

## UČNI NAČRT PREDMETA / COURSE SYLLABUS

**Predmet:** ELEKTROKEMIJA  
**Course Title:** ELECTROCHEMISTRY

Študijski program in stopnja Study Programme and Level	Študijska smer Study Field	Letnik Academic Year	Semester Semester
MAG Kemija, 2. stopnja	/	1.	2.
USP Chemistry, 2 <sup>nd</sup> Cycle	/	1 <sup>st</sup>	2 <sup>nd</sup>

**Vrsta predmeta / Course Type:**

obvezni / Mandatory

**Univerzitetna koda predmeta / University Course Code:**

Predavanja Lectures	Seminar Seminar	Vaje Tutorial	Klinične vaje Work	Druge oblike študija	Samost. delo Individual Work	ECTS
50	25	/	/	/	75	5

**Nosilec predmeta / Lecturer:**

prof. dr. Miran Gaberšček / Dr. Miran Gaberšček, Full Professor  
 izr. prof. dr. Janez Cerar / Dr. Janez Cerar, Associate Professor

**Jeziki / Languages:**

**Predavanja / Lectures:** slovenski / Slovenian

**Vaje / Tutorial:** /

**Pogoji za vključitev v delo oz. za opravljanje študijskih obveznosti:**

Študent oz. kandidat mora imeti predmet opredeljen kot študijsko obveznost.

**Prerequisites:**

The course has to be assigned to the student.

**Vsebina:**

ELEKTROKEMIJA RAZTOPIN

### Osnovni pojmi

Elektrokemija: raztopine elektrolitov, elektrodni procesi. Električni dvosloj. Voda kot najpomembnejše topilo. Vodikova vez. Sile v raztopinah. Solvatacija ionov. Hidrofobni efekt. Enostavni elektroliti. Polielektroliti. Ionske tekočine.

### Termodinamične lastnosti raztopin elektrolitov

Različni nivoji opisa raztopin elektrolitov. Preprosti model raztopine elektrolita. Poisson-Boltzmannova enačba. Debye-Hücklova teorija. Srednji elektrostatski potencial. Prostorske porazdelitvene funkcije. Osmozni

**Content (Syllabus outline):**

ELECTROCHEMISTRY OF SOLUTIONS

### Basic concepts

Electrochemistry: ionics and electrodicts. Electric double-layer. Role of water as a solvent. Hydrogen bond. Forces in solutions. Solvation of ions. Hydrophobic effect. Simple electrolytes. Polyelectrolytes. Ionic liquids.

### Thermodynamic properties of electrolyte solutions

Different levels of electrolyte solution description. Simple model of electrolyte solution. Poisson-Boltzmann equation. Debye-Hückel theory. Mean electrostatic potential. Spatial distribution functions. Osmotic pressure and activity coefficient. Experimental

tlak in koeficient aktivnosti. Eksperimentalno določanje termodinamičnih količin. Pitzerjeva teorija. Asociacija ionov. Bjerrumova teorija.

#### **Transportne lastnosti raztopin elektrolitov**

Prevodnost. Difuzija elektrolitov.

#### **Lastnosti raztopin polielektrolitov**

Manningov model nabite premice. Hoffmeisterova vrsta. Osmozni koeficient. Razredčilne toplote. Membransko ravnotežje. Topnost polielektrolitov. Raba polielektrolitov. Biopolielektroliti.

#### **ELEKTRODNI PROCESI**

Pregled teorije elektrodnih procesov: Električni dvosloj ob elektrodah, kinetika elektrodnih procesov, Butler-Volmerjeva enačba in njene limitne oblike (Taflova relacija, polarizacijska upornost). Transport snovi (difuzija, konvekcija, migracija) in vpliv transporta na hitrost elektrodnih procesov.

