A Practical Beginner’s Guide to Cyclic Voltammetry

Noémi Elgrishi, Kelley J. Rountree, Brian D. McCarthy, Eric S. Rountree, Thomas T. Eisenhart, and Jillian L. Dempsey*

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290, United States

Supporting Information

ABSTRACT: Despite the growing popularity of cyclic voltammetry, many students do not receive formalized training in this technique as part of their coursework. Confronted with self-instruction, students can be left wondering where to start. Here, a short introduction to cyclic voltammetry is provided to help the reader with data acquisition and interpretation. Tips and common pitfalls are provided, and the reader is encouraged to apply what is learned in short, simple training modules provided in the Supporting Information. Armed with the basics, the motivated aspiring electrochemist will find existing resources more accessible and will progress much faster in the understanding of cyclic voltammetry.

KEYWORDS: Upper-Division Undergraduate, Graduate Education/Research, Inorganic Chemistry, Analytical Chemistry, Distance Learning/Self Instruction, Inquiry-Based/Discovery Learning, Textbooks/Reference Books, Electrochemistry

INTRODUCTION

Motivation

Electrotransfer processes are at the center of the reactivity of inorganic complexes. Molecular electrochemistry has become a central tool of research efforts aimed at developing renewable energy technologies. As the field evolves rapidly, the need for a new generation of trained electrochemists is mounting. While several textbooks and online resources are available, no concise and approachable guide to cyclic voltammetry is available. Here, we update, modify, and streamline seminal papers to provide a single introductory text that reflects the current best practices for learning and utilizing cyclic voltammetry. Practical experiments and examples centered on nonaqueous solvents are provided to help kick-start cyclic voltammetry experiments for inorganic chemists interested in utilizing electrochemical methods for their research. The practical experiments in this text are the basis for the instruction of new researchers in our laboratory.

Electrochemistry

Electrochemistry is a powerful tool to probe reactions involving electron transfers. Electrochemistry relates the flow of electrons to chemical changes. In inorganic chemistry, the resulting chemical change is often the oxidation or reduction of a metal complex. To understand the difference between a chemical reaction and an electrochemical reduction, consider the example of the reduction of ferrocenium [Co(Cp)₂]⁺ (Cp = cyclopentadienyl), abbreviated as Fe⁺, to ferrocene [Fe(Cp)₂], abbreviated as Fc:

- At an electrode: Fe⁺ + e⁻ ⇌ Fc

Why does [Co(Cp)₂]⁺ (Cp* = pentamethylcyclopentadienyl) reduce Fe⁺? In the simplest explanation, an electron transfers from [Co(Cp)₂]⁺ to Fe⁺ because the lowest unoccupied molecular orbital (LUMO) of Fe⁺ is at a lower energy than the electron in the highest occupied molecular orbital (HOMO) of [Co(Cp)₂]. The transfer of an electron between the two molecules in solution is thermodynamically favorable (Figure 1A), and the difference in energy levels is the driving force for the reaction.

In an electrochemical reduction, Fe⁺ is reduced via heterogeneous electron transfer from an electrode; but what is the driving force for this process? An electrochemical cell is an electrical conductor, typically platinum, gold, mercury, or glassy carbon. Through use of an external power source (such as a potentiostat), voltage can be applied to the electrode to modulate the energy of the electrons in the electrode. When the electrons in the electrode are at a higher energy than the LUMO of Fe⁺, an electron from the electrode is transferred to Fe⁺ (Figure 1B). The driving force for this electrochemical reaction is again the energy difference between that of the electrode and the LUMO of Fe⁺.

Changing the driving force of a chemical reduction requires changing the identity of the molecule used as the reactant. At its core, the power of electrochemistry resides in the simplicity with which the driving force of a reaction can be controlled and the ease with which thermodynamic and kinetic parameters can be measured.

Received: May 26, 2017
Revised: September 13, 2017

© XXXX American Chemical Society and Division of Chemical Education, Inc.
Cyclic Voltammetry

Cyclic voltammetry (CV) is a powerful and popular electrochemical technique commonly employed to investigate the reduction and oxidation processes of molecular species. CV is also invaluable to study electron transfer-initiated chemical reactions, which includes catalysis. As inorganic chemists embrace electrochemistry, papers in the literature often contain figures like Figure 2.

The aim of this paper is to provide the readers with the tools necessary to understand the key features of Figure 2. The following section will provide clues to understand the data, the reason for including the experimental parameters, their meaning and influence, and a broader discussion about how to set up the experiment and what parameters to consider when recording your own data. Finally, a brief description of frequently encountered responses in cyclic voltammetry will be given. The text will be punctuated with boxes containing further information (green) or potential pitfalls (red). Additional callouts refer to short training modules provided in the Supporting Information (SI).

