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A Practical Beginner's Guide to Cyclic Voltammetry

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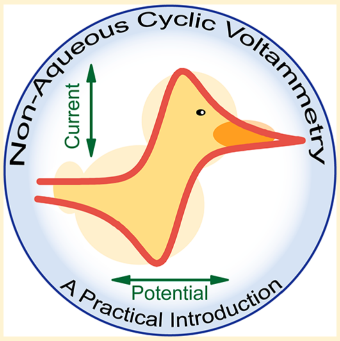
Supporting Information

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

Electron transfer 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,[1−5] as well as an increasing number of laboratories geared toward undergraduate students,[6,7] no concise and approachable guide to cyclic voltammetry for inorganic chemists is available. Here, we update, build on, and streamline seminal papers[8−11] 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 reduction and an electrochemical reduction, consider the example of the reduction of ferrocenium $[Fe(Cp)_2]^+$ (Cp = cyclopentadienyl), abbreviated as Fc^+, to ferrocene $[Fe(Cp)_2]$, abbreviated as Fc:

- Through a chemical reducing agent: $Fc^+ + [Co(Cp^*)_2] \rightleftharpoons Fc + [Co(Cp^*)_2]^+$
- At an electrode: $Fc^+ + e^- \rightleftharpoons Fc$

Why does $[Co(Cp^*)_2]$ (Cp* = pentamethylcyclopentadienyl) reduce Fc^+? In the simplest explanation, an electron transfers from $[Co(Cp^*)_2]$ to Fc^+ because the lowest unoccupied molecular orbital (LUMO) of Fc^+ 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, Fc^+ is reduced via heterogeneous electron transfer from an electrode; but what is the driving force for this process? An electrode 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 Fc^+, an electron from the electrode is transferred to Fc^+ (Figure 1B). The driving force for this electrochemical reaction is again the energy difference between that of the electrode and the LUMO of Fc^+.

Changing the driving force of a chemical reduction requires changing the identity of the molecule used as the reductant.[12] 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.

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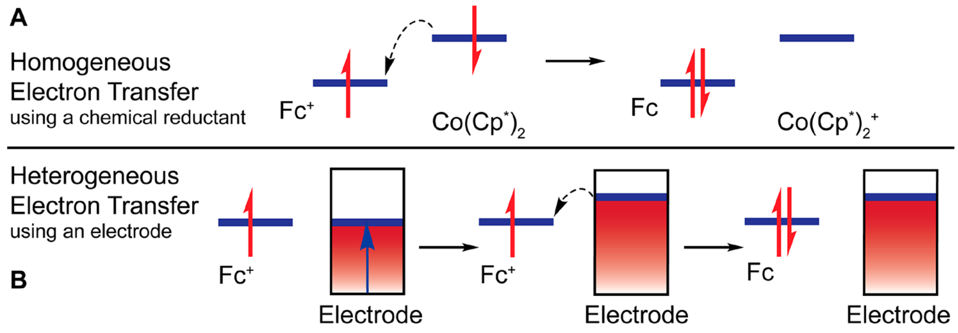


Figure 1. (A) Homogeneous and (B) heterogeneous reduction of Fc^+ to Fc. The energy of the electrons in the electrode is controlled by the potentiostat; their energy can be increased until electron transfer becomes favorable.[4]

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.

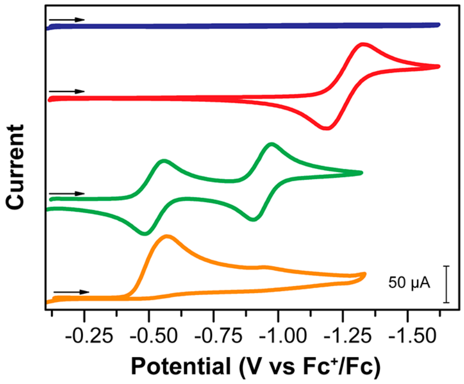


Figure 2. Voltammograms of a bare electrode under N_2 (blue trace); a bare electrode under air (red trace); $[CoCp(dppe)(CH_3CN)](PF_6)_2$ (dppe = diphenylphosphinoethane) under N_2 (green trace); $[CoCp(dppe)(CH_3CN)](PF_6)_2$ under air (orange trace). Voltammograms recorded in 0.25 M $[NBu_4][PF_6]$ CH_3CN solution at $\upsilon = 100$ mV/s with a 3 mm glassy carbon working electrode, a 3 mm glassy carbon counter electrode, and a silver wire pseudoreference electrode.

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).

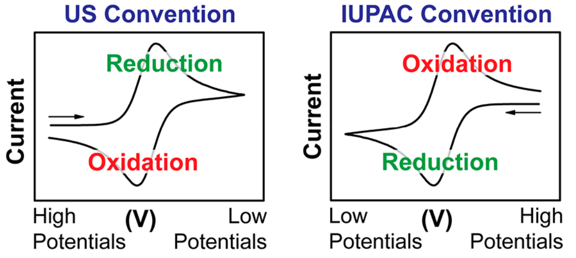
■ UNDERSTANDING THE SIMPLE VOLTAMMOGRAM

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: "$\upsilon = 100$ mV/s". This value is called the scan rate (υ). It indicates that during the experiment the potential was varied linearly at the speed (scan rate) of 100 mV per second.

Box 1. IUPAC or US convention?

Two conventions are commonly used to report CV data: the US convention, used herein, and the IUPAC convention. Visually, data reported in the two conventions will appear to be rotated by 180°.



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.[13−15]

Understanding the "Duck" Shape: Introduction to the Nernst Equation

Why are there peaks in a cyclic voltammogram? Consider the equilibrium between ferrocenium (Fc^+) and ferrocene (Fc). This equilibrium is described by the Nernst equation (eq 1). The Nernst equation relates the potential of an electrochemical

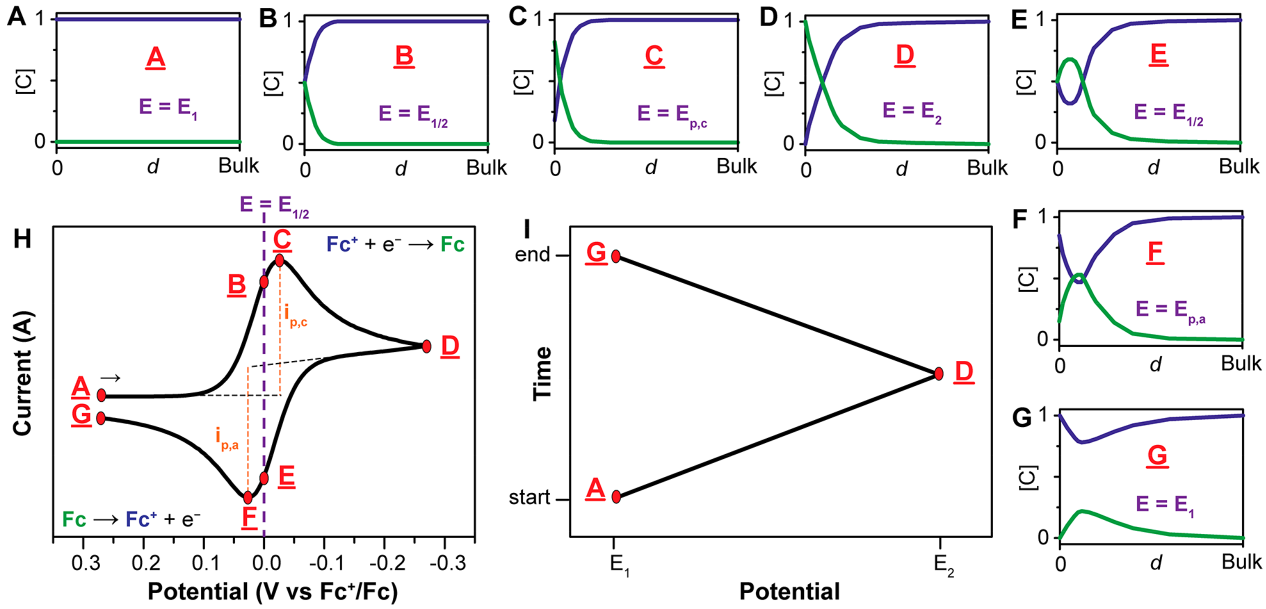


Figure 3. (A−G): Concentration profiles (mM) for Fc$^+$ (blue) and Fc (green) as a function of the distance from the electrode (*d*, from the electrode surface to the bulk solution, e.g. 0.5 mm) at various points during the voltammogram. Adapted from Reference 4. Copyright © 2011, Imperial College Press. (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).

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, *n* is the number of electrons, and *T* is the temperature

$$E = E^0 + \frac{RT}{nF}\ln\frac{(\mathrm{Ox})}{(\mathrm{Red})} = E^0 + 2.3026\frac{RT}{nF}\log_{10}\frac{(\mathrm{Ox})}{(\mathrm{Red})} \tag{1}$$

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 $E^{0\prime}$, and *n* is set equal to 1:

$$E = E^{0\prime} + \frac{RT}{F}\ln\frac{[\mathrm{Fc}^+]}{[\mathrm{Fc}]} = E^{0\prime} + 2.3026\frac{RT}{F}\log_{10}\frac{[\mathrm{Fc}^+]}{[\mathrm{Fc}]} \tag{2}$$

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 $E = E^{o\prime} \approx E_{1/2}$ 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 ($i_{p,c}$) 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** → **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 $E^{0\prime}$ 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 (ΔE_p), 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.[3] 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 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 ΔE_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.[2,3] 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 υ (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.

$$i_p = 0.446nFAC^0\left(\frac{nF\upsilon D_o}{RT}\right)^{1/2} \tag{3}$$

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."

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 $\upsilon^{1/2}$ should be linear. For an electrode-adsorbed species, the current response is described by:[2]

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

where Γ^* 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 υ.

For an analyte that is thought to be a freely diffusing species, deviations from linearity in plots of i_p vs. $\upsilon^{1/2}$ 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.

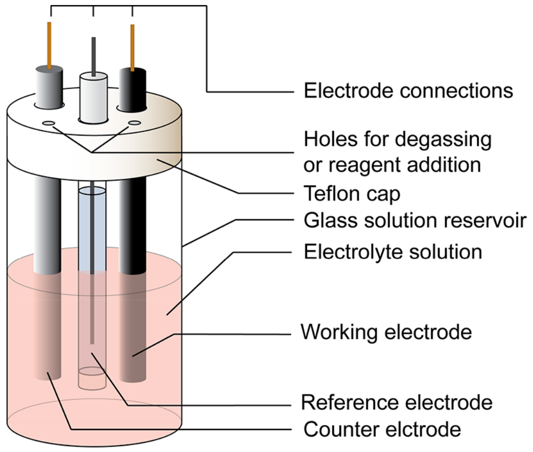


Figure 4. Schematic representation of an electrochemical cell for CV experiments.

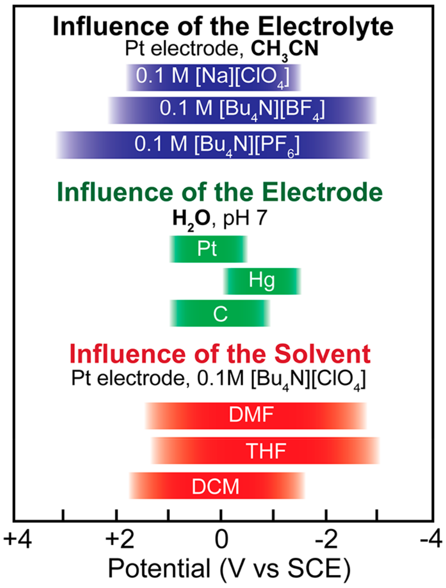
Solvent. A good solvent has these characteristics:

- It is liquid at experimental temperatures.
- 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]



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.[2] 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 ($^+NBu_4$) 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 $[B(C_6F_5)_4]^-$, $[B(C_6H_5)_4]^-$, $[PF_6]^-$, $[BF_4]^-$, and $[ClO_4]^-$. 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 $[NBu_4][PF_6]$ 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 $[NBu_4][PF_6]$ in CH_3CN), 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.

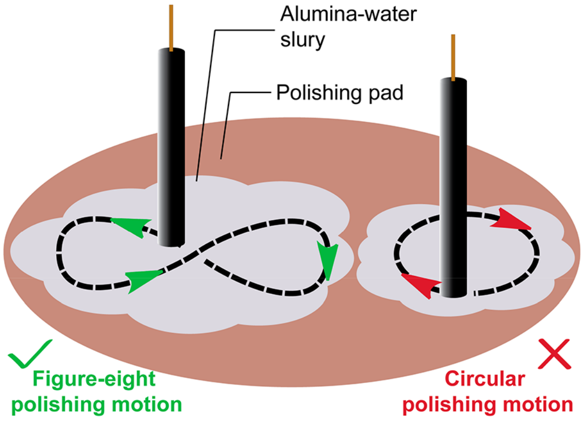
Working Electrode (WE). The working electrode carries out the electrochemical event of interest. A potentiostat is used to control the applied potential of the working electrode as a function of the reference electrode potential. The most important aspect of the working electrode is that it is composed 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.[17] It is often also 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

Box 4. How to polish glassy carbon electrodes?

A simple way to polish electrodes is with figure-eight motions on a cloth polishing pad in a water-alumina slurry. When using circular motions, the polishing is often uneven, and the surface can become slanted.



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 $E^{0\prime}$. 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.[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.

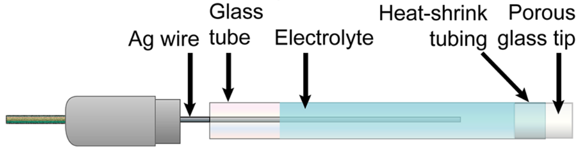
Box 5. What does it mean when data are reported as referenced to “Ag^+/Ag electrode”?

As we have seen, this can encompass many different electrodes, as the use of different reference electrode compositions (e.g., salt identity, concentration) leads to the reported redox potentials to be effectively on different scales.

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_2O/Ag couple. This method eliminates the possibility of silver salts leaks but requires the presence of an internal standard.

Box 6. How to assemble a simple RE

One easy way to assemble a silver-based reference electrode is to feed a silver wire in a small glass tube fitted with a frit and fill the tube with electrolyte solution.



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

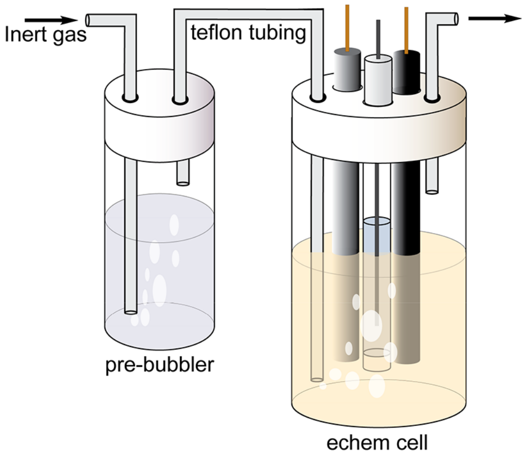
Recording a Background Scan. Now that the components are ready, the cell can be assembled, and voltammograms can be recorded. When no electroactive species have been added to the electrolyte solution, voltammograms should exhibit the profile of the blue trace in Figure 2. A small current is still flowing 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 $[NBu_4][PF_6]$ 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 the potential is scanned cathodically (Figure 2, red trace). In the reverse scan, another peak emerges that seems related to the first peak. Why are these peaks observed in the absence of the analyte? The answer lies in the fact that the solution was prepared in open atmosphere. While nitrogen is electrochemically inert within this window, oxygen is not. Oxygen undergoes a reversible one-electron reduction to form the oxygen radical anion (superoxide, $O_2^{\bullet -}$). The peaks in the red trace of Figure 2 is attributed to the reduction of oxygen and then the subsequent reoxidation. Note that in solvents besides acetonitrile, the reduction of oxygen may not be cleanly reversible.

In electrochemical experiments, the presence of oxygen can also alter the electrochemical response of analytes. For example, under inert atmosphere, $[CoCp(dppe)(CH_3CN)][PF_6]_2$ undergoes two reversible, one-electron reductions (Figure 2, green trace).[23] However, if oxygen is introduced, reversibility is lost as the reduced anzalyte can transfer an electron to dissolved O_2, becoming oxidized through this chemical step (Figure 2, orange trace). To avoid interference from dissolved O_2, all electrolyte solutions should be sparged with an inert gas before measurements are taken (see Box 7). Once all the O_2 is removed from the cell, the Teflon tubing used for sparging is placed above the surface of the solution to continue flushing the headspace while 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.



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 Fc^+ 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_{sol} in the electrochemical cell (Figure 5). While some potentiostats can compensate for most of this solution resistance (R_c), there remains a portion of uncompensated resistance (R_u) between the WE and the RE (technically between the WE and the entire equipotential surface that traverses the tip of the RE, as explained in references 24 and 25). During electrochemical measurements, the potential that the instrument records may not be the potential experienced by the

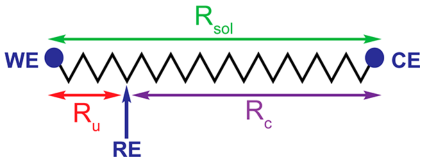


Figure 5. Representation of an electrochemical cell as a potentiostat. Adapted from ref 1. Copyright © 2006, with permission from Elsevier. Increasing the conductivity of the solution diminishes R_{sol} and, therefore, R_u. Diminishing the distance between WE and RE diminishes R_u. R_c is generally compensated by the potentiostat.

analyte in solution due to R_u. 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_u. For large values of R_u or i, the resulting ohmic drop may be unacceptably 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_u, by increasing the conductivity of the solution with higher electrolyte concentrations; and (3) decrease R_u directly (and increase R_c) by diminishing the distance separating the reference and working electrodes (see Figure 5).[3,25]

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_u and compensate for it in real time (Experimental Module 2: Experimental Determination of the Uncompensated Resistance).

Recording 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_u 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.[2,3,26,27] 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_rE_r

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

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

Many complexes can undergo multiple reversible redox processes.[2] For simplicity, we will only consider two electrochemical steps. The voltammogram appearance is dependent upon the difference in formal potential of the two electrochemical steps. If the second electrochemical step is thermodynamically more favorable than the first,[2] the voltammogram appears identical to a Nernstian two-electron transfer, and the peak-to-peak separation (ΔE_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, ΔE_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 ΔE_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_rC_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_rC_i mechanism

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

$$\mathrm{Red} \xrightarrow{k} \mathrm{Z}$$

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).[2,4] 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.[2,3] For an experimental example of extracting kinetic information from voltammograms of a E_rC_i mechanism in an inorganic complex reacting with an acid source, see reference 23. For discussion

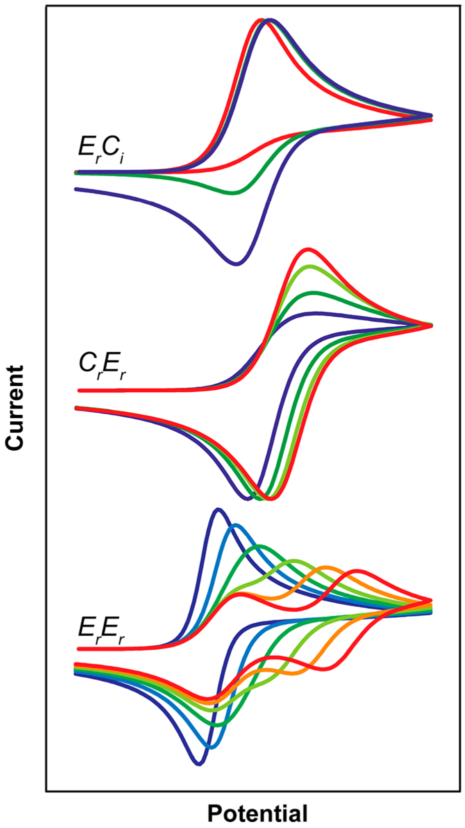


Figure 6. Examples of voltammograms modeled using DigiElch simulation software for three common mechanisms. The currents are normalized. E_rC_i mechanism: increasing the scan rate (from $\upsilon = 0.1$ (red) to 1 (green) to 10 V s^{-1} (blue)) restores reversibility (rate constant for the C_i step $k = 5\ s^{-1}$). C_rE_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^{-1} (red)). E_rE_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).

on using this methodology to estimate rates of intramolecular decomposition upon reduction/oxidation, see reference 29.

CE Coupled Reaction C_rE_r: Reversible Chemical Step Followed by a Reversible Electron Transfer

Another simple case is the C_rE_r mechanism

$$Z \rightleftharpoons Ox$$

$$Ox + e^- \rightleftharpoons Red$$

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.[2,3,30]

■ 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, DOCX)

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Notes

The authors declare no competing financial interest.

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Cyclic Voltammetry

Denis Andrienko

January 22, 2008

Literature:

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Chapter 1

Cyclic Voltammetry

1.1 Background

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. it offers a rapid location of *redox potentials* of the electroactive species.

A few concepts has to be introduced before talking about this method.

1.1.1 Electronegativity

Electronegativity is the affinity for electrons. The atoms of the various elements differ in their affinity for electrons. The term was first proposed by Linus Pauling in 1932 as a development of valence bond theory. The table for all elements can be looked up on Wikipedia: `http://en.wikipedia.org/wiki/Electronegativity`.

Some facts to remember:

- Fluorine (F) is the most electronegative element. $\chi_{\mathrm{F}} = 3.98$.
- The electronegativity of oxygen (O) $\chi_{\mathrm{O}} = 3.44$ is exploited by life, via shuttling of electrons between carbon (C, $\chi_{\mathrm{F}} = 2.55$) and oxygen (O): Moving electrons against the gradient (O to C) - as occurs in photosynthesis - requires energy (and stores it). Moving electrons down the gradient (C to O) - as occurs in cellular respiration - releases energy.
- The relative electronegativity of two interacting atoms plays a major part in determining what kind of chemical bond forms between them.

Examples:

- Sodium ($\chi_{\mathrm{Na}} = 0.93$) and Chlorine ($\chi_{\mathrm{Cl}} = 3.16$) = Ionic Bond: There is a large difference in electronegativity, so the chlorine atom takes an electron from the sodium atom converting the atoms into ions (Na^+) and (Cl^-). These are held together by their opposite electrical charge forming ionic bonds. Each sodium ion is held by 6 chloride ions while each chloride ion is, in turn, held by 6 sodium ions. Result: a crystal lattice (not molecules) of common table salt (NaCl).
- Carbon (C) and Oxygen (O) = Covalent Bond. There is only a small difference in electronegativity, so the two atoms share the electrons. a covalent bond (depicted as C:H or C-H) is formed, where atoms are held together by the mutual affinity for their shared electrons. An array of atoms held together by covalent bonds forms a true molecule.
- Hydrogen (H) and Oxygen (O) = Polar Covalent Bond. Moderate difference in electronegativity, oxygen atom pulls the electron of the hydrogen atom closer to itself. Result: a polar covalent bond. Oxygen does this with 2 hydrogen atoms to form a molecule of water.

