

ELECTROCHEMICAL ENGINEERING IN THE PROCESS LABORATORY COURSE

JAN B. TALBOT

University of California, San Diego • La Jolla, CA 92093-0411

The Chemical Engineering Program at the University of California, San Diego, has successfully operated a unique Chemical Engineering Process Laboratory since the early 1980s^[1] that is taught at the senior level over two quarters for a class size under forty. The emphasis of the laboratory is to develop skills in planning, designing, and building an experimental apparatus, performance of experimental work, analysis of data, and making proper interpretation and decisions. Learning how to make effective oral technical presentations and developing report-writing skills are also integral parts of the course.

The projects of this course range from the more traditional areas of kinetics and transport phenomena to applications in microelectronics, environmental engineering, and biotechnology. The uniqueness of this process laboratory class is its attempt to emulate industrial process development projects with one in-depth project rather than rotating through a set of unit operation equipment each quarter for each small group of students.

CHEMICAL ENGINEERING PROCESS LABORATORY

Although the philosophy of the class has remained the same since its inception,^[1] some changes have been made in the details of its execution. For each ten-week project, a proposal and a safety memorandum must be written. In the project proposal, the proposed plans and methods form the main body of the proposal and the background section must have a critical review of at least five to six pertinent research articles. A proposal should clearly identify the objectives of the project, demonstrate an understanding of the relevant

literature, establish the significance of the proposed work, and outline the approach.

The safety memorandum should be a summary of pertinent information from the MSDS of any chemicals that may be used in the specific project, should contain specific safety precautions and lab procedures, and should address the issue of waste minimization. With a better appreciation of the importance of planning, the students are required for the second quarter to prepare and use a project schedule (a so-called Gantt) chart. During each quarter, students must demonstrate experimental design on their new project and scale-up calculations as specified by their project director.

We have recently introduced a group rotation project (*e.g.*, a cooling-tower or heat-exchanger project) that is ongoing each quarter and that involves the whole class. The objective of the project is to learn group-to-group communication to achieve a common goal by having each group work on the project for one week. The students analyze their data and then write a memo that summarizes their progress and advises the next group of the new tasks to be accomplished. To communicate the success of the laboratory projects, the final

Jan B. Talbot is Professor of Chemical Engineering and Materials Science at the University of California, San Diego. She received her BS and MS in Chemical Engineering from Pennsylvania State University. She worked as a development engineer at the Oak Ridge National Laboratory for six years before returning to academia and receiving her PhD from the University of Minnesota in 1986. Her current research interests are in the areas of information display technology and electrochemical engineering, particularly electrodeposition.



This laboratory course has been an excellent vehicle for teaching and demonstrating electrochemical engineering principles.

presentation for the second quarter is a poster session meeting presented to the local professional AIChE Chapter and a Web page for their project is designed (<http://chemelab.ucsd.edu>).

ELECTROCHEMICAL ENGINEERING

This laboratory course has been an excellent vehicle for teaching and demonstrating electrochemical engineering principles. The applications of electrochemistry are diverse and the projects in the laboratory have spanned the gamut from energy conversion (fuel cell) to electroplating to environmental engineering. The electrochemical engineering projects typically involve thermodynamics, kinetics, transport processes (diffusion, convection, and electromigration), reactor design, and scale up.

The students readily determined, after reviewing the electrochemistry from their physical chemistry class, that electrochemical processes can be analyzed using chemical engineering principles. The main difference is the addition of the effects of a potential gradient. But for the experiments and analysis of data, the ability to control and measure voltage or current can often be an advantage as it gives direct information about the process. The minimum voltage may be related to ΔG of the reaction. The current density may be proportional to the rate of heterogeneous reaction. The limiting current density can be related to the mass transfer rate. The design of an electrochemical reactor is often analogous to a heterogeneous reactor in which the surface area to volume needs to be maximized. Attention must be given to potential and current distributions, however.

Table 1 (next page) lists the project statements that have been assigned in the class over the past decade. Note that the statements are all the students receive, which emphasizes the open-ended problem at hand.

The main piece of necessary laboratory equipment is a potentiostat to control voltage and measure current (average cost is about \$12,000). Also, reference electrodes are used in most experiments. The most expensive materials were ion exchange-membranes or dimensionally stable electrodes, which were used in as small amounts as possible when required.

