

## ELEKTROKEMIJA

2 + 1

akad. godina 2018/2019.

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## oblici nastave:

predavanja

vježbe

kolokviji

## fizikalna kemija

- Elektroliti (otopine i taline)
- Elektroliza - stehiometrija (Faradayevi zakoni)
- Električna vodljivost elektrolita
- Migracija iona u električkom polju; ionska pokretljivost, prijenosni broj
- Električna vodljivost jakih elektrolita
- Električna vodljivost i ionizacija slabih elektrolita
- Teorijski opis jakih elektrolita (Debye i Hückel)
- Ravnoteže u otopinama slabih elektrolita

## fizikalna kemija

- Elektrokemijski članci; Daniellov članak
- Ravnotežni napon (elektromotivnost) – definicija i mjerenje
- Nernstova jednažba
- Standardni ravnotežni napon i  $K^\circ$
- Elektrodni potencijal
- Elektrode I. i II. vrste, redoks-elektrode
- Definicija i mjerenje pH; staklena elektroda
- Potenciometrijska titracija

## što je elektrokemija?

- grana kemije koja se bavi međudjelovanjem električnih i kemijskih efekata
- proučavanje kemijskih promjena uzrokovanih prolaskom električne struje

## što je elektrokemija?

- elektroanalitička kemija; elektroanalitičke metode
- mjerenje električnih svojstava (jakosti struje, naboja) i njihove ovisnosti o kemijskim parametrima

## elektrokemija jučer, danas, sutra

- Substances are frequently spoken of as being electro-negative, or electro-positive, according as they go under the supposed influence of direct attraction to the positive or negative pole....I propose to distinguish such bodies by calling those *anions* which go to the anode of the decomposing body; and those passing to the cathode, *cations*; and when I have the occasion to speak of these together, I shall call them *ions*.

M. Faraday, 1834.

## elektrokemija jučer, danas, sutra

- 1894. - osnovano "Njemačko elektrokemijsko društvo" (*Deutsche Elektrochemische Gesellschaft*) - Wilhelm Ostwald
- 1902. - širi se u "Njemačko Bunsen-društvo za primijenjenu fizikalnu kemiju" (*Deutsche Bunsen-Gesellschaft für angewandte physikalische Chemie*)

## International Society of Electrochemistry

### 55<sup>th</sup> Annual Meeting, Patras, Greece

**Frumkin Award Lecture**  
"Surfaces and Interfaces in Electrochemistry"  
Professor S. Trasatti

**Plenary Lectures**  
"From 1 to 1000 nm: Regular Nanostructures by Templated Electrodeposition"  
Professor P.N. Bartlett

"Electrochemical Nanotechnology for New Materials Design"  
Professor T. Osaka

"New Electrocatalysts for Low Temperature Fuel Cells:  
A Materials by Design Approach"  
Professor P.N. Ross

"Fuel Cells: From Nanometers to Systems"  
Professor U. Stimming

<b>Topic 1</b> Fundamental Electrochemistry Traditional studies of the electrochemical interface - Modern microscopic or spectroscopic techniques - Liquid-liquid interfaces	<b>Topic 2</b> Organic Electrochemistry and Bioelectrochemistry Organic electrosynthesis - Oscillation of cyclic reactor mechanisms - Organometallic and organometallic electrochemistry - Bioelectronic devices - Conformational and biological cells
<b>Topic 3</b> Environmental Electrochemistry Electrochemical and photochemical purification processes - Cell and reactor design - Recovery, recycling and reuse - Separation processes - Electrochemical generation of decontamination agents	<b>Topic 4</b> Electroanalysis and Electrochemical Sensors New modifications/combinations of analytical methods - Flow injection and SP-C electrochemical detection - Capillary electrophoresis - New designs and miniaturization of sensors
<b>Topic 5</b> Electrodeposition and Electroplating Processes Kinetics of electrodeposition - Properties of electrodeposits - Metal and semiconductor/polymer composites - Intermetallic compounds in electrodeposits	<b>Topic 6</b> Electrocatalysis Surface structure and electrode kinetics - Oxidation of organic fuels - Kinetics of oxygen and hydrogen reactions - In situ spectroscopy and microscopy of catalysis
<b>Topic 7</b> Corrosion Science and Technology Molecular aspects of corrosion, passivity and passivity breakdown - Material protection - Non-aqueous state techniques - Oscillation and/or chaos in corrosion/passivation processes	<b>Topic 8</b> Electrochemical Production and Applications of New Materials Conducting polymers - Coatings - Composites - Solid ionic conductors - Conductive materials - Diamond and diamond-like electrodes
<b>Topic 9</b> Electrochemical Power Sources and Energy Conversion Hydrogen and reformate fuel cells - Direct methanol fuel cell - Fuel cell materials - Scaling-up and commercialization - Lithium batteries - Advances in aqueous batteries	<b>Topic 10</b> Micro-scale and Nano-scale Electrochemistry Pulsing through templates - Electrochemical fabrication or properties of microsystems - Micro and nano-electrode arrays - Patterning and replication - Conductivity/impedance modification by SPM and SECM
<b>Topic 11</b> Industrial Electrochemistry and Electrochemical Engineering Industrial electrolysis - Membranes - Chlorine technology - Industrial materials and cell design	<b>Topic 12</b> General Session