UNDERSTANDING THE SIMPLE VOLTAMMOGRAM

Cyclic Voltammetry Profile

The traces in Figure 2 are called voltammograms or cyclic voltammograms. The x-axis represents a parameter that is imposed on the system, here the applied potential ($E$), while the y-axis is the response, here the resulting current ($i$) passed. The current axis is sometimes not labeled (instead a scale bar is inset to the graph). Two conventions are commonly used to report CV data, but seldom is a statement provided that describes the sign convention used for acquiring and plotting the data. However, the potential axis gives a clue to the convention used, as explained in Box 1. Each trace contains an arrow indicating the direction in which the potential was scanned to record the data. The arrow indicates the beginning and sweep direction of the first segment (or “forward scan”), and the caption indicates the conditions of the experiment. A crucial parameter can be found in the caption of Figure 2: $\nu = 100 \text{ mV/s}$. This value is called the scan rate ($\nu$). It indicates that during the experiment the potential was varied linearly at the speed (scan rate) of 100 mV per second.

Panel I of Figure 3 shows the relationship between time and applied potential, with the potential axis as the x-axis to see the relation with the corresponding voltammogram in panel H. In this example, in the forward scan, the potential is swept negatively from the starting potential $E_1$ to the switching potential $E_2$. This is referred to as the cathodic trace. The scan direction is then reversed, and the potential is swept positively back to $E_1$, referred to as the anodic trace.

Understanding the “Duck” Shape: Introduction to the Nernst Equation

Why are there peaks in a cyclic voltammogram? Consider the equilibrium between ferrocenium ($\text{Fc}^+$) and ferrocene ($\text{Fc}$). This equilibrium is described by the Nernst equation (eq 1).

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Fc}]}{[\text{Fc}^+]}$$

Figure 1. (A) Homogeneous and (B) heterogeneous reduction of $\text{Fc}^+$ to $\text{Fc}$. The energy of the electrons in the electrode is controlled by the potentiostat; their energy can be increased until electron transfer becomes favorable.

Figure 2. Voltammograms of a bare electrode under $\text{N}_2$ (blue trace); a bare electrode under air (red trace); [CoCp(dppe)(CH$_3$CN)][PF$_6$], (dppe = diphenylphosphinoethane) under $\text{N}_2$ (green trace); [CoCp-(dppe)(CH$_3$CN)][PF$_6$] under air (orange trace). Voltammograms recorded in 0.25 M [NBu$_4$][PF$_6$] CH$_3$CN solution at $\nu = 100 \text{ mV/s}$ with a 3 mm glassy carbon working electrode, a 3 mm glassy carbon counter electrode, and a silver wire pseudoreference electrode.
cell \(E\) to the standard potential of a species \(E^0\) and the relative activities\(^{16}\) of the oxidized (Ox) and reduced (Red) analyte in the system at equilibrium. In the equation, \(F\) is Faraday’s constant, \(R\) is the universal gas constant, \(T\) is the temperature, \(n\) is the number of electrons, and \(E\) is the formal potential

\[
E = E^0 + \frac{RT}{nF} \log \left( \frac{[Ox]}{[Red]} \right) = E^0 + 2.303 \frac{RT}{nF} \log \left( \frac{[Ox]}{[Red]} \right)
\]

(1)

In application of the Nernst Equation to the one-electron reduction of Fc\(^+\) to Fc, the activities are replaced with their concentrations, which are more experimentally accessible, the standard potential \(E^0\) is replaced with the formal potential \(E^0\), and \(n\) is set equal to 1:

\[
E = E^0 + \frac{RT}{F} \log \left( \frac{[Fc^+]}{[Fc]} \right) = E^0 + 2.303 \frac{RT}{F} \log \left( \frac{[Fc^+]}{[Fc]} \right)
\]

(2)

The formal potential is specific to the experimental conditions employed and is often estimated with the experimentally determined \(E_{1/2}\) value (Figure 3, average potential between points \(F\) and \(C\) in panel H). The Nernst equation provides a powerful way to predict how a system will respond to a change of concentration of species in solution or a change in the electrode potential. To illustrate, if a potential of \(E = E^0 \approx E_{1/2}\) is applied to our example Fc\(^+\) solution, the Nernst equation predicts that Fc\(^+\) will be reduced to Fc until \([Fc^+] = [Fc]\), and equilibrium is achieved. Alternatively, when the potential is scanned during the CV experiment, the concentration of the species in solution near the electrode changes over time in accordance with the Nernst equation.

When a solution of Fc\(^+\) is scanned to negative potentials, Fc\(^+\) is reduced to Fc locally at the electrode, resulting in the measurement of a current and depletion of Fc\(^+\) at the electrode surface. The resulting cyclic voltammogram is presented in Figure 3 as well as the concentration–distance profiles for Fc\(^+\) (blue) and Fc (green) at different points in the voltammogram. Crucially, the concentrations of Fc\(^+\) vs Fc relative to the distance from the surface of the electrode are dependent on the potential applied and how species move between the surface of the electrode and the bulk solution (see below). These factors all contribute to the “duck”-shaped voltammograms.

