

Introduction to Electrochemistry and the Use of Electrochemistry to Synthesize and Evaluate Catalysts for Water Oxidation and Reduction

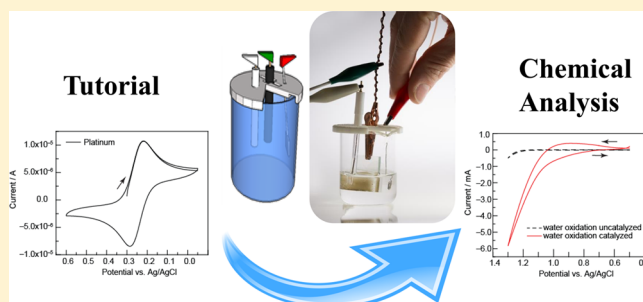
Samuel J. Hendel and Elizabeth R. Young*

Department of Chemistry, Amherst College, Amherst, Massachusetts 01002, United States

S Supporting Information

ABSTRACT: Electrochemical analysis is an important skill to teach in chemistry curricula because it is a critical tool in current high-impact chemical research. Electrochemistry enables researchers to analyze a variety of systems extending from molecules to materials that encompass research themes ranging from clean energy to substrate activation in biological systems. Specifically, it can reveal information about catalytic efficiency, the role of catalysts, and the nature of chemical reduction and oxidation (redox) processes. Researchers working in the area of catalysis rely heavily on electrochemistry, using it to identify effective catalysts and optimize reaction conditions. This laboratory experiment begins with an introductory tutorial to electrochemistry by guiding students through the use of several electrochemical techniques using the ferricyanide/ferrocyanide redox couple as a model system. The techniques covered in the tutorial include cyclic voltammetry, differential pulse voltammetry, Tafel analysis, and bulk electrolysis. The protocol then applies these techniques to electrocatalysis by identifying and characterizing catalysts for hydrogen and oxygen generation in the water electrolysis reaction. Electrochemical methods are connected to current chemical research by focusing on catalysis in the context of renewable energy, which is a current societal and curricular imperative. The entire laboratory protocol described herein is conducted in groups of two to three students in a four hour laboratory period and is suitable for upper-level physical, analytical, or inorganic chemistry.

KEYWORDS: Electrochemistry, Water/Water Chemistry, Green Chemistry, Catalysis, Physical Chemistry, Laboratory Instruction, Inorganic Chemistry, Analytical Chemistry, Upper-Division Undergraduate, Hands-On Learning/Manipulatives



INTRODUCTION

Electrochemistry permeates the undergraduate chemistry curriculum in various contexts. Most general chemistry courses introduce redox chemistry through discussions of galvanic cells.¹ Biology and biochemistry courses consider how redox potentials lead to a flow of electrons in the electron transport chain and how that energy is harvested to power oxidative phosphorylation.² Upper-level courses in inorganic, analytical, and physical chemistry as well as other specialized topics include discussion of electrochemical processes in various frameworks, including environmental and industrial chemistry.³ While students are exposed to the concepts of electrochemistry throughout the undergraduate curriculum, experimental techniques used to garner quantitative electrochemical characterization and analysis may not be encountered. Quantitative electrochemistry is an important tool for chemical research. In fact, the *ACS Guidelines and Evaluation Procedures for Bachelor's Degree Programs* in chemistry identifies, as part of its infrastructure needs, electrochemistry as a category of on-site instrumentation with which undergraduates should gain familiarity.⁴ Electrochemistry is one of the five instrumentation categories from which at least four must be supported (in

addition to NMR) for a department to maintain an ACS-approved program.⁴ For these reasons, incorporation of electrochemistry into the laboratory curriculum may be of interest at many institutions.

Electrochemical techniques, including potentiometry, amperometry, coulometry, and voltammetry, are used in chemical research to measure redox potentials, characterize reversibility of a chemical process, assemble or synthesize materials, and analyze the efficiency and function of catalysts, among many other uses. To familiarize students with electrochemistry, this laboratory experiment first introduces the fundamentals of experimental electrochemistry through a tutorial section that demonstrates and explains several electrochemical techniques. The students then conduct electrochemical analyses of the water electrolysis reaction and identify catalysts for both hydrogen and oxygen generation in the reductive and oxidative half-reactions, respectively.

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Water electrolysis (or water splitting) was chosen because of many students' familiarity with the reaction and because it forms the foundation of an energy storage fuel cycle urgently needed by the global community. By converting water into molecular hydrogen, a fuel, and oxygen, water electrolysis provides a means for energy storage. When linked with solar energy-harvesting processes, hydrogen generated by this reaction produces clean, renewable fuels. To make this process more energetically feasible, new efficient catalysts must be designed and characterized. The overall water-splitting reaction and component half-reactions are typically covered in the introductory level. Therefore, students will more easily grasp the electrochemical concepts behind these reactions. The techniques introduced in this protocol allow students to demonstrate the efficacy of catalysts for reduction and oxidation half-reactions. Students will gain insight into research methods used to identify pathways for renewable energy production. Indeed, the water oxidation catalyst used in this protocol was published recently in *Science*,⁵ and students are directed to an M.I.T. video production⁶ that provides an overview of the research challenges of water splitting and highlights the researchers who carried out the work.

To date, electrochemical techniques have been utilized in a wide range of applications in experimental laboratory procedures reported in this journal, including measurement of redox potentials,^{7–11} determination of diffusion coefficients,^{12,13} modification of electrode surfaces,^{14–17} biochemical analysis,¹⁸ measurement of changes to redox potentials as ligand or micellar environments are modified,^{19–23} and monitoring of isomerization reactions,²⁴ among many others.^{25,26} The first tutorial section of this laboratory experiment is well-positioned as a foundational experience in electrochemistry that could precede any number of other experiments that employ electrochemical analysis and characterization. This protocol contains an additional application section that draws real-world connections between electrochemistry and chemical research through the lens of clean, renewable energy, which is currently of massive global importance.

OVERVIEW AND BRIEF INTRODUCTION OF ELECTROCHEMISTRY CONTENT

The tutorial component introduces cyclic voltammetry (CV) and differential pulse voltammetry (DPV) and includes an optional Tafel analysis experiment. Bulk electrolysis is introduced and utilized in the second portion of the experiment that contains an advanced section describing electrocatalysis. A brief description of these techniques is outlined here, and a table of symbols and abbreviations is included in [Table S1](#).

CV and DPV are two techniques to measure redox potentials. CV is a linear potential sweep method that varies an applied potential in an electrochemical cell while recording the resulting current.²⁷ The redox potential, $E_{1/2}$, is determined using two peaks that arise as the applied potential is cycled to a switching potential and then back to the starting potential. E_{pc} and E_{pa} are the peaks observed on the cathodic and anodic scans, respectively. For a perfectly reversible system, the voltage difference between the two peaks in a CV scan should be close to

$$|E_{pc} - E_{pa}| = \frac{2.3RT}{nF} \quad (1)$$

where R is the gas constant, F is Faraday's constant, n is the number of electrons involved in the electrochemical event, and T is temperature (K). At 298 K, $\frac{2.3RT}{nF} = 0.059$ V for a one-electron process. Further,

$$\frac{i_{pc}}{i_{pa}} = -1 \quad (2)$$

where i_{pc} and i_{pa} are the cathodic and anodic peaks, respectively. The ratio of the peak currents should be negative one because the absolute value of the heights should be the same on the forward and reverse scans, and one current is positive (i_{pc} for a reduction and i_{pa} for an oxidation) while the other is negative (i_{pc} for an oxidation and i_{pa} for a reduction). Taken together, the ratio of peak currents and the difference between the peak potentials reveal the reversibility of the reaction; the closer the peak current ratio is to negative one and the closer the peak potential difference is to $\frac{2.3RT}{nF}$, the more fully thermodynamically reversible, or Nernstian,²⁸ the reaction is. For systems with irreversible redox events, DPV is a useful electrochemical method because the technique relies on a successive pulses in only one direction, yielding a value of E_p at the peak potential. The production of an unstable product does not affect the results as it does in a CV.

