CHEM465/865 – Electrochemistry

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- Office hours (room C9034) :
  - Friday: 1 – 2 pm
  - Monday, Wednesday: 10:30 – 11:30 am

- Tutorials (Dr. Ata Roudgar), starting next week

- Problem sets (7-8 assignments, starting next week)
  Comment: What is the objective? How to do problem sets?
  Encourage discussion, collaboration…

- Projects in computational electrochemistry (October):
  groups of 3, adjusted grading scheme, register next week
  Topics: Molecular Dynamics, Monte-Carlo Simulations
  Requirements: tutorial sessions, calculations, report

- **Exams**
  - **Midterm: Oct. 23rd, 2006 (during class)**
  - **Final: Dec. 7th, 2006, 15.30 – 18.30**

- **Grading**
  - **25% midterm**
  - **25% problem sets**
  - **50% final exam**

  with computational electrochemistry project:
  - **20% midterm**
  - **20% problem sets**
  - **20% project**
  - **40% final exam**

Questions, suggestions???

**"The important thing is not to stop questioning…
Never loose a holy curiosity."
Albert Einstein, 1879-1955**

**"Judge a man by his questions rather than by his answers."
Voltaire, 1694-1778**

**"A wise man's question contains half the answer."
Solomon Ibn Gabirol, 1021-1058**

**"It is not every question that deserves an answer."
Publilius Syrus, ~100 BC**

Always welcome, helpful!

Outline

1. Introduction (1 week)

1.1 Preliminaries

1.2 Interdiscplinarity

1.3 What is electrochemistry?

1.4 Overview of electrochemical systems and applications

Outline

2. Fundamentals of Electrochemistry (5 - 6 weeks)

2.1 Thermodynamics (interfaces and energy conversion)

2.2 Electrochemical potential, electrode potential and electrode configurations

2.3 Metal solution interface and electrode processes

2.4 Adsorption on metal electrodes

2.5 Kinetics of electrode reactions (phenomenological)

2.6 Microscopic theory of charge transfer (electrons, protons, ions)

2.7 Semiconductor electrochemistry and photoelectrochemistry

2.8 Mass transfer in electrochemical systems

2.9 Electrochemical reactions in complex systems

2.10 Complex reactions, mixed potentials and corrosion

Outline

3. Experimental methods (electrochemistry, surface science) (3 weeks)

3.1 Transient techniques

3.2 Cyclic voltammetry

3.3 Impedance spectroscopy

3.4 STM-based techniques

3.5 Raman, IR spectroscopy

Outline

4. Selected topics in electrochemistry (3 weeks)

4.1 Electrochemical energy conversion

4.2 Theory of fuel cells: structures and processes in charge

4.3 Random heterogeneous media – distributed systems (length scales, processes, theoretical tools, experimental techniques), pore structure

4.4 Nanoparticle electrocatalysis (exp., kinetic theory, MC simulations)

4.5 PEM operation: structure formation, proton/solvent/polymer dynamics, theoretical tools (charge transfer theory, MD simulations)

Literature

Recommended texts:

Introductory textbook, concisely covers all important aspects:
W. Schmickler**, Interfacial Electrochemistry**,
Oxford University Press, NY, 1996

Classical textbooks, from basic concepts to applied aspects:
A.J. Bard, L.R. Faulkner, **Electrochemical Methods**,
2nd Ed., Wiley & Sons, New York, 2000.

V.S. Bagotzky, **Fundamentals of Electrochemistry**,
2nd Ed., Wiley & Sons, New York, 2006.

C.M.A. Brett and A.M.O. Brett, **Electrochemistry**, Oxford Univ. Press, Oxford, 1993.

Selected Chapters from

Handbook of fuel cells: fundamentals, technology, and applications,
editors, Wolf Vielstich, Arnold Lamm, Hubert A. Gasteiger, New York, Wiley, 2003.

Encyclopedia of electrochemistry, edited by A.J. Bard and M. Stratmann,
Weinheim, Wiley-VCH, 2002-.

Theory of charge transfer in biology, chemistry and physics:

J. Ulstrup, A.M. Kuznetsov, **Electron transfer in chemistry and biology: an introduction to the theory,** John Wiley, New York, 1998.

