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

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Measuring techniques

Electrochemical measurements

1) Measurement at zero Faradaic current:
– potentiometry;
2) Measurements with an applied external voltage (nonzero Faradaic current):
- polarography;
- voltammetry;
- amperometry;
- electrogravimetry;
- coulometry.

Electrochemical measurements

3) Methods without the course of electrode reaction:
- conductometry;
4) Methods using alternating current:
- impedance measurement;
- admittance measurement.

Potentiometry

Potentiometry is one of the most popular and the most important methods in electrochemistry.

Potentiometry – in other words measurement of the potential difference between electrodes (measurement of the electromotive force EMF).

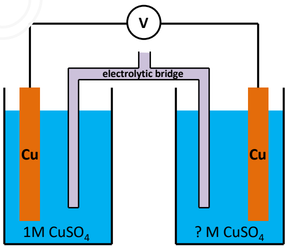
Measuring system consists of two electrodes and a voltmeter.

Such a system often requires calibration (pH).

Potentiometry - example

Scheme of the concentration cell is shown below. Its EMF in the 1. second of the operation is 24 mV. Estimate the initial electrolyte concentration in the cell (the one on the right in the scheme).

Available data:
$T = 25°C$
$E°_{Cu2+/Cu} = 0.34$ V



Solution

The general form of the Nernst equation is:
$E = E^0 + R \cdot T/(z \cdot F) \cdot \ln([ox]/[red])$

Nernst equation at 25°C:
$E = E^0 + 0.059/z \cdot \log([ox]/[red])$

In both cells the following reactions take place:
A: $Cu \rightarrow Cu^{2+} + 2e^-$
K: $Cu^{2+} + 2e^- \rightarrow Cu$ z – exchanged charge = 2

Solution cont'd

In both cells the oxidized form is Cu^{2+}.

After substitution to the Nernst equation one gets:

$E_1 = 0.34 + 0.059/2 \cdot \log(1) = 0.34$ V
$E_2 = 0.34 + 0.059/2 \cdot \log(a_{Cu2+})$
$EMF = E_1 - E_2 = 0.024$ V
$E_2 = E_1 - EMF = 0.34 - 0.024 = 0.316$ V
$0.316 = 0.34 + 0.059/2 \cdot \log(a_{Cu2+})$
$-0.024 = 0.059/2 \cdot \log(a_{Cu2+})$
$-0.024 \cdot 2/0.059 = \log(a_{Cu2+})$
$a_{Cu2+} = 10^{-0.814}$
$a_{Cu2+} = 0.15$ M

Potentiometry - applications

- EMF measurements;
- pH measurements – using combined glass electrode → change of the measured potential difference is related to the H_3O^+ ions concentration change in the solution;
- measurements with use of the selective electrodes (measurement of the selected ions concentration in the solution);
- possibility of the biologically active substances measurements – with use of enzymatic electrodes.

Coulometry

It uses Faraday laws: $m = M \cdot I \cdot t/(F \cdot z)$

It consists in measuring electrode mass change due to the investigated electrode process or the charge passed through the system.

This kind of measurement does not require calibration prior to use.

It is used in two variants: by enforcing constant potential between electrodes or by enforcing constant current passage between them.

Coulometry

Alternatively, this measurement process can be called electrolysis.

It enables obtaining pure metals or gases, like Cl_2.

This method is used for quantitative determination of ions concentration in multicomponent systems, where its components differ in standard potentials.

Voltammetry (LSV)

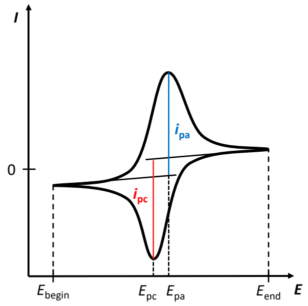
It is an investigation of changes of current flowing through the cell. This current results from linear change (increase or decrease) of applied potential between electrodes. Thus the name: Linear Sweep Voltammetry.

During measurement, when at the given potential some electrode reaction starts to occur, the current peak is observed. It is slightly shifted compared to $E°$ of this process due to overpotential existence (potential required for the process to happen in the given conditions).

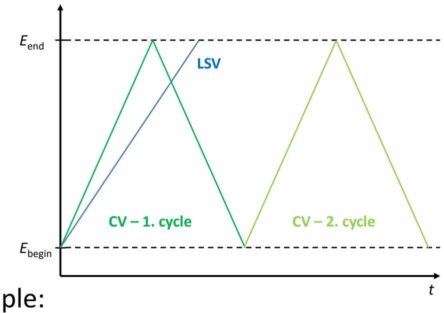
Cyclic Voltammetry (CV)

It is an investigation consisting in cyclic changes of direction of the linear potential sweep.

For instance, measurement starts at E_{begin} goes down/up to E_{end} and goes back to the initial potential (E_{begin}).



LSV vs CV



Example:
In the figure LSV measurement is carried out with the lower rate than CV measurement.

LSV and CV

In both methods scan rate is measured in mV/s. The higher scan rate, the higher peaks are expected.

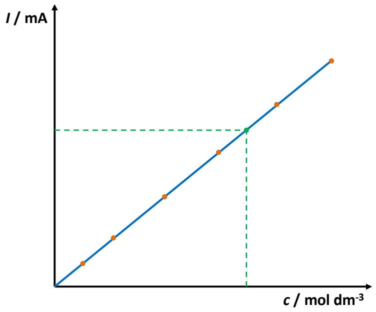
Both methods are employed in analytical determination of ionic concentrations (as low as trace level).

It is also possible to determine material stability. It is particularly important when it comes to battery materials (electrodes/electrolyte) – in order to measure in what potential range are they stable. Thus, in what range the cell can work.

LSV and CV – quantitative determination

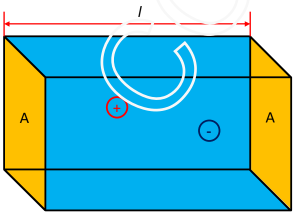
It is crucial to measure so-called calibration curve first. In order to do that, one should measure (with the same scan rate) few solutions with known concentrations. The higher concentration of the given component, the bigger is observed peak coming from its reaction. Next, one measure the sample (of unknown concentration). Basing on the peak size, one can determine its concentration from the calibration curve.

Calibration curve



Conductometry

Measurement of the solution's conductivity is called conductometry.



From the 2. Ohm's law:

$R = \rho \cdot l/A$
$\kappa = 1/\rho = 1/R \cdot l/A$
$\kappa = k/R$

where:
$k = l/A$

Conductometry

It is a method that requires calibration first. It means that one need to know what is the cell constant k, before starting measurements.

The method allows to determine, which electrolyte is better conducting and due to this, which one will cause smaller energy losses during cell recharging, for instance. When electrolyte resistance is high, then the energy is used to heat the cell, not to recharge it (overheating may lead to explosion).

EIS – Electrochemical Impedance Spectroscopy

One of the methods gaining popularity in last years due to its low cost and relatively fast measurement. It consists in impedance measurement, which is resistance of the sample under alternative current. In standard measurement, the sample is treated with sinusoidal voltage signal with low amplitude (up to 15 mV). The alternative current response is measured, which is usually different in both amplitude and phase. Repeating the measurement at various frequencies allows to plot so-called EIS spectrum (spectrum only in name).

EIS – cont'd

By employing this method one can form so-called equivalent circuit of the investigated system. It is built of the RLC elements (resistor, coil, capacitor). EIS plot of the parallel R and C elements system is depicted below: