Chemistry 445: Electroanalytical Chemistry

Prof. Jeffrey E. Dick (he, him, his), Ph.D @ UT Austin w/ Allen J. Bard (jedick@email.unc.edu)
T/Th 9:30 – 10:45 AM, Venable G311
Graduate Research Consultant: Jackson Hall (jrobha@live.unc.edu) for inquiries regarding the project
Office Hour by Appointment

Prerequisites for Chem 445: Chemistry 480 or 481. Your final grade in this course will be based on two hour exams, a project, and homework. I do not give make-up hour exams; if you are absent you either have a valid excuse or a zero. Exam coverage will be announced in class.

Sweepstat: In this course, you will master electrochemistry while working on a project designed to have a broad impact on society. Almost all aspects of the project will be completed during our allotted class time:

1.) You will be placed in pre-determined groups of 3 for the project.
2.) You will be required to build your own device that is capable of voltammetric and amperometric measurements in the Makerspace (schedule orientation at: https://beam.unc.edu/events.php). All materials will be provided.
3.) These devices should be donated to universities or high schools interested in integrating electrochemistry into their curricula. You should identify a home for your devices and start these conversations early.
4.) You will be trained in 3D printing and will design a box and a logo for your device, also in the BEAM Makerspace. Be creative here!
5.) You will test your device on a real electrochemical system, such as the oxidation of ferrocyanide. Low current devices will use ultramicroelectrodes, and you will test the efficacy of 'blocking' collision experiments. Each group will screen the difference in the electrochemical collision signal for different nanoparticles with a pre-chosen electrocatalytic amplification reaction.
6.) You will be required to simulate your electrochemical results using the COMSOL Digital Simulation platform.

Important Dates (Attendance will be taken at all special class time activities so that points can be allotted):

- **Tuesday, September 4th:** HW1 Due (25 pts.), Device Home Progress Report (10 pts.)
- **Tuesday, September 18th:** HW2 Due (25 pts.), 3D Printing Training in class - BEAM @ Murray (10 pts.)
- **Thursday, September 20th:** Fusion 360 Workshop in class (10 pts.), BRING A LAPTOP
    - https://www.autodesk.com/products/fusion-360/students-teachers-educators
- **Tuesday, September 25th:** First Design of Box and Logo Due (10 pts.), Guest Lecture by CJM &MDV
- **Tuesday, October 2nd:** HW3 Due (25 pts.), Device Building, led by CJM BEAM @ Murray (10 pts.)
- **Thursday, October 4th:** Murray Device Building, led by CJM BEAM @ Murray (10 pts.)
- **Tuesday, October 9th:** HW4 Due (25 pts.), Device Home Due with E-mail Verification (10 pts.)
- **Thursday, October 11th:** COMSOL Homework (Laminar Flow) Due (25 pts.)
- **Tuesday, October 16th:** Midterm (200 pts.)
- **Thursday, October 25th:** Decision on Final Exam, Final Box (25 pts.) and Logo Due (25 pts.)
- **Week of October 29th:** Laboratory Device Testing (100 pts.)
- **Tuesday, November 8th:** COMSOL Homework (Electric Field) Due (25 pts.)
- **Tuesday, November 13th:** DigiElch Homework Due (100 pts.)
- **Friday, November 15th:** COMSOL Voltammetry @ Macrodisc (25 pts.) & Edge Effect Sims Due (25 pts.)
- **Tuesday, November 27th:** Final Write-Up Due (200 pts.)§
- **Tuesday, December 4th:** Great Hall, Student Union, Presentations (50 pts.)
- **TBA:** Final Exam (200 pts)§, EC Quiz Due: *Bad Science* & *The Myth of Icarus* (50 pts.)

§Choice of written exam or project write-up

Grades: Graduate Students: HP: >93% P: 75-92.999% LP: 70-74% F: < 70%
Undergraduates: A+: >95%, A: 90-95, A-: 85-90, B+:80-85, B: 75-80, B-:70-75, C+: 70-75, C:65-70, C-:60-65, D+:55-60, D: 50-55, F: 0-50

Texts: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd Ed., 2001.
Oldham, K. B.; Myland, J. C.; Bond, A. M. *Electrochemical Science and Technology: Fundamentals and Applications*.

Homework: HW is available on Sakai and due on the due dates listed above. Late HW will not be accepted. For each homework, you will be required to read a paper and answer questions regarding that paper. These questions will be graded for accuracy. Only one of the remaining questions will be graded for accuracy, and this will be decided by using a random number generator.

