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 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.

**Capacity of a capacitor:**

\[ C = \varepsilon \varepsilon_0 \frac{A}{d} \]

where:
- \( \varepsilon \) – relative permittivity of a dielectric (dielectric constant);
- \( \varepsilon_0 \) – 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).

**Supercapacitors**

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).

\[ C = 15 \cdot 8\cdot10^{-12} \text{ F/m} \cdot 1000 \text{ m}^2 / 10^{-10} \text{ m} = 10 \text{ F} \]

**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.

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/Pb²⁺ potential is ~0.125 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=σC], 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.

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).

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

Work $A$ has two components $\alpha$ and $\beta$ ($\alpha + \beta = 1$), called transition factors. $\alpha A$ and $\beta A$ 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:

$C' = C_0 \exp(-z_i F \psi / (R - T))$ 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 ($\psi$ – between metal crystalline network and ions of the double layer) and to the drop of potential in the diffuse layer ($\psi_1$ – 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**

Thus all previous electrode processes activation energy formulae transform:

$E_a = E_0 - a z F \psi = E_0 - a z F (E_{eq} + \eta - \psi_1 - \text{const})$

$E_C = E_0 + b z F \psi = E_0 + b z F (E_{eq} - \eta + \psi_1 + \text{const})$

• Partial currents result from the partial processes:

$I_a = z F v_a = z F K_a \exp(-E_a/(RT))$
$I_C = z F v_C = z F K_C C_0 \exp(-z F \psi/(RT)) \exp(-E_C/(RT))$

**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

$I = I_a - I_C = I_a$

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

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

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

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 $(1+\text{exponent})$. Then:

$I_A = I_0 \exp(\alpha z i F \eta / (R T)) \approx I_0 (1 + \alpha z i F \eta / (R T))$

$I_C = I_0 \exp(-\beta z i F \eta / (R T)) \approx I_0 (1 - \beta z i F \eta / (R T))$

As $I = I_A - I_C$ then $I = I_0 ((\alpha + \beta) z i F \eta / (R T))$

Thus $\eta = R T / (z i F) \cdot I / I_0$

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

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

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.

$\eta = R T \ln(k c_i^0/(k c_i^0-I_0 z I_F)), \text{ where } k = z F D_i / ((1-t_i) \Delta x_0)$

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

where:

$D_i$ - $i$ ions diffusion coefficient
$t_i$ - $i$ ions transference number
$C_i^0$ - ionic concentration in the bulk of electrolyte
$\Delta x_0$ - 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).