

A Course in

ELECTROCHEMICAL AND CORROSION ENGINEERING

JOHN VAN ZEE

University of South Carolina
Columbia, SC 29208

THE NEED TO EDUCATE chemical engineering students in the principles of electrochemical and corrosion engineering is still as important as when Alkire [1], Jorne [2], and Locke and Daniels [3] described their courses in these disciplines. Electrochemical industries are energy intensive, and engineering of new membrane reactors for the chlorine/caustic industry, for example, could lead to significant savings in operating costs [4]. Familiarity of chemical engineering graduates with the principles of corrosion engineering would be particularly beneficial to the speciality chemicals industry.

Graduate students frequently view electrochemical and corrosion engineering as dichotomous disciplines. This may be the case because corrosion engineering is often taught at the undergraduate level in terms of material selection or environmental conditions, whereas electrochemi-

cal engineering may be taught as an extrapolation of reactor engineering to fuels cells and batteries. For graduate students this division is arbitrary and unnecessary because each discipline is actually built from the same constitutive equations which have a basis in the fundamentals of thermodynamics, kinetics, mass transfer, and potential theory.

The course discussed here was designed to show the similarities between the two disciplines and to demonstrate to graduate students that electrochemical and corrosion engineering can be accomplished by extending their knowledge of chemical engineering models. That is, once the constitutive equations relevant to electrochemical systems are mastered, students can apply their understanding of transport phenomena and differential continuum mechanics to obtain the set of governing equations for a problem. The solution of these equations can be accomplished by using the analytical and numerical mathematical techniques which are familiar to second-semester graduate students. Then, quantitative engineering predictions for design in each discipline can be made with the solutions of these models. Obviously, in trying to synthesize two disciplines it is not possible to consider a large number of examples of each. Nevertheless, for an introductory course the students have a chance to work a great number of advanced problems which are significant to electrochemical reactor design and corrosion prevention.



John Van Zee obtained his BSChE in 1975 from the University of California (Berkeley) where he studied porous electrodes under the direction of John Newman. He worked in Chiapas, Mexico, building potable water systems for 3 years before obtaining his MS in 1982 and his PhD in 1984, both under the direction of Ralph White at Texas A&M University. He joined the chemical engineering department at the University of South Carolina in 1984 where he continues his research interest in the modeling of electrochemical and corroding systems.

TEXTBOOK SELECTION

Two textbooks are used for the course. *Electrochemical Systems*, by Newman [5], is used to provide the theory and fundamentals of the constitutive equations. Appendix C of his text also provides the student with a listing of computer codes for the solution of coupled nonlinear differential equations. *Corrosion Engineering*, by Fontana and Greene [6], is used for the qualitative description of the behavior of corroding systems. Two papers by Newman [7, 8] are used to provide an over-

© Copyright ChE Division, ASEE, 1985

view of model formulation in the two disciplines. Homework and example problems are formulated from these four references and from texts by Pickett [9], Pletcher [10], and Selley [11]. Numerous handouts and additional references are used as described below.

COURSE DESCRIPTION

As seen in Table 1, the course is divided into four sections. The first section considers the fundamentals of thermodynamics, kinetics, mass transfer, and potential theory. It concentrates on the development of constitutive equations for electrochemical systems. The second section deals with steady state applications in which these four fundamental topics interact. The third section is concerned with time-dependent applications of the fundamentals. Selected readings in both texts are used in all three of these sections as discussed below. The fourth section of the course deals with the application of statistics for the development of new models, constitutive equations, and better parameter estimates for electrochemical systems.

The first topic in the fundamentals section is the thermodynamics of electrolytic solutions. The historical difference between reduction and oxidation half-cell potentials is presented. The sign difference between electrolyzers (*i.e.*, cells which

Graduate students frequently view electrochemical and corrosion engineering as dichotomous disciplines The course discussed here was designed to show the similarities . . .

require energy) and spontaneous or galvanic corrosion cells is discussed and a large number of back-of-the-envelope homework problems are assigned. The objective of these problems is for the student to obtain the ability to determine the initial direction of the total cell reaction, the thermodynamic conversion of the reactor, the minimum decomposition voltage of the reactor, and the tendency for a system to corrode. It is observed that even though these calculations are typically required in an undergraduate physical chemistry course, the majority of the students do not have a consistent methodology for proceeding with the calculations. Hence, they make numerous sign errors on the first homework problem set, even though a large number of example problems are presented in the lectures. Initially students tend to try shortcuts and it presents a problem when the shortcuts do not work, because the direction of the reaction and the current is the key to understanding and modeling electrochemical systems. Fortunately, Newman provides a con-

