Electrochemistry
Fall 2010
Fitch/Loyola University Chicago
Tth 4:00-5:15; FH105

Content and Material

Electrochemistry is a very diverse area. It can be broadly divided into

a) **Analytical** electrochemistry which is concerned with methods of measurement involving potentiometry (pH meters etc), voltammetry, and modern sensors (generally voltammetric in nature)

b) **Physical electrochemistry** is the basis of analytical electrochemistry, but is generally concerned with the effect of electric fields, charge balance, and diffusion.

c) **Chemical electrochemistry** usually is less interested in quantitative analysis but is devoted to understanding the mechanisms of electron transfer based on chemical structure.

d) Biologic electrochemistry which can be understood as a form of physical electrochemistry (charge and fields around biomolecules) and of chemical electrochemistry (electron transfer events in biological systems)

e) Geologic and environmental electrochemistry which is concerned with all of the above as they take place in the natural environment. Of particular interest are the oxidation reduction reactions of iron, manganese, chromium, arsenic, sulfur, as these set the parameters in which life can grow and, as the oxidation state of iron has substantial implications for the stability of various minerals and their dissolution/formation.

f) Technical - in this field fall the major areas of batteries, solar energy, fuel cells, and corrosion sciences.

This class is primarily concerned with a, b, and c which will be covered in the first 2/3 of the semester. Based on student interest selected topics from d-f will be discussed.

“TextBook”

Wiley found my lecture notes from 2007 and asked me to submit a book proposal which was accepted. Consequently, in addition to the ppt lectures, you ***may*** get supplemental material which is a written description of the materials in the ppt lectures.

If you are a “book” learner and need a book, I am happy to suggest reading materials and/or loan out one or more of the common electrochemistry textbooks. I should warn you, however, that the vast majority of electrochemistry texts are highly equation driven, hence Wiley’s interest in our approach to presenting electrochemical material.

Table of Contents

The chapters are arranged in order of ascending complexity of the system electrochemistry. As necessary, the appropriate research methods are introduced, with the ascending complexity. Several chapters then build upon detailed analysis of industrial system electrochemistry.

6. **Electrodes and Solvents, EC_i**

Chapters 1, 2-5 simplified the electrochemical system by focusing only on the electrochemistry of the compounds, while presuming that the solvent and electrode were non-participants in the electrochemistry. This chapter introduces the impact of both the electrode and the solvent on electrochemical reactions.

a. The chapter begins by assuming that many electrochemical reactions end with a radical that can interact with the solvent. Solvents are examined with respect to the Gutman donor/acceptor numbers. and how they are characterized by reactivity and polarity are examined.
b. The concept of radical production is further extended to polymerization reactions which can result in electrode fouling. Out of this we introduce the concept of deliberately polymerized materials for conducting organic surfaces (polythiophene, polyaniline, and polypyrrole).
c. The preceding topic allows a natural transition to metal surfaces. Various typical metal surfaces used in electrochemistry are examined for their behavior in strong acids (butterfly plots). The typical background currents related to oxide formation are examined.
d. Surfaces that are not so reactive end this chapter: modified electrodes, sol gel surfaces, carbon nanotubes, and surface assembled monolayer films are introduced.

7. **Quinone Case Study: Proton Coupled Electron Transfer**

(square and 9 member schemes)

Hydroquinone is examined in detail. (This introduces another biological component (ubiquinone). The growing complexity of CVs are analyzed. Methods of distinguishing between EC, CE and concerted proton/electron transfer are discussed. The role of proton transfer in biological electrochemistry is introduced.

8. **Charged Surfaces**

This chapter elaborates on the concepts begun in chapter 6.

a. Concepts covered are Poisson-Boltzman distribution, Debye length, diffuse double layer, surface charge density, Gouy-Chapman model of the surface, Stern and Helmholtz layers, zeta potentials, steaming potentials, electrophoretic mobility, ionic mobilities, resistivities. The relationship of the diffusion coefficient to ionic mobilities is discussed.
b. Further topics are solution resistance, cell configurations, and transference numbers. Methods to measure capacitance are introduced. One featured system is the change in capacitance curves in the presence of nanoparticles.
c. The final topic relates the work of bringing a charged reactant to the surface of the electrode with the activation energy for electron transfer. This will serve as a lead in to Chapter 9.

