oxidation state change
- Charge transfer
- Phase transitions

Overpotentials:

- Diffusion – transport of ions toward electrode
- Activation – charge transfer
- Reaction – initiation of a chemical process
- of the new phase formation:
  - Crystal – crystalline structure building-in
  - Gas – gas bubbles formation.

Electrode processes kinetics

Overpotentials are resistances of each of the process steps and are totalize in an overall overpotential of the whole process.

Polarization curve is an overpotential dependence of a current density.

One can influence this dependence through the minimization of individual overpotentials, like through an intensive stirring (thinner laminar layer, lack of a concentration gradient maintained artificially).

Electrode processes kinetics

Factors that influence electrode process kinetics, apart from the stirring, are: temperature (influencing viscosity, reaction rate), electrode properties (structure, energies of bonds) and additives (added on purpose) or impurities affecting the surface tension.

Investigation into those reactions kinetics usually bases on maintaining all factors influencing those kinetics steady and adjusting those factors in such a way, that in a given system only one step would be the rate determining step (rds).

Tafel equation

- Crossing of energetic barrier of the ion passing from the crystalline phase to the solution or vice versa requires certain energy input E_0, called the **activation energy of the process** (equilibrium one, as long as there is no forced current flow from the external source). Activation energy of the process at the cathode (E_C) and of the process at the anode (E_A) is the same as an equilibrium activation energy (E_0).
- If (due to the external current source) electrode is polarized, then the activation energy of one of the electrodes starts to decrease ($E_A < E_C$, for instance), thus statistically, process at this electrode starts to accelerate ($v_A > v_C$).

Tafel equation

- Rate of the process (in case of metal stripping) is:

$$v_A = K_A \cdot \exp(-E_A/(R \cdot T)) \quad \text{i} \quad v_C = K_C \cdot C' \cdot \exp(-E_C/(R \cdot T))$$

where K is **process rate constant** and C' is concentration of ions at the electrode in a given moment (in a direct double layer – at the phase boundary). C' depends on electrolyte concentration, but also indirectly on anodic reaction rate.

- Electrochemical potential difference between metal ions in the crystalline network and those in the layer at the phase boundary is equal to the electrical work required for ion to cross phase boundary (value of the potential jump at the phase boundary). $A = z_i \cdot F \cdot \psi$, where ψ is a potential drop at the phase boundary.

Tafel equation

Work A has two components α and β ($\alpha + \beta = 1$), called **transition factors**. αA and βA are drops/growths of activation energy E_0, defined as:

$$E_A = E_0 - \alpha A = E_0 - \alpha z_i F\psi$$
$$E_C = E_0 - \beta A = E_0 + \beta z_i F\psi$$

Assuming there are no hindrances in the ionic transport toward the bulk of electrolyte:

$$C' = C_0 \cdot \exp(-z_i \cdot F \cdot \psi/(R \cdot T))$$

where C_0 is a concentration in the bulk of electrolyte.

Tafel equation

Assuming that the total Galvani potential ($\Delta\Phi$) between metal and solution is equal to the drop of potential at the phase boundary (ψ – between metal crystalline network and ions of the double layer) and to the drop of potential in the diffuse layer (ψ_1 – between ions of the double layer and bulk of the solution undisturbed by the electrode polarization),

Thus $\Delta\Phi = \psi + \psi_1$ and $\psi = \Delta\Phi - \psi_1$

Tafel equation

Galvani potential itself ($\Delta\Phi$) is non-measurable (as it has been already covered), but the overpotential (η) is a difference between the cell potential (E) and equilibrium potential of the cell (E_{eq}). It is also equal to the difference between Galvani potential ($\Delta\Phi$) during cell operation and equilibrium Galvani potential ($\Delta\Phi_{eq}$):

$\eta = E - E_{eq} = \Delta\Phi - \Delta\Phi_{eq}$

thus: $\Delta\Phi = \eta + E_{eq} + const$

(constant depends on the scale – versus which electrode one measures $\Delta\Phi$ against E: $\Delta\Phi = E + const$)

Tafel equation

Thus all previous electrode processes activation energy formulae transform:

$E_A = E_0 - \alpha z_i F\psi = E_0 - \alpha z_i F(E_{eq} + \eta - \psi_1 - const)$

$E_C = E_0 + \beta z_i F\psi = E_0 - \beta z_i F(E_{eq} - \eta + \psi_1 + const)$

- Partial currents result from the partial processes:

$$I_A = z_i F v_A = z_i F\ K_A \exp(-E_A/(RT))$$

$$I_C = z_i F v_C = z_i F\ K_C C_0 \exp(-z_i F\psi/(RT)) \exp(-E_C/(RT))$$

Tafel equation

- Certain simplifications can be made: during the anodic polarization $I_A > I_C$ (otherwise the process would run in the opposite direction), so the resultant current is $I = I_A - I_C$
- If the electrolyte concentration is high enough, then the potential drop between phase boundary and bulk of the electrolyte is negligible.
- Parameters that are constant for the given system (z_i, F, E_{eq}, *const*) can be included in the constant (K_A^0, K_C^0). After introducing these changes, equations look as follows:

$$I_A = K_A^0 \exp(\alpha z_i F\eta/(RT)) \exp(-E_0/(RT))$$

$$I_C = K_C^0 C_0 \exp(-\beta z_i F\eta/(RT)) \exp(-E_0/(RT))$$

Tafel equation

During equilibrium there is no overpotential at the phase boundary (η=0) and both anodic and cathodic currents are equal and their value is the same as the exchange current:

$I_0 = I_A = I_C = K_A^0 \exp(-E_0/(RT)) = K_C^0 C_0 \exp(-E_0/(RT))$

thus

$I_A = I_0 \exp(\alpha z_i F\eta/(RT))$

$I_C = I_0 \exp(-\beta z_i F\eta/(RT))$

This equation is called the Tafel equation.

