Electrochemistry “Discovery” Course for Undergraduates

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Course Description

We recently developed a novel selected-topics course at Central State University, “Introduction to Laboratory Techniques in Electrochemistry”, to give undergraduate sophomores and juniors practical, hands-on experience with electrochemical measurements, and to recruit and prepare students for summer research in fuel cell and battery technology at the Illinois Institute of Technology (IIT). We designed this 3-credit-hour, 10-week course to focus on “electrochemistry through laboratory discovery”. Small class sizes (ca. 5 students) were preferred to maximize instructor-student interaction. Since one of our objectives was to recruit motivated sophomores for undergraduate summer research, this course has a strong hands-on focus and minimal prerequisites. The course meets 4 hours per week for lab and 2 hours per week for lecture. Lab reports comprise 60% of the course grade, with the 40% balance made up by exams and homework.

The Illinois Institute of Technology in Chicago recently received funds to develop a minority outreach program, one goal of which was to encourage more minority students to participate in fuel cell and battery research. These areas have been identified by the Army Research Office as nationally strategic technologies. Central State University is an Historically Black College-University (HBCU) in central Ohio with an enrollment of ca. 2500 students. It was one of three universities funded by IIT to design, develop, and execute an electrochemistry program to better prepare students for scientific research.

The prerequisites for Chem 321 include general chemistry (particularly thermodynamics and electrochemistry topics) and intermediate algebra. Naturally it is advantageous for students to have also taken university physics, calculus, and chemical quantitative analysis before Chem 321. Since electrochemistry is interdisciplinary, Chem 321 was marketed toward Chemistry, Physics, and Engineering majors. We try to complete about 7 labs, based on a “less is more” philosophy emphasizing analytic and creative process rather than mandatory topical coverage. In practice, we have realized both the advantages and drawbacks of “less is more” (1).

Electrochemistry Laboratory

Experiments were selected to demonstrate fundamental electroanalytical techniques with an emphasis on future applicability to fuel cell and battery research (2-12). Currently, we have 8 lab experiments available:

• Construction of zinc–copper battery stacks
• Lead acid battery charge–discharge cycles
• Conductometric titration of aspirin with ammonium hydroxide
• Ion selective electrode determination of fluoride in water
• Cyclic voltammetry of potassium ferriyride solution
• Cyclic voltammetry of sulfuric acid on platinum working electrode
• Anodic stripping voltammetry of lead ion in solution
• Differential pulse polarography of lead ion in solution

After completing a lab, students write a structured lab report (title page, objective, theory, data, calculations, graphs, results, discussion, references). We tentatively assign the theory section to be done as library research, although in practice students usually “check out” instructor materials. We strongly encourage students to use computers to assemble their lab reports, including the use of Word, Excel, Cricketgraph, and MacDraw software.

Electrochemistry Lecture

We utilize two hours of lecture per week to explain the principles that underlie laboratory observations and results. Lectures are based on a set of distributed notes extracted from sources on electrochemistry (13-17), instrumentation (18, 19), chemistry (20–22), physics (23), and applied math (24, 25). Topics covered in lectures typically include chemical definitions, electrical definitions, oxidation-reduction reactions, electrochemical series, electrodes, electrochemical cells, direct coulometry, electrolysis, electrochemical process efficiency, equilibrium potentiometry, real electrochemical cell voltages, types and design of ion selective electrodes, reference electrode designs, working electrode designs, pH buffers, cyclic voltammetry, anodic stripping voltammetry, polarography, differential pulse polarography, and simple electronic circuits for electrochemical instruments. Homework is assigned each week and solutions for difficult problems are discussed in lecture. One midterm exam and one comprehensive final exam are given, which include questions and problems from both lecture and lab.

Figure 1. Layout of electrochemistry laboratory.
Outline of Laboratory “Discovery” Experiments

Our main electrochemistry laboratory has about 26 m² of working area, divided into functional stations (Fig. 1). It contains 4 benches, 2 tables, and 1 fume hood and can comfortably accommodate about 6 students. Purified water for all experiments is produced from a Barnstead Fistreem II GlassStill in combination with a Barnstead deionization cartridge. Each student is given a guided tour of the lab and a safety seminar during the first lab meeting. We have prepared a written handout for each experiment, which presents the experiment title, main concepts, objectives, equipment, summary of procedures, and methods of data analysis. An outline of the 8 laboratory experiments follows below.

Construction of Zinc–Copper Battery Stacks

Objectives are to construct and measure the open circuit voltage (OCV) of battery stacks made from zinc, copper, and filter paper soaked with sodium chloride solution. Students explore concepts such as battery design, series circuits, and electromotive series. Stacks of copper–zinc batteries are constructed and tested for OCV using a digital voltmeter. The current discharge of one battery stack is measured as it is discharged through a series resistor. A plot of OCV vs. number of series stacks is obtained (Fig. 2). We also have students (unknowingly) construct some “short circuit” stacks. Faraday’s law of electrolysis is utilized to calculate battery lifetime for one Zn-Cu cell assuming constant discharge of ca. 1 mA. Mass- and charge-balanced electrochemical half-reactions for the battery are reported.