As the potential is scanned negatively (cathodically) from point \(A\) to point \(D\) (Figure 3), \([Fc^+]\) is steadily depleted near the electrode as it is reduced to Fc. At point \(C\), where the peak cathodic current (\(i_{pc}\)) is observed, the current is dictated by the delivery of additional Fc\(^+\) via diffusion from the bulk solution. The volume of solution at the surface of the electrode containing the reduced Fc, called the diffusion layer, continues to grow throughout the scan. This slows down mass transport of Fc\(^+\) to the electrode. Thus, upon scanning to more negative potentials, the rate of diffusion of Fc\(^+\) from the bulk solution to the electrode surface becomes slower, resulting in a decrease in the current as the scan continues (\(C \rightarrow D\)). When the switching potential (\(D\)) is reached, the scan direction is reversed, and the potential is scanned in the positive (anodic) direction. While the concentration of Fc\(^+\) at the electrode surface was depleted, the concentration of Fc at the electrode surface increased, satisfying the Nernst equation. The Fc present at the electrode surface is oxidized back to Fc\(^+\) as the applied potential becomes more positive. At points \(B\) and \(E\), the concentrations of Fc\(^+\) and Fc at the electrode surface are equal, following the Nernst equation, \(E = E_{1/2}\). This corresponds to the halfway potential between the two observed peaks (\(C\) and \(F\)) and provides a straightforward way to estimate the \(E^0\) for a reversible electron transfer, as noted above. The two peaks are separated due to the diffusion of the analyte to and from the electrode.

If the reduction process is chemically and electrochemically reversible, the difference between the anodic and cathodic peak potentials, called peak-to-peak separation (\(\Delta E_{pp}\)), is 57 mV at 25 °C (2.22 \(RT/F\)), and the width at half max on the forward scan of the peak is 59 mV.\(^{9}\) Chemical reversibility is used to denote whether the analyte is stable upon reduction and can subsequently be reoxidized. Analytes that react in homogeneous chemical processes upon reduction (such as ligand loss or

---

Figure 3. (A–G): Concentration profiles (mM) for Fc\(^+\) (blue) and Fc (green) as a function of the distance from the electrode (d, from the electrode surface to the bulk solution, e.g. 0.5 mm) at various points during the voltammogram. Adapted from Reference 4. Copyright © 2011, Imperial College Press. (H): Voltammogram of the reversible reduction of a 1 mM Fc\(^+\) solution to Fc, at a scan rate of 100 mV s\(^{-1}\). (I): Applied potential as a function of time for a generic cyclic voltammetry experiment, with the initial, switching, and end potentials represented (\(A, D,\) and \(G,\) respectively).
degradation) are not chemically reversible (see discussion below on EC Coupled Reactions). Electrochemical reversibility refers to the electron transfer kinetics between the electrode and the analyte. When there is a low barrier to electron transfer (electrochemical reversibility), the Nernstian equilibrium is established immediately upon any change in applied potential. By contrast, when there is a high barrier to electron transfer (electrochemical irreversibility), electron transfer reactions are sluggish and more negative (positive) potentials are required to observe reduction (oxidation) reactions, giving rise to larger $\Delta E_p$. Often electrochemically reversible processes—where the electron transfers are fast and the processes follow the Nernst equation—are referred to as "Nernstian.”

**Importance of the Scan Rate**

The scan rate of the experiment controls how fast the applied potential is scanned. Faster scan rates lead to a decrease in the size of the diffusion layer; as a consequence, higher currents are observed. For electrochemically reversible electron transfer processes involving freely diffusing redox species, the Randles-Sevcik equation (eq 3) describes how the peak current $i_p$ (A) increases linearly with the square root of the scan rate $\nu$ (V s$^{-1}$), where $n$ is the number of electrons transferred in the redox event, $A$ (cm$^2$) is the electrode surface area (usually treated as the geometric surface area), $D_o$ (cm$^2$ s$^{-1}$) is the diffusion coefficient of the oxidized analyte, and $C_0$ (mol cm$^{-3}$) is the bulk concentration of the analyte.

$$i_p = \frac{0.446nFA^2D_o^{1/2}}{RT}$$ (3)

The Randles–Sevcik equation can give indications as to whether an analyte is freely diffusing in solution, as explained in Box 2. As analytes can sometimes adsorb to the electrode surface, it is essential to assess whether an analyte remains homogeneous in solution prior to analyzing its reactivity. In addition to verifying that the analyte is freely diffusing, the Randles–Sevcik equation may be used to calculate diffusion coefficients (Experimental Module 4: Cyclic Voltammetry of Ferrocene: Measuring a Diffusion Coefficient).$^2$

**COLLECTING DATA**

**Introduction to the Electrochemical Cell**

In the experimental section of papers describing electrochemical measurements, a brief description is generally given for the experimental setup used to collect the data. The vessel used for a cyclic voltammetry experiment is called an electrochemical cell. A schematic representation of an electrochemical cell is presented in Figure 4. The subsequent sections will describe the role of each component and how to assemble an electrochemical cell to collect data during CV experiments.