A Tafel analysis is used to reveal the nature of the transition state, equilibrium kinetics at the electrode, and kinetic limitations of an electrochemical system. A Tafel plot is constructed by plotting the applied overpotential for an electrochemical process versus the log of the current. In the Tafel region, the data yield a straight line that (for a cathodic reaction) takes the functional form

$$\ln(i) = \ln(i_0) - \frac{\alpha F}{RT} \eta \quad (3)$$

where, i_0 is the exchange current, α is the charge transfer coefficient, and η is the overpotential.

Bulk electrolysis is the application of an applied potential in an electrochemical cell for an extended period of time while monitoring the current passing through the cell. Bulk electrolysis may be used to carry out chemical transformations or condition electrodes for specific experiments, among other things.

EQUIPMENT AND MATERIALS

An electrochemical workstation is used for data acquisition and analysis. A CH Instruments (CHI) 630 or 730 (or higher model numbers), which includes CV, DPV, bulk electrolysis and full CV simulation and fitting program, possesses the necessary features. A single-compartment electrochemical cell comprised of a standard 50 mL beaker is used to accommodate the three-electrode experimental configuration as shown in [Figure 1](#). A three-dimensional (3D) printable cap was designed to fit on a 50 mL beaker, simplifying the electrochemical cell setup ([Figure 1](#), printing schematic provided in the [Supporting Information](#)). Otherwise, a ring stand and clamps are used to support and position the electrodes. Smaller beakers or commercial electrochemical cells may be used (see the [Supporting Information](#)); however, care must be taken to ensure that conducting parts of the electrodes do not come in contact with metallic regions of the clamp or each other. Four different working electrodes are used: (1) a glassy carbon, (2) an (optional) gold, (3) a platinum electrode, and (4) a fluorine-

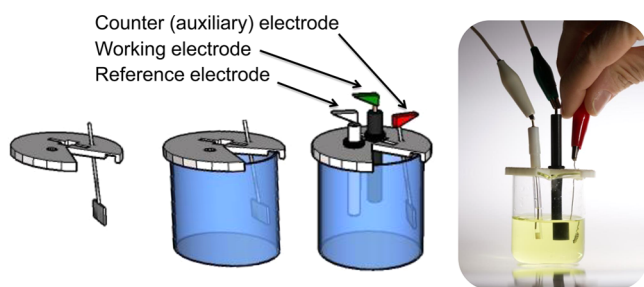


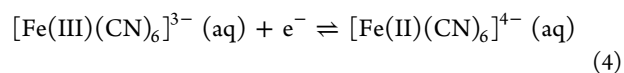
Figure 1. Schematic diagram of the electrochemical cell with the 3D printed cap. The Pt mesh counter electrode is inserted into the cap, and the cap is placed on the beaker. The working and reference electrodes can then be inserted into the cap. O-rings on the working and reference electrodes are used to position the height of the electrodes in the solution. A picture of the completed cell is shown on the right. Additional pictures of the electrochemical cell are provided in the [Supporting Information](#).

doped tin oxide (FTO)-coated glass slide. A Ag/AgCl reference electrode and a Pt mesh or Pt coil counter electrode are used in all experiments. The three electrolyte solutions needed are (1) 2 mM $K_3[Fe(III)(CN)_6]/0.2$ mM $Na_4[(Fe(II)(CN)_6)]/1$ M KCl, (2) 100 mM KCl, and (3) 100 mM potassium phosphate (pH 7). Cobalt(II) nitrate hexahydrate ($Co(II)(NO_3)_2 \cdot 6H_2O$) in solid form is needed during the experiment in addition to a stir plate and small stir bar. Product information and CAS numbers for electrodes and chemicals are provided in the [Supporting Information](#). Preparation of electrodes for electrochemical measurements are described in the [Supporting Information](#). *Mathematica* code is used to work up Tafel Plot data (provided in the [Supporting Information](#)). If *Mathematica* is not available, the Tafel data can be analyzed manually using standard plotting software (instructions provided in the [Supporting Information](#)).

