Electrochemical reaction

- electrochemistry
- electrochem. reaction mechanism
- electrode potential
- Faradays law
- electrode reaction kinetics

Electrochemistry in industry

Chlor-Alkali
galvano industry
production of other inorganic/organic compounds
recycling
wastes treatment and reprocessing
dezinfection / toxic wastes elimination
contaminated soils treatment
electric energy sources (battery, fuel cells, ...)
electroanalytical methods

Advantages

- versatile
  - direct oxidation or reduction
  - mediated oxidation or reduction
  - simple construction
  - scalable

- selective
  - electrode potential
  - material of electrode (overpotentials)
  - separation of electrode chambers

- ecological
  - electron - clean reactant
  - recycling of raw materials
  - waste treatment

Disadvantages

- expensive
  - Faradays law + price of electric energy
  - electrode materials

- mass transfer
  - heterogeneous process - concentrations limited by mass transfer
Electrochemical reactions - the transfer of electrons between the electrode surface and molecules in the electrolyte.

- reactant: electron
- rate of electron flow: electric current
- oxidation/reduction power: potential (voltage)
- amount of electrons: electrical charge

Separation of electrode reactions in a reactor enables to proceed processes hardly realizable (or unrealizable) by other means.

### Basic terms

**Electrode** – (from a technological point of view) a piece of electrically conductive matter (of suitable shape) where electrode reaction takes place (on its surface)

- **Anode** – electrode with oxidative reaction
- **Cathode** – electrode with reductive reaction

**Electrolyte** – an ion-conductive medium. Mainly solutions with dissociated molecules (ions).

### Basic terms I

**Electrolyser** - to do electrolysis i.e. redox reaction driven by external voltage on the anode and cathode

**Galvanic cell** – batteries, accumulators

**Elchem. generators** - fuel cells

**Separator** – permeable barrier for anodic and cathodic chamber separation. Membrane or diaphragm.

### Basic terms II

**Electrochemical reactors:**

- **Electrolyser** - to do electrolysis i.e. redox reaction driven by external voltage on the anode and cathode
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Electrode reaction

reaction with electron as a reactant or product

\[ aA + n\,e^- = m\,M \]

Simultaneously on the second electrode another reaction occurs to enable charge flow.

\[ bB = z\,Z + n\,e^- \]

total reaction in the system is the sum of both electrode reactions

\[ aA + bB = mM + zZ \]

¹ Electrode reactions occur at electrodes separated by electrolyte. One electrode is called half cell

Electrochemical reaction

Baghdad Battery 2000 BC
Mechanism of electrode reaction

reaction mechanism consists from several steps
transport to the electrode
adsorption on the el. surface
reaction on electrode
products desorption from he surface
transport to the bulk
more than one electron reaction – less probable – usually sequence of individual steps

\[ \text{NO}_3^- + 3 \text{H}_2\text{O} + 5 e^- = \frac{1}{2} \text{N}_2 + 6 \text{OH}^- \]

Polarisation curve

Polarization curve - dependence of current on voltage refers to the course of events on the electrode in the system

Electrode potential

Galvani potential – the work done in moving a unit positive charge from infinity to that point

Usually difference of potentials

Standard (reference) electrode – electrode of known potential resistive to the potential shift (calomel, mercurousulphate, Ag/AgCl)

For solutions in protic solvents, the universal reference, \( \text{H}^+ / \text{H}_2 \) is zero at all temperatures:

SHE

\[ 2 \text{H}^+ (aq) + 2e^- \Leftrightarrow \text{H}_2 (g) \]
Fundamental relationships I

Current density – \( j = I / A \)

El. charge – \( Q = \int_0^t I(t) \cdot dt \)

Faraday’s law – \( m = \frac{Q}{n} \cdot \frac{M}{N_A} = \frac{1}{q} \cdot \frac{Q \cdot M}{n} = \frac{1}{q} \cdot \frac{Q \cdot M}{F} \cdot \frac{F}{N_A} = \frac{Q}{96,485} \cdot \frac{N_A}{n} \)

- \( m \) is the mass of the substance produced at the electrode (in grams).
- \( Q \) is the total electric charge that passed through the solution.
- \( n \) is the valence number of the substance as an ion in solution (electrons per ion).
- \( F \) is Faraday’s constant,
- \( M \) is the molar mass of the substance (in grams per mole), and
- \( N_A \) is Avogadro’s number = 6.022 x 10^{23} ions per mole.

\[ \text{Current} \times \text{time (in seconds)} \times A \text{ is electrode area} \]

Fundamental relationships II

Electrode reaction potential – \( \Delta G = - n \cdot F \cdot E \)

Relation between el. potential and Gibbs energy

Nernst equation – \( E = E^0 + \frac{RT}{N_A} \ln \left( \frac{q_{+}^c}{q_{+}^a} \right) \)

electrode potential calculation

Tafel equation – \( \rho = a + b \times \log t \)

where \( a \) and \( b \) are characteristic constants of the electrode system.