*Metode za študij elektrodnih procesov in ugotavljanje mehanizma elektrodnih procesov:* Potenciostatsko in galvanostatsko merjenje polarizacijskih krivulj, tranzientne tehnike (kronoamperometrija, kronokulometrija, kronopotenciometrija), ciklična voltometrija, impedančna spektroskopija. Simulacija elektrodnih procesov. Mehanizem izločanja vodika (HER) in redukcije kisika (ORR).

#### *Elektrokemija materialov*

- Elektrodepozicija, elektrosinteza in tehnike za študij procesov. Samosestavljive monoplasti-SAM, podnapetostno izločanje-UPD, elektrokemijska kvarčna mikrotehnična-EQCMB.

- Elektrokemijska korozija: vrste korozije, termodinamski in kinetični vidiki (Pourbaix, Wagner-Traud), korozijski tok in korozijski potencial, Evansovi diagrami, elektrokemijske metode za študij korozijskih procesov, inhibicija korozije, pasivacija in protikorozijska zaščita.

- Elektrokemijski viri energije: elektrokemijski vidiki primarnih in sekundarnih virov energije (učinkovitost, gostota energije), pregled

determination of thermodynamic quantities. Pitzer theory. Ion association. Bjerrum theory.

#### **Transport properties of electrolyte solutions**

Conductivity. Diffusion of electrolytes.

#### **Properties of polyelectrolyte solutions**

Manning model. Hoffmeister series. Osmotic coefficient. Enthalpies of dilution. Membrane equilibrium. Solubility of polyelectrolytes. Application of polyelectrolytes. Biopolyelectrolytes.

#### **ELECTRODE PROCESSES**

*Overview of the theory of electrode processes:* electrical double layer at electrodes, kinetics of electrode processes, Butler-Volmer equation and the limiting cases (Tafel relation, polarisation resistance). Transport of matter (diffusion, convection, migration) and the influence on the rate of electrode processes.

Methods for study of electrode processes and identification of their mechanisms: potentiostatic and galvanostatic measurements of polarisation curves, transient techniques (chronoamperometry, chronocoulometry, chronopotentiometry), cyclic voltammetry, impedance spectroscopy. Simulation of electrode processes. Mechanism of hydrogen (HER) and oxygen (OER) evolution reactions. Materials electrochemistry: electrodeposition, electrosynthesis and related phenomena. Self assembled monolayers (SAMs) underpotential deposition (UPD), electrochemical quartz crystal microbalance (EQCMB).

-Electrochemical corrosion: types of corrosion, thermodynamic and kinetic aspects (Pourbaix, Wagner-Traud), corrosion current and potential, Evans diagrams, electrochemical methods for investigation of corrosion, corrosion inhibition, passivation and anticorrosion protection.

-Electrochemical energy sources (efficiency, energy density), overview of conventional and advanced systems (Zn/MnO<sub>2</sub>, Pb/PbO<sub>2</sub>, Ni/Cd, Ni/MH, Li/Li<sup>+</sup>, fuel cells), photovoltaic systems.

klasičnih in naprednih sistemov (Zn/MnO<sub>2</sub>, Pb/PbO<sub>2</sub>, Ni/Cd, Ni/MH, Li/Li<sup>+</sup>, gorivne celice), fotovoltaični sistemi.

### Temeljna literatura in viri / Readings:

#### Literatura (temeljna):

J. O'M. Bockris in A.K.N. Reddy *Modern Electrochemistry: ionics* (2. izdaja), New York: Plenum Press, 1998, 769 str. (cca 15 %).

J.O' M. Bockris, A.K.N. Reddy, *Modern Electrochemistry, Electrode Processes in Chemistry, Engineering, Biology, and Environmental Science*, Vol. 2B, 2<sup>nd</sup> Ed., Kluwer Academic/Plenum Publishers, New York, 2000.

M. Mandel *Physical Properties of Polyelectrolyte Solutions*, Pisa: Pacini Editore, 1999, 190 strani, (20 %).

#### Dodatna literatura:

M. R. Wright *An introduction to aqueous electrolyte solutions*, Chichester : J. Wiley, 2007, 574 str.

S. Forster in M. Schmidt, *Physical Properties of Polymers: Polyelectrolytes in Solution*, v *Advances in Polymer Science*, Berlin: Springer-Verlag, 1995.