EXPERIMENTAL PROCEDURE

The laboratory protocol consists of (1) an introductory tutorial on electrochemistry that introduces several electrochemical techniques used in research laboratories²⁹ and (2) an analysis section that implements these techniques to characterize water electrolysis half-reactions. A flowchart outlining the experimental protocol is shown in [Figure 2](#). The experiments are carried out in groups of two to three students in a four hour laboratory period, and discussion questions and calculations are assigned with the laboratory write-up. The protocol typically takes three hours, which allows students time to begin work on the postlaboratory assignment. This experimental protocol was performed several times,³⁰ and pre- and postlab surveys indicated that students successfully engaged the material and achieved the desired learning goals.³¹

In the tutorial portion of the laboratory experiment (*Electrochemistry Tutorial: One-electron Reduction of Potassium Ferricyanide*), students are introduced to experimental electrochemistry techniques by measuring the one-electron reduction of ferricyanide to ferrocyanide:



Students perform CV and DPV to measure the reduction potential. Students then perform a Tafel analysis on the ferricyanide/ferrocyanide reaction. A CV simulation is employed to model the experimental CV data to extract k_0 (self-exchange rate), E_0 (thermodynamic cell potential), and α (charge transfer coefficient), which allow students to predict i_0 (the exchange current). The fitted Tafel plot analysis produces an experimental value for i_0 , which is compared to the value obtained from CV simulation parameters, providing a link between experiment and theory.

In the application section of the experiment (*Electrochemical Analysis: Water Electrolysis and Catalysis*), students apply the electrochemical techniques introduced in the tutorial portion to

Introduction to Electrochemical Techniques

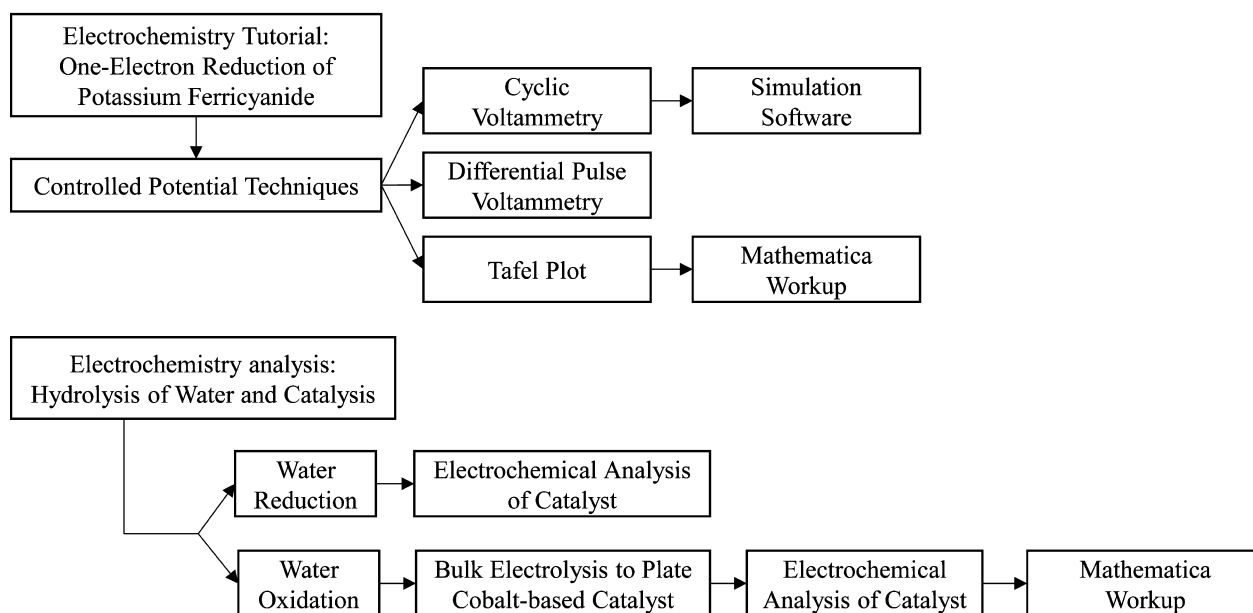


Figure 2. Flowchart describing the two portions of the laboratory protocol.