Molecules, like water, with polar covalent bonds are themselves polar; that is, have partial electrical charges across the molecule; may be attracted to each other (as occurs with water molecules); are good solvents for polar and/or hydrophilic compounds. May form hydrogen bonds.

1.2 Electrode Reactions

A typical electrode reaction involves the transfer of charge between an electrode and a species in solution. The electrode reaction usually referred to as electrolysis, typically involves a series of steps:

1. Reactant (O) moves to the interface: this is termed mass transport
2. Electron transfer can then occur via quantum mechanical tunnelling between the electrode and reactant close to the electrode (typical tunnelling distances are less than 2 nm)
3. The product (R) moves away from the electrode to allow fresh reactant to the surface

The 'simplest' example of an electrode reaction is a single electron transfer reaction, e.g. $Fe^{3+} + e^{-} = Fe^{2+}$. Several examples are shown in Fig. 1.1

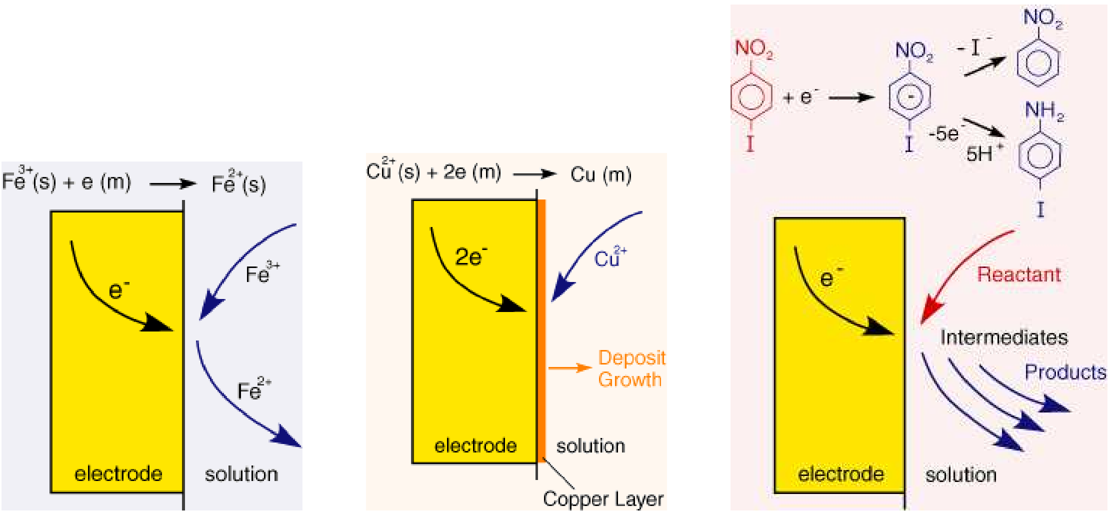


Figure 1.1: Simple electrode reactions: (left) A single electron transfer reaction. Here the reactant Fe^{3+} moves to the interface where it undergoes a one electron reduction to form Fe^{2+}. The electron is supplied via the electrode which is part of a more elaborate electrical circuit. For every Fe^{3+} reduced a single electron must flow. By keeping track of the number of electrons flowing (ie the current) it is possible to say exactly how many Fe^{3+} molecules have been reduced. (middle) Copper deposition at a Cu electrode. In this case the electrode reaction results in the fomation of a thin film on the orginal surface. It is possible to build up multiple layers of thin metal films simply by passing current through appropriate reactant solutions. (right) Electron transfer followed by chemical reaction. In this case an organic molecule is reduced at the electrode forming the radical anion. This species however is unstable and undergoes further electrode and chemical reactions.

1.3 Electron Transfer and Energy levels

The key to driving an electrode reaction is the application of a voltage. If we consider the units of volts

$$V = \text{Joule}/\text{Coulomb} \tag{1.1}$$

we can see that a volt is simply the energy required to move charge. Application of a voltage to an electrode therefore supplies electrical energy. Since electrons possess charge an applied voltage can alter the 'energy' of the electrons within a metal electrode. The behaviour of electrons in a metal can be partly understood by considering the Fermi-level. Metals are comprised of closely packed atoms which have strong overlap between one another. A piece of metal therefore does not possess individual well defined electron energy levels that would be found in a single atom of the same material. Instead a continuum of levels are created with the available electrons filling the states from the bottom upwards. The Fermi-level corresponds to the energy at which the 'top' electrons sit.

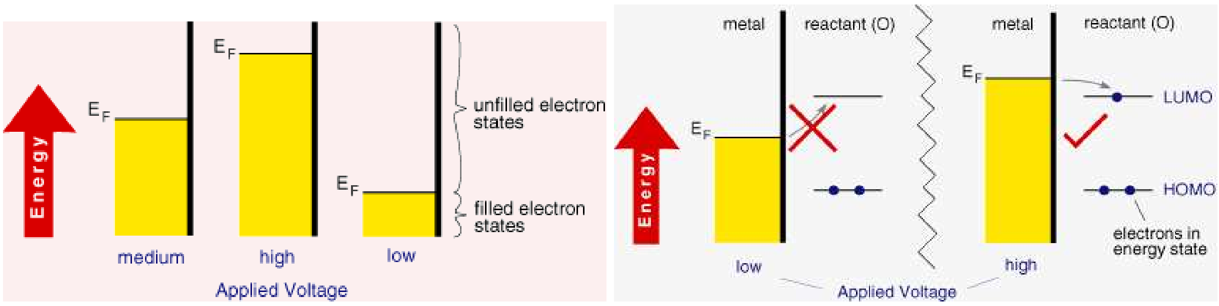


Figure 1.2: Representation of the Fermi-Level in a metal at three different applied voltages (left). Schematic representation of the reduction of a species (O) in solution (right).

This level is not fixed and can be moved by supplying electrical energy. Electrochemists are therefore able to alter the energy of the Fermi-level by applying a voltage to an electrode.

Figure 1.2 shows the Fermi-level within a metal along with the orbital energies (HOMO and LUMO) of a molecule (O) in solution. On the left hand side the Fermi-level has a lower value than the LUMO of (O). It is therefore thermodynamically unfavourable for an electron to jump from the electrode to the molecule. However on the right hand side, the Fermi-level is above the LUMO of (O), now it is thermodynamically favourable for the electron transfer to occur, ie the reduction of O.

Whether the process occurs depends upon the rate (kinetics) of the electron transfer reaction and the next document describes a model which explains this behavior.

1.4 Kinetics of Electron Transfer

In this section we will develop a quantitative model for the influence of the electrode voltage on the rate of electron transfer. For simplicity we will consider a single electron transfer reaction between two species (O) and (R)

$$O + e^- \xrightarrow{k_{\text{red}}} R \tag{1.2}$$

$$R \xrightarrow{k_{\text{ox}}} O + e^- \tag{1.3}$$

The current flowing in either the reductive or oxidative steps can be predicted using the following expressions

$$i_O = FAk_{\text{ox}}c_R \tag{1.4}$$

$$i_R = -FAk_{\text{red}}c_O \tag{1.5}$$

For the reduction reaction the current i_R is related to the electrode area A, the surface concentration of the reactant c_O, the rate constant for the electron transfer k_{red} and Faraday's constant F. A similar expression is valid for the oxidation, now the current is labelled i_O, with the surface concentration that of the species R. Similarly the rate constant for electron transfer corresponds to that of the oxidation process. Note that by definition the reductive current is negative and the oxidative positive, the difference in sign simply tells us that current flows in opposite directions across the interface depending upon whether we are studying an oxidation or reduction. To establish how the rate constants k_{ox} and k_{red} are influenced by the applied voltage we will use transition state theory.

In this theory the reaction is considered to proceed via an energy barrier, as shown in Fig 1.3. The summit of this barrier is referred to as the transition state. Using this picture the corresponding reaction rates are given by

$$k_{\text{red,ox}} = Z \exp\left(\frac{-\Delta G_{\text{red,ox}}}{k_B T}\right) \tag{1.6}$$

If we plot a series of the free energy profiles as a function of voltage the free energy of R will be invariant with voltage, whereas the right handside (O + e) shows a strong dependence.

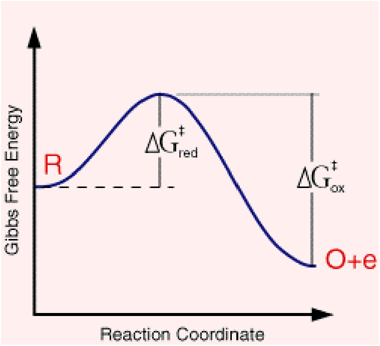


Figure 1.3: Transition occurs via a barrier ΔG.

This can be explained in terms of the Fermi level diagrams noted earlier: as the voltage is altered the Fermi level is raised (or lowered) changing the energy state of the electrons.

However it is not just the thermodynamic aspects of the reaction that can be influenced by this voltage change as the overall barrier height (ie activation energy) can also be seen to alter as a function of the applied voltage. We might therefore predict that the rate constants for the forward and reverse reactions will be altered by the applied voltage. In order to formulate a model we will assume that the effect of voltage on the free energy change will follow a linear relationship (this is undoubtedly an over simplification). Using this linear relationship the activation free energies for reduction and oxidation will vary as a function of the applied voltage as follows (Buttler-Volmer model)

$$\Delta G_{\text{red}} = \Delta G_{\text{red}}(V=0) + \alpha F V \tag{1.7}$$

$$\Delta G_{\text{ox}} = \Delta G_{\text{ox}}(V=0) - (1-\alpha) F V \tag{1.8}$$

The parameter α is called the transfer coefficient and typically is found to have a value of 0.5. Physically it provides an insight into the way the transition state is influenced by the voltage. A value of one half means that the transition state behaves mid way between the reactants and products response to applied voltage. The free energy on the right hand side of both of the above equations can be considered as the chemical component of the activation free energy change, ie it is only dependent upon the chemical species and not the applied voltage. We can now substitute the activation free energy terms above into the expressions for the oxidation and reduction rate constants, which gives

$$k_{\text{red}} = Z \exp \frac{-\Delta G_{\text{red}}^{V=0}}{k_B T} \exp \frac{-\alpha F V}{k_B T} \tag{1.9}$$

$$k_{\text{ox}} = Z \exp \frac{-\Delta G_{\text{ox}}^{V=0}}{k_B T} \exp \frac{(1-\alpha) F V}{k_B T} \tag{1.10}$$

These results show us the that rate constants for the electron transfer steps are proportional to the exponential of the applied voltage. So the rate of electrolysis can be changed simply by varying the applied voltage. This result provides the fundamental basis of the experimental technique called voltammetry which we will look at more closely later.

In conclusion we have seen that the rate of electron transfer can be influenced by the applied voltage and it is found experimentally that this behaviour can be quantified well using the simple model presented above. However the kinetics of the electron transfer is not the only process which can control the electrolysis reaction. In many circumstances it is the rate of transport to the electrode which controls the overall reaction.

1.5 Mass transport

In the electrode kinetics section we have seen that the rate of reaction can be influenced by the cell potential difference. However, the rate of transport to the surface can also effect or even dominate the overall reaction rate and in this section we look at the different forms of mass transport that can influence electrolysis reactions.

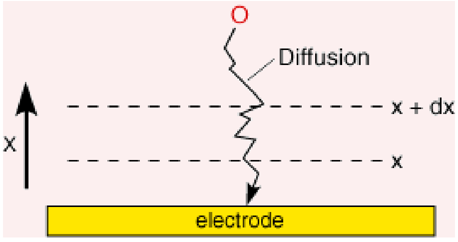


Figure 1.4: Diffusion of the reactants to the electrode

We have already seen that a typical electrolysis reaction involves the transfer of charge between an electrode and a species in solution. This whole process due to the interfacial nature of the electron transfer reactions typically involves a series of steps.