DigiElch Homework: You will be required to download a free version of the DigiElch software (https://www.gamry.com/digielch-electrochemical-simulation-software/). Be careful – you only have 2 weeks. You will use this software to simulate voltammograms at macroelectrodes for the following mechanisms: Er, Ei, Eq, CrEr, ErCr, ErCi, ErC2i (dimerization), ErCi' (also ErCiCiEr, catalytic), ErC2i' (catalytic disproportionation), ErEr, ErCiEr, ErCrEr, ECE. For each mechanism, you must obtain: ΔE_p, $i_p*(\nu)^{-1/2}$, i_{pa}/i_{pc} and provide insight into how changing reaction kinetics might change these diagnostic criteria. Answer the following questions regarding *JACS*, **2013**, *135*, 17671 – 17674: (a) What are the main issues the paper deals with? (b) What is the main point of contention with previous work? (c) How is CV used to argue for the point of view in this paper?

Book Assignment: *Bad Science: the Short Life and Weird Times of Cold Fusion* by Gary Taubes & *The Myth of Icarus*. Book quiz on Sakai. The quiz is worth a maximum of 50 extra credit points.

COMSOL Homework: For these assignments, you are encouraged to work together. You will have free access to the COMSOL Finite Element software beginning September 17th, and you are to answer the following questions using your own simulations: Homework 1 – How is laminar flow perturbed by introducing a defect in a pipe? Homework 2 – How does the electric field change between two electrodes in solution as a function of electrolyte conc. and electrode size? These simple simulations will help you prepare for simulations necessary for the project. There are many valuable references to guide you for solving the edge effect, and you can find many examples online (i.e., https://www.comsol.com/models).[1-4]

Final Write-Up/Final Exam: After the Midterm, you will have a choice of writing a final paper or taking a final exam. The Final Exam will be similar in breadth and depth to the Midterm. The final paper must be completed as a journal article as though we would submit this for publication in the *Journal of Chemical Education*. At the end of the semester, if a paper or collection of papers are good enough for publication, students may have a chance to be co-authors on this study. Papers should be complete with a title, abstract, introduction, detailed methods, results/discussion, and conclusions. Figures must be very high (publication) quality and made on Adobe Illustrator.

Major Topics Covered (~Chronological Order): (Introduction) Back to basics, Electron Transfer & Solid State Physics, (1) Electrochemical Thermodynamics & Pourbaix Diagrams, (2) Electrode Surface Structure, (3) Electrochemical Kinetics & Marcus Theory of Electron Transfer, (4) Potentiometry, Amperometry, & Coulometry (5) Voltammetry & Coupled Chemical Reactions, (6) Rotating Disc Electrode, (7) Rotating Ring Disk Electrode & Scanning Electrochemical Microscopy, (8) Spectroelectrochemistry: Electrogenerated Chemiluminescence and Semiconductor Photoelectrochemistry, (9) Ultramicro & nanoelectrodes, (10) Organometallic Electrochemistry & Electrosynthesis, (11) Double Layer Structure, Adsorption Isotherms, Inner Sphere Reactions, and Electrocatalysis, (12) Single Atoms, Molecules, and Nanoparticles

Some specific learning objectives:

Back to Basics: Band Theory of Solids, Brillouin Zones, Wave Diffraction and the Reciprocal Lattice

1.) Understand how one can predict relative $E^{0'}$ values from effective nuclear charge.
2.) Be able to explain metals, semiconductors, and insulators using ideas in solid state physics (Band Theory, Density of States, Brillouin Zones)

Ch. 1 & 2, B&F

3.) Know the difference between faradaic and non-faradaic reactions.
4.) Describe a potential step in terms of the equivalent circuit.
5.) Understand factors affecting electrode reaction rate (and the current), including mass transfer, electron transfer, chemical reactions, adsorption/desorption/crystallization.
6.) Understand liquid junction potentials in terms of transference numbers of ions & how to minimize liquid junction potentials (including ITIES).
7.) Be able to describe the surface structure of an electrode. For HMD, what's an easy way of finding PZC?
8.) Know how to use and generated Pourbaix diagrams.
9.) Begin thinking about thermodynamics at the nanoscale.

Ch. 3, B&F

10.) Be able to derive the Butler-Volmer formalism for electrode kinetics & understand its limitations.
11.) Design a spreadsheet to model simple, one-electron reactions at UMEs.
12.) Understand qualitatively Marcus Theory of electron transfer and its genesis from Libby's work and the Franck-Condon principle. Understand the inverted region predicted by Marcus Theory and explain how it comes about and first experimental evidence for its existence.

Ch. 4, B&F

13.) Understand three modes of mass transfer.
14.) Understand diffusional processes as outlined in Anderson, L. B.; Reilley, C. N. J. Chem. Ed., 1967, 44(1),9.
15.) Describe methods to increase mass transfer.

Ch. 5, B&F

16.) Derive the Cottrell Equation for disc and spherical electrodes.
17.) Be aware of experimental and instrumental limitations under Cottrell conditions.
18.) Describe how concentration profiles change as a function of time for semi-infinite linear diffusion.
19.) Describe the roughness factor and how to calculate it.
20.) Explain why diffusion controlled currents are different at macro electrodes than micro electrodes.
21.) Understand steady-state voltammetry. Why is it so powerful?