A generic electrochemical reactor that could be used repeatedly was a project one year and it has been used by other

groups for many experiments. Note that four of the projects (6 through 9) are of an environmental engineering nature, which is of great interest to the students. There is the added benefit to the professor in actually observing how these various processes work.

It is also possible to incorporate the experiments given in Table 1 into a more traditional unit operations laboratory with a focus on kinetics or mass transport aspects. The experimental stations, such as the reciprocating-paddle system to be discussed, were built in our shop with inexpensive materials such as plexiglass and used simple pumps and motors (at a total cost of less than \$200).

EXAMPLE EXPERIMENT

To illustrate the development of one of the lab projects, a study of copper electrodeposition with a reciprocating-paddle system will be used as an example to show how the principles of electrochemical engineering were explored by the students in a design context. It was one of the most successful projects; this very motivated and industrious group wrote a journal note^[2] from the results of their project.

The group of students was given the problem statement (#3, Table 1), and they proceeded to design and build (with help from a technician) their experimental apparatus based on information from a patent^[3] in which a reciprocating paddle cell had been used to deposit magnetic alloy films. A schematic of their experimental apparatus is shown in Figure 1.

The plating cell was a plexiglass tank to be filled with

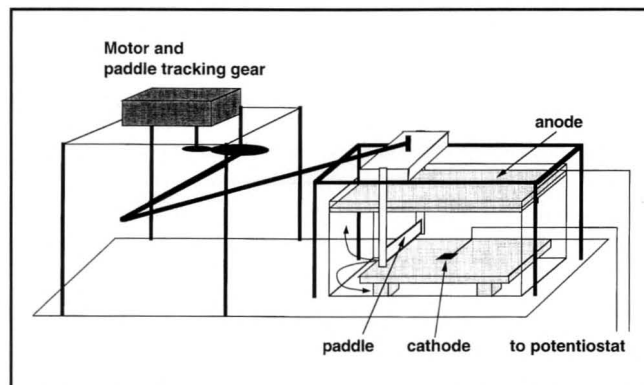


Figure 1. Reciprocating paddle cell experimental apparatus.

TABLE 1
Project and Scale-Up Design Problem Statements

Project Statement

Scale-Up Design Problem

1) Methanol-air fuel cell

Fuel cells can be useful power sources (particularly for operation in remote areas) due to their high energy density and quiet operation. However, in a methanol-air fuel cell, methanol is soluble in the aqueous electrolyte and can diffuse to the cathode where it can oxidize. Our client is interested in an application of a methanol-air fuel cell, but is aware that there are problems. The problem of diffusion of methanol to the cathode is an important problem to our client that needs to be investigated. Please develop an experimental plan and design an appropriate apparatus to conduct your study.

- 1a)** It has been proposed to use a methanol fuel cell system remotely in small cabins for weekend recreational power usage. Please design a fuel-cell system for this purpose. Discuss the power requirements and costs.
- 1b)** Our client was very pleased with the design of the batch apparatus for the methanol-air fuel cell study. However, for continuous use, our client would like the fuel cell to be designed as a continuously stirred tank reactor with recycle of the electrolyte.
- 1c)** Our client would like a design of a cross-flow array assembly of methanol-air fuel cells to supply back-up power to a personal computer for eight hours. Base this design on the results of your experimental study of a methanol-air fuel cell.

2) Electrolytic gas evolution

In conventional bioreactors, oxygen is provided to the cells by bubbling air through the growth medium. This method has several disadvantages, however, including nonuniform distribution of oxygen, destruction of fragile cells from induced shear, and risk of contamination. In past studies of mass transfer of oxygen in both air-lift and bubble-column reactors, our development engineers have determined that achievement of an adequate gas-liquid mass transfer coefficient was not possible. However, a novel electrochemical aeration system has been suggested to enhance mass transfer by evolving oxygen electrolytically as finely dispersed bubbles. Please develop an experimental plan and design a system to conduct your investigation.

Our client would like a design of a 10-liter aerobic bioreactor to produce penicillin using electrolytically evolved oxygen and air sparging in a bubble column. Compare the costs associated with using electrolysis and compressed oxygen.

3) Reciprocating paddle electroplating cell

3a) An electroplating process is being used by our client to produce thin alloy films for magnetic recording heads. Our client would like us to investigate the use of a reciprocating paddle as a means of electrolyte agitation. Please develop an experimental plan and design an appropriate apparatus to conduct your investigation.
3b) Our client was satisfied with the investigation of the use of a reciprocating paddle as a means of electrolyte agitation for copper deposition which was initiated during the last quarter. However, we have been informed that organic agents are routinely added to the plating baths to enhance the quality of the electrodeposition. We need to understand if these additives affect the mass transfer and the kinetics of deposition. Please develop an experimental plan to conduct your investigation.

