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:

• A.C. Fisher, "Electrode Dynamics", Oxford University Press 1996, #34 in the "Oxford Chemistry Primers" series, [pb, ISBN 978-0198556909] $30. If you want something more comprehensive than any of the above, then:

• A.J. Bard, L.R. Faulkner, "Electrochemical Methods: Fundamentals & Applications", Wiley 2001, ISBN 0471043729 [hc] $115. QD553.B37.2001, is more or less 'the bible' of electrochemical theory and methods. *On reserve in Hagerty Library.*

• R.G. Compton & C.E. Banks, "Understanding Voltammetry". Imperial College Press, 2011. ISBN978-1-84816-585-4. Hagerty QD116.V64.C66.2011. PChem basics, CV and RDE methods, with a touch of pulses.

• R.G. Compton, C. Batchelor-McAuley & E.J.F. Dickinson, “Understanding Voltammetry – Problems & Solutions”. Imperial College Press, 2012. ISBN978-1-84816-730-8. Hagerty QD116.V64.C66.2012. Examples, with the attendant things mentioned, without which you usually can’t turn data into results.

• D.T. Sawyer, A. Sobkowiak & J.L. Roberts, "Electrochemistry for Chemists" (Hardcover), Wiley-Interscience 1995. Hardcover, ISBN 0-471-59468-7, $120, QD553.S32.1995.
Fairly practical, with a chapter on examples, though there are a few things I don’t “get” just yet .....

• R. Holze, “Experimental Electrochemistry: a Laboratory Textbook”. Wiley-VCH 2009 [pb], ISBN= 978-3-527-31098-2, $40. A few nice experiments one could do, but thin on what for me passes as “theory”; not as useful a book as one might have hoped.

• R.G. Compton, C. Batchelor-McAuley & E.J.F. Dickinson, “Understanding voltammetry : problems and solutions”. Imperial College Press/World Scientific Publishing, 2012. QD116.V64 C66 2012.

• K. Izutsu, “Electrochemistry in Nonaqueous Solutions”, Wiley-VCH Weinheim, 2nd. Edn. 2009, QD555.6.N56.I98.2009. Not bad - both practical stuff and useful theory - easier than HH&V. The Library also has hardcopy & e-versions of the 2002 edition.

• 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)

• Eds. Weissberger and Rossiter, "Techniques of Chemistry" —> "Physical Methods of Chemistry" —> "Electrochemical Methods": Wiley-Interscience: supposedly at QD61.P47.1986; 2-4 volumes on electrochemical data and methods for analytical, organic chemistry.
  • 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.

• "Electrochemistry at Solid Electrodes", R.N. Adams, Marcel Dekker New York, NY, 1969. A still-useful classic with definitive info about doing voltammetry & RDE polarography.

• 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

• *Data compilation:* Eds. A. J. Bard, R. Parsons & J. Jordan, “Standard potentials in aqueous solution”. M. Dekker, New York, 1985. QD571.S74 1985. A biggish book with many inorganic redox potentials.

• *Data compilation:* L. Meites, “CRC Handbook Series in Inorganic Electrochemistry” CRC Press, 1977-1980. Tables of redox potentials for inorganic ions and complexes; QD557.C73, five volumes. Its classic forebear is Clark’s book.

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., *iQ* 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, Ilkoviç equation.
• Rotating disk electrode, Levich eqn., Gregory/Riddiford eqn. Reversible & irreversible processes, electron-transfer rates. The ring-disk electrode, kinetics studies.
• 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.

• **E**lectrochem. **I**mpedance **S**pectroscopy: variation of response with AC frequency; Nyquist (impedance) plots.
• Chronocoulometry: analyte adsorption. Double potential step chronocoulometry for reversible processes.
• Chronopotentiometry.
• CV for quasireversible, 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 interpretion of the results.

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