In the section on electrode kinetics we saw how the electrode voltage can effect the rate of the electron transfer. This is an exponential relationship, so we would predict from the electron transfer model that as the voltage is increased the reaction rate and therefore the current will increase exponentially. This would mean that it is possible to pass unlimited quantities of current. Of course in reality this does not arise and this can be rationalized by considering the expression for the current that we encountered in the electrode kinetics section

Clearly for a fixed electrode area (A) the reaction can be controlled by two factors. First the rate constant k_{red} and second the surface concentration of the reactant (C_O^{surf}). If the rate constant is large, such that any reactant close to the interface is immediately converted into products then the current will be controlled by the amount of fresh reactant reaching the interface from the bulk solution above. Thus movement of reactant in and out of the interface is important in predicting the current flowing. In this section we look at the various ways in which material can move within solution - so called mass transport.

There are three forms of mass transport which can influence an electrolysis reaction

- Diffusion
- Convection
- Migration

In order to predict the current flowing at any particular time in an electrolysis measurement we will need to have a quantitative model for each of these processes to complement the model for the electron transfer step(s).

Diffusion occurs in all solutions and arises from local uneven concentrations of reagents. Entropic forces act to smooth out these uneven distributions of concentration and are therefore the main driving force for this process. One example of this can be seen in the animation below. Two materials are held separately in a single container separated by a barrier. When the barrier is removed the two reagents can mix and this processes on the microscopic scale is essentially random. For a large enough sample statistics can be used to predict how far material will move in a certain time - and this is often referred to as a random walk model. Diffusion is particularly significant in an electrolysis experiment since the conversion reaction only occurs at the electrode surface. Consequently there will be a lower reactant concentration at the electrode than in bulk solution. Similarly a higher concentration of product will exist near the electrode than further out into solution.

The rate of movement of material by diffusion can be predicted mathematically and Fick proposed two laws to quantify the processes. The first law

$$J_O = -D_O \frac{\partial c_O}{\partial x} \tag{1.11}$$

relates the diffusional flux J_O (ie the rate of movement of material by diffusion) to the concentration gradient and the diffusion coefficient D_O. The negative sign simply signifies that material moves down a concentration gradient i. e. from regions of high to low concentration. However, in many measurements we need to know how the concentration of material varies as a function of time and this can be predicted from the first law. The result is Fick's second law

$$\frac{\partial c_O}{\partial t} = -\frac{\partial J_O}{\partial x} \tag{1.12}$$

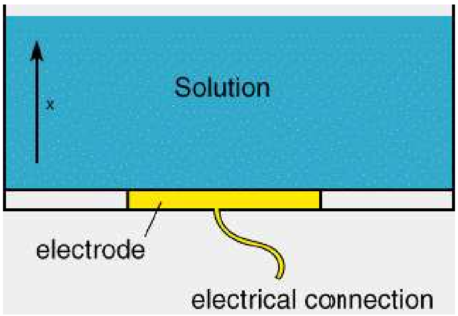


Figure 1.5: Schematic of the setup.

In this case we consider diffusion normal to an electrode surface (x direction). The rate of change of the concentration c_O as a function of time t can be seen to be related to the change in the concentration gradient. So the steeper the change in concentration the greater the rate of diffusion. In practice diffusion is often found to be the most significant transport process for many electrolysis reactions.

Fick's second law is an important relationship since it permits the prediction of the variation of concentration of different species as a function of time within the electrochemical cell. In order to solve these expressions analytical or computational models are usually employed.

1.6 Voltammetry

Voltammetry is one of the techniques which electrochemists employ to investigate electrolysis mechanisms. There are numerous forms of voltammetry

- Potential Step
- Linear sweep
- Cyclic Voltammetry

For each of these cases a voltage or series of voltages are applied to the electrode and the corresponding current that flows monitored. In this section we will examine potential step voltammetry, the other forms are described on separate pages

For the moment we will focus on voltammetry in stagnant solution. The figure below shows a schematic of an electrolysis cell. There is a working electrode which is hooked up to an external electrical circuit. For our purposes at the moment we will not worry about the remainder of the circuit, obviously there must be more than one electrode for current to flow. But as we shall see later it is only the so called working electrode that controls the flow of current flow in the electrochemical measurement. The essential elements needed for an electolysis measurement are as follows:

- The electrode: This is usually made of an inert metal (such as Gold or Platinum)
- The solvent: This usually has a high dielectric constant (eg water or acetonitrile) to enable the electrolyte to dissolve and help aid the passage of current.
- A background electrolyte: This is an electrochemically inert salt (eg NaCl or Tetra butylammonium perchlorate, TBAP) and is usually added in high concentration (0.1 M) to allow the current to pass.
- The reactant: Typically in low concentration 10^{-3} M.

1.6.1 Potential Step Voltammetry

In the potential step measurement the applied voltage is instantaneously jumped from one value V_1 to another V_2 The resulting current is then measured as a function time. If we consider the reaction

$$\mathrm{Fe}^{3+}(s) + e^- \xrightarrow{k_\mathrm{red}} \mathrm{Fe}^{2+}(s) \tag{1.13}$$

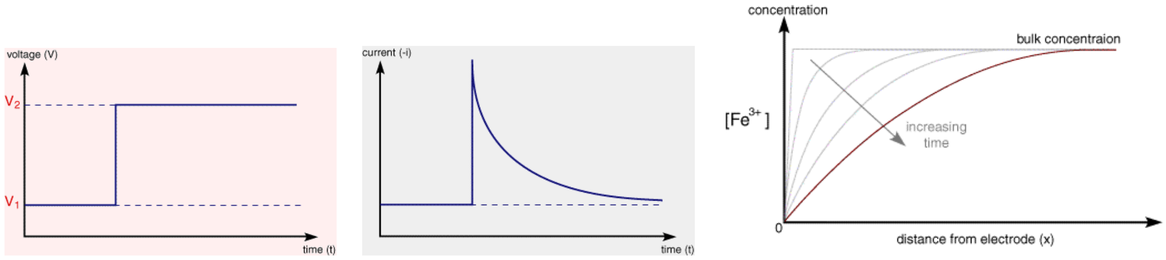


Figure 1.6: Potential step voltammetry: voltage vs time, current versus voltage, and concentration versus distance from the electrode plotted for several times.

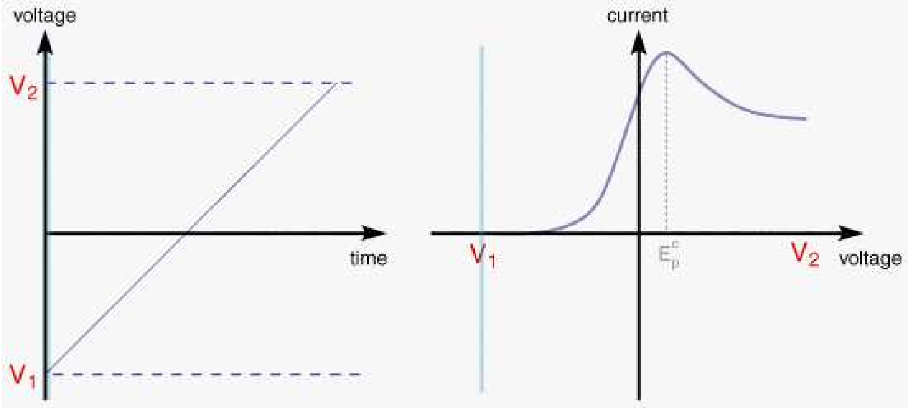


Figure 1.7: Linear increase of the potential vs time.

Usually the voltage range is set such that at V_1 the reduction of (Fe^{3+}) is thermodynamically unfavorable. The second value of voltage (V_2) is selected so that any Fe^{3+} close to the electrode surface is converted to product (Fe^{2+}). Under these conditions the current response is in Fig. 1.6.1

The current rises instantaneously after the change in voltage and then begins to drop as a function of time. This occurs since the instant before the voltage step the surface of the electrode is completely covered in the reactant and the solution has a constant composition below

Once the step occurs reactant (Fe^{3+} is converted to product Fe^{2+} and a large current begins to flow. However now for the reaction to continue we need a supply of fresh reactant to approach the electrode surface. This happens in stagnant solution via diffusion. As we noted in a previous section the rate of diffusion is controlled by the concentration gradient. So the supply of fresh Fe^{3+} to the surface (and therefore the current flowing) depends upon the diffusional flux. At short times the diffusional flux of Fe^{3+} is high, as the change in concentration between the bulk value and that at the surface occurs over a short distance

As the electrolysis continues material can diffuse further from the electrode and therefore the concentration gradient drops. As the concentration gradient drops (see concentration profiles below) so does the supply of fresh reactant to the surface and therefore the current also decreases.

Solving the mass transport equation in 1D case we obtain

$$i = nFAk_{\mathrm{red}}c_O^{\mathrm{bulk}}\sqrt{\frac{D}{\pi t}} \propto t^{-1/2} \tag{1.14}$$

Here the current is related to the bulk reactant concentration. Step voltammetry allows the estimation of the diffusion coefficients of the species to be obtained.

1.7 Linear Sweep Voltammetry

In linear sweep voltammetry (LSV) a fixed potential range is employed much like potential step measurements. However in LSV the voltage is scanned from a lower limit to an upper limit as shown below. The characteristics of the linear sweep voltammogram depend on a number of factors including:

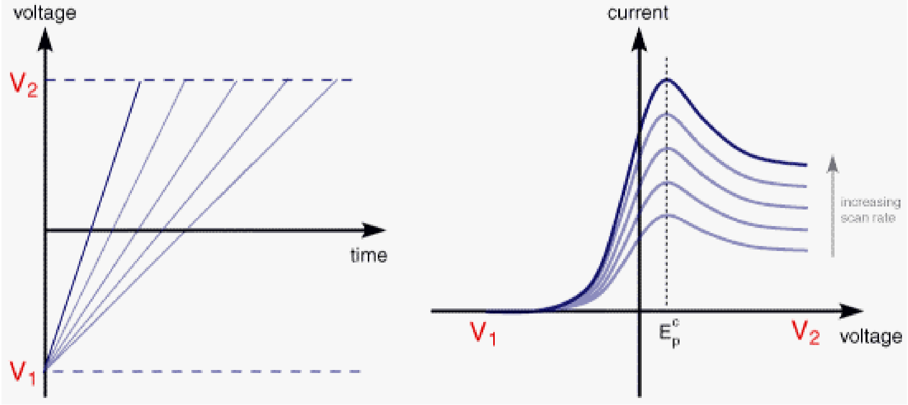


Figure 1.8: Linear increase of the potential vs time.

- The rate of the electron transfer reaction(s)
- The chemical reactivity of the electroactive species
- The voltage scan rate

In LSV measurements the current response is plotted as a function of voltage rather than time, unlike potential step measurements.

The scan begins from the left hand side of the current/voltage plot where no current flows. As the voltage is swept further to the right (to more reductive values) a current begins to flow and eventually reaches a peak before dropping. To rationalise this behaviour we need to consider the influence of voltage on the equilibrium established at the electrode surface. Here the rate of electron transfer is fast in comparsion to the voltage sweep rate. Therefore at the electrode surface an equilibrum is established identical to that predicted by thermodynamics. You may recall from equilibrium electrochemistry that the Nernst equation

The exact form of the voltammogram can be rationalised by considering the voltage and mass transport effects. As the voltage is initially swept from V_1 the equilibrium at the surface begins to alter and the current begins to flow. The current rises as the voltage is swept further from its initial value as the equilibrium position is shifted further to the right hand side, thus converting more reactant. The peak occurs, since at some point the diffusion layer has grown sufficiently above the electrode so that the flux of reactant to the electrode is not fast enough to satisfy that required by the Nernst equation. In this situation the curent begins to drop just as it did in the potential step measurements. In fact the drop in current follows the same behaviour as that predicted by the Cottrell equation.