**Preparation of Electrolyte Solution**

As electron transfer occurs during a CV experiment, electrical neutrality is maintained via migration of ions in solution. As electrons transfer from the electrode to the analyte, ions move in solution to compensate the charge and close the electrical circuit. A salt, called a supporting electrolyte, is dissolved in the solvent to help decrease the solution resistance. The mixture of the solvent and supporting electrolyte is commonly termed the "electrolyte solution.”

**Solvent:** A good solvent has these characteristics:

- It is liquid at experimental temperatures.

**Box 2. Freely diffusing or adsorbed on the electrode?**

For electrochemically reversible electron transfer processes involving freely diffusing redox species, the Randles-Sevcik Equation describes the dependence of the peak current on scan rate and reveals that plots of $i_p$ versus $\nu^{1/2}$ should be linear. For an electrode-adsorbed species, the current response is described by:

$$i_p = \frac{n^2F^2}{4RT}\nu A \Gamma^*$$

where $\Gamma^*$ is the surface coverage of the adsorbed species in mol cm$^{-2}$.

The current response for an adsorbed species is expected to vary linearly with $\nu$.

For an analyte that is thought to be a freely diffusing species, deviations from linearity in plots of $i_p$ vs. $\nu^{1/2}$ suggest either (a) electrochemical quasi-reversibility or (b) that electron transfer may be occurring via surface-adsorbed species. Examination of the peak-to-peak separation can help distinguish the cause of the deviation. For an electrochemically quasi-reversible process, the peak-to-peak separation shifts with scan rate, while for a surface-adsorbed species, no peak-to-peak separation is observed.

**Figure 4.** Schematic representation of an electrochemical cell for CV experiments.

- It dissolves the analyte and high concentrations of the supporting electrolyte completely.
- It is stable toward oxidation and reduction in the potential range of the experiment.
- It does not lead to deleterious reactions with the analyte or supporting electrolyte.
- It can be purified.

The potential windows of stability ("solvent window") of some common solvents used for inorganic electrochemistry are shown in Box 3. Experimenters are advised to rigorously ensure
Box 3. How wide is the electroactive window?

The electrolyte, solvent, and nature of the working electrode all influence the potential window that can be used for a CV experiment.1,2

<table>
<thead>
<tr>
<th>Influence of the Electrolyte</th>
<th>Pt electrode, CH₃CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M [NBu₄][ClO₄]</td>
<td></td>
</tr>
<tr>
<td>0.1 M [Bu₄N][BF₄]</td>
<td></td>
</tr>
<tr>
<td>0.1 M [Bu₄N][PF₆]</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Influence of the Electrode</th>
<th>H₂O, pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Influence of the Solvent</th>
<th>Pt electrode, 0.1M [Bu₄N][ClO₄]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>+4</td>
</tr>
<tr>
<td>DCM</td>
<td>+2</td>
</tr>
<tr>
<td>DCM</td>
<td>0</td>
</tr>
<tr>
<td>THF</td>
<td>-2</td>
</tr>
<tr>
<td>DCM</td>
<td>-4</td>
</tr>
</tbody>
</table>

The electrolyte, solvent, and nature of the working electrode all influence the potential window that can be used for a CV experiment.3

Solvents are free of impurities and, if necessary, rigorously anhydrous.

Supporting Electrolyte. A good supporting electrolyte has these characteristics:

- It is highly soluble in the solvent chosen.
- It is chemically and electrochemically inert in the conditions of the experiment.
- It can be purified.

Large supporting electrolyte concentrations are necessary to increase solution conductivity. As electron transfers occur at the electrodes, the supporting electrolyte will migrate to balance the charge and complete the electrical circuit. The conductivity of the solution is dependent on the concentrations of the dissolved salt. Without the electrolyte available to achieve charge balance, the solution will be resistive to charge transfer (see How To Minimize Ohmic Drop below). High absolute electrolyte concentrations are thus necessary.

Large supporting electrolyte concentrations are also necessary to limit analyte migration. Movement of the analyte to the electrode surface is controlled by three modes of mass transport: convection, migration, and diffusion. A species that moves by convection is under the action of mechanical forces (e.g., stirring or vibrations). In migration, ionic solute moves by action of an electric field (e.g., positive ions are attracted to negative electrodes). Diffusion arises from a concentration difference between two points within the electrochemical cell; this concentration gradient results in analyte movement from areas of high to areas of low concentration. All theoretical treatments and modeling exclude migration and convection of the analyte. To ensure that these mechanisms of mass transport are minimized, convection is reduced by the absence of stirring or vibrations, and migration is minimized through the use of electrolyte in high concentration.4 High electrolyte concentration relative to the analyte concentration ensures that it is statistically more probable that the electrolyte will migrate to the electrode surface for charge balance.

