CHEM.774 Electrochemistry for Chemists.

Winter, 2014.

“Everything you always wanted to know about electrochemistry but were afraid to ask” (with apologies to W. Allen)

Usual instructor: Prof. A. W. Addison. (AddisonA@drexel.edu; 12-418; x2646).

This course incorporates both lecture sessions (Weds. & Fri.) and laboratory activities (Fridays). Your grade will be based on your treatment of your experimental data/results, and on the homework assignments; I do not plan a final exam. The field of electrochemistry has, like others, exploded in scope over the last decade or two. The 774 coverage is aimed at using electrochemical techniques to reveal the thermodynamic and kinetic properties of molecules, rather than for quantitative chemical analysis (determination of concentration/amount). Numerous other aspects (e.g., electroplating, storage devices) will also not be covered. The lab revolves mainly around the Department’s BASi Epsilon Electrochemistry System. If we can beg, borrow or steal from CoE a unit capable of doing EIS, that would be great!

Text sources:

• C.H. Hamann, A. Hamnett & W. Vielstich, "Electrochemistry", Wiley-VCH 2007, $80. ISBN= 978-3-527-31069-2. Fairly comprehensive, but a bit thin on how to use various instrumentation-based methods, with more coverage of ‘applied’ and of ‘traditional’ electrochem. theory. Better than the original 1998 edition, which had lots of typos (and is on reserve at Hagerty Library: QD553.H29.1998) It may actually now be cheaper than the text I initially recommended:

• C.M.A. Brett & A.M.O. Brett, "Electrochemistry: Principles, Methods & Applications", Oxford U.P. 1993 [ISBN 978-0198553885]; QD553.B74.1993. Fairly wide coverage, though some methods are short on detail/examples. Nonetheless it’s fairly readable, and costs a fair bit less than the alternatives, so if you want to buy a book that has general utility, this is a reasonable choice. Another nice little book with a good summary of matters electrodic is:


• P.T. Kissinger & W.R. Heineman, "Laboratory Techniques in Electroanalytical Chemistry", Second Edn., Marcel Dekker, 1996, $100. This has been a pretty good book, though I’ve not seen this 2nd edition yet (it’s checked out of Hagerty right now)

  • Volume-1, Part-IIA is on various electrochemical techniques.
  • Volume-2 is about properties of solvents - a useful lab volume.
  • Data compilation: Volume-5, Part-II: Ed. Weinberg: pp667-1056, H. Siegerman, “Oxidation & Reduction Potentials of Organic Compounds” (Tables); QD251.W362. These volumes are in general rather poorly catalogued and can thus be hard to find in libraries; confusion/obscurity as to edition, volume, publication year and part numbers.

• F.C. Anson, "Electroanalytical Chemistry", ACS Audio Course (six one-hour audio cassettes and workbook): Hagerty Library Non-Print Division, *Phonotape E387*.

• W.M. Clark, “Oxidation-Reduction Potentials of Organic Systems”, Williams & Wilkins, Baltimore, 1960. Has many short data tables; expounds on several principles, and was The Source for early practitioners of biological redox chemistry; Far from contemporary - based on potentiometry. QD281.09.C55


**Topics.** The order, accentuation and coverage is not set in stone, though the more ‘fundamental’ stuff obviously needs to come first.

• Some simple electrochemical thermodynamics reviewed: Nernst eqn., cells, half-cells, standard cells, the SHE & standard electrode potentials.
• Units & definitions. Redox indicators, redox buffers.
• Kohlrausch’s laws, ion mobility, LJP’s, intro. to nonaqueous.
• LUMO/HOMO correlation with E°. Electrical double layer.
• Reference electrodes.
• Potentiometry, diffusion layer, migration current.
• Chronoamperometry, Cottrell Eqn., iΩ plots, capacitive current.
• Electrode & cell technology, solvents, supporting electrolytes, nonaqueous solutions; reference electrodes, diffusion coefficients, viscosities, Walden’s Rule. The unfortunate consequences of solution resistance; iR compensation.
• Dropping mercury electrode polarography, Ilković equation.
• Heterogeneous electron-transfer kinetics.
• Cyclic voltammetry: Randles/Sevcik & Nicholson/Shain results for planar and spherical electrodes. Potential and current characteristics.
• CV for simple (binding) equilibria; some structural influences on E_{1/2}’s.
• CV at cylindrical electrodes by Stephens/Moorhead, Aoyagi/Matsuda & Addison models.
• Sequential processes, stripping voltammetry. Contrast CV with RDE.
• Pulse methods: pulse polarography/voltammetry, Tast polarography, Osteryoung square-wave voltammetry.
• AC techniques: phase-selected results in AC voltammetry.
• **Electrochem. Impedance Spectroscopy:** variation of response with AC frequency; Nyquist (impedance) plots.
• **Chronocoulometry:** analyte adsorption. Double potential step chronocoulometry for reversible processes.
• **Chronopotentiometry.**
• **CV for quasi-reversible, irreversible & EC processes.**
• **Electron-transfer kinetics by Nicholson/Shain & Matsuda/Ayabe methods.**
• **Electron-transfer kinetics by DPSCC.**
• **CV for EC & CE processes, adsorption.**
• **DPSCC for EC processes.**
• **Spectroelectrochemistry**

**Goals of the course:**
To learn how to do electrochemical experiments which reveal the thermodynamic, kinematic and kinetic properties of molecular systems, through analysis of the experimental data and interpretation of the results.

Prof. A. Addison  12-418   215-895-2646   AddisonA@drexel.edu