The above voltammogram was recorded at a single scan rate. If the scan rate is altered the current response also changes. The figure 1.8 shows a series of linear sweep voltammograms recorded at different scan rates. Each curve has the same form but it is apparent that the total current increases with increasing scan rate. This again can be rationalised by considering the size of the diffusion layer and the time taken to record the scan. Clearly the linear sweep voltammogram will take longer to record as the scan rate is decreased. Therefore the size of the diffusion layer above the electrode surface will be different depending upon the voltage scan rate used. In a slow voltage scan the diffusion layer will grow much further from the electrode in comparison to a fast scan. Consequently the flux to the electrode surface is considerably smaller at slow scan rates than it is at faster rates. As the current is proportional to the flux towards the electrode the magnitude of the current will be lower at slow scan rates and higher at high rates. This highlights an important point when examining LSV (and cyclic voltammograms), although there is no time axis on the graph the voltage scan rate (and therefore the time taken to record the voltammogram) do strongly effect the behaviour seen. A final point to note from the figure is the position of the current maximum, it is clear that the peak occurs at the same voltage and this is a characteristic of electrode reactions which have rapid electron transfer kinetics. These rapid processes are often referred to as reversible electron transfer reactions.

This leaves the question as to what would happen if the electron transfer processes were ‘slow’ (relative to the voltage scan rate). For these cases the reactions are referred to as quasi-reversible or irreversible

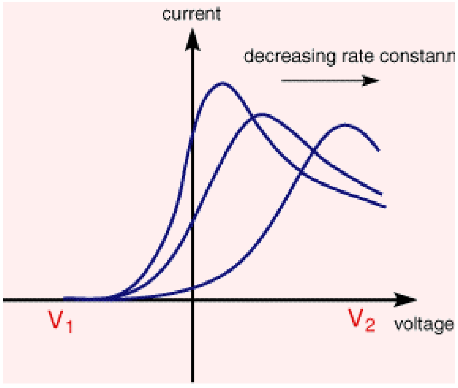


Figure 1.9: Change of the rate constant.

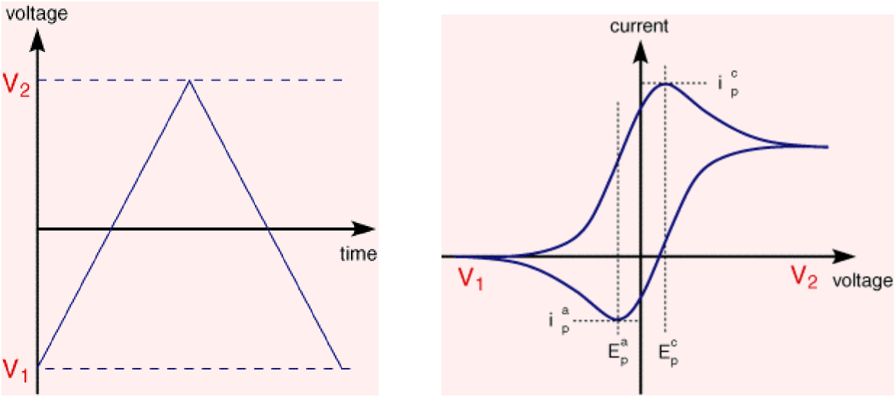


Figure 1.10: Voltage as a function of time and current as a function of voltage for CV

electron transfer reactions. The figure below shows a series of voltammograms recorded at a single voltage sweep rate for different values of the reduction rate constant k_{red}

In this situation the voltage applied will not result in the generation of the concentrations at the electrode surface predicted by the Nernst equation. This happens because the kinetics of the reaction are 'slow' and thus the equilibria are not established rapidly (in comparison to the voltage scan rate). In this situation the overall form of the voltammogram recorded is similar to that above, but unlike the reversible reaction now the position of the current maximum shifts depending upon the reduction rate constant (and also the voltage scan rate). This occurs because the current takes more time to respond to the the applied voltage than the reversible case.

1.7.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is very similar to LSV. In this case the voltage is swept between two values (see below) at a fixed rate, however now when the voltage reaches V_2 the scan is reversed and the voltage is swept back to V_1

A typical cyclic voltammogram recorded for a reversible single electrode transfer reaction is shown in below. Again the solution contains only a single electrochemical reactant

The forward sweep produces an identical response to that seen for the LSV experiment. When the scan is reversed we simply move back through the equilibrium positions gradually converting electrolysis product (Fe^{2+} back to reactant (Fe^{3+}. The current flow is now from the solution species back to the electrode and so occurs in the opposite sense to the forward seep but otherwise the behaviour can be explained in an identical manner. For a reversible electrochemical reaction the CV recorded has certain well defined characteristics.

1. The voltage separation between the current peaks is
2. The positions of peak voltage do not alter as a function of voltage scan rate

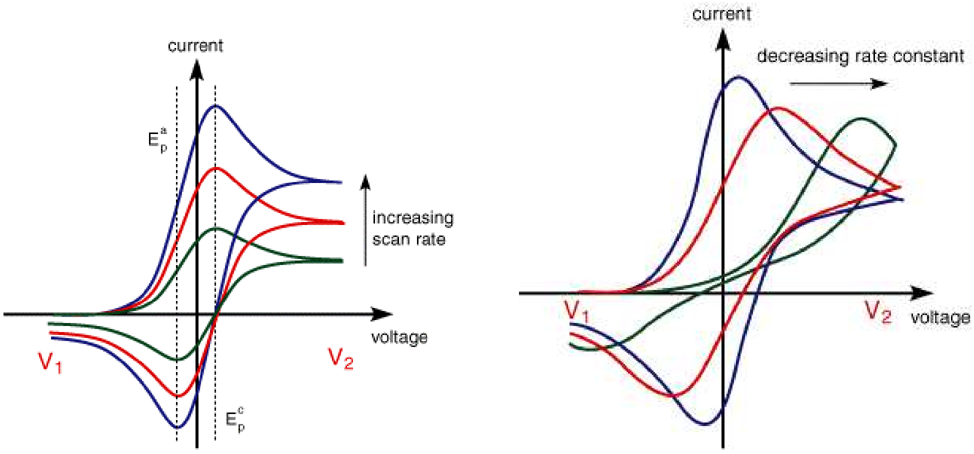


Figure 1.11: Scan rate and rate constant dependence of the I-V curves.

3. The ratio of the peak currents is equal to one
4. The peak currents are proportional to the square root of the scan rate

The influence of the voltage scan rate on the current for a reversible electron transfer can be seen in Fig. 1.11 As with LSV the influence of scan rate is explained for a reversible electron transfer reaction in terms of the diffusion layer thickness. The CV for cases where the electron transfer is not reversible show considerably different behaviour from their reversible counterparts.

By analysing the variation of peak position as a function of scan rate it is possible to gain an estimate for the electron transfer rate constants.

CYCLIC Voltammetry

⇒ **read more:**

- **C.M.A. Brett & A.M.O. Brett, “Electrochemistry”, Oxford University Press, Oxford, 1993** → **chapter 9**
- **E. Gileadi, “Electrode Kinetics for Chemists, Chemical Engineers and Materials Scientists”, VCH, Weinheim, 1993** → **chapter 25**

Different ways to do voltammetry:

- **Potential step**
- **Linear sweep**
- **Cyclic Voltammetry (CV)**

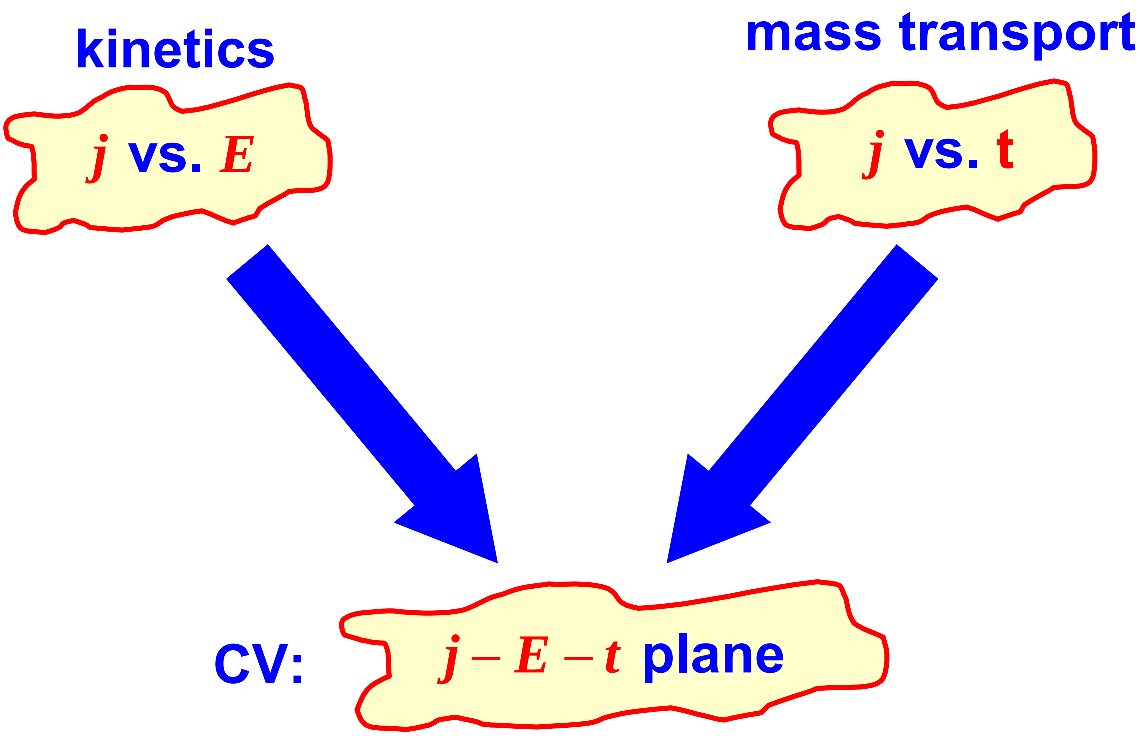
CV: widely used technique for studying electrode processes (particularly by non-electrochemists)

Principle of CV: Apply continuous cyclic potential E to working electrode

⇒ **Effects**

- **Faradic reactions: oxidation/reduction of electroactive species in solution**
- **Adsorption/desorption due to E**
- **Capacitive current: double layer charging**