- 3a)** Our client would like a design of a copper-plating system using a reciprocating-paddle means of electrolyte agitation to plate multilayer circuit board through-holes.
- 3b)** Our client would like a design of a system for uniform electroplating of a 1- μm film of copper on a 1m x 1m device. Please design a commercial-scale electroplating process that uses the reciprocating paddle for agitation. Also include a procedure for operating the electroplating system that you design.

4) Electroplating of through-holes

Plated through-holes provide electrical connections between the different layers of printed circuit boards. However, the trend in the development of multilayer printed circuit boards is towards more layers and narrower diameter through-holes. Therefore, as through-hole aspect ratio (length-to-diameter) increases, uniform electro-deposition of a through-hole becomes very challenging. We wish to study the electro-deposition of copper in a through-hole in order to characterize the important process variables that affect plating uniformity. Please develop an experimental plan and design an appropriate apparatus to conduct your investigation.

Our client would like a design of a copper-plating system to plate the through-holes of a multilayer circuit board. The 0.381-cm (150 mils) thick circuit board has an array of 100 through-holes, each with a radius of 0.064 cm (25 mils) with a hole-to-hole distance of 0.254 cm. The minimum thickness of 0.0025 cm (1 mil) of copper is required at the center of each through-hole. In your design, consider agitation of the electrolyte solution by pumping the solution. Estimate the cost of power required for electroplating and pumping of the solution.

5) Electroforming process

An electroforming process is being used by our client in making orifice plates for their thermal ink jet printer. Our client wants a study of an electroplating process to better understand the effects of various important system parameters, such as anode-cathode orientation, applied potential drop, and electrolyte concentration. Develop an experimental plan and design an appropriate apparatus to conduct your investigation.

Our client was very impressed with the design of the parallel-plate electroplating process considering the effects of the primary current distribution. However, our client would like to consider a system for uniform electroplating with flow through parallel plate electrodes. Please design a commercial scale electroplating process for a flowing electrolyte.

Continued on next page

about 10 liters of the plating solution. A 1-cm² copper cathode was mounted in the center of a platform raised above the tank floor. The raised platform was added to allow fluid displaced by the paddle to flow underneath it to minimize waves induced from the tank walls. Flow visualization was performed by the students with this system.

A simple rectangular block fixed on a tracking system was used as the paddle driven by a motor in a reciprocating motion at various velocities and heights above the cathode surface. A copper anode was placed parallel above the cathode support. The anode area was about 250 times that of the cathode, to allow it to function as a relatively unpolarized reference electrode as well as a counter electrode. The solution was either a binary electrolyte 0.05M CuSO₄ or a supporting electrolyte solution of 0.05M CuSO and 1.7M H₂SO₄. One of the students mentioned that this project kept him in style with "acid-washed" jeans, which were very popular at that time.

The quality of the 1- μ m thick film was determined by using microscopy and profilometry. Applied potential and current were controlled and measured, respectively, by a potentiostat, connected by copper-wire leads to the electrodes.

Before building the apparatus, the first step for this project was to learn about the thermodynamics, kinetic, and mass transport of electrochemical systems. Often, a comfortable place for a student (or a faculty member) to begin is the chapter on electrochemistry in a physical chemistry textbook.

There are also several good basic books on electrochemistry and electrochemical engineering (see Table 2) appropriate for the novice. Extra time has not been needed to lecture to the students on electrochemistry; this information is garnered through specific technical problems the students encountered either in reading literature or in conducting an experiment.

Table 1, continued.

6) Packed-bed electrode system

A local manufacturer of printed circuit boards requires a waste treatment system to recover plating wastes generated in their copper electroplating process. The manufacturer is interested in a high-surface area rotating electrode cell metal recovery system. Please develop an experimental plan and design an appropriate apparatus to conduct your investigation.

6a) A typical average discharge rate from a plating shop is 50,000 gal/day. Based on your bench-scale packed-bed electrode system, design a waste-treatment system to accommodate this flowrate that meets the EPA discharge standards.

