Warsaw PhD School of Natural and BioMedical Sciences [Warsaw-4-PhD]

Specialization Lecture

Basic Physical Chemistry V: ELECTROCHEMISTRY

30 hours, 3 ECTS

Institute of Physical Chemistry
Polish Academy of Sciences
Kasprzaka 44/52, 01-224 Warsaw
~~Bldg. 9, Assembly hall "Aula"~~
Online

Wednesdays 12:00 – 13:30 CET/CEST
March 2, 2022 through June 22, 2022
~~May 25, June 8~~

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Syllabus:

1. **The scope of electrochemistry and applications**

Industrial electrolysis and electrosynthesis. Electrowinning. Electrorefining. Electroplating. Energy storage. Batteries. Fuel cells. Supercapacitors. Electrochemical sensors.

2. **Electrochemical cells, thermodynamics and potentials**

Electrochemical cells. Electrolyzer cell. Galvanic cell. Concentration cell. Reversibility of electrode processes. Equilibrium. Thermodynamics. Electric, chemical and electrochemical potentials. Galvani potential. Half reactions and electrodes. Nernst equation. Formal potential. Diffusion potential. Ionic conductivity. Transference numbers. Liquid junction potential. Potential difference measurement.

3. **Electrified interfaces and electrodes**

Classification of electrodes. Polarizability. Graphic conventions. Reference electrodes – calibration and conservation. Ion-selective electrodes. Faraday laws of electrolysis.

4. **The electrical double layer (EDL)**

Surface charge density. Capacity. Charging current. Porous electrode – roughness factor. Diffuse layer. Surface energy. Surface tension. Differential capacitance. Electrocapillary curves. EDL structure – Helmholtz model, Gouy-Chapman theory, Stern modification. EDL influence on electrode processes. Colloids and electrokinetic phenomena (electrophoresis, electroosmosis). The zeta potential.

5. **Mass transport (I)**

Diffusion. Migration. Convection. Mixed mass transport.

6. **Mass transport (II)**

Supporting electrolyte. Steady-state. Diffusion-limited current at electrodes. Diffusion layer. Linear and spherical diffusion. Microelectrodes. Microelectrode arrays. Fick's laws of diffusion. Hydrodynamic systems - rotating disc electrode, microfluidics, dropping electrode. Diffusion as a stochastic process.

7. **Electron transfer mechanism and kinetics**

Mechanism of electron transfer in the homogeneous systems - Marcus theory. Kinetics of electron transfer in heterogeneous systems. Tafel plot. Irreversible and quasi-reversible electrode processes. Butler-Volmer equation. Transfer coefficient. Exchange current. Parameters affecting ET kinetics. Tunneling. Outer-sphere and inner sphere ET.

8. **Principles of electrode processes studies**

Principles of electric circuits. Time constant. Three electrode electrochemical cell. Measurements at equilibrium and away from equilibrium. Electrode potential control – potentiostats. Ohmic drop compensation. Bipotentiostat – rotating ring-disk electrode, interdigitated electrodes, generator-collector systems. Current control - galvanostat. Low current measurements. Data acquisition. Electrode materials. Preparation and cleaning. Removal of oxygen.

9. **Basic potential and current step methods**

Chronoamperometry (Cottrell equation, microelectrodes – steady-state current). Sampled current voltammetry (complexation, irreversible processes, multicomponent systems, multistep reactions). Chronocoulometry (adsorption, EDL). Pulse voltammetry. Chronopotentiometry. Analysis of batteries and fuel cells. Bulk electrolysis (electrosynthesis).

10. Polarography and pulse techniques

Hanging mercury electrode. Dropping mercury electrode. Ilkovic equation. Staircase voltammetry. Normal pulse voltammetry (NPV). Reverse pulse voltammetry. Differential pulse voltammetry (DPV). Square wave voltammetry (SWV). Stripping voltammetry.

11. Cyclic voltammetry (I)

Linear sweep voltammetry. Planar electrodes and microelectrodes. Reversible, irreversible and quasi-reversible systems. Influence of EDL and uncompensated resistance. Scan rate. Multiple electron transfer and multicomponent systems.

12. Cyclic voltammetry (II)

Liquid-liquid electrochemistry (liquid junction). Linear and staircase CV. Adsorbed species. Coupled homogeneous reactions. Electrocatalysis. Rotating ring-disc electrode (RRDE). Interdigitated electrodes (generator-collector).

13. Alternating current techniques

Instrumentation. Alternating voltage. Circuit elements. Impedance. Electrochemical impedance spectroscopy (EIS). Interpretation of the impedance. Components of equivalent circuits. Kinetic measurements. Mass transport impedance. AC voltammetry.

14. Scanning electrochemical microscopy (SECM) and other techniques to study electrode processes

Principles. Instrumentation. Operation Modes. Reaction rate measurements. Imaging. Microfabrication. Scanning ion-conductance microscopy (SICM), Scanning electrochemical cell microscopy (SECCM) Spectroscopies. Quartz crystal microgravimetry. Mass spectrometry, etc.

15. Corrosion of metals and prevention

General. Localized. Atmospheric. Galvanic. Pitting. Mixed potential theory. Corrosion potential. Oxidation state diagrams (Pourbaix diagrams). Thermodynamics and kinetics. Electrochemical measurements. Passivation. Cathodic protection.