9. **Electron Transfer Kinetic Models**

a. The rate of electron transfer is examined via the Butler-Volmer formulation, Tafel plots. The alpha parameter is discussed as a proxy for the effect of the geometry of bond breaking. CVs are examined for the effect of the alpha parameter. Exchange currents are discussed with the re-introduction of the Levich equation for the RDE.
b. Marcus theory for outer sphere electron transfer is developed. The relationship of the alpha parameter to the quadratic is shown and literature examples introduced.
c. The electrochemistry of transition metal complexes is re-examined in light of electron transfer theory. The viability of the Marcus cross- reaction is tested.

10. **Proteins**

Understanding metalloproteins and their electrochemistry

Marcus theory as applied to the rate of electron transfer in proteins is examined. The role of porphyrins and conductive “wires” in charge propagation discussed. Electron hopping pathways introduced.

Thin layer optical cells are introduced in order to study some data on hemoglobins in detail.

11 **The Respiratory Chain**

This chapter draws together all of the previous concepts: transition metal complexes, aromatics, potential modulation of aromatics to control the direction of electron transfer, etc. Focus on all complexes of the electron transport chain with special emphasis on Complex III and IV.
Work on enzymatic, microbial, and organelle-based biofuel cells presented.
Membrane potentials as a complication to the system highlighted and used to set up subsequent chapter on membrane potentials.

12. **<u>Membrane Potentials and potentiometric sensors</u>**

Membrane potentials more fully (mathematically) developed leading to the Henderson equation, . Briefly relates potentials to applications in biology. Ends by looking at methods based on potential measurements (Potentiometric sensors and "Noses and Tongues").

13. **<u>Biologically Based Amperometric Sensors</u>**

Uses the concepts introduced in Chapters 10 and 11 to examine sensors based porphyrins (volcano plots), enzymes, and DNA. Methods of localizing these materials are discussed (SAMS and hairpin DNA). The role of orientation and biomolecule stabilization are examined. The model system for this chapter is the glucose oxidase sensor.

13. **<u>Metal and Metal Oxide Surfaces</u>**

This chapter introduces the following concepts 111,100 surface structures, Pourbaix diagrams, galvanostatic methods, chronopotentiometry (Sand equation), electrochemical impedance spectroscopy, under potential deposition, theory and mathematics of current deposition, use of deposition in semiconductor industry for integrated devices.

14. **<u>Photoelectrochemistry</u>**

a. Photosynthesis is used to introduce a variety of Photoelectrochemical systems.
b. Excited state electron transfer uses the Weller equation. The system next examined chemiluminescence and the $Ru(bpy)_3^{2+}$ technologies. Immunoassays based on $Ru(bpy)_3^{2+}$ are examined.
c. Solar cells are examined which requires the introduction of the mathematics of voltammetry at semiconductor electrodes (Gartner Eq.) and pulls apart the technology of solar cell systems with particular notice of the chemistry previously discussed. This chemistry includes sensitizing dyes (old film technology).
d. Photodegradation of pollutants is the last topic in this chapter.

15. **<u>Batteries</u>**

The ability to store and access chemical energy based on interfacial surface structures explained. The mathematics and effects of porosity are covered. The focus is primarily on the lead acid and Li batteries. Various Pourbaix plots are used as well as EIS to explore the structure of the battery electrode interface.

16. **<u>Fuel Cells</u>**

The general concept of fuel cells is introduced. The importance of transport in fuel cells emphasized. Information is related to UPD and volcano diagrams, as well as to membrane potentials, and kinetics. The issue of membrane potentials is related back to proton transfer. The system examined is that of Pt, including the prognosis for future use of Pt.

17. **<u>Iron Oxides (I) Corrosion</u>**

Corrosion of iron is introduced, and examined in the case of uranium storage systems, batteries.

18. **<u>Iron Oxides (II) Microbial Environmental Electrochemistry</u>**

This chapter integrates concepts of proteins as terminal redox functional at the cell membrane, acid mine drainage, bio mining, and microbial fuel cells.