⇒ **deviations from steady state, i.e.** $\frac{\mathrm{d}c}{\mathrm{d}t} \neq 0$



kinetics

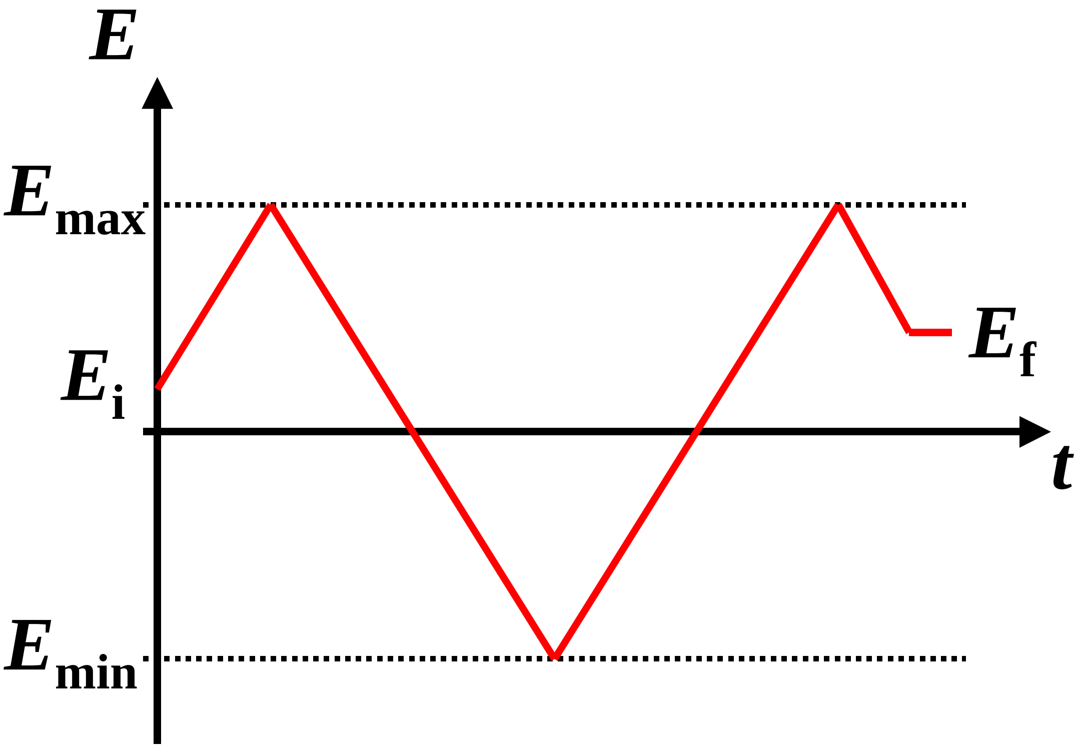
j vs. E

mass transport

j vs. t

CV: $j - E - t$ plane

- Potential changed at a constant sweep rate, $v = \left|\frac{\mathrm{d}E}{\mathrm{d}t}\right|$
- Cycled forward and backward between fixed values
- Current plotted as a function of potential



In principle: useful…

- ❑ Unknown electrochemical system
  - → start analysis with CV
  - → survey over processes, kinetics
  - → identify involved species and mechanisms
  - ⇒ qualitative understanding

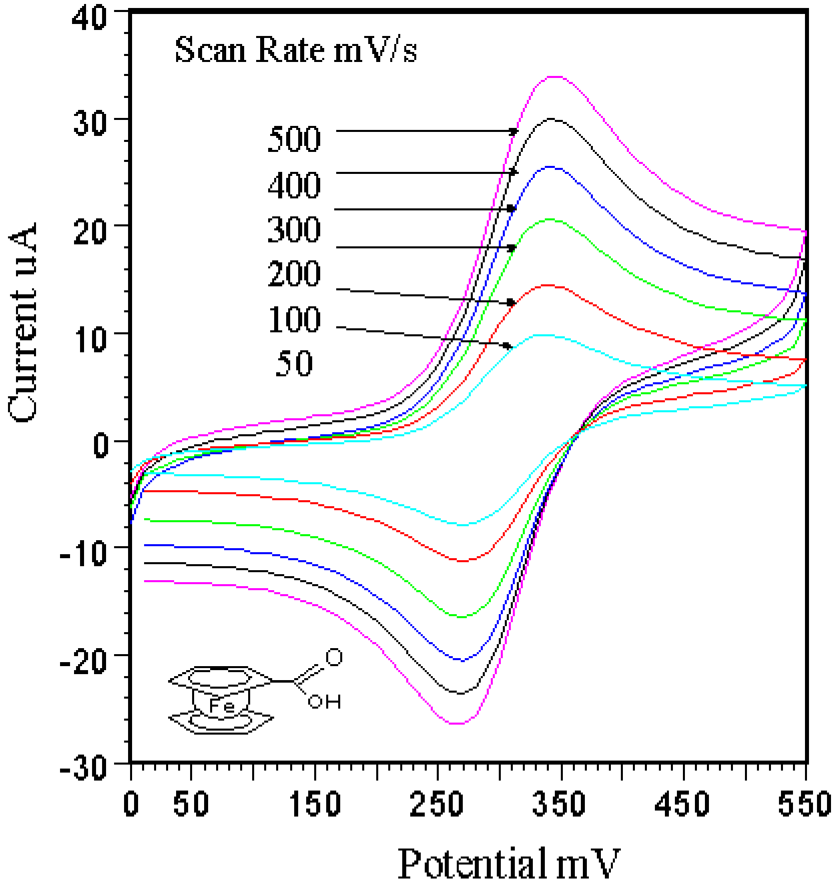
- ❑ Semi-quantitative analysis
  - → diagnostic capabilities

… but difficult to understand and analyze

→ a lot of information

→ difficult to discern!!!

How do typical cyclic voltammograms look like?



Measured Current

faradaic current + capacitive current

electrode reaction ↓ | double layer charging ↓

→ total current density:

$$\begin{aligned} j &= j_{\mathrm{F}} + j_{\mathrm{C}} \\ &= j_{\mathrm{F}} + C_{\mathrm{d}} \frac{\mathrm{d}E}{\mathrm{d}t} \end{aligned}$$

$$\boxed{j = j_{\mathrm{F}} + vC_{\mathrm{d}}}$$

rate constants ↙ ↘ double layer correction

Double layer correction important if v is large!

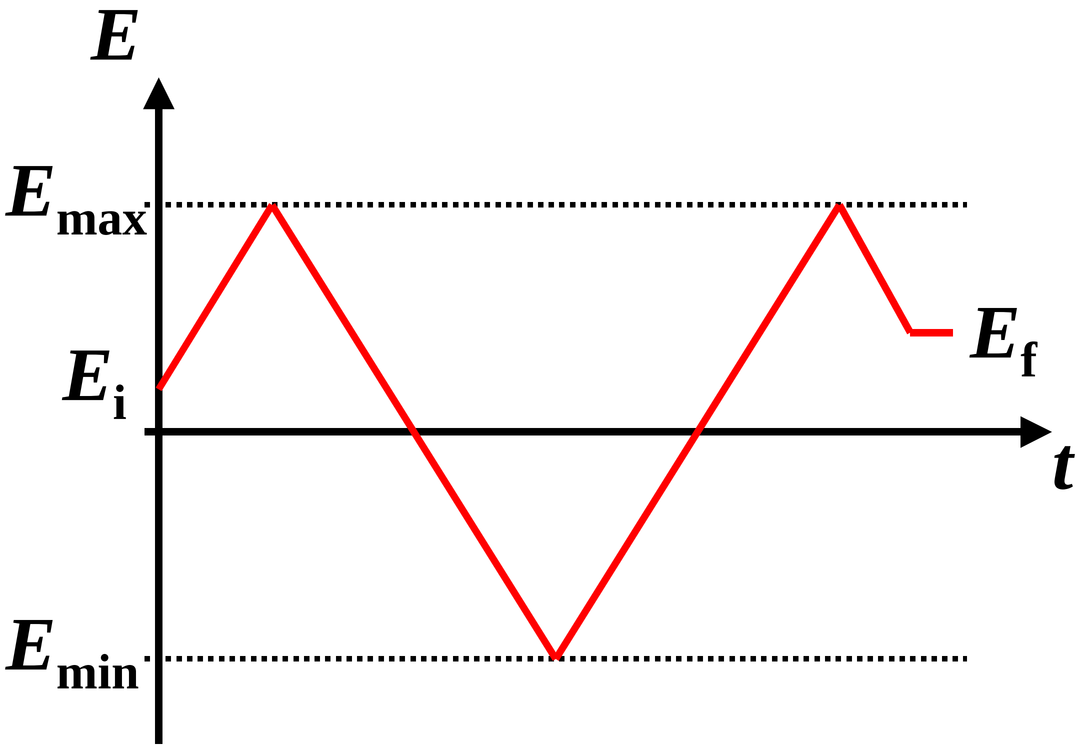
What do we need?

- Nernst-equation → equilibrium
- Butler-Volmer equation → kinetics
- Diffusion equation → mass transport
- Double layer charging
- Adsorption

⇒ anything new??

What is controlled in CV?

Variation of applied potential with time



Important parameters:

- Initial potential , E_i
- Initial sweep direction
- Sweep rate, v [mV s^{-1}] → ~ mV s^{-1} to 10^3-10^4 V s^{-1}
- Maximum potential, E_{max}
- Minimum potential, E_{min}
- Final potential, E_f

E_{max}, E_{min} → solvent stability

Sweep rate: 3 ranges of operation

(1) very slow sweeps (→ nothing new!)

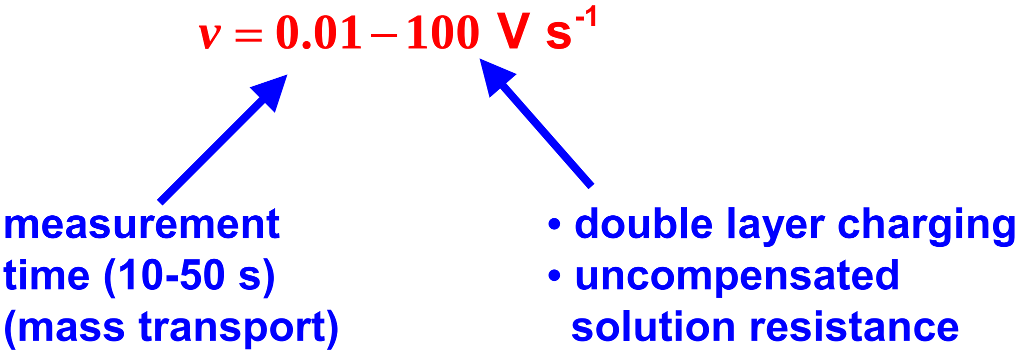
$$v = 0.1 - 2\ \text{mV s}^{-1}$$

quasi-steady state conditions

sweep rate and reversal: no effect on j/E relationship

- ☐ corrosion
- ☐ passivation
- ☐ fuel cell reactions

(2) Oxidation or reduction of species in the bulk

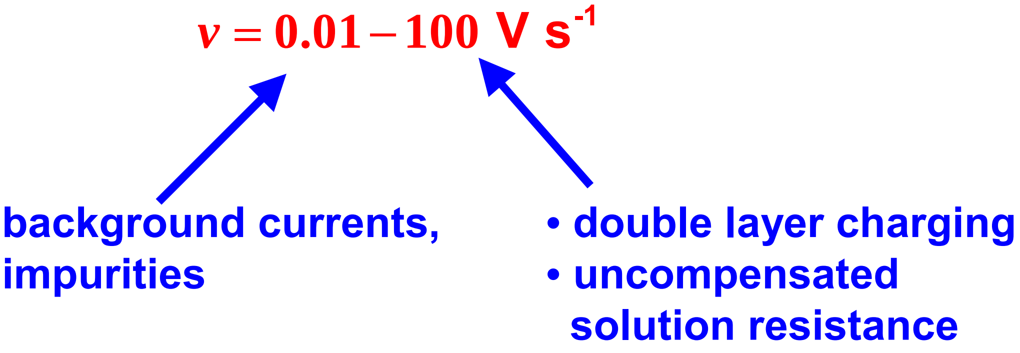


$$v = 0.01 - 100\ \text{V s}^{-1}$$

measurement
time (10-50 s)
(mass transport)