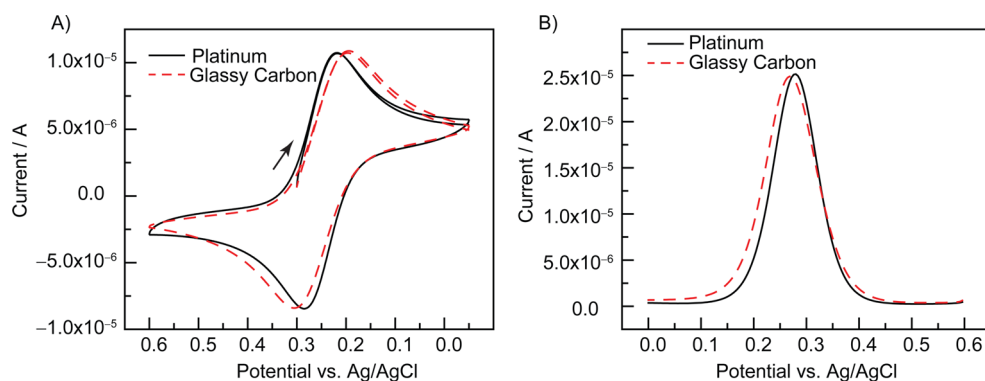


Figure 3. (A) Typical CV and (B) DPV scans for the ferricyanide/ferrocyanide solutions with the glassy carbon and platinum working electrodes. Acquisition parameters are provided in the [Supporting Information](#).

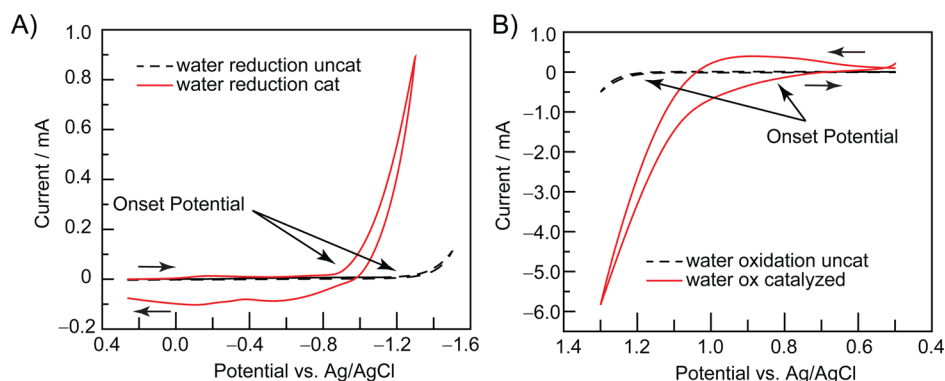
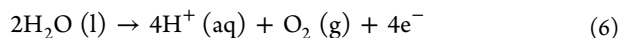


Figure 4. CV scans of (A) water reduction using a gold (uncatalyzed) and platinum (catalyzed) working electrode and (B) water oxidation using a blank FTO-coated glass slide (uncatalyzed) and the cobalt-based catalyst (catalyzed). Acquisition parameters are provided in the [Supporting Information](#).

examine water splitting. First, the reaction of relevance in water reduction, namely hydrogen ion reduction



is carried out with a gold electrode (glassy carbon could also be used) and then with a platinum working electrode. Platinum itself is a catalyst for hydrogen production. Thus, the CV taken with the platinum electrode reveals features of catalysis, which are detailed in the [Discussion](#). Second, for analysis of water oxidation,



students electrochemically synthesize a cobalt-phosphate water oxidation catalyst on an FTO-coated glass slide electrode.⁵ They evaluate the performance of the catalyst compared to the bare FTO-coated slide. A Tafel analysis is performed on the water oxidation catalyst.

HAZARDS

$\text{K}_3[\text{Fe}(\text{III})(\text{CN})_6]$, $\text{Na}_4[(\text{Fe}(\text{II})(\text{CN})_6)]$, and $\text{Co}(\text{II})(\text{NO}_3)_2$ are harmful if swallowed and cause irritation to the eyes and skin. Cobalt nitrate is an oxidizer and must be stored separately from other materials.

