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Perspective

Reinvigorating electrochemistry education

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SUMMARY

Electrochemistry is an established discipline with modern frontiers spanning energy conversion and storage, neuroscience, and organic synthesis. In spite of the expanding opportunities for academic and industrial electrochemists, particularly in the growing energy-storage sector, rigorous training of electrochemists is generally lacking at academic institutions in the United States. In this perspective, we highlight the core concepts of electrochemistry and discuss ways in which it has been historically taught. We identify challenges faced when teaching inherently interdisciplinary electrochemical concepts and discuss how technology provides new tools for teaching, such as inexpensive electronics and open-source software, to help address these challenges. Finally, we outline example programs and discuss how new tools and approaches can be brought together to prepare scientists and engineers for careers in electrochemical technology where they can accelerate the research, development, and deployment of the clean energy technology essential to combat climate change in the coming decades.

INTRODUCTION

Electrochemistry underlies critical aspects of modern civilization and is the key to developing the sustainable CO₂-emission-free economy that is essential to mitigate climate change (Davis et al., 2018). The widespread electrification of society, which is required to reach net-zero CO₂ emissions and is being driven by the dramatically decreasing cost of electricity from solar and wind (Haegel et al., 2017), requires energy-dense durable batteries and fuel cells for the transportation sector (Crabtree, 2019), and inexpensive electrolyzers to produce hydrogen gas as a feedstock chemical and fuel for long-distance transport and long-duration grid-scale energy storage (Dowling et al., 2020). Capacitive deionization is a promising route for desalination and separations (Liu et al., 2020) and organic electrosynthetic cells may improve chemical processes (Minteer and Baran, 2020). Ion-selective polymer membranes, a core electrochemical technology, are essential for these and other applications (Strathmann, 2010). The capacity of electrochemistry to contribute at immense scale is proven: Production of chlorine via the chloralkali process and aluminum via the Hall-Héroult process have taken place at industrial scales for over a century (Pletcher and Walsh, 2012). Electrochemistry is also central to interfacing electronics with biology, for example, to enable brain-machine interfaces via neural sensing and stimulation as well as for electroceuticals (Famm, 2013; Silversmith et al., 2021). Implementation of these technologies, along with many others, relies on a body of scientists and engineers trained in fundamental and applied electrochemistry to make the requisite scientific discoveries and engineering innovations in the laboratory and translate those to devices employed at scale.

Despite the vital role of electrochemistry in the future of diverse industries, education in electrochemical science, engineering, and technology is lacking across US universities. At the undergraduate level, science and engineering students usually see only a brief introduction to electrochemistry in their general chemistry courses. Graduate students in PhD programs may have access to one course, typically focused on electroanalytical chemistry. Several universities offer an electrochemical engineering course, but rarely are the two courses coordinated. Given the importance of electrochemical science, engineering, and technology to the prosperity of human civilization, electrochemistry education deserves a reinvigoration and reinvention to meet the needs of the 21st century.

ELECTROCHEMISTRY EDUCATION

Teaching electrochemistry is a challenge. Chemists familiar with homogeneous chemical reactions in beakers and flasks must translate their experience to heterogeneous reactions at interfaces while learning the fundamentals of transport and strengthening physics concepts such as electrostatics. Understanding electrochemical

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instrumentation and troubleshooting electrochemical cells requires an understanding of amplifier and feedback circuits. Students must be proficient in differential equations and multivariable calculus to develop foundational understanding of the relationships among thermodynamics, kinetics, and transport. As a result, most dedicated courses in electrochemistry are at the graduate level and build on assumed prior exposure to chemical kinetics, electrostatics, thermodynamics, and mass-transfer; topics from courses that span many departments and thus are unlikely to be mastered by any single entry-level graduate student.