Lead Acid Battery Charge–Discharge Process

Students are introduced to the chemistry of a 12-V, 6-cell car battery:

\[ \text{PbO}_2(s) + \text{Pb}(s) + 4\text{H}^+(aq) + 2\text{SO}_4^{2-}(aq) \rightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O(liq)} \]

A resistive discharge circuit is set up to record discharge time, current, and voltage for about 1 h at an initial discharge rate of ~20 A. For this, voltmeters, ammeters, timers, and rheostats are used; we use 3 rheostats connected in parallel. From raw data on current, voltage, instantaneous charge, and time, plots are constructed such as that in Figure 3. Using Microsoft Excel, the total charge capacity of the battery is calculated by numeric integration of the total area under the [current, time] plot. Students are expected to submit a cutaway sketch of the internal anatomy of a lead–acid battery.

AC Conductometric Titration of Aspirin with Ammonium Hydroxide

Concepts of ac conductivity and conductometric titrations are considered. Students determine the cell constant “k” of an ac conductivity electrode, and the nominal conductivities of various water samples (deionized, distilled, tap water), and they find the mass of salicylic acid acetate in an aspirin tablet. A Fisher Accumet 50 meter is used along with 3 conductivity electrodes (\( k = 10^{-1}, 10^{0}, 10^{1} \) cm\(^{-1} \)). Procedurally, students first determine the electrode cell constant using 0.01000 M KCl solution. Conductances for various water samples are measured next. An aspirin tablet is weighed on an analytical balance and dissolved in 250 mL of water. Two 100-mL portions are titrated with standard 0.100 M ammonium hydroxide solution. The titration endpoint is estimated from a plot of conductivity vs. volume of titrant added, and the mass of aspirin is calculated. Such a conductivity plot can be seen in Figure 4. The mass-balanced aspirin–ammonium hydroxide reaction is reported.

Potentiometric Voltage Response of an Ion Selective Electrode (ISE)

Concepts such as high-impedance voltmeters, ion-selective electrodes, electrochemical cells, formal concentration, and chemical activity are explored. Ion-selective electrodes (e.g., fluoride and sulfide) are used to seek the empirical relation between cell voltage and ion activity-concentration (activity coefficients for dilute ion solutions are provided to
Cyclic Voltammetry of Potassium Ferricyanide Solution

Electrochemical reversibility is studied using the versatile technique of cyclic voltammetry. Students collect cyclic voltammograms of the ubiquitous K$_3$Fe(CN)$_6$ system on platinum (or glassy carbon) working electrode. Cell voltages are plotted and fitted against ion concentration (and logarithm of concentration) over at least 3 orders of magnitude of concentration. The effects of ion charge, ionic strength, and pH are also considered. Figure 5 shows typical data for an Orion fluoride-selective electrode at fixed pH and ionic strength.

Figure 5. Calibration curve for a fluoride electrode, showing equilibrium cell voltage (vs. SCE) as a function of added fluoride molarity. Ionic strength and pH were approximately fixed. Note the linear slope of ca. 58 mV.

A general ISE math equation is presented, which relates equilibrium cell voltage to ion activity. Selected CV peaks are tentatively assigned to electrochemical half-reactions. The same type of electrochemistry hardware is utilized as in the K$_3$Fe(CN)$_6$ experiment. A solution of 0.50 M H$_2$SO$_4$ in deionized water is tried; it would be interesting to repeat the cyclic voltammetry in various acids.

Students discover that platinum itself can be electrochemically reactive in sulfuric acid (and the solvent water) at extreme potentials. The important idea of "potential window" is discussed, as well as surface adsorption–desorption. Selected CV peaks are tentatively assigned to electrochemical half-reactions. The same type of electrochemistry hardware is utilized as in the K$_3$Fe(CN)$_6$ experiment. A solution of 0.50 M H$_2$SO$_4$ in deionized water is tried; it would be interesting to repeat the cyclic voltammetry in various acids.

Multiple scans (electrode cycling) on platinum are recorded at fixed scan rate. The platinum-electrode surface is examined under a 30-power stereomicroscope before and after CV. Experimental variants on this procedure could in-
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volve systematically changing the scan rate, initial scan direction, initial potential, cathodic potential limit, anodic potential limit, or working electrode material (platinum, gold, glassy carbon, etc.).