Ammonium salts have become the electrolyte of choice for inorganic electrochemistry experiments performed in organic solvents as they fulfill the three conditions of electrolyte choice. For dichloromethane or acetonitrile solutions, tetrabutylammonium (NBu₄) salts are commonly used. For less polar solvents like benzene, tetrahexylammonium salts are more soluble. While ammonium salts have become the standard cation, the choice of counteranion is less standardized as anions tend to be more reactive with transition metal analytes. The most commonly used anions are [B(C₆F₅)₄]⁻, [B(C₆H₅)₄]⁻, [PF₆]⁻, [BF₄]⁻, and [ClO₄]⁻. The more coordinating the anion, the more likely it is to have unwanted interactions with the cation, the solvent, or the analyte. We have found [NBu₄][PF₆] salts to be ideal supporting electrolytes in acetonitrile for their stability, noncoordinating nature, ease of purification, and solubility. Purity of the electrolyte is paramount because of the high concentrations required (we routinely use 0.25 M [NBu₄][PF₆] in CH₃CN), meaning even the slightest impurity can reach a concentration sufficient to interfere with the measurement. For information on the purification of common electrolyte salts, we direct the reader to page 70 of reference 1.

Choosing Electrodes and Preparing Them for Use

The caption of Figure 2 indicates that a three-electrode setup was used, including a glassy carbon working electrode, glass carbon counter electrode, and Ag+/Ag pseudoreference electrode. This setup (Figure 4) is typical for common electrochemical experiments, including cyclic voltammetry, and the three electrodes represent a working electrode, counter electrode, and reference electrode, respectively. While the current flows between the working and counter electrodes, the reference electrode is used to accurately measure the applied potential relative to a stable reference reaction.

Working Electrode (WE). The working electrode carries out the electrochemical event of interest. A potentiostat is used to control the applied potential of the working electrode as a function of the reference electrode potential. The most important aspect of the working electrode is that it is composed of redox-inert material in the potential range of interest. The type of working electrode can be varied from experiment to experiment to provide different potential windows or to reduce/promote surface adsorption of the species of interest (see Box 3 for examples).

Because the electrochemical event of interest occurs at the working electrode surface, it is imperative that the electrode surface be extremely clean and its surface area well-defined. The procedure for polishing electrodes varies based on the type of electrode and may vary from lab to lab. When using electrodes such as glassy carbon or platinum, clean electrodes surfaces can be prepared via mechanical polishing (Box 4). To remove particles, the electrode is then sonicated in ultrapure water.4 It is often necessary to perform several CV scans in simple electrolyte across a wide potential window to remove any adsorbed species left over from the polishing procedure. This can be repeated until the scans overlap, and no peaks are observed. This procedure is sometimes referred to as “pretreating” the electrode.18

For glassy carbon electrodes, the surface is very reactive once activated via polishing. When impurities are present in the solvent, they can preferentially adsorb to the carbon surface of...
the electrode, leading to modifications of the voltammograms. To limit adsorption of solvent impurities, a treatment of the solvent with activated carbon can be used.\(^{17}\)

It is necessary to polish the electrode prior to measurements, and often, electrodes need to be repolished between measurements over the course of an experiment because some analytes are prone to electrode surface adsorption. To determine if an analyte is adsorbed to the electrode surface, a simple rinse test can be performed: after recording a voltammogram, the WE is rinsed and then transferred to an electrolyte-only solution. If no electrochemical features are observed by CV, this rules out strong adsorption (although not weak adsorption). Since electrodes are capable of adsorbing species during an experiment, it is good practice to polish them after every experiment. Ideally, separate polishing pads are used before and after experiments to avoid contamination.

Different electrode materials can also lead to varying electrochemical responses, such as when electron transfer kinetics differ substantially between electrode types, when adsorption occurs strongly on only certain electrode materials, or when electrode-specific reactivity with substrates occurs. As such, changing the electrode material is a good first step to diagnose and assess these issues.\(^7\)

**Reference Electrode (RE).** A reference electrode has a well-defined and stable equilibrium potential. It is used as a reference point against which the potential of other electrodes can be measured in an electrochemical cell. The applied potential is thus typically reported as “vs” a specific reference. There are a few commonly used (and usually commercially available) electrode assemblies that have an electrode potential independent of the electrolyte used in the cell. Some common reference electrodes used in aqueous media include the saturated calomel electrode (SCE), standard hydrogen electrode (SHE), and the AgCl/Ag electrode. These reference electrodes are generally separated from the solution by a porous frit. It is best to minimize junction potentials by matching the solvent and electrolyte in the reference compartment to the one used in the experiment.