6b) ELTECH Systems Corporation (Sugarland, TX) sells a heavy-metal recovery electrochemical cell with an extended surface area provided by use of a "reticulated" metal sponge cathode. The cathode presents an actual surface area almost 15 times its geometrical area. The cathodes are used in a cell as porous flow-through electrodes that are placed in series with flow-through anodes. The typical cell operating conditions for a copper sulfate stream are a feedrate of 3 gal/min with an inlet concentration of 250 ppm and an outlet concentration of 5 ppm. The average rate of removal is 0.36 lb/hr. The process conditions are a cell current of 200 amps and a voltage between 1.5 and 5.5 V. Please design a packed-bed cathode cell (or a series of cells) that can compete with the ELTECH system. Discuss the power requirements.

7) Electrokinetic soil remediation

Our company has been asked to evaluate an electrokinetic processing system for the treatment of pollutants in sand. Your group needs to determine the appropriate technology, a chemical system to study, and a plan of development for a sand-treatment system.

Geokinetics, Inc., claims to have used the electrokinetic soil remediation to reduce the copper concentration of 8100 ft³ of soil from a former paint-factory waste facility from 1200 ppm to <200 ppm. Please design an electrokinetic soil remediation system for this purpose, considering there is 10% clay by weight in the soil. Discuss the power requirements and costs.

8) Electrochemical oxidation of organics

Our company has been asked to evaluate using an electrochemical oxidation system for the treatment of organic constituents in a wastewater stream. A recent article is attached that briefly reviews both indirect and direct oxidation processes. Your group needs to determine the appropriate technology, a chemical system to study, and a plan of development for a wastewater treatment system.

8a) Based on your bench-scale experimental results and information from the literature, design a scaled-up system to treat phenol at 200 ppm from 1000 gal/day of wastewater to U.S. effluent water standards. Please consult with the other two groups (Fenton's Reagent Group, UV Oxidation Group) in order for us to make a "fair" comparison of these technologies.

8b) Design a cell (or a series of cells) with the ELTECH-type system (see 6b) with an inlet concentration of 150 ppm of phenol. Discuss the power requirements and costs.

9) Electrochemical ion exchange

Our company has been asked to evaluate an electrochemical ion exchange system for the treatment of toxic metal ions in a wastewater stream. Your group needs to determine the appropriate technology, a chemical system to study, and a plan of development for a wastewater treatment system.

Design an EIX cell (or a series of cells) that can compete with the ELTECH system (see 6b). Discuss the power requirements. Also, consider elution of the resin to recycle make-up stream to a plating operation that uses a concentration of 200 g/l CuSO₄.

The important reactions that the students must consider are the electroplating of copper and hydrogen evolution at the cathode and the corrosion of copper at the anode. An explanation of the relationship between free energy change of reaction (ΔG) to electrochemical potential through the Nernst equation and then use of a Pourbaix diagram^[4] (potential vs. pH) give a direct use of thermodynamics. The students readily determined and demonstrated the minimum potential required for electroplating of copper (and also in order to avoid hydrogen evolution).

By connecting the electrodes in a solution in a beaker (which is typically done first to understand the basics of anodic and cathodic reactions) and then in the actual plating apparatus, the student stepped (or ramped) the potential difference, E , and measured current, i (to attain a polarization curve).

For this experiment, the applied potential was decreased in steps beyond the mass transfer limiting current plateau until a sharp increase in current was observed, indicating the dominance of H_2 evolution, as shown in Figure 2. The current efficiency of copper electrodeposition was determined by measuring the weight gain of a sample at limiting current over a specified period of time, using Faraday's law. Therefore, the kinetics of copper plating and at very cathodic potentials, hydrogen evolution, were illustrated.

Due to the reciprocating motion of the paddle, the current transients at a set applied potential were periodic. Therefore, an average of the maximum and minimum current values at each applied potential difference associated with the reciprocating paddle

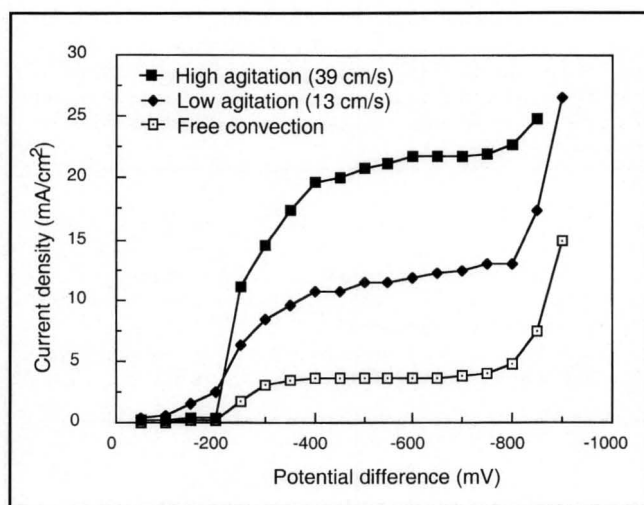


Figure 2. Polarization curve from copper deposition in 0.5 M $CuSO_4$ and 1.7M H_2SO_4 in a reciprocating paddle cell.