- double layer charging
- uncompensated solution resistance

(3) Oxidation/reduction of species on surface

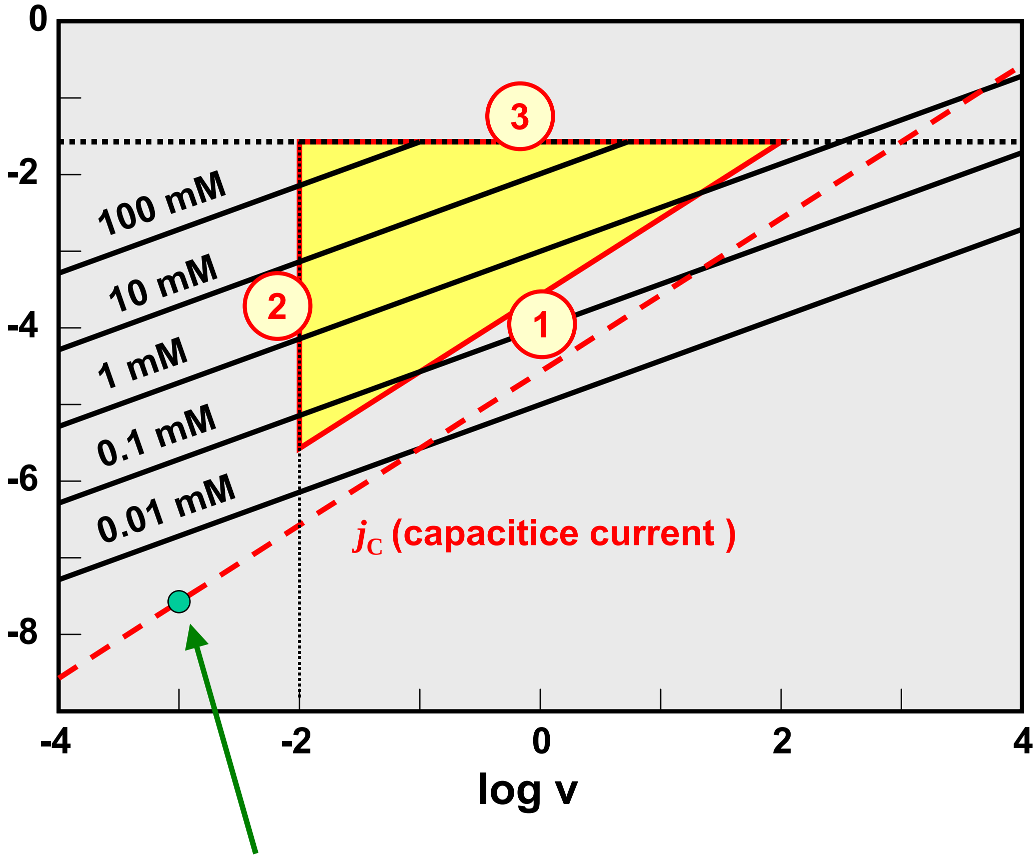


$$v = 0.01 - 100\ \text{V s}^{-1}$$

background currents,
impurities

- double layer charging
- uncompensated solution resistance

Optimum range of concentration and sweep rate



at 1 mV s^{-1}: j_C = 20 nA cm^{-2}

(1) j_F (at peak) $\geq 10\,j_C$

(2) $v > 10$ mV s^{-1} (avoid convection)

(3) j_F (at peak) < 20 mA cm^{-2}

(minimize effect of uncompensated solution resistance)

(4) $c^b \leq 100$ mM

(permit addition of supporting electrolyte)

but: $c^b > 0.1$ mM (double layer charging)

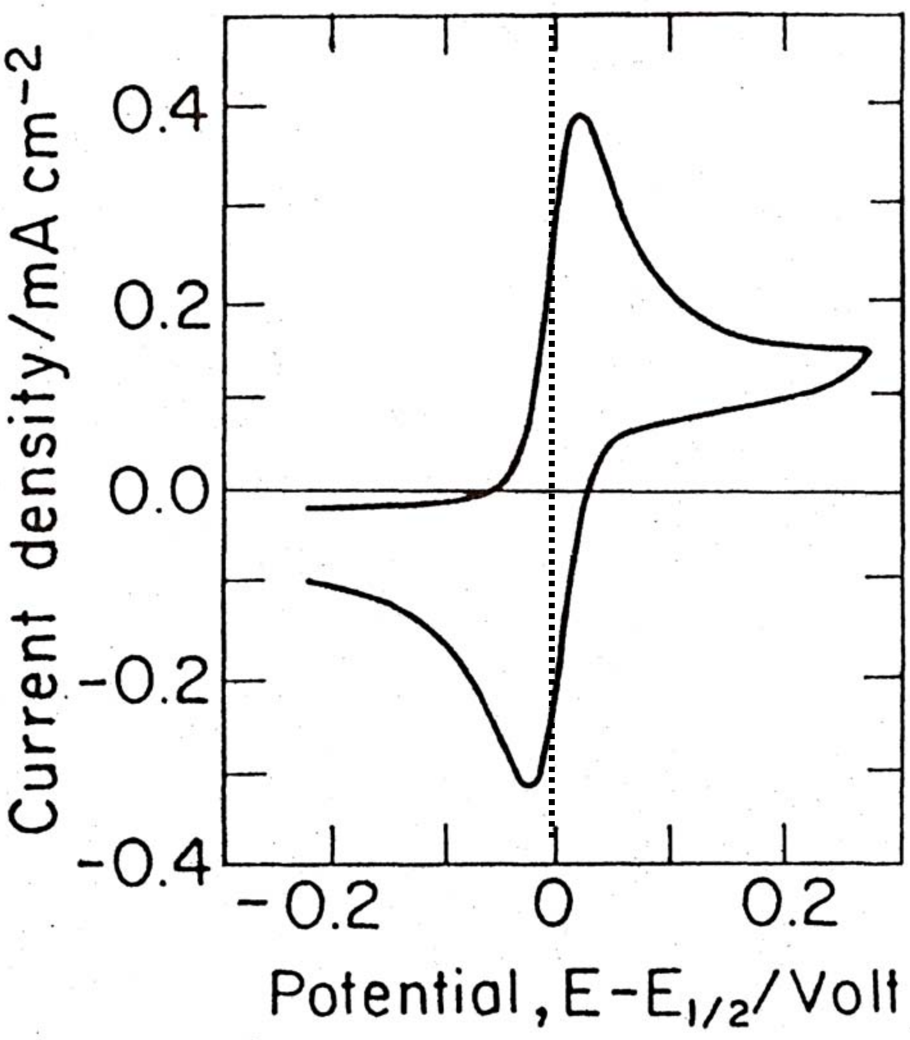
What about porous (rough) electrodes? Would they help improving the range of sweep rates?

Let’s look at some typical CVs

Consider CV for simple electron transfer process

e.g. $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$ (M) (anodic) – which quadrant?

$Fe^{3+} + e^{-}$ (M) $\rightarrow Fe^{3+}$ (cathodic) – which quadrant?



Why is a peak observed in this plot?

Why is $j = 0$ at $E < E^{eq}$ (or why is CV asymmetric)?

Let’s start in …

- ☐ **Lower left corner (cathodic region):**

  $E < E^{\mathrm{eq}} \Rightarrow$ **cathodic current (< 0)**

  c_{ox} **consumed (depleted near electrode)**

  c_{red} **produced (enhanced near electrode)**

  $\Rightarrow j = 0$ **at** $E < E^{\mathrm{eq}}$ **(remember Nernst equation!)**

- ☐ E **increases** → **towards upper right corner (anodic)**

  c_{red} **depleted**

  c_{ox} **produced**

  $\Rightarrow$ **peak is reached at** $j = j_{\mathrm{p}},\ E = E_{\mathrm{p}}$

What causes occurrence of peak?

???

Of course: Interplay of diffusion and mass transport!

Consider: simple phenomenology

kinetics	➡	**activation control**	j_{ac}
mass transport	➡	**diffusion control**	j_{diff}

Resulting current: $$\frac{1}{j} = \frac{1}{j_{\mathrm{ac}}} + \frac{1}{j_{\mathrm{diff}}}$$

- ☐ **initially:** $j_{\mathrm{ac}} << j_{\mathrm{diff}} \Rightarrow j = j_{\mathrm{ac}}$

  → j **increases with** E **(and** t **)**

- ☐ t **proceeds,** E **grows** ➡ $j_{\mathrm{ac}} \nearrow$ **and** $j_{\mathrm{diff}} \searrow$

  until $j_{\mathrm{ac}} \approx j_{\mathrm{diff}}$ ➡ **MAXIMUM t**

- ☐ **further progress:** $j_{\mathrm{ac}} >> j_{\mathrm{diff}} \Rightarrow j = j_{\mathrm{diff}}$

  → j **decreases with** E **(and** t **)**

You see: Same phenomena (and equations) as before!

Now: More detail!

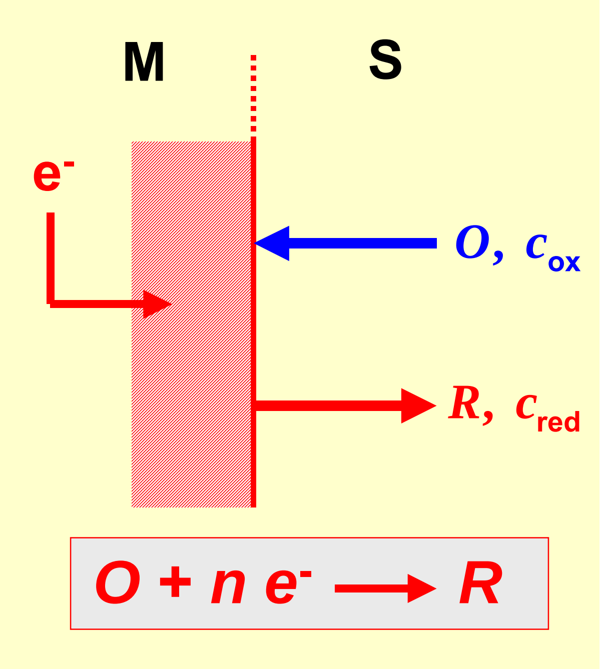
Distinguish:

reversible region ↔ **Tafel region (“irreversible”)**

Which fundamental parameter is this distinction related to?

Semi-quantitative treatment of CV

(1) Simple, reversible electron transfer planar electrode



$$O + n\,e^- \longrightarrow R$$

Diffusion equations (both species):

$$\boxed{\begin{aligned}\frac{\partial c_{\text{ox}}}{\partial t} &= D_{\text{O}}\frac{\partial^2 c_{\text{ox}}}{\partial x^2}\\[2ex] \frac{\partial c_{\text{red}}}{\partial t} &= D_{\text{R}}\frac{\partial^2 c_{\text{red}}}{\partial x^2}\end{aligned}}$$

Initial and boundary conditions:

$t = 0,\ x = 0$ (interface): $c_{\text{ox}}^{\text{s}} = c_{\text{ox}}^{\text{b}}$ (1), $c_{\text{red}}^{\text{s}} = c_{\text{red}}^{\text{b}} = 0$ (2)

$t > 0,\ x \to \infty$ (bulk): $c_{\text{ox}} \to c_{\text{ox}}^{\text{b}}$ (3), $c_{\text{red}} \to 0$ (4)

Mass balance:

flux of “ox” (reaching surface) = flux of “red” (leaving surface)

$$D_{\text{O}}\frac{\partial c_{\text{ox}}}{\partial x} + D_{\text{R}}\frac{\partial c_{\text{red}}}{\partial x} = 0 \quad (5)$$

(careful: provided that both species are soluble!)

One condition is missing! – “The reversible case”

What does “reversibility” mean in this context?