## TEME

- 1) IONIKA
- 2) ELEKTRODIKA
- 3) ELEKTROANALITIKA

## IONIKA

strukture ionskih otopina i talina  
svojstva ionskih otopina

jaki i slabi elektroliti

kiselinsko-bazne i ligacijske ravnoteže  
modeli elektrolitne otopine

## IONIKA

modeli elektrolitne otopine

model "ionskog oblaka" (Debye & Hückel)

model ionske asocijacije (Bjerrum)

numeričke simulacije

## ELEKTRODIKA

- ravnoteža u elektrokemijskim člancima
  - definicija i mjerenje pH
- staklena elektroda, ion-selektivne elektrode
  - stacionarna voltametrija
    - DC polarografija
- ciklička voltametrija, pravokutnovalna voltametrija
- voltametrija anodnog i katodnog otapanja

## literatura

- A. J. Bard i L. R. Faulkner, *Electrochemical Methods*, Wiley, New York 2001.
- J. Wang, *Analytical Electrochemistry*, Wiley, New York, 2000.
- P. W. Atkins, *Physical Chemistry*, 3. izdanje (i sva kasnija izdanja), Oxford Univ. Press, Oxford, 1987.

## literatura

- I. Piljac, *Elektroanalitičke metode*, RMC, Zagreb, 1995.
- VI. Simeon, *Termodinamika*, Školska knjiga, Zagreb, 1980.
- VI. Simeon, *Equilibria in Electrolyte Solutions*, u: N. Kallay (ur.), *Interfacial Dynamics*, M. Dekker, New York, 2000.
- VI. Simeon i V. Tomišić, *Kem. Ind.* **46** (1997) 319-326.

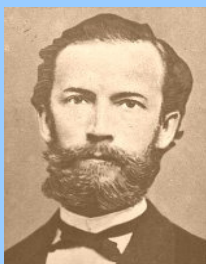


## IONIKA

elektrolit

- neka tvar prisutna u otopini ili u talini koja je barem djelomično u obliku nabijenih čestica

- Vodljivost (*conductance*)  $G / S$
- Provodnost (*conductivity*)  $\kappa / S \text{ m}^{-1}$
- Molarna provodnost  $\Lambda / S \text{ cm}^2 \text{ mol}^{-1}$
- Molarna provodnost pri beskonačnom razrijeđenju  $\Lambda_0 / S \text{ cm}^2 \text{ mol}^{-1}$



**Friedrich Wilhelm Georg Kohlrausch**

14. listopada, 1840., Rinteln, Njemačka

17. siječnja, 1910., Marburg, Njemačka



## Kohlrausch

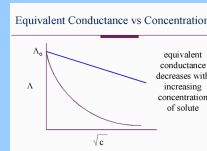


Kohlrausch i suradnici (npr. Arrhenius, Nernst),  
Wuerzburg, 1886.

## jaki i slabi elektroliti

- ovisnost molarnih provodnosti o koncentraciji:
- dva tipa ovisnosti - iz toga zaključak o dva tipa elektrolita
- jaki elektroliti - potpuno disocirani
- slabi elektroliti - prisutan u otopini i u ionskom i u molekulskom obliku