TABLE 2	
List of Recommended References	
<i>For the Novice</i>	
•	<i>Electrochemical Engineering Principles</i> , G. Prentice, Prentice-Hall (1991)
•	<i>Industrial Electrochemistry</i> , 2nd ed., D. Pletcher, F.C. Walsh; Chapman & Hall (1990)
•	<i>Electrochemistry: Principles, Methods, and Applications</i> , C.M.A. Brett, A.M. Oliveira-Brett; Oxford Science (1993)
<i>For the More Advanced</i>	
•	<i>Electrochemical Science</i> , J. O'M. Bockris, D.M. Drazic; Taylor & Francis (1972)
•	<i>Modern Electrochemistry, Vols 1 & 2</i> , J. O'M. Bockris, A.K.N. Reddy; Plenum Press (1977)
•	<i>Surface Electrochemistry</i> , J.O'M. Bockris, S.U.M. Khan; Plenum Press (1993)
•	<i>Electrochemical Methods: Fundamentals and Applications</i> , A.J. Bard, L.F. Faulkner; John Wiley & Sons (1980)
•	<i>Electrochemical Systems</i> , 2nd ed., J.S. Newman; Prentice-Hall (1991)
•	<i>Electrode Processes and Electrochemical Engineering</i> , F. Hine; Plenum Press (1985)
•	<i>Electrochemical Reactor Design</i> , D.J. Pickett; Elsevier (1979)
•	<i>Environmental Electrochemistry</i> , K. Rajeshwar, J. Ibanez; Academic Press (1997)

motion was used in Figure 2.

The mass transfer limiting current plateau for copper electrodeposition is easily identifiable in Figure 2. The limiting current densities for the binary electrolyte were higher than the supporting electrolyte, as expected—indicating the influence of electrical migration on the transport of copper ions for the binary electrolytic solution. The effect of forced convection is also readily observable

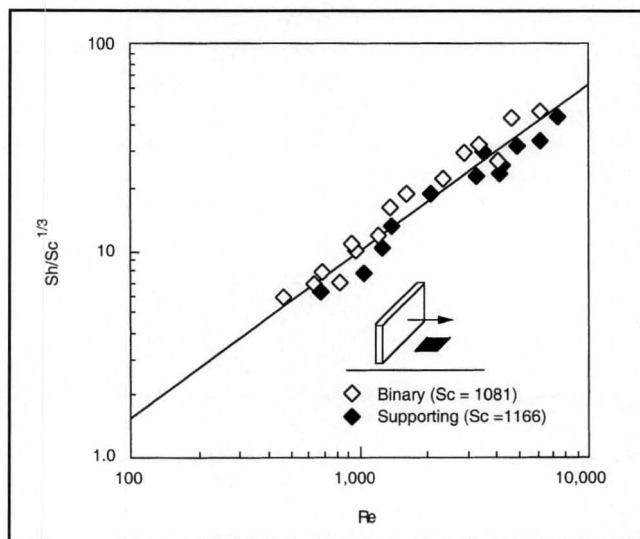


Figure 3. Mass transfer correlation.

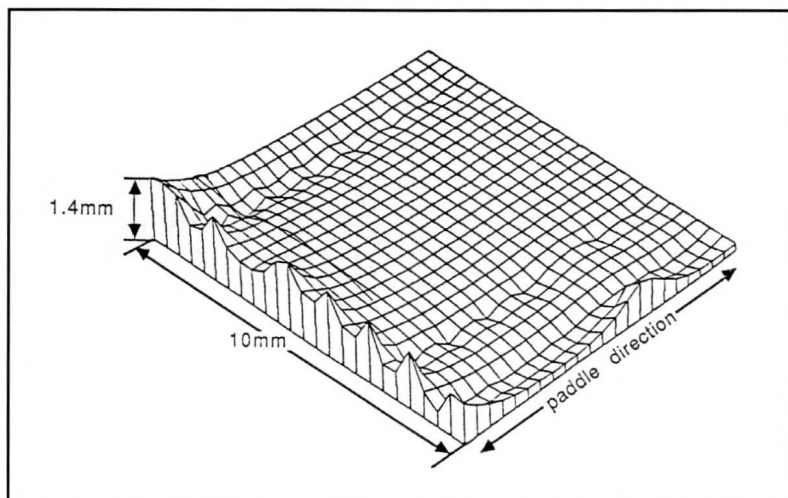


Figure 4. Topography of the copper deposit from a binary electrolyte at a high velocity with a paddle height of 1 cm above the cathode.

