**Fundamentals of electro-transport processes in membrane systems**

**Intensive multidisciplinary course: physics, chemistry, programming, simulation**

***Lectures&Problem solving - 30 hrs***

*Governing transport equations*

Basic transport equations. The microscopic and irreversible thermodynamics approaches. Onsager and Kedem-Katchalsky equations. The Nernst-Planck equation and the linear equations of Fick, Ohm, Darcy and Fourier. Applications to homogeneous and heterogeneous media. Basics of effective medium theory.

The conservation equations. Conservation of mass, matter, energy. Conservation of momentum. The Navier-Stokes equation. Hagen-Poiseuille flow between membranes.

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| *Structure of charged membranes* |  |  |

Structure of the electric double layer at the interfaces: diffuse and dense parts of the EDL; models by Helmholtz, Gouy-Chapman, Stern. Equilibrium at interfaces. Boltzmann and Donnan equations.

Structure of charged membranes and its model description. Structuring in dry membranes, formation of multiplets; evolution of structure when swelling. Similarity with biological membranes, phase separation, micro-, meso- and macropores, the pore size dependence of the parameters of the structure (chain length, the concentration of functional groups). Structural models by Gierke, Kreuer, Haubold. Capillary space-charge models. Effective medium theory; multiphase models; microheterogeneous model: basic equations and parameters, calculation of the membrane conductivity, permeability and transport numbers as functions of concentration and structural parameters.

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| *Ion and water transport in charged membranes* |  |  |

Homogeneous medium approach: Teorell-Meyer-Sievers (TMS) model. Transport in heterogeneous medium. Combination of the Onsager, Kedem-Katchalsky or Nernst-Planck equations with the microheterogeneous model. Osmosis and electroosmosis.

Ion transfer combined with parallel chemical reactions. Ampholyte transport.

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| *Concentration polarization* |  |  |

Current-induced changes in the electrolyte concentration at the membrane / solution interface. The concept of the diffusion layer. Limiting current density. 1D and 2D classical models. Calculation of the transmembrane potential and the total potential difference including diffusion layers. Stationary and transient processes. Basics of physicochemical hydrodynamics. Probstein’s convective diffusion model of electrodialysis.

Overlimiting transfer mechanisms. Water splitting at the interface: mono- and bipolar IEMs. Catalytic role of functional groups. Coupled convection: the gravitational convection and electroconvection. Rubinstein’s 1D model of overlimiting transfer: extended space charge region. 2D basic model of overlimiting transfer enhanced by electroconvection.

Surface modification of IEMs and its effect on the mass transfer characteristics. Controlling the rate of water splitting (generation of H+ and OH− ions) at the interface. Suppression of electroconvection by water splitting. Role of surface hydrophobicity. The role of the electrical and geometrical heterogeneity of the membrane surface.

*Bipolar membranes. Ion transport and water splitting*

Current-voltage characteristics of bipolar membranes. Mechanism of water splitting. Use of bipolar membranes in production of acids and bases from salt solutions. Semi-bipolar membranes.

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| *Membrane electrochemical characterization*  |  |  |

Membrane transport properties: electrical conductivity, diffusion permeability, ion and water transport numbers. Measurements, modelling by using microheterogeneous model.

Voltammetry, chronopotentiometry, electrochemical impedance spectrometry.

Randles-Ershler equivalent circuit, Warburg and Gerisher impedances. Dependence of impedance spectrum on the direct current bias. Measurements, theory, dependence on membrane bulk and surface structure, the role of coupled phenomena (electroconvection, water splitting). Impedance spectra of monopolar and bipolar membranes.

***Practicums – 42 hrs***

*Theoretical: calculations using software for 1D and 2D models – 8 hrs*

*Experimental: membrane electrochemical characterization* (electrical conductivity, diffusion permeability, transport numbers; voltammetry, chronopotentiometry, electrochemical impedance spectrometry) *– 34 hrs*

**Literature**

1. R.B. Bird, W.C. Stewart, and E.N. Lightfoot, Transport Phenomena. J. Wiley & Sons, NY, 2007.
2. E.N. Lightfoot, Transport Phenomena and Living Systems. John Wiley, New York, 1974.
3. V.G. Levich, Physicochemical Hydrodynamics, N.Y., Prentice-Hall, Englewood Cliffs, 1962.
4. J.S. Newman, Electrochemical systems, Prentice Hall PTR, 1991.
5. R.F. Probstein, Physicochemical Hydrodynamics: An Introduction, John Wiley & Sons, Inc., Hoboken, NJ, (2005)
6. D.K. Kondepudi, I. Prigogine, Modern Thermodynamics: From Heat Engines to Dissipative Structures. Wiley, 2005.
7. H Strathmann, Ion-Exchange Membrane Separation Processes, Elsevier, 2004.
8. Y. Tanaka, Ion Exchange Membranes: Fundamentals and Applications, Elsevier, 2007.
9. K. Konturri, L. Murtomaki, J. Manzanares, Ionic transport processes in electrochemistry and membrane science, Oxford University Press, 2008.
10. I. Rubinstein, Electrodiffusion of Ions. SIAM, Philadelphia, PA, 1990.
11. V.I. Zabolotsky, V.V. Nikonenko, Ion transport in membranes, Moscow, Nauka (Science) (in Russian), 1996.
12. V.V. Nikonenko, A.B. Yaroslavtsev, G. Pourcelly, Ion transfer in and through charged membranes. Structure, properties, theory. In: Ionic Interactions in Natural and Synthetic Macromolecules, Ciferri, A and Perico, A. Eds.; Wiley: Hoboken, NJ, 2012, pp. 267-336.
13. E.M.V. Hoek, M. Guiver, V. Nikonenko, V.V. Tarabara, A.L. Zydney, Membrane Terminology. In *Encyclopedia of Membrane Science and Technology*; E.M.V. Hoek, V.V. Tarabara, Eds.; Wiley: Hoboken, NJ, 2013; Vol.3; pp 2219-2228.

**Programming and Simulation of electro-membrane processes: Visual Basic, COMSOL Multiphysics**

***Lectures&Practicum - 18 hrs***

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| *Algorithms for solving 1D problems.**Comsol: principles of programming, solving 2D problems with Nernst-Planck, Poisson and Navier-Stokes equations*.  |  |  |

**Literature**

1. COMSOL Multiphysics, User’s guide, <http://nf.nci.org.au/facilities/software/COMSOL/4.3/doc/pdf/mph/COMSOLMultiphysicsUsersGuide.pdf>
2. A.M. Uzdenova, A.V. Kovalenko, M.K. Urtenov, V.V. Nikonenko, Mathematic modelling of membrane processes by using Comsol Multiphysics 4.3, Kuban State University, Krasnodar, 2013 (in Russian).