## jaki i slabi elektroliti



## Kohlrauschov zakon

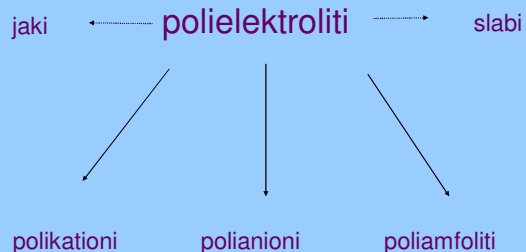
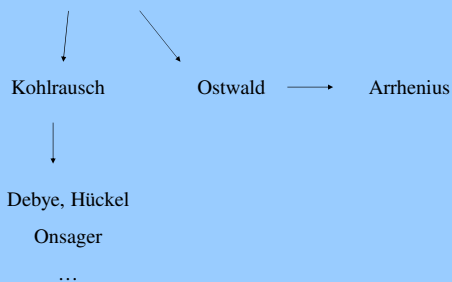
- $\Lambda(\text{KCl}) = \Lambda_0(\text{KCl}) - b c(\text{KCl})^{1/2}$
- $\Lambda_0(\text{KCl}) = \lambda_0(\text{K}^+) + \lambda_0(\text{Cl}^-)$
- $\Lambda_0(\text{MgCl}_2) = \lambda_0(\text{Mg}^{2+}) + 2\lambda_0(\text{Cl}^-)$

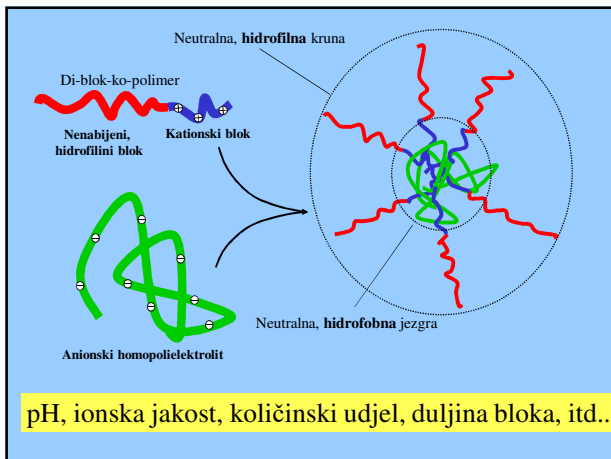
## slabi elektroliti

- $\alpha = \Lambda / \Lambda_0$
- $K(\text{CH}_3\text{COOH}) = \alpha^2 [\text{CH}_3\text{COOH}] / (1 - \alpha)$
- Ostwaldov zakon razrjeđenja

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{\kappa}{\Lambda_0^2 K}$$

- Faraday





**PAMA** poli(dimetil-aminoetil-metakrilat)  
Poly(di-methyl-Amino-ethyl-MethAcrylate)

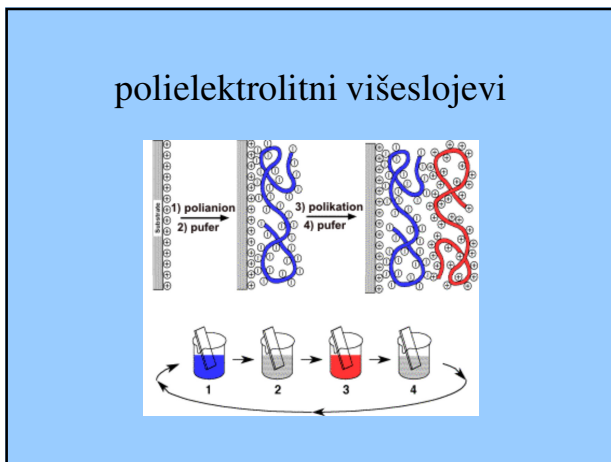
$$\left[ \begin{array}{c} \text{CH}_3 \\ | \\ \text{C}-\text{CH}_2 \\ | \\ \text{C}=\text{O} \\ | \\ \text{O} \\ | \\ \text{CH}_2 \\ | \\ \text{CH}_2 \\ | \\ \text{N}(\text{CH}_3)_2 \end{array} \right]_n$$

$M_w = 20 \text{ kg/mol}$   
 $M_s = 157 \text{ g/mol}$

**PAA** poli(akrilna kiselina)  
Poly(Acrylic Acid)

$$\left[ \begin{array}{c} \text{CH}-\text{CH}_2 \\ | \\ \text{C}=\text{O} \\ | \\ \text{OH} \end{array} \right]_n$$

$M_w = 12.5 \text{ kg/mol}$   
 $M_s = 72 \text{ g/mol}$



- konceptualni modeli ionske otopine
- model “ionskog oblaka” (Debye & Hückel)
- model ionske asocijacije (Bjerrum)