To date, students have been directed to assign CV peaks to specific electrochemical half-reactions with help from the literature. Figure 7 shows a sample CV of 0.50 M H₂SO₄ on Pt electrode after the system has been purged with dry nitrogen. In the future, we will have the Pt working electrode area quantitated two ways: geometrically (area = πr²), and electrochemically from steady-state CV peak areas for PtH → Pt + H⁺ + e⁻. Students integrate the area under the CV peaks (voltage vs time), and then use the surface factor 1.3 × 10¹⁵ Pt atoms cm⁻² to estimate electrode area.

Figure 8. (a) Anodic stripping voltammograms (ASVs) of lead ion added to 50 mL of 0.1 M KNO₃ at pH 4. Nine different mass additions of lead ion are depicted (0 ppm to 28 ppm). Applied potential ranged from -0.80 to +0.10 V vs. SCE at the scan rate of 0.1 V s⁻¹. Maximum cathodic peak current was ca. 5.2 µA. (b) ASVs of 6.3 ppm of lead ion at 8 different cathodic deposition times (0 min to 30 min). Maximum cathodic peak current was ca. 4.6 µA. Arrows denote zero volts vs. SCE.

Anodic Stripping Voltammetry of Lead Ion

Anodic stripping voltammetry is used to develop an analytical calibration curve for lead ion concentrations. Preconcentration on the working electrode is introduced as a tool for trace analysis. Once again, the cyclic voltammetry hardware described above is used. Pb(NO₃)₂ solutions of concentration 1–10 × 10⁻⁶ M are prepared in 0.1 M KNO₃ at pH 4 and purged with dry argon immediately before use.

The procedure involves plating lead from lead ion in solution onto the working electrode surface at cathodic deposition potential (E_app = -0.800 V vs. Ag–AgCl electrode). After an electroreduction period of 15 min, the applied potential is linearly scanned in the anodic direction. This results in “anodic stripping” of the preconcentrated lead, which yields a maximum peak current proportional to both bulk lead ion concentration (Fig. 8a) and cathodic deposition time (Fig. 8b). We found that graphs of anodic peak current vs. concentration were empirically best fit by a quadratic function (Fig. 9). Further, plots of peak current vs. deposition time (at fixed concentration) were also best fit by a quadratic function (Fig. 10). Students are prompted to comment on the analytical sensitivity of stripping voltammetry in comparison with cyclic voltammetry.

Lead Calibration Curve by Differential Pulse Polarography

A concentration calibration curve for lead ion is constructed using differential pulse polarography (DPP). Concepts of direct calibration, pulse polarography, difference currents, and differential pulse polarography are explored. For this lab we “recycled” a PAR Model 174A polarographic analyzer, constructed a homemade dropping mercury electrode (DME) using a buret and glass capillary tube, and utilized a PAR mercury drop timer assembly 174-70, a PAR 75-mL electrochemical cell, a saturated calomel reference electrode (SCE), a platinum auxiliary electrode, and a Linseis 16100-II xy-recorder.

After pipetting 50.00 mL of 0.1 M KNO₃ into the cell and purging with argon for ~15 min, background DPP polarograms are recorded. To do this, it is first necessary to synchronize the timing between the PAR 174A drop timer and the DME (one “knock” equals one Hg drop). Next an exact mass of dry Pb(NO₃)₂ is added to the cell and the differential pulse polarogram is recorded. Mass additions of 0, 2, 5, 10, 15, and 20 mg of Pb(NO₃)₂ are tried. The applied potential is swept from +0.5 to +1.0 V vs. SCE at a scan rate of 0.01 V s⁻¹.

Figure 9. Plot of anodic peak current vs. added lead ion from Figure 8a. Note the quadratic mathematical relation at fixed deposition time.

Figure 10. Plot of anodic peak current vs. cathodic deposition time from Figure 8b. Note the quadratic mathematical relation at fixed lead ion concentration.
Results for one such DPP data set are given in Figure 12. Data workup involves calculating the formal concentrations of Pb\textsuperscript{2+} in the solution for each Pb(NO_3)_2 mass addition. Peak currents (heights) from peak baseline tangents are measured and recorded. A plot of peak current vs. Pb\textsuperscript{2+} concentration is constructed, and the most probable linear relation for the data is determined by a least squares method. Results for one such DPP data set are given in Figure 12.

Summary

This electrochemistry discovery course focuses on practical laboratory techniques. Since we start with “learning by doing”, the course is suitable for undergraduates from sophomore to senior levels. By incorporating a “less is more” approach, deductive and inductive thought is emphasized at the expense of maximum coverage of topics. By analogy to recent lab courses (26, 27), we tried to incorporate experimental techniques useful for modern research. Students gain hands-on experience with electrochemical equipment, techniques, concepts, and data analysis. Preliminary student feedback from the course has been very positive, particularly with regard to preparation for research.

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Literature Cited