Tafel equation solutions

In case of the strong polarization (derivation for anodic polarization is presented below, for cathodic one is identical):

If $\eta >> 0$ (strong polarization), then $I_A >> I_C$, so

$I = I_A - I_C \approx I_A$

Thus, $I = I_0 \exp(\alpha z_i F\eta/(RT))$

Upon taking logarithm of both sides of the formula and transforming to gain formula for overpotential:

$\eta = -RT \ln(I_0)/(\alpha z_i F) + RT \ln(I)/(\alpha z_i F)$

Thus, overpotential is a linear function of the logarithm of a current here:

$\eta = a + b \ln(I)$

Tafel equation solutions

For a very weak polarization (whichever one):

If $\eta \approx 0$, then the exponential term due to the power close to zero can be expanded into a power series. The only non-negligible are the first two terms of the series (1+exponent). Then:

$I_A = I_0 \exp(\alpha z_i F\eta /(RT)) \approx I_0 (1 + \alpha z_i F\eta /(RT))$

$I_C = I_0 \exp(-\beta z_i F\eta /(RT)) \approx I_0 (1 - \beta z_i F\eta /(RT))$

As $I = I_A - I_C$ then $I = I_0 ((\alpha+\beta)z_i F\eta /(RT))$

And as $\alpha + \beta = 1$ then $I = I_0 z_i F\eta /(RT))$

Thus $\eta = RT/(z_i F) \cdot I/I_0$

Overpotential is a linear function of a current here.

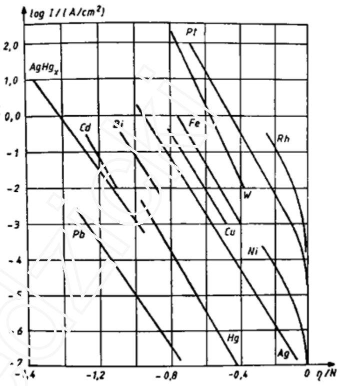
Tafel equation in practice

Polarization curves of the cathodic hydrogen evolution from the aqueous acid solution on the different metals.

a has a very high value for Pt and Rh, and very low for Pb and Hg.

Calculated I_0 (from a) is
10^{-1} A/cm^2 for Pt
10^{-12} A/cm^2 for Hg

$b \approx 118$ mV ($\approx 59.2 \cdot 2$, $\alpha=0.5$)



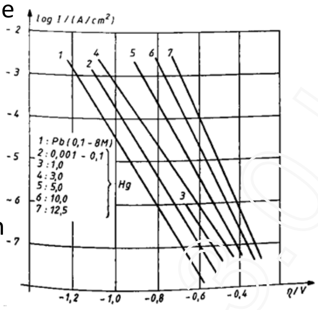
W. Ufnalski, Elementy elektrochemii, OWPW 1996

Tafel equation in practice

Polarization curves of the cathodic hydrogen evolution at the lead electrode from the H_2SO_4 solution and at the mercury electrode from the HCl solution.

Slope coefficient is
$b \approx 118$ mV ($\approx 59.2 \cdot 2$, $\alpha=0.5$)

Coefficient a (and thus, the exchange current I_0) changes by orders of magnitude depending on concentration (with its increase at the mercury electrode).



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Tafel equation in practice

Presence of the electrode poison (substance that blocks electrode by almost irreversible adsorption at the catalytic centers of the metal surface) causes an exchange current drop, but not the slope coefficient drop (reaction potential).

Diffusion resistance reduction (by means of stirring, electrode spinning, *etc.*) works only up to a certain point (linear current increase), after which it is not causing further current increase. It means, that after such a point another step of the process starts to be the RDS.

Diffusion overpotential in practice

Increasing of the electrode polarization causes linear current increase only for the small currents. At one point current almost stops increasing due to the diffusion-related restrictions and increase asymptotically towards certain value of I_{max}. Achievement of this value means that each ion reaching electrode, reacts immediately (lack of ions at the phase boundary). Surpassing value of I_{max} means that the increasing applied external potential reached the level at which different electrode process starts to occur.

Diffusion overpotential in practice

$\eta = R\,T \ln(k\,c_i^0/(k\,c_i^0 - I))/(z_i\,F)$, where
$k = z_i F D_i/((1-t_i)\Delta x_0)$

$I_{max} = k\,c_i^0 = z_i F D_i c_i^0/((1-t_i)\Delta x_0)$

where:
D_i – i ions diffusion coefficient
t_i – i ions transference number
c_i^0 – ionic concentration in the bulk of electrolyte
Δx_0 – laminar layer thickness (layer of the fluid in which the flow is lower due to the wall/obstacle vicinity).

Conclusion: maximum current is a result of an ion concentration in the electrolyte and of the character of the electrolyte itself (D_i, t_i).

Reactions reversibility

Reversibility of the reaction can have different meanings.

One of the meanings is a thermodynamic one, which describes reaction/process as an infinitely slow one.

Other meaning, more common in a traditional chemistry, is that a given reaction can be reversible or not in a given conditions. That is, if equilibrium in which reaction occurs, can be changed to this reaction going backwards in a certain range of conditions (temperature, pressure, concentrations, *etc.*).

Reactions reversibility

From the practical point of view, if the process/reaction occurs in a real-world system (vial or other vessel, for instance), some reactions can be irreversible. This happens if one of the products is gaseous (it escapes from the reaction vessel and loses contact with the reacting system) or when one of the products is precipitating, and the precipitate reaches the bottom, losing proper contact with other reagents in some way (in a given temperature in a given solvent there is no contact with it, so there can be no reaction with it).