



SCIENTIFIC AND METHODS MODULE

Module name	Catalysts
Number	2013-MatCatNet02
Aims	<p>The module links molecular sciences to catalysis on complex, multicomponent and multifunctional active sites.</p> <ol style="list-style-type: none"> 1. General aspects, principles of catalysis, history and development, classification, methodology 2. Green chemistry concepts, design of safer, more efficient processes, use of alternative, more specific forms of energy 3. Carbon-carbon bond formation, synthetic utility and potential 4. Metal-organic frameworks (MOFs), synthesis and applications in catalysis 5. Generation and handling of nanoparticles, catalytic properties 6. Modern concepts of heterogeneous photo-catalysis in industrial and environmental processes 7. Solid acid catalysts for the petrochemical industry 8. Electrocatalysis, charge transfer processes, heterogeneous electrocatalysis with noble metal nanoparticles 9. Protein-film voltammetry, electron transfer reactions, redox biochemistry, bio-relevant processes 10. Biocatalysis, efficiency, sustainability and biological compatibility, important methodology, key unsolved problems, current challenges
Basics	Basic understanding of catalytic chemical processes and kinetics; organometallic compounds, transition metal complexes; nanoparticles; chirality; basic knowledge of analytical and physical chemistry; fundamentals of environmental protection
Contents	<ol style="list-style-type: none"> 1. Homogeneous, heterogeneous and biocatalysis, definitions, history, activity, selectivity, standard reactions, catalytic cycle, terms, mechanisms, industrial processes 2. Microwave irradiation, dielectric heating, thermal/kinetic and non-thermal effects, phase transfer catalysis, heterogeneous catalysis, transition metal catalysis 3. C-C bond formation, Baylis-Hillman reactions, methodology, application in the total synthesis of natural products 4. MOFs, ligands, linkers, metal ions, metal clusters, improved anchored catalysts in heterogeneous catalysis 5. Preparation of nanoparticles, their properties and application as catalysts 6. Photo-catalysis, titania-based catalysts, modern techniques, sustainable development, environmental issues 7. Noble metal-promoted acid catalysts, liquid and/or solid acid catalysts 8. Homogeneous and heterogeneous electrocatalysis, electron transfer, ion transfer, coupled electron-ion transfer, two-phase interfaces, typical examples 9. Redox reactions of relevant enzymes as main biocatalysts, relevant thermodynamic/kinetic data of the redox processes of enzymes 10. Biocatalysts, examples important in energy, commodity production, fine/selective organic synthesis, bulk biomaterials
Type	Two-day block course
Date (month/year)	16 to 17 October 2013
Time	Day 1: 8:30 – 18:30, Day 2: 8:30 – 18:30