by the increase in the limiting current density. Since the flux of an ionic species is related to the current density, the average mass transfer coefficient, k (cm/s), can be determined from the limiting current density, i^* (A/cm²)

$$k = \frac{\epsilon i^*}{nFC_b} \quad (1)$$

where n is the number of electrons transferred, F is Faraday's constant (9.6485×10^4 C/equiv), ϵ is the current efficiency, and C_b is the bulk reactant concentration (mol/cm³). For our system, we anticipated that the characteristic parameters were the linear paddle velocity (U) and paddle height above the cathode surface (L), to be related by

$$Sh = a Re^b Sc^c \quad (2)$$

where $Sh = kL/D$ is the Sherwood number, $Re = UL/\nu$ is the Reynolds number, $Sc = \nu/D$ is the Schmidt number, and ν is kinematic viscosity of the fluid. The power of the Schmidt number, c , was estimated as 1/3 based on correlations in the literature. A log-log plot of $Sh/Sc^{1/3}$ versus Re for all the experiments in both supporting and binary electrolytes is given in Figure 3. The coefficients of the correlation in Eq. (2) were determined to be $a = 0.039$ and $b = 0.80$. This correlation was then used for the scale-up design problem.

One of the difficulties in electrochemical engineering is understanding the potential and current distributions inherent in such systems. To explore these concepts, the students measured the topography of the plated copper layer by a stylus profilometer, as shown in Figure 4. The thickness of the films was observed to be greatest at the cathode edges, as shown in the topographical maps in Figure 4, and decreased as the paddle was raised up to about 1 cm.^[2] Comparison of deposition uniformity between a free convective and a highly agitated plating bath, as determined by the topo-

logical survey of the copper deposit, showed that the paddle motion seemed to improve the deposition uniformity at the cathode edges parallel to the paddle motion.

The effect of thiourea on copper deposition was also studied. Thiourea ($SC(NH_2)_2$) is often added to plating solutions to refine the grain size and brighten the deposit. The addition of thiourea to the plating solutions did not influence the limiting current density for copper deposition, but did affect the surface kinetics and properties of the deposit.

CONCLUSIONS

During the two quarters of the design lab (10 weeks each), two groups of chemical engineering seniors designed, built, and operated a reciprocating-paddle electrochemical system. A correlation was determined to describe the mass transfer limited operation of an electroplating bath using this device in which binary and supporting electrolyte solutions exhibited the same power law correlation. This correlation would allow scaling the system for industrial applications.

To optimize deposition rate and uniformity, the highest paddle velocity (43 cm/s) and a paddle height of 1.0 cm above the cathode was recommended. Comparison of the deposition surfaces with and without agitation showed no loss of uniformity with agitation, while increasing the deposition rate by at least five times.

The other experiments listed in Table 1 followed a similar procedure, with varying degrees of success. The principles of chemical engineering and design were readily demonstrated in each of the experiments. A few students became interested in the specialization of electrochemical engineering and later they even took my graduate course on electrochemical engineering.

ACKNOWLEDGMENTS

The author acknowledges the contributions of colleagues, Professors Pao Chau and Richard Herz, who have also taught and improved this course over the years. The laboratory has been skillfully managed by Victor Gruol.

REFERENCES

1. Rochefort, S., S. Middleman, and P.C. Chau, "An Innovative ChE Process Laboratory," *Chem. Eng. Ed.*, **19**(3), 150 (1985)
2. Rice, D.A., D. Sundstrom, M.F. McEachern, L.A. Klumb, and J.B. Talbot, "Copper Electrodeposition Studies with a Reciprocating Paddle," *J. of Electrochem. Soc.*, **135**(11), 2777 (1988)
3. Powers, J.V., and L.T. Romankiw, U.S. Patent 3,652,442 (1972)
4. Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, New York, NY (1966) □