Kinetic factor of electrochemical reaction

Faraday’s law

\[ m = \frac{Q}{n} \cdot \frac{M}{N_A} = \frac{1}{q} \cdot \frac{Q \cdot M}{n} = \frac{1}{q} \cdot \frac{Q \cdot M}{F} \cdot \frac{F}{N_A} = \frac{Q}{96,485} \cdot \frac{N_A}{n} \]

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Task: calculate volume and weight of produced Cl\(_2\) during 1h in the case of total current 10 kA, pressure 101,3 kPa and temp. 25°C. Current efficiency is 95 %.

\[ Q = I \times t = 10,000 \times 3600 = 3.6 \times 10^7 \text{ C} \]

\[ \text{Mr (Cl}_2\text{)} = 70.9 \text{ g/mol} \]

\[ Q \cdot \text{Mr(Cl}_2\text{)} = 3.6 \times 10^7 \times 0.95 = 3.42 \times 10^7 \text{ C} \]

\[ m(\text{Cl}_2) = 3.42 \times 10^7 / (96.485 \times 2) = 177.23 \text{ mol} \]

\[ V = \frac{n \cdot R \cdot T}{P} = \frac{177.23 \times 8.314 \times 298}{101,3 \times 10^3} = 4.3346 \text{ m}^3 \]

\[ \text{in} = \rho \cdot \text{M} = 177.23 \times 70.9 = 12565.5 \text{ g} = 12,565.5 \text{ kg} \]
**Electrode potential calc.**

The Nernst equation is used to calculate electrode potentials:

\[
E = E^\circ - \frac{RT}{nF} \ln \left( \frac{a_{products}}{a_{reactants}} \right)
\]

in tables potentials in the reduction direction.

**Task:** Calculate the potential of the hydrogen electrode in HCl at conditions pH=1, pressure H₂=99.8 kPa, and temperature 25°C.

**Reaction:**

\[
2H^+ (aq) + 2e^- \rightarrow H_2 (g)
\]

**Solution:**

\[
a(H^+) = 10^{-pH} = 10^{-1} = 0.1
\]

\[
a(H_2) = \frac{p(H_2)}{p_{std}} = \frac{99.8}{101.3} = 0.985
\]

\[
E = E^\circ - \frac{RT}{2F} \ln \left( \frac{a(H_2)}{a(H^+)} \right)
\]

\[
E = 0 - \frac{(8.314 \times 298)}{(2 \times 96500)} \times \ln(0.985/0.1) = -0.0589 \text{ V}
\]

**Cell potential**

For cell potential, the difference between electrodes (cathode and anode) is calculated.

In practice, both electrodes are calculated in the reduction form, and the final cell potential is calculated as:

\[
E_{cell} = E_{kat} - E_{anode}
\]

\[
U_{elz} = -E_{cell}
\]

**Task:** Calculate the theoretical cell potential for HCl electrolysis in the system from the previous task.

\[
E(H^+/H_2) = -0.0589 \text{ V}
\]

\[
E(Cl_2/Cl^-) = 1.358 \text{ V}
\]

\[
E(\text{Cl}_2/\text{Cl}^-) = 1.358 - \frac{(8.314 \times 298)}{(2 \times 96500)} \times \ln(0.1/0.985) = 1.417 \text{ V}
\]

\[
E_{cell} = E_{kat} - E_{anode} = -0.0589 - 1.417 = -1.476 \text{ V} \Rightarrow U_{elz} = -E_{cell} = 1.476 \text{ V}
\]

**Counter electrode reaction**

Electric energy demand is very high with respect to the requested charges/currents (100 kA). Each small decrease of potential causes high energy savings.

Production of Cl₂ by HCl electrolysis. Replacement of cathode hydrogen production – for 1 t Cl₂ it is necessary 1000 kWh besides 1700 kWh.

\[
E(H^+/H_2)=0.000 \text{ V}; E(\text{O}_2/\text{H}_2\text{O})=1.229 \text{ V}; E(\text{Cl}_2/\text{Cl}^-)=1.358 \text{ V}
\]
Galvanizing Industry

Proper selection of galvanic bath composition it is possible to deposit simultaneously more metals (bronzes, brasses)

\[
\begin{align*}
\text{Cu}^{2+} + 2e^- &= \text{Cu} \quad E^\circ = 0.337 \text{ V} \\
\text{Zn}^{2+} + 2e^- &= \text{Zn} \quad E^\circ = -0.763 \text{ V} \\
\text{Sn(OH)}_6^{2–} + 2e^- &= \text{HSnO}_2^– + 3\text{OH}^- + \text{H}_2\text{O} \quad E^\circ = -0.93 \text{ V} \\
\text{HSnO}_2^– + \text{H}_2\text{O} + 2e^- &= \text{Sn} + 3\text{OH}^- \quad E^\circ = -0.909 \text{ V}
\end{align*}
\]

Rate of electrochemical reaction is dependent on various parameters:
electrode material, electrolyte composition, temperature etc.