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Work load	15 contact hours/ 45 hours self-study
Examination	written
Credit points	2
Responsible scientists	Valentin Mirceski (MK), Rubin Gulaboski (MK), Avni Berisha (KOS), Blaga Radovanovic (SER), Aleksandra Zarubica (SER), Ahmed Jashari (MK)
Guest lecturers	Castelia Cristea (RUM), Radu Silaghi-Dumitrescu (RUM), Evamarie Hey-Hawkins (DE)
Recommendations for literature, e-learning	<ul style="list-style-type: none"> • G. Rothenberg, <i>Catalysis - Concepts and Green Applications</i>, 1. Edition, Wiley-VCH, Weinheim, 2008 • D. Steinborn, <i>Fundamentals of Organometallic Catalysis</i>, 1. Edition, Wiley-VCH, Weinheim, 2011 • P. W. N. M. van Leuween, <i>Homogeneous Catalysis – Understanding the Art</i>, Kluwer Academic Publishers, 2004 • M. Lancaster, chapter in: <i>Green Chemistry, an Introductory text</i>, Cambridge UK, 2002 • T. Welton, Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis, <i>Chem. Rev.</i> 1999, 99, 2071 • A. Loupy, <i>Microwaves in Organic Synthesis</i>, Wiley-VCH, 2002 • C. O. Kappe, A. Stadler, <i>Microwaves in Organic and Medicinal Chemistry</i>, Wiley-VCH, 2005 • C. Guazhong, <i>Nanostructures & Nanomaterials</i>, Imperial College Press, 2004 • B. Bharat (Ed.), <i>Springer Handbook of Nanotechnology</i>, Springer, 3rd ed, 2010 • F. A. Armstrong, <i>Voltammetry of Proteins</i>, in: A. J. Bard, M. Stratmann, G. S. Wilson (eds), <i>Encyclopedia of Electrochemistry</i>, vol. 9, Wiley VCH, 2002 • F. A. Armstrong, <i>Voltammetric Investigations of Iron-sulfur Clusters in Proteins</i>, in: A. Brajter-Toth, J. Q. Chambers (eds), <i>Electroanalytical Methods for Biological Materials</i>, Marcel Dekker, Basel 2002 • S. Kaskel, <i>Handbook of Porous Solids</i>, Vol. 2, Wiley-VCH, 1190, 2002 • S. Kitagawa, R. Kitaura, S. Noro, <i>Angew. Chem. Int. Ed.</i> 2004, 43, 2334 • K. Buchholz, V. Kasch, U. Bornscheuer, <i>Biocatalysis and Enzyme Technology</i>, Wiley-VCH, 2004 • L. Poppe, L. Novak, <i>Selective Biocatalysis</i>, Wiley-VCH • 1992 • A. J. Bard, L. R. Faulkner, <i>Electrochemical Methods: Fundamentals and Applications</i>, John Wiley & Sons, 2001 • K. B. Oldham, J. C. Myland, A. M. Bond, <i>Electrochemical Science and Technology. Fundamentals and Applications</i>, John Wiley & Sons, 2012 • F. G. Banica, A. Ion, <i>Electrocatalysis-based Kinetic Determination</i>, in: R. A. Meyers (ed.) <i>Encyclopedia of Analytical Chemistry</i>, Wiley, Chichester, 2000 • G. D. Yadav, J. J. Nair, <i>Micropor. Mesopor. Mater.</i> 1999, 33, 1 • H. A. Prescott, M. Wloka, E. Kemnitz, <i>J. Molecul. Catal. A: Chem.</i> 2004, 223, 67 • J. McMurry, <i>Organic Chemistry</i>, 5th ed., Brooks/Cole, 2000 • N. Miyaura, A. Suzuki, <i>Chem. Rev.</i> 1995, 95, 2457.

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SCHEDULE 2013

Time	Lecturer	Programme	Location
Day 1			
8:30-9:30	Evamarie Hey-Hawkins (Leipzig)	Introduction to catalysis	Cluj-Napoca, RUM
9:30-09:40	<i>Break</i>		
9:40-11:40	Castelia Cristea (Cluj-Napoca)	Microwave activation in organic and organometallic synthesis	Cluj-Napoca, RUM
11:40-12:00	<i>Coffee Break</i>		
12:00-13:00	Ahmed Jashari (Tetovo)	Baylis-Hillman reactions	Cluj-Napoca, RUM
13:00-14:30	<i>Lunch</i>		
14:30-15:30	Evamarie Hey-Hawkins (Leipzig)	Metal-organic frameworks: Application in catalysis	Cluj-Napoca, RUM
15:30-15:45	<i>Coffee Break</i>		
15:45-16:30	Aleksandra Zarubica (Nis)	Solid acid catalysts – application in petrochemical industry	Cluj-Napoca, RUM
16:30-17:00	<i>Coffee Break</i>		
17:00-18:30	Castelia Cristea (Cluj-Napoca)	Microwave activation – experimental	Cluj-Napoca, RUM
Day 2			
08:30-10:00	Aleksandra Zarubica (Nis), Blaga Radovanovic (Nis)	Titania for heterogeneous photocatalytic degradation processes	Cluj-Napoca, RUM
10:00-10:100	<i>Coffee Break</i>		
10:10-11:20	Avni Berisha (Prishtina)	Nanostructures – synthesis, characterization and catalytic properties	Cluj-Napoca, RUM
11:20-11:40	<i>Coffee Break</i>		
11:40-12:40	Valentin Mirceski (Skopje)	Electrochemical methods, techniques and electrode kinetics	Cluj-Napoca, RUM
12:40-14:00	<i>Lunch</i>		
14:00-15:00	Valentin Mirceski (Skopje)	Electrocatalysis	Cluj-Napoca, RUM
15:00-15:10	<i>Coffee Break</i>		
15:10-16:10	Rubin Gulaboski (Stip)	Protein-film voltammetry – Electrochemical spectroscopy for probing the redox features of biocatalysts	Cluj-Napoca, RUM
16:10-16:30	<i>Coffee Break</i>		
16:30-18:30	Radu Silaghi-Dumitrescu (Cluj-Napoca)	Biocatalysis	Cluj-Napoca, RUM
19:00-...	<i>Get-together dinner</i>		