A.J. Bard, M. Stratmann, Eds., *Encyclopedia of Electrochemistry*, Vol. 2, *Interfacial Kinetics and Mass Transport*, Vol. Ed. E.J. Calvo, Wiley-VCH, Weinheim, 2003.

R. Greef, R. Peat, L.M. Peter, D. Pletcher, J. Robinson, *Instrumental Methods in Electrochemistry*, Ellis Horwood Lim., Chichester, 1985.

### Cilji in kompetence:

#### Cilji:

Spoznavanje teorijskih pristopov pri obravnavi termodinamičnih in transportnih lastnosti raztopin elektrolitov in polielektrolitov.

Poglobljen študij elektrokemijskih zakonitosti, ki so podlaga za raziskave na področju elektroanaliznih tehnik, elektrokemije materialov, korozije in elektrokemijskih virov energije.

#### Kompetence:

Razumevanje fizikalnih pojavov v raztopinah elektrolitov in polielektrolitov ter elektrokemijskih procesov na elektrodah.

Uporaba tega znanja tako pri tehnoloških kot pri bioloških procesih.

Pridobljena znanja so usmerjena v razumevanje in usposabljanje za raziskovalno delo na teh področjih.

### Objectives and Competences:

#### Objectives:

To get insight into basic theoretical approaches used in studies of thermodynamic and transport properties of both electrolyte and polyelectrolyte solutions.

In-depth study of electrochemical laws which represents the basis for understanding electroanalytical techniques, corrosion, materials electrochemistry and electrochemical energy sources.

#### Competences:

Understanding of physical phenomena occurring in electrolyte and polyelectrolyte solutions as well as electrochemical processes at electrodes. Application of this knowledge for comprehension of technological and biological processes.

Acquired knowledge is the basis for training and applied work either in research or in routine laboratory work in the field of electrochemistry.

### Predvideni študijski rezultati:

### Intended Learning Outcomes:

<p><u>Znanje in razumevanje</u> Študent pridobi temeljna znanja potrebna za razumevanje elektrokemijskih procesov in spozna uporabo elektrokemijskih zakonitosti na različnih področjih. Obvlada instrumentacijo in razume principe elektrokemijskih tehnik potrebnih za študij in raziskave povezanih z elektrokemijo.</p>	<p><u>Knowledge and Comprehension</u> The student acquires base knowledge needed for understanding electrochemical processes and is acquainted with selected applications of electrochemical phenomena in various fields. The student also acquires selected laboratory skills and techniques related to electrochemistry.</p>
<p><u>Uporaba</u> Pridobljeno znanje je usmerjeno v aplikacijo elektrokemijskih zakonitosti in pojavov na področjih kot so: korozija, preiskave in razvoj novih materialov, elektrokemijska sinteza in elektrokemijski viri energije, elektroanalizne metode, ipd. Študent se na teh področjih usposobi za samostojno raziskovalno delo in spozna načine prenosa in uporabe teoretskih zakonitosti v praksi.</p>	<p><u>Application</u> Acquired base knowledge is implemented in selected applications such as: corrosion, investigation and development of new materials, electrochemical synthesis, electrochemical energy sources, electroanalytical methods etc. Student becomes qualified for independent research in the field and gets knowledge about transfer of theoretical concepts into practice.</p>
<p><u>Refleksija</u> Pridobljeno teoretično znanje omogoča študentu poglobljen vpogled v osnovne koncepte in zakonitosti na področju elektrokemije. Dodatno študent pridobi veščine prenosa osnovnih znanj na izbrane praktične primere. Vsebina in izvedba predmeta predstavlja dobro osnovo za kasnejše aktivno in samostojno udejstvovanje na področju raziskav in uporabe elektrokemijskih znanj v praksi.</p>	<p><u>Analysis</u> Acquired theoretical knowledge enables a profound insight into main concepts and laws in the field of electrochemistry. Additionally, the student acquires the ability to apply knowledge base into selected practical examples. The curriculum represents a solid background for later active and independent research in the fields of basic and applied electrochemistry.</p>
<p><u>Prenosljive spretnosti</u> Pridobi veščine na področju elektrokemije, zna uporabljati znanstveno in strokovno literaturo ter pravilno predstaviti in razlagati merske rezultate. Pridobi znanja potrebna za projektno in timsko delo.</p>	<p><u>Skill-transference Ability</u> Student acquires experimental skills in the field of electrochemistry, masters the use of scientific and professional literature and develops the skill of presenting and explaining complex and specific results to wider audience. Competences needed for project and team work are also developed.</p>