In nonaqueous solvents, reference electrodes based on the Ag\(^+\)/Ag couple are commonly employed. These consist of a silver wire in a solution containing an Ag\(^+\) salt, typically AgNO\(_3\). Conversion tables exist which enable referencing of data obtained with an Ag\(^+\)/Ag electrode to other types of reference electrodes for several silver salt, solvent, and concentration combinations.\(^{19}\) The potential of Ag\(^+\)/Ag reference electrodes can vary between experiments due to variations in [Ag\(^+\)], electrolyte, or solvent used (see Box 5), so it is important to note the specific details of a nonaqueous reference electrode. To circumvent these problems, reduction potentials should be referenced to an internal reference compound with a known \(E^0\). Ferrocene is commonly included in all measurements as an internal standard, and researchers are encouraged to reference reported potentials vs the ferrocene couple at 0 V vs Fc\(^-\)/Fc\(^0\).\(^ {20,21}\) Care should be taken to ensure that the potential window of the analyte’s redox processes do not overlap with those of ferrocene and that the analyte does not interact with ferrocene. If this is the case, a number of other internal standards with well-defined redox couples can be used (such as decamethylferrocene).\(^ {22}\) Since nonaqueous reference electrode potentials tend to drift over the course of an experiment, we recommend having ferrocene present in all measurements rather than adding it at the end of a measurement set.

Leaking of Ag\(^+\) into the rest of the analyte solution has sometimes been reported as an issue,\(^ {18}\) which can then interfere with electrochemical measurements. Thus, great care must be taken to minimize this possibility. One option, in conjunction with use of an internal standard, is to do away with the Ag\(^+\) salt and use a silver wire in electrolyte, separated from the analyte by a frit (see Box 6). This silver wire pseudoreference electrode presumably takes advantage of the natural oxide layer on the silver wire, using the resulting ill-defined Ag\(_2\)O/Ag couple. This method eliminates the possibility of silver salts leaks but requires the presence of an internal standard.

**Counter Electrode (CE).** When a potential is applied to the working electrode such that reduction (or oxidation) of the
analyte can occur, current begins to flow. The purpose of the counter electrode is to complete the electrical circuit. Current is recorded as electrons flow between the WE and CE. To ensure that the kinetics of the reaction occurring at the counter electrode do not inhibit those occurring at the working electrode, the surface area of the counter electrode is greater than the surface area of the working electrode. A platinum wire or disk is typically used as a counter electrode, though carbon-based counter electrodes are also available.1

When studying a reduction at the WE, an oxidation occurs at the CE. As such, the CE should be chosen to be as inert as possible. Counter electrodes can generate byproducts depending on the experiment, therefore, these electrodes may sometimes be isolated from the rest of the system by a fritted compartment. One example is the oxidative polymerization of THF that can occur at the CE when studying a reductive process in THF at the WE.

Steps toward Data Acquisition

Recording a Background Scan. Now that the components are ready, the cell can be assembled, and voltammograms can be recorded. When no electroactive species have been added to the electrolyte solution, voltammograms should exhibit the profile of the blue trace in Figure 2. A small current is still flowing between the electrodes, but no distinct features are observed. This background current is sometimes called capacitive current, double-layer current, or non-Faradaic current. The intensity of the current varies linearly with the scan rate used (see below). The background scan is essential to test if all the components of the cells are in good condition before adding the analyte as well as to quantify the capacitive current.

Importance of an Inert Atmosphere. Once the electrolyte solution is prepared, and the cell is assembled, one may begin experiments. Consider a 0.25 M [NBu4][PF6] solution in acetonitrile prepared in a fume hood. From Box 3, the potential window for this acetonitrile solution is wide. If the potential is scanned within this window, no redox events should be observed (i.e., the current response should be relatively flat). However, if this experiment is performed with the solution prepared as described above, one would instead see an unexpected peak as if this experiment is performed with the solution prepared in a fume hood. As such, the CE should be chosen to be as inert as possible. Counter electrodes can generate byproducts depending on the experiment, therefore, these electrodes may sometimes be isolated from the rest of the system by a fritted compartment. One example is the oxidative polymerization of THF that can occur at the CE when studying a reductive process in THF at the WE.

Measuring the Open Circuit Potential. When the cell is assembled, and the analyte has been added, a potential develops at the electrodes. For example, when Fe3+ is added to a cell, the potential of the electrode equilibrates with the solution (so that no current flows). The potential observed when no current is flowing is called the open circuit potential (OCP). The OCP can give information about the redox state of species in the bulk solution as well as the concentration of different species when the solution contains a mixture (Experimental Module 1: OCP Measurements of Ferrocene/Ferrocenium Solutions: Evolution with Solution Composition).

Minimizing Ohmic Drop. The electrochemical cell considered so far was assumed to be ideal. However, electrolytic solutions have an intrinsic resistance $R_{\text{sol}}$ in the electrochemical cell (Figure 5). While some potentiostats can compensate for not perturbing the solution in the cell. Another option is to feed electrode cables into an inert atmosphere glovebox and run electrochemical experiments using previously deoxygenated solvents.