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Baylis-Hillman Reactions

Ahmed Jashari

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Carbon-carbon bond formation is one of the fundamental reactions in organic synthesis. The most important types include the aldol reaction, Friedel-Crafts reaction, Grignard reaction, Diels-Alder reaction, Wittig reaction [1] and the well-known Heck, Kumada, Suzuki and Sonogashira reactions [2]. The development of efficient methods for the formation of carbon-carbon bonds is still a challenging effort which requires the design of miscellaneous catalysts. The Baylis-Hillman reaction [3] may be broadly defined as: "a process of carbon-carbon formation as a result of the reaction between the α -position of one activated alkene and an electrophilic electron-deficient sp^2 carbon (usually an aldehyde), under the influence of a suitable catalyst (particularly a tertiary amine), producing multifunctional molecules" [4]. Nowadays, this reaction is of enormous synthetic utility and potential [5], especially its application in the total synthesis of natural products. Furthermore, the simplicity of this reaction in the easy formation of a C-C bond under green conditions and its ability to accommodate a wide range of electrophiles, activated alkenes, and catalysts will provide opportunities and also challenges to organic chemists to discover innovative methodologies to understand and solve problems in drugs synthesis and other important molecules of biological importance, in the following years.

References:

- [1] J. McMurry, *Organic Chemistry*, 5th ed., Brooks/Cole, 2000.
- [2] a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, 95, 2457; b) H. Remmele, A. Kollhofer, H. Plenio, *Organometallics* **2003**, 22, 4098; c) R. F. Heck, *Acc. Chem. Res.* **1979**, 12, 146.
- [3] A. B. Baylis, M. E. D. Hillman, German Patent 2155113, **1972**, *Chem. Abstr.* 197Z, 77, 34174q.
- [4] D. Basavaiah, P. Dharma Rao, R. Suguna Hyma, *Tetrahedron* **1996**, 52, 8001.
- [5] D. Basavaiah, A. Jaganmohan Rao, T. Satyanarayana, *Chem. Rev.* **2003**, 103, 811.

Solid acid catalysts – application in petrochemical industry

Aleksandra Zarubica

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Saturated hydrocarbons constitute a significant fraction of fuels. However, due to the low octane number of *n*-alkanes, their isomerization to branched counterparts is necessary. Poor reactivity of traditional catalysts in isomerization reactions imposed the need for new and more active catalysts such as noble metal promoted acid catalysts, liquid and/or solid acid catalysts. Among the solid acid catalysts, sulfated zirconia and promoted sulfated zirconia have exhibited high activity for the isomerization of light alkanes at low temperatures.

The present lecture highlights the selected original results which indicate that the modification of sulfated zirconia by incorporation of selected elements significantly affects catalytic performances in *n*-hydrocarbon conversion reaction. Attention is also paid to the recently developed solid acid catalysts used in other reactions of hydrocarbon conversions in petrochemical industry.