TABLE 1
Course Outline

- | | |
|--|--|
| <p>I. Fundamentals</p> <p>A. Thermodynamics of Electrochemical Systems</p> <ol style="list-style-type: none"> 1. Driven electrolyzers 2. Galvanic/Corrosion cells 3. Solubility products 4. Pourbaix diagrams <p>B. Electrochemical Kinetics</p> <ol style="list-style-type: none"> 1. Butler-Volmer expression for elementary step reactions 2. Analogies with thermal kinetic expressions 3. Multiple step reaction expressions <p>C. Mass Transfer</p> <ol style="list-style-type: none"> 1. The rotating disk electrode (RDE) 2. The Graetz and Leveque problems <p>D. Potential Theory</p> <ol style="list-style-type: none"> 1. Primary current distributions 2. Secondary current distributions 3. Tertiary current distributions <p>II. Analysis of Steady-State Behavior</p> <p>A. Mixed Potential Graphs for Corroding Systems</p> <ol style="list-style-type: none"> 1. Mass transfer effects 2. Passivation phenomena 3. Cathodic protection schemes <p>B. Coupled Behavior at a RDE</p> <ol style="list-style-type: none"> 1. Effect of ionic migration | <ol style="list-style-type: none"> 2. Potential dependent reaction rates 3. Simultaneous reactions 4. Effect of homogeneous reactions <p>C. Electrolyzers</p> <ol style="list-style-type: none"> 1. Diaphragm-type chlorine/caustic cells 2. Parallel plate reactors <p>D. Porous Electrodes</p> <ol style="list-style-type: none"> 1. Zinc/bromine batteries 2. Dilute metal-ion recovery reactors <p>III. Analysis of Time-Dependent Behavior</p> <p>A. Diaphragm-type electrolyzers</p> <p>B. Porous electrodes</p> <p>C. Stress corrosion</p> <p>D. Oxide film formation</p> <p>IV. Applications of Statistics</p> <p>A. Statistical Experimental Designs</p> <ol style="list-style-type: none"> 1. Factorial designs 2. Nonlinear sequential designs <p>B. Interpretation of Experimental Data</p> <ol style="list-style-type: none"> 1. Parameter estimation 2. Confidence intervals <p>C. Use of Experimental Data for Reactor Design</p> <ol style="list-style-type: none"> 1. Confidence limits on predictions 2. Model discrimination |
|--|--|

sistent methodology for these calculations in Chapter 2. Solubility products and the phase behavior inherent in Pourbaix diagrams are also discussed.

The basic constitutive kinetic expressions are studied by considering Chapter 8 in Newman. The differences between homogeneous thermally-driven chemical reaction rate expressions and heterogeneous voltage-driven electrochemical kinetics are emphasized. Analogies are made between heterogeneous reaction rates and the current density. The concentration-independent and concentration-dependent forms of the Butler-Volmer rate expression are discussed for elementary step reactions. Linear and logarithmic rate expressions are shown to be subsets of this expression. Multiple step reactions are analyzed in this fundamental section by considering the typical physical

. . . once the constitutive equations relevant to electrochemical systems are mastered, they can apply their understanding of transport phenomena and differential continuum mechanics to obtain the set of governing equations for a problem.

chemistry concepts of rate determining steps and dynamic equilibrium. Simultaneous reactions are discussed in the next section of the course and statistical interpretation of kinetic data is discussed in the fourth section of the course.

The fundamentals of mass transfer in electrochemical and corroding systems are analyzed by first neglecting the effect of ionic migration. As discussed in Chapter 17 of Newman, this assumption results in the convective diffusion equation, which should be familiar to chemical engineering graduate students. For homework, the students derive the analytical solutions for the problems of mass transfer to a rotating disk electrode (RDE) and to a wall of a tube in which Poiseuille flow prevails. An example of the use of these solutions in the design of electrowinning cells is used to illustrate the usefulness of the analysis.

The last fundamental to be considered is potential theory. Graduate chemical engineering students are familiar with the governing differential equations of the primary and secondary potential distributions because of their experience with the Laplace equation for heat conduction. The differences between the primary and secondary current distributions are discussed in terms of changes in the boundary conditions. Students are quick to draw their own analogies

between thermally and electrically insulated surfaces. Homework problems concerning analytical solutions to these current distributions are assigned. The tertiary current distribution is the students' first exposure to the coupled nature of electrochemical systems. That is, since the effect of ionic migration is now included and since the potential distribution is nonlinear, neither the governing material balances nor the boundary conditions are linear. The approach in this fundamental section is to write the equations and boundary conditions only. The solution of these equations is postponed until the next part of the course.

The second part of the course considers the steady-state interactions of the four fundamentals. Predictions of corrosion currents (*i.e.*, rates) are emphasized first. A 45-minute film, "Corrosion in Action," produced by the International Nickel Company, is shown to present an overview of corrosion phenomena. Students find that the film supplements Chapters 2 and 3 in Fontana and Greene. Chapters 9 and 10 in Fontana and Greene provide background for quantitative predictions which can be made from mixed potential graphs. The basis for these graphs is that the anodic and cathodic currents are equal and opposite in sign at the corrosion potential. The graphs show the interactions of thermodynamics, kinetics, and mass transfer and their effects on the corrosion potential and corrosion currents. These graphs are also used to predict the effect of passivation (*i.e.*, the decrease in corrosion rate as the potential is increased). Finally, cathodic protection schemes are studied from Chapter 6 in Fontana and Greene.

In the next section of the second part of the course, the interactions of the four fundamentals are illustrated by considering a RDE system. The governing equations for mass transfer with the effect of ionic migration are developed by considering Chapter 19 of Newman. The MIGR computer code found in Appendix C of Newman is used for the simultaneous numerical integration of the coupled nonlinear differential equations. The explanation of Newman's technique and the subroutine BAND(J) of Appendix C by White [12] is helpful for the students. It should be noted that BAND(J) solves the boundary value problem by a multiple variable Newton-Raphson technique and that students are familiar with the technique from their distillation courses. In one homework problem, the students use MIGR to calculate the increase in the limiting current due to ionic migration for copper deposition at a RDE. The comput-

er code is given to the students and they modify it to solve the problem. The next homework problem is to extend MIGR to include the nonlinear Butler-Volmer kinetic expression at the RDE; this expression and modification allows the prediction of potential-dependent currents at a RDE. Then, the next week, the program is extended to include simultaneous potential-dependent reactions such as simultaneous hydrogen evolution and copper deposition. A handout on references 13 and 14 is used to explain the required modifications. The last assigned problem in this section is the prediction of the effect of homogeneous reactions on the potential dependent simultaneous reactions. This extension follows the treatment in reference 15.

Other lectures on the steady-state behavior include the analysis of diaphragm-type chlorine/caustic electrolyzers, parallel-plate reactors, porous electrodes for zinc/bromine batteries, and flow-through porous electrodes for the recovery of metal ions from dilute solutions. The lectures concentrate on the modeling of these systems by writing the differential material balances, including the constitutive equations, and specifying the boundary conditions. Homework problems are assigned which give students practice in setting up the problems for numerical solution by programs similar to MIGR.

The lectures in the third part of the course focus on time-dependent behavior. The lectures emphasize the minor extensions of MIGR-type programs which are required to allow integration of the time-dependent equations. Implicit stepping in time is used with BAND(J) to integrate the resulting parabolic partial differential equations. Examples for the analysis of diaphragm-type cells and porous electrodes are shown. With respect to corrosion, constitutive equations for stress corrosion cracking and oxide film formation are proposed and discussed. The qualitative discussions in Fontana and Greene are useful in the development of these equations.

The last topic of the course is the application of statistics to electrochemical and corrosion engineering. The reduction of experimental effort which can be achieved by using factorial experimental design is discussed. These lectures are prepared with the aid of reference 16. Examples of designs which helped identify measurable properties for the diaphragm in chlorine/caustic cells [17] are discussed. The estimation of electrochemical kinetic parameters and their confidence inter-

The lectures concentrate on the modeling of these systems by writing the differential material balances, including the constitutive equations, and specifying the boundary conditions.

vals is illustrated with experimental data from references 18 and 19. A computer code for these nonlinear regressions is given to the students, and homework problems which use this code are assigned. These problems illustrate the use of experimental data with simple models of chlorine/caustic cells to predict reactor behavior. Confidence limits on the predictions are discussed and used to determine the need for additional data and new models. Thus, the statistics can point to the need for a better description of the fundamental constitutive equations. These better descriptions may, for example, take the form of a concentrated solution expression for the flux for use in the differential material balances. These better descriptions are left for more advanced, separate courses in electrochemical reactor engineering or corrosion engineering which are currently under development.

CONCLUSIONS

Electrochemical and corrosion engineering need not be viewed as separate disciplines for an introductory course for chemical engineering graduate students. Each discipline is based on the same set of fundamentals, and students welcome the chance to draw analogies between standard chemical engineering concepts and those of electrochemical and corrosion engineering. The students can successfully solve the advanced differential equation models for quantitative predictions of the behavior of electrochemical systems. This success builds confidence in their ability to analyze chemical engineering problems in general. In addition, the familiarity of chemical engineering graduate students with both electrochemical reactor design and corrosion engineering concepts will aid the chemical industry in the future.

REFERENCES

1. Alkire, R., "Electrochemical Engineering," *Chem. Eng. Ed.*, 10, 158 (1976).
2. Jorne, J., "Electrochemical Engineering," *Chem. Eng. Ed.*, 11, 164 (1977).
3. Locke, C. E., and R. D. Daniels, "Corrosion Control," *Chem. Eng. Ed.*, 7, 164 (1973).

Continued on page 213.

adequately illustrated through examples. The number, and more importantly the variety, of exercise problems in many chapters should have been increased. Use of experimental data as the basis for problem formulation is rarely attempted in the book. A refreshing exception is provided by the example problem under dimensional analysis dealing with the formation of bubbles of one phase in another. I also wish that the problem statements were more interesting than they presently are throughout the book in order to capture the students' interest. One would have expected to see in the Third Edition examples and problems illustrating the application of transport theory to modern chemical engineering problems—those that have become important in the years since the Second Edition of the book.

Overall, *Momentum, Heat, and Mass Transfer* by Bennett and Myers has firmly established itself as a textbook for those choosing to study unit operations guided by transport theory. While one or another feature of the book may be found less than satisfactory by different instructors, they could easily be improved by the use of supplementary material prepared by instructors. Until a more appealing approach to teaching transfer operations emerges, the book by Bennett and Myers will remain prominently in many students' bookshelves. □

12. White, R. E., "On Newman's Numerical Technique for Solving Boundary Value Problems," *Ind. Eng. Chem. Fundam.*, 17, 367 (1978).
13. White, R. E., S. L. Lorimer, and R. Darby, "Prediction of the Current Density at an Electrode at Which Multiple Electrode Reactions Occur under Potentiostatic Control," *J. of the Electrochem. Soc.*, 130, 1123 (1983).
14. White, R. E., and J. Newman, "Simultaneous Reactions on a Rotating-Disk Electrode," *J. Electroanal. Chem.*, 2, 173 (1977).
15. Hsueh, L., and J. Newman, "The Role of Bisulfate Ions in Ionic Migration Effects," *Ind. Eng. Chem. Fundam.*, 10, 615 (1971).
16. Box, G. E. P., W. G. Hunter, and J. S. Hunter, *Statistics for Experimenters*, John Wiley and Sons, NY (1978).
17. Poush, K. A., D. L. Caldwell, J. W. Van Zee, and R. E. White, "Characterization of Asbestos Diaphragms for Chlor-Alkali Electrolysis," *Modern Chlor-Alkali Technology: Vol. 2*, C. Jackson, Ed., Ellis Horwood Ltd., Chichester, West Sussex, England (1983).
18. Van Zee, J., and R. E. White, "Using Parameter Estimation Techniques with a Simple Model of a Diaphragm-type Electrolyzer to Predict the Electrical Energy Cost of NaOH Production," *J. Electrochem. Soc.*, 132, 818 (1985).
19. Van Zee, J., and R. E. White, "An Analysis of a Back-Fed Porous Electrode for the Bromine/Bromide Redox Reaction," *J. Electrochem. Soc.*, 130, 2004 (1983). □

CORROSION ENGINEERING

Continued from page 197.

4. Caldwell, D. L., "Production of Chlorine," in *Comprehensive Treatise of Electrochemistry*, Vol. 2, J.O'M. Bockris, B. E. Conway, E. Yeager, and R. E. White, Eds., 105, Plenum Press, NY (1981).
5. Newman, J. S., *Electrochemical Systems*, Prentice-Hall, Inc., Englewood Cliffs, NJ (1973).
6. Fontana, M. G., and N. G. Greene, *Corrosion Engineering*, 2nd edition, McGraw-Hill, Inc., New York (1978).
7. Newman, J., "Engineering Design of Electrochemical Systems," *Ind. Eng. Chem. Fundam.*, 60, 12 (1968).
8. Newman, J., "Mass Transport and Potential Distribution in Geometries of Localized Corrosion," *Localized Corrosion*, National Association of Corrosion Engineers, NACE-3, 45 (1974).
9. Pickett, D. J., *Electrochemical Reactor Design*, Elsevier Scientific Publishing Co., New York (1979).
10. Pletcher, D., *Industrial Electrochemistry*, Chapman and Hall, NY (1984).
11. Selley, N. J., *Experimental Approach to Electrochemistry*, John Wiley and Sons, Inc., NY (1977).

GENERIC QUIZ

Continued from page 181.

- I think the only thing about it that makes me feel uncomfortable is the grading. While in some cases it may be pretty obvious the person didn't work hard it seems to me that in others a person might come up with a good comprehensive test, but just not be in the type of format the grader may be looking for. This feeling would be hard to verify, though.
- If it had a drawback it was in the time required to do a decent job. Clearly, this was an assignment which could absorb as much time as one was willing to give to it.
- I think it is very difficult to be creative and yet produce reasonable questions. This made the exercise somewhat frustrating and time consuming.
- Nothing. I couldn't wait to work on it.

Things gained from the experience

Students also volunteered comments on what they had gained from the experience. Many repeated points they made in the "Things liked" category regarding the depth of study required to make up a good examination. One comment I