Week #	Week begins on	Topic
1	Aug 30	Introduction
2	Sept 6	Beginnings of electron transfer rates; metal complexes
3	Sept 13 **<u>Thurs. Sept. 16</u>** Chemistry Depart. Seminar Shelley Minteer: BioFuel cells – class attendance mandatory in place of regular class (Life Sciences Bldg. Room 142 4-5:15 pm)	Potentials, Nernst Eq, and measurements
4	Sept 20	Organic Electroactive groups
5	Sept 27	Controlled Potential Methods
6	Oct 4	**Exam I. First consultation due**
7	Oct 11 (Tues. Oct 12 no Classes) Electrochemical Society Meets Las Vegas	Kinetics Effects in Organic Electrochemistry
8	Oct 18	Photochemical Electrochemistry
9	Oct. 25	Biological Electrochemistry
10	Nov. 1	**Exam 2, Second Consultation** Simulations and Delivery of pdf documents
11	Nov 8	Membrane Potentials; Ion Selective Electrodes
12	Nov. 15 Eastern Analytical Society meets N. J.	Selected Topics (H2 & O2 rxs)
13	Nov. 22 (Thurs. Noc. 25 no classes)	Selected Topics (e.g. corrosion)
14	Nov. 29	Selected Topics, **Exam 3**

Grading and Assignments

1. Exams (Three exams) (Drop one)=200 points
2. Final Exam =100 points
3. Simulation (Each student will be assigned one simulation problem)=100 points
4. Literature Paper = 100 points (10 points for each consultation; 20 for the articles delivered; 30 for presentation; 30 for written paper)

Grade	%	400
A	92	368
A-	90	360
B+	88	352
B+	82	328
B-	80	320
C+	78	312
C	72	288
C-	70	280
D+	68	272
D	60	240
F	<60	<240

Simulation

Part of understanding electrochemistry is visualizing movement of ions in response to a concentration gradient which has been established by an applied potential. In order to better understand these gradients each student will perform one simulation using an excel spread sheet. The simulations will be variable, but still reasonably simple. Students will present their simulation in class with an appropriate set of graphs to show the concentration gradients.

Literature Search and Presentation=100 points

You will conduct a literature search for your article. This search should be done on **SciFinder Scholar**. http://libraries.luc.edu/research/scifinderscholar/

Example searchers are ABiofuel Cells Shewanella@ AElectron Transfer mechanisms clays@ These searches should generate somewhere between 50-100 hits. Of those hits you should be able to get 10 pdf articles via electron journal subscriptions of Loyola (http://hn9yf5lh6v.search.serialssolutions.com/) or via a request for interlibrary loan (http://pluto-lib.ls.luc.edu/illiad/logon.html). You must submit the electronic version of the 10 pdf documents to me.

Week of	Presenter
Aug 27	
Sept 3	
Sept 10	
Sept 17	
Sept 24	Paper topic due
Oct 1	
Oct 8	Mid Semester Break
Oct 15	
Oct 22	
Oct 29	Search Results due
Nov 5	Presentations begin
Nov 12	
Nov 19	Thanksgiving Week - no meeting
Nov 26	
Dec 3	

Literature Presentation Evaluation Form

Date:___________________

Name of Presenter:_____________________________

Name of Evaluator: ______________________________

	Criteria	Poss Pts	Pts
1	Did the student send a copy of the article in pdf format to each group member one week before the presentation?	10	
2	Did the student use power point for his/her presentation?	10	
3	In opening the discussion did the presenter indicate why he/she chose this particular article	10	
4	In opening the discussion did the presenter indicate what background the authors have in the area that would lead a reader to expect some excellence from the article.	10	
5	In opening the discussion did the presenter indicate did the presenter read and present conclusions from any relevant prior work that was discussed in the article?	10	
6	Did the presenter clarify the purpose the authors had in mind?	10	
7	Did the presenter indicate which data/graphs were significant in demonstrating the point the authors wished to make? (Were these graphs expanded to be projected in a form that facilitated discussion of the data?)	10	
8	Did the presenter allow for a reasonable discussion from within the group?	10	
9	Did the presenter summarize the relevant points of the article?	10	
10	Did the presenter and relate them to research to topics covered the class?	10	
	Total	100	

Constructive Comments: Please write below any comments that you feel will help the presenter in future presentations

Late and/or Missed Assignments

No make up exams will be provided as it is difficult to reproduce equivalent materials for all students. Because no make up exam is provided one of three exams will be dropped in calculating the final grade.

Late assignments will be graded as follows:

On time	100% possible
1 week late	90% possible
2 weeks late	80% possible
3 weeks late	70% possible

No assignments accepted after three weeks.

If an assignment is late due to medical illness the student should provide third party documentation, in which case the student gets a one week reprieve before the discounting of points begins.