References:

- [1] G. D. Yadav, J. J. Nair, *Sulfated zirconia and its modified versions as promising catalysts for industrial processes*, *Micropor. Mesopor. Mater.* **1999**, 33, 1.
- [2] H. A. Prescott, M. Wloka, E. Kemnitz, *Supported sulphated zirconia catalysts and their properties*, *J. Molecul. Catal. A: Chem.* **2004**, 223, 67.
- [3] A. Zarubica, B. Jovic, A. Nikolic, P. Putanov, G. Boskovic, *Temperature imposed textural and surface synergism affecting the isomerization activity of sulphated zirconia catalysts*, *J. Serb. Chem. Soc.* **2009**, 74, 1429.
- [4] G. Boskovic, A. Zarubica, M. Kovacevic, P. Putanov, *Precursor memory effect determining structural properties of sulphated zirconia*, *J. Therm. Anal. Calor.* **2008**, 91, 849.
- [5] A. Zarubica, M. Randjelovic, M. Momcilovic, N. Stojkovic, M. Vasic, N. Radulovic, *The balance between acidity and tetragonal phase fraction in the favorable catalytic act of modified zirconia towards isomerized *n*-hexane(s)*, *Optoelect. Adv. Mater. – Rapid Comm.* **2013**, 7, 62.

Titania for heterogeneous photocatalytic degradation processes

Aleksandra Zarubica, Blaga Radovanovic

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The goal of the lecture is to present the most modern concepts of heterogeneous photo-catalysis in industrial and environmental processes. The lecture will provide advanced knowledge of application of modern techniques towards sustainable development.

Heterogeneous photocatalysis is widely efficient in numerous fields, such as selective oxidation reactions of various reactants, synthesis of fine chemicals, environmental photocatalysis, etc.. Photocatalysis has been based on the ability of the photocatalyst to adsorb reactants and/or react with them, and to efficiently absorb photons. In addition, photocatalysis alternatively induces mild and/or selective oxidation reactions, and also total oxidation reactions.

Titania-based catalysts can be synthesized by using different preparation methods. The physico-chemical properties of the catalysts can be characterized using the Brunauer-Emmett-Teller method (BET), X-ray Diffraction (XRD) and Scanning Electron Microscopy/Transmission Electron Microscopy (SEM/TEM) techniques, etc.. These characterization techniques provide information on the nano-structure of the catalyst, porous system, and morphology of the catalyst's surface. These features of the catalysts have an influence on the catalytic performance and will be discussed in a model reaction, the photo-degradation of pollutants.

References:

- [1] M. Lancaster, chapter in: *Green Chemistry, an Introductory text*, Cambridge UK, 2002.
- [2] T. Welton, *Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis*, *Chem. Rev.* **1999**, 99, 2071.
- [3] P. Vijayan, Ch. Mahendiran, C. H. Sursh, K. Shanthi, Photocatalytic activity of iron doped nanocrystalline titania for the oxidative degradation of 2,4,6-trichlorophenol, *Catalysis Today* **2009**, 141, 220.



Module Catalysts – Cluj-Napoca, October 2013

Nanostructures – synthesis, characterization and catalytic properties

Avni Berisha

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An introduction to the field of nanosciences and nanotechnology will be given. The first part of the lecture will present the short history of the beginnings of nanosciences, followed by a short introduction on selected important topics of physical chemistry of solid surfaces, such as: surface energy, chemical potential, electrostatic stabilization and the interaction between two particles. The classification and the formation of 0 D (nanoparticles), 1 D (nanowires and nanorods) and 2 D (thin films) nanostructures and also some other special nanomaterials (such as carbon fullerenes, carbon nanotubes) will be discussed briefly. Some physical methods for the formation (lithographic techniques, nano-manipulation, etc.) and the characterization (X-ray diffraction - XRD, scanning electron microscopy - SEM, transmission electron microscopy - TEM, X-ray photoelectron spectroscopy - XPS, infrared spectroscopy - IR etc.) of nanomaterials will be introduced. The general utility of nanomaterials with a focus on the use of their catalytic properties will be presented.

References:

- [1] C. Guazhong, *Nanostructures & Nanomaterials*, Imperial College Press, 2004.
- [2] B. Bharat (Ed.), *Springer Handbook of Nanotechnology*, Springer, 3rd ed, 2010.