22.) Should the potential change as a function of electrode size? Explain your answer to this question qualitatively.
23.) In totally irreversible systems, what techniques can be used to obtain kinetic parameters? (p. 203, B&F).
24.) Understand the mathematics behind bulk electrolysis theory. Describe analytical advantages of coulometry.

Ch. 6, B&F

25.) Understand the shape of voltammograms for semi-infinite linear diffusion.
26.) Understand the effect of double layer capacitance and uncompensated resistance on the voltammogram.
27.) Explain why CV may not the best quantitative electrochemical method.
28.) Understand the correction that Nicholson has proposed for the peak current in CV.
29.) Use the Randles-Sevcik equation to calculate values from experimental data.
30.) Understand applications of UMEs to fast scan cyclic voltammetry, voltammetry in low-conductivity media, etc.
31.) Understand rotating disc electrode mathematics and origins. Be able to calculate kinetic parameters.

Rotating Ring Disc Electrode and Scanning Electrochemical Microscopy

32.) Describe how one can study follow-up chemical reactions with RRDE and SECM.
33.) Describe negative and positive feedback approach curves.
34.) Understand surface interrogation SECM.
35.) Describe other scanning electrochemical experiments, SECCM, SICM, etc.
36.) What advantages does SECM offer over RRDE? How can one extract kinetic information from SECM?

Ch. 1-6, Elements of Molecular and Biomolecular Electrochemistry, J. M. Saveant; Ch. 12, B&F

37.) Broadly, understand and describe how the characteristics of a voltammogram should change with coupled chemical reactions.

Structure of the Double Layer, Adsorption, Inner Sphere Reactions, and Electrocatalysis

38.) Understand the double layer in terms of Debye-Huckel and Guoy Chapman.
39.) Derive expressions for Frumkin and Langmuir Isotherms.
40.) Describe mechanistic considerations for Tafel analyses, particularly for the Tafel/Volmer/Heyrovsky Mechanisms .

Special Topic 1: Electrogenerated Chemiluminescence & Electrodeposition.

41.) Describe reaction mechanisms that contribute to ECL mechanisms and its general importance in bioanalysis.
42.) Understand classical nucleation and growth as outlined by Kelvin, Plieth, Fleischmann, and Scharifker.

Special Topic 2: Organometallic Electrochemistry and Electrosynthesis

43.) Understand use of electrochemistry for synthesis.
44.) Understand considerations for choosing solvents and electrolytes, including donor number, anion charge, etc.
45.) Be able to completely understand voltammetric considerations for non-aqueous systems.
46.) Understand benefits of electrochemistry in non-aqueous systems and experimental methods for these systems.

Special Topic 3: Single Molecule and Nanoparticle Electrochemistry

47.) Describe how to detect the following nanoparticles: conductive, insulating, catalytic, soft (emulsion droplets, vesicles).
48.) Understand why it is important to study single entities versus ensemble particles.
49.) Calculate statistical properties of stochastic processes.

The professor reserves the right to make changes to the syllabus, including project due dates, test dates, and grading scale when unforeseen circumstances occur. These changes will be announced as early as possible so that students can adjust their schedules.

HONOR CODE: Policy adopted by the faculty of the Department of Chemistry on Sept. 9, 1977:
“Since all graded work (including homework to be collected, quizzes, papers, midterm examinations, final examinations, research proposals, laboratory results and reports, etc.) may be used in the determination of academic progress, no collaboration on this work is permitted unless the instructor explicitly indicates that some specific degree of collaboration is allowed. This statement is not intended to discourage students from studying together or working together on assignments which are not to be collected.”

References:

1 Park, J. H., Boika, A., Park, H. S., Lee, H. C. & Bard, A. J. Single Collision Events of Conductive Nanoparticles Driven by Mi gration. *Journal of Physical Chemistry C* **117**, 6651-6657, doi:10.1021/jp3126494 (2013).

2 Boika, A., Thorgaard, S. N. & Bard, A. J. Monitoring the Electrophoretic Migration and Adsorption of Single Insulating Nanoparticles at Ultramicroelectrodes. *Journal of Physical Chemistry B* **117**, 4371-4380, doi:10.1021/jp306934g (2013).

3 Boika, A. & Bard, A. J. Electrophoretic Migration and Particle Collisions in Scanning Electrochemical Microscopy. *Analytical Chemistry* **86**, 11666-11672, doi:10.1021/ac502944n (2014).

4 Fosdick, S. E., Anderson, M. J., Nettleton, E. G. & Crooks, R. M. Correlated Electrochemical and Optical Tracking of Discrete Collision Events. *Journal of the American Chemical Society* **135**, 5994-5997, doi:10.1021/ja401864k (2013).