Box 7. How to sparge a solution with minimal concentration changes

Using a pre-bubbler to saturate the inert gas with solvent vapors helps reduce the loss of solvent in the electrochemical cell due to evaporation during the sparge process.
analyte in solution due to $R_o$. This phenomenon is called ohmic drop. A telltale sign of ohmic drop in CV is increased peak-to-peak separation in the voltammogram for a redox event that is known to be electrochemically reversible (Experimental Module 3: Cyclic Voltammetry of Ferrocene: Influence of the Concentration of Electrolyte on the Peak-to-Peak Separation as an Indication of the Solution Resistance). The potential difference due to ohmic drop, per Ohm’s Law, equals the current passed ($i$) times the resistance, $R_o$. For large values of $R_o$ or $i$, the resulting ohmic drop may be unacceptable large and affect the accuracy of the data.

Ohmic drop can be mitigated by three methods: (1) diminish $i$, by reducing the size of the working electrode or restricting the experiment to slow scan rates; (2) decrease $R_{sol}$ and therefore decrease $R_o$, by increasing the conductivity of the solution with higher electrolyte concentrations; and (3) decrease $R_e$ directly (and increase $R_w$) by diminishing the distance separating the reference and working electrodes (see Figure 5).

For most experiments, these approaches will reduce ohmic drop enough that its overall effect will be negligible. There are times, however, when experimental conditions restrict the employment of these methods. To account for this, many potentiostats have software to experimentally determine $R_w$ and compensate for it in real time (Experimental Module 2: Experimental Determination of the Uncompensated Resistance).

**Recoding the Cyclic Voltammogram**

Once the cell has been assembled and sparged of oxygen and precautions have been taken to minimize ohmic drop, experiments can be run. The electrodes are connected to the potentiostat, and the experimental parameters are selected through the potentiostat software. While different software will require different parameters, fundamental ones are the potential window that will be scanned (defined by the initial, switching, and final potentials), the scan rate, and the number of segments/scans. Some potentiostats allow one to start the scan at the OCP, where the solution is at equilibrium, and no net current is passed. Advanced parameters include an automatic or manual compensation of $R_w$, and are generally specific to each manufacturer’s instrument.

### BEYOND THE SIMPLE ONE-ELECTRON REVERSIBLE VOLTAMMOGRAM: IRREVERSIBILITY, COUPLED CHEMICAL REACTIONS, AND MULTIELECTRON PROCESSES

Several processes can give rise to voltammograms more complicated than the data seen for simple, reversible, one-electron transfer reactions. In the simplest cases, the voltammogram is modified by slow electron transfer or multielectron transfers, and cyclic voltammetry can provide useful information for these pure electron transfer reactions. Further, when electron transfers are coupled to chemical reactions, cyclic voltammetry can provide kinetic and mechanistic information. In many cases, these coupled reactions can be related to a specific type of mechanism that has been previously described; as such, careful examination of a voltammogram can assist in diagnosing which homogeneous reaction mechanism is occurring as well as the kinetics of these reactions.

The notation used to describe various coupled reaction scenarios deserves a brief explanation: $E$ indicates an electron transfer step, $C$ indicates a homogeneous chemical reaction (a chemical step). In addition, the subscript $r$ indicates reversibility, and subscript $i$ indicates irreversibility. Each reaction is described for the reduction of the analyte Ox to Red. The same concepts can be readily extended to oxidative reactions.

### Electrochemical Irreversibility

When electron transfer at the electrode surface is slow compared to mass transport, the process is termed “electrochemically irreversible.” As noted above in the Cyclic Voltammetry Profile section, slow electrode kinetics necessitate significantly more negative applied potentials for appreciable current to flow. As a result, peak-to-peak separation is larger than the 57 mV anticipated for an electrochemically reversible one-electron redox couple (Experimental Module 5: Cyclic Voltammetry of Oxygen: Evaluating Electrochemical Reversibility).

**Two Sequential Electron Transfer Reversible Process $E_i E_f$**

$$\text{Ox} + e^- \rightleftharpoons \text{Red}$$

$$\text{Red} + e^- \rightleftharpoons \text{Q}$$

Many complexes can undergo multiple reversible redox processes. For simplicity, we will only consider two electrochemical steps. The voltammogram appearance is dependent upon the difference in formal potential of the two electrode steps. If the second electrochemical step is thermodynamically more favorable than the first, the voltammogram appears identical to a Nernstian two-electron transfer, and the peak-to-peak separation ($\Delta E_p$) will be 28.5 mV instead of the 57 mV predicted for a one-electron process. As the second electron transfer becomes less thermodynamically favorable, $\Delta E_p$ grows until it reaches a maximum value of just over 140 mV; at that point, the wave separates into two resolvable waves, each with $\Delta E_p = 57$ mV (Figure 6). See reference 28 for an experimental example of a two-electron wave in the voltammogram of an inorganic complex.