Microwave activation in organic and organometallic synthesis

Castelia Cristea

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According to the *green chemistry* philosophy, the design of safer, more efficient processes, as well as the use of alternative more specific forms of energy, is highly beneficial for chemists attempting to develop new processes and products capable to meet the evermore stringent demands of the modern society with improved performance but with a lower financial and environmental price tag. Catalysis and microwave chemistry may bring increasingly important contributions in this direction.

Since the early pioneering experiments in 1986, a tremendous amount of research was dedicated to microwave chemistry mainly due to the fact that it provides a rapid “in core” heating allowing enhanced reaction rates and fast optimization of the reaction conditions. Other *green* advantages of microwave chemistry are the safety aspects related to the use of solvents imposed by microwave heating which led to many reactions being carried out in water, ionic liquids or under solvent-free conditions.

This lecture will describe the fundamentals of dielectric heating, the thermal/kinetic and nonthermal effects induced by microwave irradiation in organic synthesis, phase transfer catalysis, heterogeneous catalysis and transition metal catalysis.

References:

- [1] A. Loupy, *Microwaves in Organic Synthesis*, Wiley-VCH, 2002.
- [2] C. O. Kappe, A. Stadler, *Microwaves in Organic and Medicinal Chemistry*, Wiley-VCH, 2005.
- [3] C. O. Kappe, *Controlled Microwave Heating in Modern Organic Synthesis*, *Angew. Chem. Int. Ed.* **2004**, 43, 6250.
- [4] P. Lidstrom, J. Tierney, B. Wathey, J. Westman, *Microwave Assisted Organic Synthesis - a Review*, *Tetrahedron* **2001**, 57, 9225.

Introduction to Catalysis

Evamarie Hey-Hawkins

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This lecture gives an introduction to catalysis in general and an overview for the main aspects of catalysis:

History and development, types of catalysts, activity, and selectivity; homogeneous catalysis: elementary reactions; heterogeneous catalysis and immobilisation; biocatalysis (metalloenzymes).

Selected examples will be presented for each type of catalysis (homogeneous, heterogeneous and biocatalysis).

The aims of this lecture are to understand the basic principles of homogeneous and heterogeneous catalysis in industry, synthesis and biology.

References:

- [1] G. Rothenberg, *Catalysis - Concepts and Green Applications*, 1. Edition, Wiley-VCH, Weinheim, 2008.
- [2] D. Steinborn, *Fundamentals of Organometallic Catalysis*, 1. Edition, Wiley-VCH, Weinheim, 2011.
- [3] P. W. N. M. van Leuween, *Homogeneous Catalysis – Understanding the Art*, Kluwer Academic Publishers, 2004.
- [4] R. M. Roat-Malone, *Bioinorganic Chemistry: A short course*, 2nd edition, Wiley VCH, 2007.
- [5] *Concepts and Models in Bioinorganic Chemistry*, ed. H.-B. Kraatz, N. Metzler-Nolte, Wiley VCH, 2006.

Metal-organic frameworks: Application in catalysis

Evamarie Hey-Hawkins

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Metal-organic frameworks (MOFs) are a class of inorganic–organic hybrid materials in which metal ions or inorganic clusters (so-called secondary building units (SBUs), often formed in situ) are bridged by multidentate ligands to form polymeric coordination networks.^[1] This relatively new class of porous polymers are promising materials for technical applications in separation, storage and heterogeneous catalysis, and the growing number of publications and patents focussed on metal-organic frameworks reflects the worldwide current interest in this research area.^[1,2]

The diversity of ligands as possible linkers and of metal ions and metal clusters as building units (nodes) is the basis for the variety of structural topologies with corresponding special properties.^[1,3] MOFs are valuable supplements to the already known zeolite materials and mesoporous molecular sieves. An essential advantage of MOFs compared with mesoporous materials is their crystalline structure. This results in uniform, strictly regular pore and cavity sizes and the possibility of detailed structural investigation by X-ray analysis. Compared to zeolites, the presence of linkers in MOFs allows tailoring of a wide variety of pore sizes (from 2 to 100 nm).

These porous coordination polymers are formed in organic solvents by self-assembly on reacting metal salts or complexes with the corresponding linkers. A promising field of application for porous coordination networks is heterogeneous catalysis, where MOFs can offer completely new possibilities and perspectives for employment as catalysts or for the synthesis of improved anchored catalysts. This area is still largely unexplored^[3] and will be the main focus of this lecture.

References:

- [1] (a) S. Kaskel, *Handbook of Porous Solids*, Vol. 2, Wiley-VCH, 1190, 2002; (b) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334.
- [2] K. Sanderson, *Nature* **2007**, *448*, 746.
- [3] *Chem. Soc. Rev.* **2009**, *38*, Special Issue on “*Metal-Organic Frameworks*”.

Biocatalysis

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Living organisms offer a good selection of catalysts that have been “optimized” and “tested” for efficiency, sustainability and biological compatibility over many millions of years. Scientifically-driven use of such catalysts, as well as of biologically-inspired “mimics”, should therefore be a prime option for process designers. Examples would include reactions important in energy (e.g., splitting water into O₂ and H₂, producing H₂ from protons, producing biodiesel), commodity production (e.g., producing sugars from atmospheric CO₂, or ammonia from N₂, or methanol from methane), fine/selective organic synthesis (e.g., enantiomer separation, highly selective derivatization of complex organic molecules, amide production from nitriles), or even synthesis of bulk biomaterials. On a different note, the multitude of enzymes available so far offer at least just as many, if not more, options for selective analyte measurements; enzymes such as peroxidases, phosphatases or glucose oxidases are illustrative success stories commercially. The lecture will review these topics, illustrating interesting achievements, important methodology points, key unsolved problems, and current challenges.

References:

- [1] K. Buchholz, V. Kasch, U. Bornscheuer, *Biocatalysis and Enzyme Technology*, Wiley-VCH, 2004.
- [2] L. Poppe, L. Novak, *Selective Biocatalysis*, Wiley-VCH, 1992.
- [3] A. Liese, K. Seelbach, C. Wandrey, *Industrial Biotransformations*, Wiley-VCH, 2001.
- [4] R. Silaghi-Dumitrescu, *Redox activation of small molecules at biological metal centers, Structure & Bonding* **2013**, 150, 97.
- [5] H. B. Kraatz, N. Metzler-Nolte, *Concepts and Models in Bioinorganic Chemistry*, Wiley-VCH, 2006.

Protein-film voltammetry - Electrochemical spectroscopy for probing the redox features of biocatalysts

Rubin Gulaboski

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As we know, life on Earth depends significantly on the occurrence of reactions involving an exchange of electrons between two or more systems. Reactions comprising an electron transfer are responsible for the functioning of many proteins in important bio-relevant processes. The photosynthesis and respiration, for example, are fundamental processes where the conversion of the energy occurs through a complex sequence of electron transfer reactions involving different enzymes. Electron transfers also occur in many other biological processes ranging from cell defense to gene control. Since many diseases are mainly associated with malfunctioning redox biochemistry in humans, the understanding of these processes has also a big medical significance.

In the case of proteins, the use of voltammetry as a tool for getting insight into their redox chemistry is a quite difficult task. The main problems are seen in the huge protein size and the presence of big “electroinactive” lipophilic tails that hinder the “access” of electrons to the protein’s redox-active site(s). Nearly 20 years ago, a promising voltammetric methodology had been developed for studying the redox chemistry of various redox-active proteins. The method had been named “protein-film voltammetry” (PFV).

In this lecture, we focus on the main achievements and experimental challenges of the protein-film voltammetry. Special attention will be paid to the application of PFV for studying various redox reactions of relevant enzymes that are main biocatalysts. We will also focus on relevant theoretical models developed to study various electrode mechanisms under conditions of square-wave voltammetry (SWV). We will present simple ways to get access to relevant thermodynamic/kinetic data of the redox processes of many enzymes.

References:

- [1] F. A. Armstrong, *Voltammetry of Proteins*, in A. J. Bard, M. Stratmann, G. S. Wilson (eds), *Encyclopedia of Electrochemistry*, vol. 9, Wiley VCH, 2002.
- [2] F. A. Armstrong, *Voltammetric Investigations of Iron-sulfur Clusters in Proteins*, in: A. Brajter-Toth, J. Q. Chambers (eds), *Electroanalytical Methods for Biological Materials*, Marcel Dekker, Basel 2002.
- [3] F. A. Armstrong, *J. Chem. Soc. Dalton Trans* **2002**, 5, 661.
- [4] F. A. Armstrong, *Applications of Voltammetric Methods for Probing the Chemistry of Redox Proteins*, in: G. Lenaz, G. Milazzo (eds), *Bioelectrochemistry: principles and practice*, vol. 5, Birkhauser Verlag AG, Basel 1997.
- [5] P. N. Barlett, *Bioelectrochemistry: Fundamentals, Experimental Techniques and Application*, Wiley, Chichester 2008.
- [6] R. Gulaboski, V. Mirčeski, I. Bogeski, M. Hoth, *J. Solid State Electrochem.* **2012**, 16, 2315.



Module Catalysts – Cluj-Napoca, October 2013

Introduction to electrode processes

Valentin Mirceski

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The main goal of the lecture is to provide basic knowledge on the heterogeneous charge transfer processes (electron transfer, ion transfer or coupled electron-ion transfer) occurring across an interface between two different phases (mostly solid/liquid and liquid/liquid), in order to understand the governing principles of electrochemical techniques. The fundamental terms and concepts employed in describing the electrode reactions are introduced. In addition, before embarking on a detailed consideration of the methods for studying electrode processes and their rigorous mathematical representations, an approximate theoretical consideration of several types of electrode processes is given. In particular, the lecture is focused on defining the following terms: electrochemical cell and electrochemical reactions, conductors of the first and second kind, electrical potential and current, interface and the strength of the electric field at the interface electrode/electrolyte, standard electrode potential, Faraday law, anodic and cathodic current, sign convention, polarisability, potential window, faradic and non-faradic processes, structure of the double electric layer at the interface, and electrode kinetics.

References:

- [1] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, 2001.
- [2] K. B. Oldham, J. C. Myland, A. M. Bond, *Electrochemical Science and Technology. Fundamentals and Applications*, John Wiley & Sons, 2012.

Electrocatalysis

Valentin Mirceski

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The lecture aims to provide a basic understanding of the catalysis in the field of electrochemistry. In particular, it is focused on the catalysis of an electrode reaction, known as electrocatalysis. The effect of electrocatalysis is an increase of the standard rate constant of an electrode reaction, which results in an increase of the faradaic current. As the current increase can be masked by other non-electrochemical rate-limiting steps, the most straightforward indication for the electrocatalytic effect is the shift of the electrode reaction to a lower overpotential at a given current density. The electrocatalysis is commonly divided into homogeneous and heterogeneous catalysis. In homogenous electrocatalysis, both the catalyst and the substrate are in the same phase, frequently dissolved in the bulk solution. Typical examples are reductions of hydrogen peroxide, hydroxyl amine, and anionic inorganic oxidant such as chlorate, chlorite, perchlorate, bromate, iodate, nitrate, nitrite, and persulfate, catalyzed by transition metal ions. For the heterogeneous electrocatalysis, most frequently the catalyst is immobilized on the electrode surface, or the electrode itself plays the role of a catalyst. The catalytic effects of various electrode materials on the hydrogen evolution reaction are typical examples for the heterogeneous electrocatalysis. Particular attention is given to the heterogeneous electrocatalysis with noble metal nanoparticles, taking into account their electrochemical *in situ* preparation. Finally, attention is given to specific heterogeneous electrocatalytic reactions at the interface between two immiscible liquid phases. State-of-the-art techniques for preparation of nanoparticles at the liquid interfaces are described in detail, considering their catalytic effects to ion and electron transfer processes.

References:

- [1] K. B. Oldham, J. C. Myland, A. M. Bond, *Electrochemical Science and Technology. Fundamentals and Applications*, John Wiley & Sons, 2012.
- [2] F. G. Banica, A. Ion, *Electrocatalysis-based kinetic determination*, in: R. A. Meyers (ed.) *Encyclopedia of analytical chemistry*, Wiley, Chichester, 2000.