Several electrochemistry and electrochemical-engineering textbooks have been published over the past decades. Selecting the appropriate text(s) for a course depends as much on the educational history of the students as it does on the course content. Each textbook has valuable examples and homework problems at a range of difficulties spanning fundamental concepts and applications. These problems are useful independent of what book or books are used in a given electrochemistry course. The comprehensive electroanalytical approach taken by Bard and Faulkner prepares students to interpret many types of electroanalytical data and derive expressions for the polarization response of different electrodes, but can be challenging for beginning electrochemists because of its mathematical and analytical rigor (Bard and Faulkner, 2000). Other texts offer an approach rooted in physical chemistry that is suited for scientists seeking to understand electrode kinetics and surface properties (Eliaz and Gileadi, 2019; Schmickler and Santos, 2010; Bockris and Reddy, 1973) or focusing on understanding voltammetry in detail (Compton and Banks, 2018). Electrochemical engineering texts are available, which introduce fundamental electrochemistry concepts while covering a broad range of electrochemical devices such as batteries and fuel cells, and applications in corrosion and electrodeposition (Fuller and Harb, 2018; Newman and Balsara, 2021). Fuller and Harb provides multiple chapters on the design of scaled up battery packs and fuel cell stacks, essential content for students entering the electrochemical industry. The recently updated text from Newman and Balsara includes a mathematically rigorous treatment of the physics required to build comprehensive models of electrochemical devices as well as new and expanded content on electrochemical impedance spectroscopy and Li-ion batteries.

Despite the diversity of approaches and subject matter in the texts above, a few topics have been neglected. Ion-conducting polymers (ionomers) are implemented in electrolyzers, fuel cells, solid-state batteries, and dialysis, but are mostly introduced in the context of a specific application and rarely provided an independent section. Thoughtful reviews are available to instructors (Meyer, 1998; Kusoglu and Weber, 2017), but dedicated chapters covering the structure and function of ionomers have yet to appear in electrochemistry textbooks (Strathmann, 2010). Lastly, with the dramatic decreases in the costs of microelectronics, inexpensive potentiostats are now readily available for teaching. Simple descriptions of how electrodes and cells are assembled and tested in the laboratory would be a welcome addition to future textbooks to augment more detailed compendiums on practical electrochemical methods (Zoski 2006). Some pedagogical electrochemistry laboratory resources are available from the Oregon Center for Electrochemistry (<https://electrochemistry.uoregon.edu/education/>), UC Irvine (<https://www.chem.uci.edu/~ardo/echem.html>), and the peer-reviewed literature (Elgrishi et al., 2017).

For all its challenges, electrochemistry provides a rich set of opportunities to introduce chemists, physicists, and engineers to instrumental analysis, multiscale modeling, and device design, while solidifying their understanding of core thermodynamics, kinetics, transport, and materials-science concepts. To avoid misconceptions in introductory courses, it is important to expose students to a broad variety of examples: electrolytic and galvanic cells, solid and liquid conducting electrolytes, and processes occurring over multiple length-scales (Sanger and Greenbowe, 1999; Subramanian and Braatz, 2010). Learning such breadth of content may be facilitated by experiences in the laboratory. A ten-week experience in fuel-cell engineering at the University of Washington serves as an example of electrochemistry as a platform for teaching a variety of interdisciplinary concepts (Stuve, 2006). Similar experiences tailored toward a survey of electrochemical devices could help solidify concepts from lecture courses, mitigate common mistakes related to potentials and ionic current, and expand career opportunities for appropriately trained graduates. Gaps in the current way electrochemistry is commonly taught at the graduate level include introductions to cell configurations of interest to electrochemical industry (Botte, 2010), application of software to model multi-scale processes (Subramanian and Braatz, 2010), and exposure to a greater breadth of technical skills (Faulkner, 2012). Addressing these gaps will lead to versatile students who can adapt to the needs of a rapidly changing industry and succeed in academic research and innovation.

CORE CONCEPTS AND FUNDAMENTALS OF ELECTROCHEMISTRY

Misconceptions and misunderstandings are rife in the field of electrochemistry. The equations behind electrochemical equilibria are often simple to introduce but difficult for students, and many practitioners, to fully understand and appropriately apply. Generally, equilibrium between phases – such as the electrode and solution – is determined by the concept of the “electrochemical potential” which brings together electric potentials from electrostatics with chemical potentials as determined by the Gibbs free energy used in chemistry (Boettcher et al., 2020). Students must be comfortable with the use of reference states and the difference between intensive and extensive properties before being tasked with deriving cell potentials. Because half-cell potentials are intimately tied to laboratory measurements and the concept of a reference reaction/electrode, students benefit from practical experience, measuring standard potentials for themselves. It is often overlooked that all measured half-cell potentials are in fact full-cell potentials measured versus a reference electrode/state, a point that helps one conceptualize the initial and final states of the electron in all coupled redox reactions. With this knowledge, it becomes clear how measurements of half-cell potentials include contributions to differences in electric potential in the electrolyte between the electrode of interest and its reference state, such as membrane potentials, liquid-junction potentials across frits, and ohmic potential drops due to uncompensated resistance when current is flowing. Notably, the widespread use of cyclic voltammetry in chemistry research to approximate thermodynamic standard-state solution potentials oftentimes leads to a misunderstanding of the differences in standard-state and actual electrode and solution potentials.

Extending measurements of the equilibrium cell potential to non-equilibrium situations where current is flowing introduces new challenges. Students often struggle to balance the current carried by electrons with ions carrying the charge through the electrolyte (Sanger and Greenbowe, 1997). Some misconceptions about ionic current and net charges on electrodes can be traced back to literal interpretations of poorly designed descriptions and diagrams (Sanger and Greenbowe, 1999). Exposure to chemically reversible cells, such as rechargeable batteries, help prevent misconceptions about the relationship between positive and negative electrodes to cell anodes and cathodes and the direction of ionic current. Furthermore, students should be provided opportunities to directly assess the contributions of convection, diffusion, and migration to mass transport required for sustained currents. At the graduate level, students struggle to understand the various contributions to the overpotential under current flow and how those develop across interfaces and through the cell. Issues with connecting overpotentials to the spatial dependence of the electrochemical potential, chemical potential, and electric potential are carried over into the published electrochemical literature. Laboratory experiences to explore these concepts could work hand-in-hand with analytical and numerical modeling of transport and electron-transfer processes.

The use of Butler-Volmer-type kinetic models is commonplace when analyzing electrode current-voltage behavior and the performance of energy conversion and storage devices. The common assumptions in these models, including a surface concentration, coverage, and transfer coefficient that do not vary with potential, are not likely to be the case for many electrodes and reactions. A misunderstanding or misrepresentation of these equations, particularly with regards to the so-called symmetry factor and its relation to the empirical transfer coefficient (Guidelli et al., 2014), is further related to unsolved problems in the field of electrochemical kinetics (Gileadi, 2011). Much can be done to clarify these assumptions and their resulting relationship to the empirical “Tafel slope” for different reactions. Research in electrocatalysis, from energy conversion to organic electrosynthesis, will be facilitated by improving our understanding of the relationship between homogeneous and heterogeneous redox reactions (Jackson and Surendranath, 2019). Students would benefit from an education that emphasizes the appropriate and inappropriate use of Butler-Volmer and Tafel relationships and includes a clear discussion of the underlying assumptions in connecting polarization data to microscopic mechanisms (Boettcher and Surendranath, 2021).

REINVIGORATING THE CLASSROOM

Modern classrooms provide a number of tools that can be used to support students of electrochemistry in the lecture hall and laboratory. A reinvigorated electrochemistry curriculum should balance learning experiences that involve flipped classrooms, laboratory experiences, and independent data analysis and simulations (Figure 1).

Flipped classrooms, where students participate in lectures on their own time and work through problems in class, are often found to increase student engagement with the textbook (Weaver and Sturtevant, 2015).

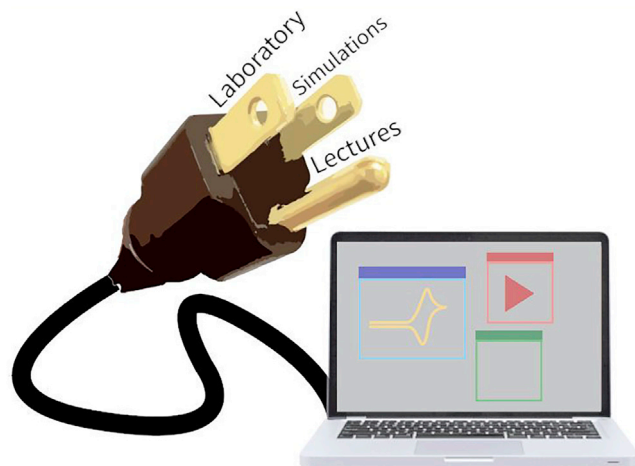


Figure 1. A “three-pronged approach” to teaching electrochemistry, grounded in fundamentals.

Concurrent laboratory and simulation courses connect to traditional lecture material, reinforce fundamentals, and provide useful skills for academic and industry research and development.

Meta-analyses of courses that include online and active-learning components have shown positive correlations with improved engagement, increased test scores, and decreased failure rates, independent of either student quality or instructor identity (Freeman et al., 2014; Means et al., 2009). This approach has now been adopted for a wide variety of STEM students, from those in introductory physics classes to medical students (Prober and Heath 2012; Deslauriers et al., 2011). Active learning could be part of the solution to narrowing achievement gaps and addressing the “leaky pipeline” for minority students within STEM programs in the US (Freeman et al., 2014; Theobald et al., 2020). Outcomes have not yet been quantified for electrochemistry education, but our experience suggests a judicious mix of pre-recorded and live content delivery to be useful. The pre-recorded content allows students to review key material and address gaps in understanding (e.g., electrostatics, thermodynamics) on their own time while simultaneously enabling instructors to supervise and model the problem-solving process when introducing new examples in the classroom. Recorded video lectures have the added benefit of broadening the impact of specialized electrochemistry courses at the graduate level, which can be made available to a global audience.

Inexpensive consumer electronics have likewise made instrumental design not only accessible for graduate curriculum, but also undergraduate and even high school classrooms. Multiple designs for home-built, inexpensive potentiostats, the instruments required for three-electrode measurements that are central to electrochemistry, are freely available (Li et al., 2018; Meloni, 2016; Mott et al., 2014). The JUAMI design is notable for being compatible with an open-source, Python-based graphical user interface. Chemists and chemical engineers are often not exposed to circuits as part of a core undergraduate curriculum and benefit from learning to read circuit diagrams, understanding the electrical response of operational amplifiers, resistors, and capacitors, and using this knowledge to build a potentiostat. Although many commercially available potentiostats come with software packages which include a variety of useful analytical and modeling tools, direct coding of these procedures in LabView, MATLAB, or Python is a useful exercise for solidifying concepts and practicing coding languages. While learning electrochemistry, opportunities to develop practical skills that are important not only in academia, but are also critical for industrial scientists and engineers, are numerous.

Finite element simulation methods are well developed and can be implemented on a personal computer, even for relatively complicated electrochemical systems. Concurrent simulations and laboratory courses are mutually beneficial. Laboratory coursework informs simulations by providing students with practical experience with systems; simulations coursework informs laboratories by forcing students to understand and apply appropriate governing equations and boundary conditions for processes they carry out in the laboratory. New questions arise from features of the experimental data that are not reproduced in the simulation results, prompting students to think critically about their measurements and assumptions of the models. Furthermore, visualization of time-variant mass-transport processes occurring at the micro

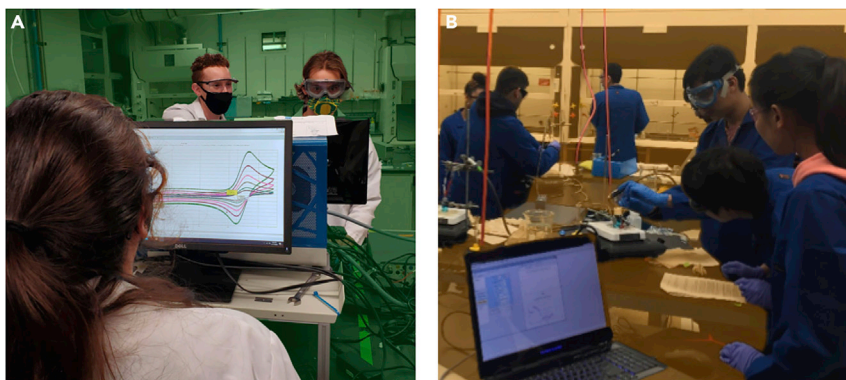


Figure 2. Electrochemists in training

Students from (A) the Oregon Center for Electrochemistry's founding cohort in 2020, collecting voltammetry data as part of the laboratory course, and (B) the first cohort of students to take part in laboratory activities as part of Prof. Ardo's CHEM 248 Electrochemistry course in Winter Quarter, 2017.

and nanoscales is nearly impossible without the assistance of simulations. Animations or videos of these processes in lectures increase accessibility of the material. Instructors can make use of software like COM-SOL, or other simpler mathematics packages, to create manipulatable applications that students can use to explore and understand limits and parameter spaces.

Laboratories that incorporate statistical methods and design-of-experiments concepts will better prepare scientists and engineers who aim to transition to careers in electrochemical industry. Students are quite familiar with *time* constraints on the number of experiments they can perform but are less familiar with *resource* constraints. Practical exposure to large datasets is rarely encountered in teaching laboratories, but electrochemical experiments are readily designed for combinatorial, "high-throughput" chemistry (Gregoire et al., 2013; Baeck et al., 2002). This approach has been shown to be practical in high school laboratories and could be implemented at the undergraduate and graduate level (McKone et al., 2014; Parkinson, 2010). Developing an understanding of statistical methods is in itself a challenge, so students will benefit most from this type of laboratory curriculum when accompanied by lecture material, which could be pre-recorded, on statistics and design of experiments.

AN EXAMPLE PROGRAM

At the graduate level, electrochemistry-related courses might include an electroanalytical-focused course taught in the chemistry department, an engineering-focused course, perhaps an energy technology course, and in rare cases, a course in corrosion. Usually, these courses are not coordinated and overlap in material is common. Courses taught with laboratory experiences, simulations, and/or practical skills are typically missing. Within the Oregon Center for Electrochemistry, we have developed an accelerated graduate program focused on electrochemical technology and a related program is being planned at UC Irvine (Figure 2). The Oregon program is distinguished from traditional electrochemistry education by tight integration of laboratory, simulation, and practical skills. Students at the master's level complete six months of intense coursework before a nine-month internship in industry or a national laboratory doing electrochemical research and development that completes the degree. Students in the PhD program take a subset of the courses depending on their interests as they start their PhD research.

The core program at Oregon consists of six quarter-long courses. The first course is a lecture course that focuses on the fundamental theories of electrochemistry, with coupled use of hands-on laboratory activities and numerical simulations. The course generally follows Bard and Faulkner's text, with some additions. After providing an overview of electrochemistry theory and applications, a review of electrostatics, and introduction to basic three-electrode measurements under mass-transfer control in the first week, the focus shifts to foundational concepts. First, thermodynamics are covered, starting from basic physical-chemistry equations and derivations of the relationship between free energy and the cell potential, then proceeding to discussions of the electrochemical potential and its use in describing equilibrium and interface effects. Students learn how to construct Pourbaix diagrams from thermodynamic data and use them to predict

reactions. Electrochemical kinetics is discussed using transition-state and Marcus theory leading to the current-overpotential, Butler-Volmer, and Tafel equations. Double-layer theory is discussed in the context of showing how the resulting electric potential drop affects electron- and ion-transfer kinetics and the free-energy surface for the reaction. Transport by diffusion and migration is introduced in the context of the electrochemical-potential gradient and students are introduced to the transference number for ionic transport. Next, electroanalytical potential step, linear sweep voltammetry, and cyclic voltammetry experiments are discussed. The current-time and current-voltage expressions are not derived in class as they include the use of relatively tedious methods in solving differential equations. Instead, the emphasis is placed on defining and understanding boundary and initial conditions, as well as the meaning and difference between steady-state and transient responses. A brief discussion of multistep electrochemical mechanisms and interpreting voltammetry follows. Students use simple commercial software to simulate the effects of transport, electrochemical kinetics, and mechanism on the resulting shape of voltammograms (such as that provided as part of the Bio-Logic software package, EC-Lab). The course ends with a discussion of alternating current (AC) circuits and impedance analysis. Students typically struggle to use complex numbers to manipulate and represent AC responses and often need to review basic circuits. The students learn to derive basic expressions for Randles equivalent circuits and to fit experimental data to identify charge transfer and diffusional impedances as well as the ohmic resistance and double-layer capacitance.

The graduate level course at UC Irvine is structured similarly to the above outline but has historically also included a larger lecture, and laboratory, component on thermodynamic activity and its application to underpotential deposition, liquid-junction potentials, membrane potentials, and ion-selective electrode. Each student is required to give a 10–15 min presentation on an application or technique that aims to bridge concepts, knowledge, and nomenclature learned in the course to their particular topic and to critically evaluate a recent peer-reviewed publication related to it, in lieu of extensive lecture material covering applications of electrochemistry and several techniques.

Both lecture courses are coupled tightly with laboratory courses (two three-hour sessions per week at Oregon and one two-hour session per week at UC Irvine). The laboratories focus on typical three-electrode electrochemical experiments and techniques that form the basis for analytical electrochemistry and build basic electrochemistry knowledge and intuition with respect to thermodynamics, kinetics, and mass transport. Students learn practical skills such as circuit design and electrode preparation. Laboratory modules include building a potentiostat, potential-step and potentiometric measurements, deposition and Tafel analysis of heterogeneous electrocatalysts, cyclic voltammetry of soluble species, and impedance spectroscopy and analysis. Instead of writing laboratory reports, the students in the Oregon Center for Electrochemistry submit Python notebooks, which makes it possible to evaluate and provide feedback on the process of data work up and analysis while teaching valuable programming skills. Additional laboratories at UC Irvine have explored ion-selective electrodes and liquid-junction potentials. Students have historically analyzed and interpreted their results to connect them more broadly to the physical processes occurring in their experiments supported by numerical simulations.

At the Oregon Center for Electrochemistry, both the lecture and laboratory content runs parallel to a course in numerical simulation of electrochemical systems, currently taught using the commercial COMSOL package. The course emphasizes (1) understanding the math and physics principles underlying finite-element numerical simulation, (2) constructing robust electrochemical models, including defining boundary conditions, interfaces, transport, kinetics, and thermodynamic model inputs, and (3) interpreting data from numerical simulations in the context of a simple physical picture to develop electrochemical intuition. Example projects include polarization of an inert electrolyte and formation of a double layer, diffusion-controlled voltammetry, and cyclic voltammetry with planar and radial geometries. Students also perform an independent project to apply their skills in an area of interest, for example, batteries.

The second term of the core electrochemistry graduate program at Oregon focuses on engineering and devices. A lecture course on electrochemical engineering follows Fuller and Harb, with emphasis on porous electrode theory, batteries and battery packs, fuel cells and systems, corrosion, electrodeposition, and industrial electrolysis. Lectures are tightly coupled with a substantial laboratory course that applies the concepts learned in the lecture while also emphasizing practical skills that are valuable in careers, including numerical simulations, programming, and design of experiments. Students work in small teams to build Li-ion battery devices, water electrolyzers, and fuel cells. They test the performance and response of these

devices compared to theory and modeling, applying experimental design and statistical analysis methods. Laboratory projects also include those focused on electrodeposition and corrosion. Open laboratory times are typically established for students to work in teams at their own pace and on their own schedule on the assigned projects, after appropriate safety training and with oversight and mentoring as needed. For both the lecture and laboratory engineering and device courses, feedback from industry partners drives content evolution to keep the courses relevant.

As a “capstone” to the on-campus curriculum, students in the Oregon Master’s program take a projects course where they join as teams (2–4 students) to solve open-ended research and development projects in electrochemistry. The applied research and development projects for the course come from industry and academic or national laboratory partners. This allows the students to develop skills solving unstructured problems representative of what they will face in their careers. One example in the first year of the program included building alkaline-membrane electrolyzers with earth-abundant oxygen-evolution catalysts and understanding the design parameters that drive energy efficiency and durability that are currently unknown in the field. Senior PhD students with expertise in the project content typically mentor and work with the teams of electrochemistry Master’s students. The outputs are formal reports to the industry sponsor and/or academic peer-reviewed publications where the students are co-authors. The students also learn to use materials characterization tools such as electron and atomic-force microscopies to augment electrochemical analyses.

OUTLOOK

Electrochemistry as a field is growing at a tremendous rate. It was central to the emergence of chemistry as a discipline through the discovery of elements, and is now poised to revolutionize energy, neuroscience, and organic synthesis, among more traditional applications in corrosion prevention and electrodeposition. A reinvigoration of electrochemical education is important to support emerging industries with the talent they need and will ensure the rigor of the rapidly growing literature that reports electrochemical data.

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