Overvoltage – difference between potential at OCP and potential at current density

\[
\eta = E^\circ - E
\]

Exponential dependence of current (reaction speed) on overvoltage

Anode – positive sign

Various types:
activation – rate determining step – electron transfer between electrolyte and electrode
concentration (diffusion) – mass transfer to the electrode surface
other overvoltages- sorption, preceding reaction, surface reaction...
Kinetics of electrochemical reaction

overpotential – irreversibility of reaction - activation

\[ \eta = E(j) - E. \]

- concentration

Butler-Volmer equation:

\[
\begin{align*}
    j &= j_0 \left( \frac{c_0^a}{c_0^c} \right) \exp \left( \frac{1}{nF} \eta \frac{RT}{1} \right) - c_0^a \exp \left( - \frac{1}{nF} \eta \frac{RT}{1} \right) \\
    j &= j_0 \exp \left( \frac{1}{nF} \frac{RT}{1} \right) - \exp \left( - \frac{1}{nF} \frac{RT}{1} \right)
\end{align*}
\]

\( j \) is the anodic or cathodic current density;
\( a = \) charge transfer barrier or symmetry coefficient for the anodic or cathodic reaction. \( a \) values are typically close to 0.5;
\( \eta \) = overpotential = \( E_{an} - E_{eq} \), i.e. positive for anodic polarization and negative for cathodic polarization;
\( n = \) number of participating electrons;
\( R = \) gas constant;
\( T = \) absolute temperature;
\( F = \) Faraday = 96485 C mol\(^{-1}\).

Tafel equation

\[ \eta = a + b \log j \]

or for anode

\[
\begin{align*}
    \eta &= a_0 + \beta_0 \log j_0 \\
    \eta &= 2.303RT \frac{a}{nF} \log j_0 \\
    \beta &= 2.303RT \frac{a}{nF}
\end{align*}
\]

Kinetics of electrode reaction

**Task:** Calculate potential of anode for chlorine production, \( j = 60 \text{ A/dm}^2 \) and temp. = 70 °C.

Activity coeff. for Cl\(^-\) and Cl\(_2\) are \( \alpha(\text{Cl}^-) = 1 \), \( \alpha(\text{Cl}_2) = 1 \). Concentration of chlorides \( c(\text{Cl}) = 1 \text{ mol/L} \).

Reaction operates at pressure 760 mm Hg.

1) On graphite - Tafel plot for 70 °C

\[ a_{\eta} = 0.6 + 0.12 \log j \]

\[ j = [\text{A/cm}^2] \]

2) on ATA – Tafel plot

\[ a_{\eta} = 0.2 + 0.06 \log j \]

\[ j = [\text{A/cm}^2] \]

\( E = 1.3595 \text{ V} \) at 25 °C

\[ \frac{\Delta E}{\Delta T} = -0.389 \text{ mV/K} \]

\( \text{pH}_2\text{O} = 233 \text{ mm Hg} \)
**Kinetics of electrode reaction**

Electrode reaction: \( \text{Cl}_2 + 2e^- = 2\text{Cl}^- \)

Electrode potential from Nernst eq.

\[ E = E^0 - \frac{RT}{nF} \ln \left( \frac{a_{\text{Cl}^-}}{a_{\text{Cl}_2}} \right) \]

\[ E = 1.342 - \frac{8.314 \times 273.15 \times 70}{2 \times 8.314 \times 273.15} \ln \frac{1}{0.01} \]

Graphite overvoltage: 60 A/dm\(^2\) = 0.6 A/cm\(^2\)

\[ \eta = \delta \gamma \]

ATA overvoltage

\[ \eta = 0.2 + 0.06 \log 0.6 + 0.2 - 0.0008 = 0.1992 \text{ V} \]

\[ E = 1.337 + 0.199 = 1.536 \text{ V} \]

**Concentration overvoltage**

Transport of ion from bulk to the electrode surface

\[ J = D \frac{c_s - c_0}{\delta_x} \]

**Importance of overvoltage – galvanotechnics**

Additives for increased concentration overvoltages – smooth surface
**NaCl electrolysis**

High overvoltage for O\textsubscript{2} enable production of Cl\textsubscript{2}

\[ E^0 (O_2/H_2O) = 1.229 \text{ V} \]

\[ E^0 (Cl_2/Cl^-) = 1.358 \text{ V} \]

**Amalgam/mercury electrolysis**

**Power sources overvoltage**

Batteries, accumulators, fuel cells