CALCULATIONS, RESULTS AND DISCUSSION

Electrochemistry Tutorial: One-Electron Reduction of Potassium Ferricyanide

Figure 3 shows typical CV and DPV scans of the ferricyanide/ferrocyanide solution with platinum and glassy carbon working electrodes. Use of two working electrodes demonstrates that the same redox reaction may display different kinetics at the electrodes and therefore different voltammetry scans. Values of $E_{1/2}$ and E_p ([Table S1](#)) for the reduction of ferricyanide obtained from CV ([Figure 3A](#)) and DPV ([Figure 3B](#)) scans as well as a complete discussion of these results are found in the [Supporting Information](#). Further, connections are developed between experimental data (Tafel plot, [Figure S1](#)) and electrochemical simulation (CV simulation) using the exchange current, i_0 , as the point of comparison. A detailed discussion of this comparison is included in the [Supporting Information](#).

Electrochemical Analysis: Water Electrolysis and Catalysis

Electrochemical analysis is applied to a real-world chemical paradigm for renewable energy research in the second section of the protocol. Students are guided through experiments to explore water reduction and oxidation that serve as energy storage reactions for a carbon-free, clean energy cycle. Students observe and describe the differences between CV scans of reversible systems (tutorial section above) and the irreversible chemical reactions that are the focus of this section. CV scans can be utilized to characterize catalytic activity in chemical reactions. For the water reduction reaction, the hydrogen ion reduction, students compare reductive CV scans using gold (or

glassy carbon) and platinum working electrodes (Figure 4A). Because platinum itself is a catalyst for water reduction, catalytic activity is observed in the CV scan. Catalytic activity is revealed by two features: (1) an earlier onset potential for observed current and (2) larger observed currents. The onset potential is the voltage at which the absolute value of the current increases from the baseline as the potential is swept to more negative potentials for reduction or to more positive potentials for oxidation. An earlier onset potential indicates that less energy is needed to drive the reaction. Increased current indicates more facile chemical reactions. For water reduction, the onset potential occurs at -1.2 V for the uncatalyzed reaction compared to -0.85 V for the catalyzed reaction. The overall current recorded with the platinum electrode is larger than that of the gold (or glassy carbon) working electrode. These two features are standard signals of catalytic activity in CV scans. Water oxidation CV scans follow a similar course (Figure 4B). A bare FTO-coated glass slide yields a high onset potential and very little current. After the cobalt-based catalyst is deposited, features of catalytic activity are clearly observed in the CV scan: the onset potential shifts from 1.2 to 0.8 V, and the absolute value of the current passing through the cell is significantly higher.

CONCLUSIONS

In this experiment, students are introduced to several electrochemical methods. Students then apply the techniques to chemical research of critical importance in the development of alternative energy sources needed to meet global energy demand. The procedure has also been utilized as a tutorial in the research laboratory setting to introduce undergraduate research students to electrochemical techniques. Discussion questions are provided to reinforce concepts from the laboratory (in the experimental protocol included in the Supporting Information). Students learn CV, DPV, and Tafel analysis. Further, students are introduced to the concepts of reversible redox processes at electrode surfaces and characteristics of chemical catalysis as they apply to electrochemical analysis. CV simulation is included to help make connections between theory and experimental measurements. The water splitting reaction and catalysis are discussed in the context of clean energy storage to promote connection of the teaching laboratory to real-world applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00230.

Experimental parameters, additional information about materials and supplies and discussion of the tutorials section, table of abbreviations, photographs of the experimental setup, manual Tafel workup protocol (PDF)

Laboratory manual (PDF, DOCX)

Answer key for the laboratory manual for instructors (PDF, DOCX)

Mathematica files and 3D printing instructions (ZIP)

AUTHOR INFORMATION

Corresponding Author

*E-mail: eyoung@amherst.edu; Fax: +1-413-542-5480.

Notes

The authors declare no competing financial interest.

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(28) At this point, we should clearly distinguish between electrochemical reversibility and chemical reversibility. An electrochemically reversible system refers to a system that behaves according to the Nernst equation, as described by eq 1 in the text. A chemically reversible system refers to a system in which the molecular species remain stable through the electrochemical event. That is, the oxidized or reduced species will not decompose into another chemical species but will remain in solution to be re-reduced or re-oxidized. A system may be chemically irreversible if the redox species decomposes or if the electrochemical event at the working electrode leads to a chemical reaction (as is the case in the advanced section of this protocol describing electrocatalysis).

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(31) Analysis of pre- and postlab assessments are provided in the [Supporting Information](#).