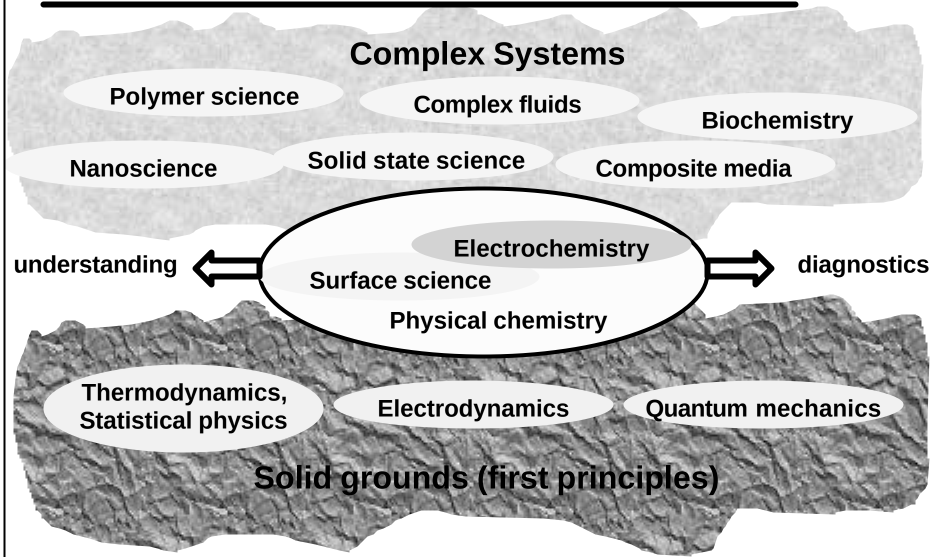
Electrocatalysis

E. Gileadi, **Electrode Kinetics**, VCH, Weinheim, 1993.

Catalysis and electrocatalysis at nanoparticle surfaces, edited by
Andrzej Wieckowski, Elena R. Savinova, Constantinos G. Vayenas,
New York, Marcel Dekker, 2003.

Electrocatalysis, edited by Jacek Lipkowski and Philip N. Ross,
New York, Wiley-VCH, 1998.

Interdisciplinarity



What is Electrochemistry?

Oxidation and reduction: loss and gain of electron density

Widespread phenomena:

- rusting of iron
- photosynthesis (solar energy ? “food”, viz. potential energy)
- metabolism (food ? kinetic energy)

Common aspect of chemical changes?

transfer of electrons from one chemical species to another

Common aspect of electrochemical changes?

<u>chemical change (redox reaction) ? flow of electrons through a wire</u>

The study of these changes is called ELECTROCHEMISTRY!

Important: Spatial separation of partial reactions

⇨ we will be dealing with heterogeneous systems

Interfaces and Energy Conversion

Electrochemistry involves interfaces: study of structures and processes at the interface between an electronic conductor (the electrode) and an ionic conductor (the electrolyte) or at the interface between two electrolytes

Electronic conductor: metal, semiconductor

Ionic conductor: electrolyte solution, molten salts, solid electrolytes

Electrochemistry involves energy conversion:
Chemical energy (driving force for chemical reactions)

voltaic cells ↓ ↑ electrolytic cells

Electrical energy (driving force for directed movement of charges)

Important Concepts in Electrochemistry

The most important concept in electrochemistry:
Electrode potential (the joystick)
Measure of energy of electrons

- ❑ **materials properties**
- ❑ **composition, morphology**
- ❑ **interfaces**

Potential distributions:

- ❑ **Electrostatics**
- ❑ **Statistical mechanics**
- ❑ **Thermodynamics**

Electrical current

- ❑ **ion transport in solution**
- ❑ **charge transfer at interface**

Measure of rate of transport/reaction

Current flux:

- ❑ **non-equilibrium thermodynamics**
- ❑ **electrode processes**
- ❑ **balance equations (fluid dynamics)**

Main interest (in practical terms):
Dependence of electrical current on potential differences.

Finely resolved structures and processes: look at detailed distributions!

How to define electrical potential?

- ❑ **nontrivial!**
- ❑ **potential scales**

What happens at a single electrode (if you wait long enough)?

- ❑ **equilibrium charge and potential distribution**

How to make a macroscopic current flow (that could perform work in cell phone, laptop, electric vehicle, etc.)?

- ❑ **need two electrodes (potential difference) forming a closed circuit**
- ❑ **stationary current: supply of reactants (open system)**