**Metode poučevanja in učenja:**

Predavanja, seminarji

**Learning and Teaching Methods:**

Lectures, seminars

**Načini ocenjevanja:**

Pisni izpit. Pisni izpit je možno opraviti tudi s pozitivno ocenjenima vmesnima pisnima kolokvijema (pozitivna kumulativna ocena).

Delež (v %) /

Weight (in %) **Assessment:**

Written exam. Written exam can be passed also by two written tests during the semester (positive cumulative grade).

#### Reference nosilca / Lecturer's references:

1. **Janez Cerar**, Jože Škerjanc: Electric transport and ion binding in solutions of fullerenehexamalic acid  $T_h-C_{66}(COOH)_{12}$  and its alkali and calcium salts. *J. Phys. Chem. B*, 2008, vol. 112, str. 892-895.
  2. **Janez Cerar**, Jože Škerjanc: Water-soluble fullerenes. 3. Alkali salts of fullerenehexamalic acid  $T_h-C_{66}(COOH)_{12}$ . *J. Phys. Chem. B*, 2003, vol. 107, str. 8255-8259.
  3. **Janez Cerar**, Jože Škerjanc: Water-soluble fullerenes. 2. Sodium fullerenehexamalonate  $T_h-C_{66}(COONa)_{12}$ , a highly asymmetric electrolyte. *J. Phys. Chem. B*, 2000, vol. 104, str. 727-730.
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1. HODNIK, Nejc, ZORKO, Milena, JOZINOVIĆ, Barbara, BELE, Marjan, DRAŽIĆ, Goran, HOČEVAR, Stanko, **GABERŠČEK, Miran**. Severe accelerated degradation of PEMFC platinum catalyst : a thin film IL-SEM study. *Electrochem. commun.*, 2013, vol. 30, str. 75-78
  2. KHATIB, R., DALVERNY, A. - L., SAUBANÈRE, M., **GABERŠČEK, Miran**, DOUBLET, M. - L. Origin of the voltage hysteresis in the CoP conversion material for Li-ion batteries. *The journal of physical chemistry. C, Nanomaterials and interfaces*, 2013, vol. 117, no. 2, str. 837-849.
  3. ATEBAMBA, Jean-Marcel, MOŠKON, Jože, PEJOVNIK, Stane, **GABERŠČEK, Miran**. On the interpretation of measured impedance spectra of insertion cathodes for lithium-ion batteries. *J. Electrochem. Soc.*, 2010, vol. 157, no. 11, str. A1218-A1228
  4. DREYER, Wolfgang, JAMNIK, Janko, GUHLKE, Clemens, HUTH, Robert, MOŠKON, Jože, **GABERŠČEK, Miran**. The thermodynamic origin of hysteresis in insertion batteries. *Nature materials*, 2010, vol. 9, str. 448-453,
  5. STRMČNIK, Dušan, **GABERŠČEK, Miran**, PIHLAR, Boris, KOČAR, Drago, JAMNIK, Janko. Copper dissolution in ammonia solutions : identification of the mechanism at low overpotentials. *J. Electrochem. Soc.*, 2009, vol. 156, no. 7, str. C222-C229.