**EC Coupled Reaction $E_i C_i$; Reversible Electron Transfer Followed by an Irreversible Homogeneous Chemical Reaction**

The simple case of a reduction followed by an irreversible chemical reaction is the $E_i C_i$ mechanism

$$\text{Ox} + e^- \rightleftharpoons \text{Red}$$

$$\text{Red} \rightleftharpoons \text{Z}$$

A slow homogeneous chemical reaction (compared to the electron transfer) results in a voltammogram that appears reversible, because the amount of Red that reacts to form Z is negligible (Figure 6). As the rate constant ($k$) of the homogeneous reaction increases, the amount of Red consumed in the chemical reaction increases, thereby moving the system from equilibrium and leading to a non-Nernstian response. The ratio of the anodic to cathodic peak currents decreases because the reduced species Red is consumed by the subsequent chemical reaction, resulting in fewer species to oxidize on the anodic scan. Experimentally, the response can be modified by varying the scan rate. As the scan rate is increased, the time scale of the experiment competes with the time scale of the chemical step, and more Red is left for reoxidation. For sufficiently fast scan rates, the electrochemical feature will regain reversibility as oxidation outcompetes the chemical reaction. Equations have been derived to extract kinetic parameters from these voltammograms.

For an experimental example of extracting kinetic information from voltammograms of a $E_i C_i$ mechanism in an inorganic complex reacting with an acid source, see reference 23. For discussion...
on using this methodology to estimate rates of intramolecular decomposition upon reduction/oxidation, see reference 29.

### CE Coupled Reaction $C,E_r$: Reversible Chemical Step Followed by a Reversible Electron Transfer

Another simple case is the $C,E_r$ mechanism

$$Z = Ox$$

$$Ox + e^- = Red$$

In this example, the amount of Ox available for the reduction is dictated by the equilibrium constant of the first step. The greater the equilibrium constant, the more reversible the voltammogram (Figure 6). In the extreme case where the equilibrium constant is so large as to be considered an irreversible reaction, the voltammogram becomes completely reversible. The equilibrium constant can be extracted from voltammograms in certain cases.$^{29,30}$

### CONCLUSION

Quantitative electrochemical analysis is a powerful tool for exploring the electron transfer reactions underpinning renewable energy technologies and fundamental mechanistic inorganic chemistry. Increasingly, emerging investigators are interested in utilizing electrochemistry to advance their research. Through this tutorial, we have aimed to provide these researchers with an approachable and comprehensive guide to utilizing cyclic voltammetry in research and education endeavors. By integrating the theoretical underpinnings of electrochemical analysis with practical experimental details, highlighting experimental pitfalls, and providing introductory training modules, this text reflects current best practices in learning and utilizing cyclic voltammetry.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.7b00361.

All modules mentioned in the text (PDF, DOXC)

### AUTHOR INFORMATION

#### Corresponding Author

*E-mail: dempseyj@email.unc.edu.

**ORCID**

Noémi Elgrishi: 0000-0001-9776-5031

Jillian L. Dempsey: 0000-0002-9459-4166

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

We thank current and past group members who tested the training modules: Will Howland, Tao Huang, Carolyn Hartley, Banu Kandemir, Daniel Kurtz, Katherine Lee, Emily Anne Sharpe, and Hannah Starr. N.E. thanks Brian Lindley for helpful discussions. J.L.D. thanks Aaron Wilson and Xile Hu as well as all of the Cyclic Voltammetry International School (CVIS) instructors: Cedric Tard, Cyrille Costentin, Marc Robert, and Jean-Michel Savéant, for insightful discussions. We also thank Pine Research Instrumentation for assistance with the method to determine cell resistance. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award DE-SC0015303 and the University of North Carolina at Chapel Hill.

### REFERENCES


**Figure 6.** Examples of voltammograms modeled using DigiElch simulation software for three common mechanisms. The currents are normalized, $E,C_r$ mechanism: increasing the scan rate (from $v = 0.1$ (red) to 1 (green) to $10$ V s$^{-1}$ (blue)) restores reversibility (rate constant for the $C_r$ step $k = 5$ s$^{-1}$). $C,E_r$ mechanism: the faster the forward rate constant of the $C_r$ step, the more reversible the voltammogram ($K_{eq} = 0.1$, $k_f = 1$ (blue), 10 (dark green), 100 (lime green), 1000 s$^{-2}$ (red)). $E,E_r$ mechanism: as the separations between the two reduction potentials ($\Delta E_{1/2}$) decreases, the peaks merge to become a single two-electron peak. $\Delta E_{1/2} = -0.05$ (dark blue), 0 (light blue), 0.05 (dark green), 0.1 (lime green), 0.15 (orange), and 0.2 V (red).


(16) The effective concentration of a species in nonideal conditions is called the activity. It corresponds to the effective chemical potential of a solution, rather than an ideal one.