Concentrations at the surface, $c^{\mathrm{s}}_{\mathrm{ox/red}}$, and potential E are related via (6)

- **Nernst-equation**

$$E(t) = E^{0} + \frac{RT}{nF}\ln\frac{c^{\mathrm{s}}_{\mathrm{ox}}(t)}{c^{\mathrm{s}}_{\mathrm{red}}(t)}$$

- **linear Tafel region (high overpotentials)**

$$nFk^{0}c^{\mathrm{s}}_{\mathrm{ox}}\exp\left(\frac{\left(1-\alpha^{\mathrm{C}}\right)F\left|E-E^{0}\right|}{RT}\right) = nFD_{\mathrm{O}}\left.\frac{\partial c_{\mathrm{ox}}}{\partial x}\right|_{x=0}$$

Potential is externally controlled function of time:

cathodic scan: $E = E_{\mathrm{i}} - vt,$ **for** $0 < t < t_{\mathrm{rev}}$

anodic scan: $E = E_{\mathrm{i}} - vt_{\mathrm{rev}} + v\left(t - t_{\mathrm{rev}}\right),$ **for** $t_{\mathrm{rev}} < t$

Overall:

Well-defined problem! Diffusion equations can be solved with given conditions in Laplace-domain – however, back-transformation into time-domain has to be done numerically

Don’t go through this!

Let’s consider instead some important parameters!

Quantitative parameters for reversible CVs

Peak potential:

$$E_{\mathrm{p}}(\mathrm{rev}) = E_{1/2} \pm 1.1\frac{RT}{nF}$$

+ : anodic sweep

- : cathodic sweep

Here: $E_{1/2}$ **is the half-wave potential at which** $j = \frac{1}{2} j_{\mathrm{diff}}$

$$E_{1/2} = E^{0} - \frac{RT}{nF}\ln\left(\frac{D_{\mathrm{O}}}{D_{\mathrm{R}}}\right)^{1/2}$$

usually: $E_{1/2} \approx E^{0}$ **since (** $D_{\mathrm{O}} \approx D_{\mathrm{R}}$ **)**

Note:

- ❑ $E_{\mathrm{p}}(\mathrm{rev})$ **is independent of** v

  (criterion for reversibility!!!)
- ❑ $E_{\mathrm{p}}(\mathrm{rev})$ **is independent of concentration!**

Peak current density:

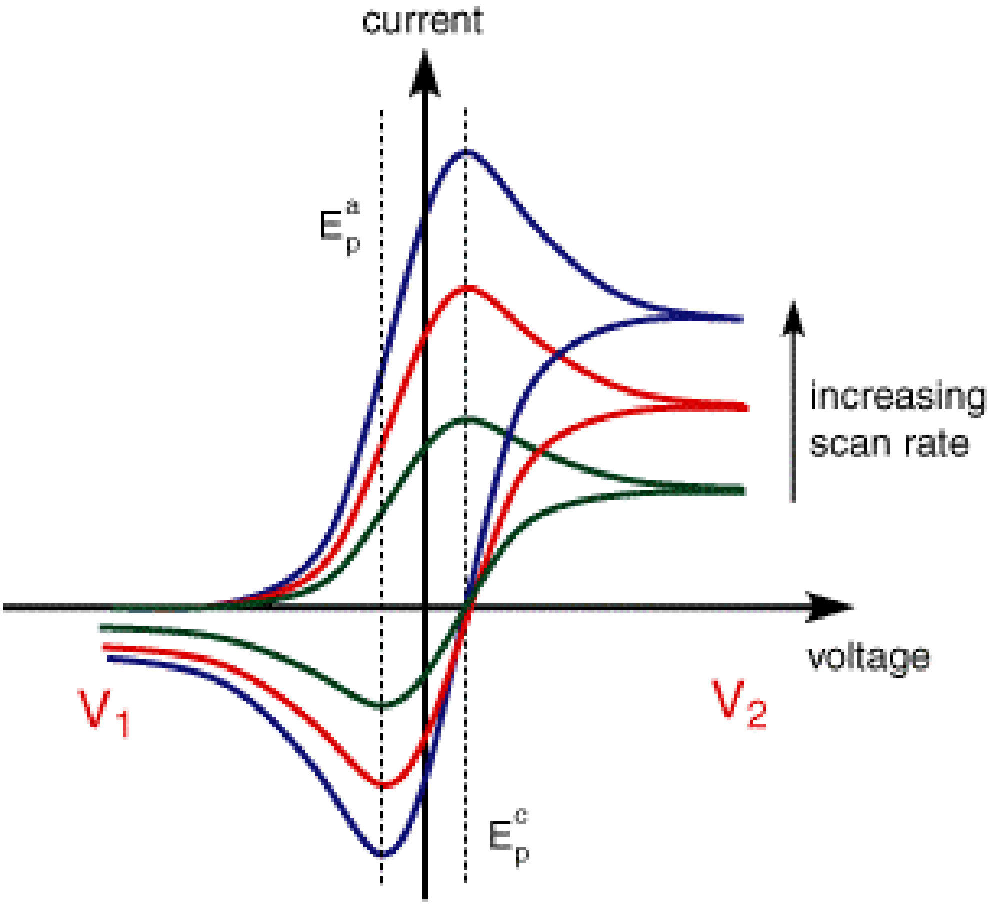
$$j_p(\text{rev}) = 0.446\,nF\left(\frac{nFD_O}{RT}\right)^{1/2} c_{ox}^{b}\,v^{1/2}$$

e.g.: $n = 1,\ D_O = 2.0\cdot10^{-5}\,\text{cm}^2\text{s}^{-1},\ c_{ox}^{b} = 10^{-4}\,\text{mol cm}^{-3}$

$$j_p(\text{rev}) = 0.12\ \text{A cm}^{-2}\ v^{1/2}[\text{in V s}^{-1}]$$

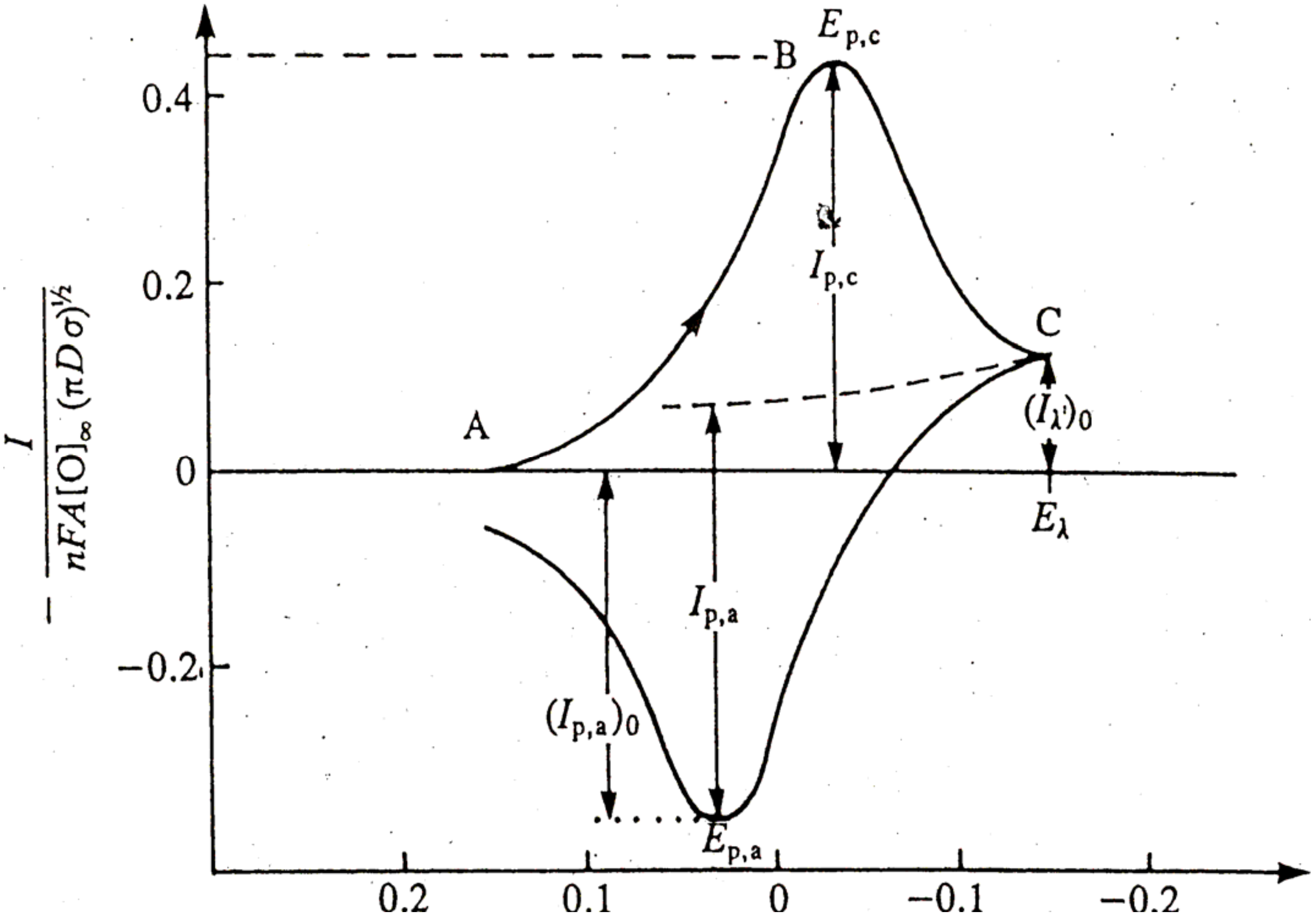
at room T:

$$\underset{\substack{\uparrow\\ \left[\frac{\text{A}}{\text{cm}^2}\right]}}{j_p}(\text{rev}) = \left[2.72\cdot10^{5}\,n^{3/2}\,\underset{\substack{\nearrow\\ \left[\frac{\text{cm}^2}{\text{s}}\right]}}{D_O^{1/2}}\,\underset{\substack{\uparrow\\ \left[\frac{\text{mol}}{\text{cm}^3}\right]}}{c_{ox}^{b}}\right]\underset{\substack{\nwarrow\\ \left[\frac{\text{V}}{\text{s}}\right]}}{v^{1/2}}$$

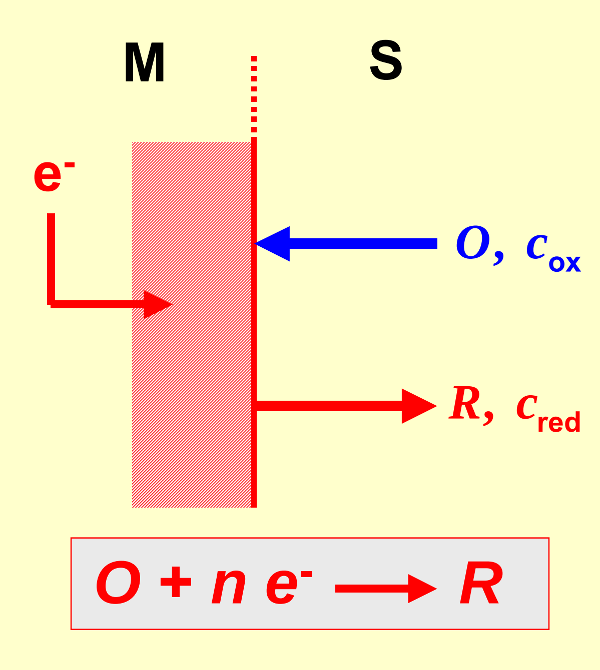


Diagnostic information in reversible CV:

- ☐ $j_\mathrm{p} \propto v^{1/2}$
- ☐ E_p independent of v
- ☐ $\left|E_\mathrm{p} - E_\mathrm{p/2}\right| = \frac{56.6}{n}\mathrm{mV}$, where $E_\mathrm{p/2} = E\left(I = I_\mathrm{p}/2\right)$
- ☐ $E_\mathrm{p,a} - E_\mathrm{p,c} = \frac{57}{n}\mathrm{mV}$
- ☐ $\left|I_\mathrm{p,a}/I_\mathrm{p,c}\right| = 1$



(2) Irreversible ET at planar electrode, linear Tafel region



$$O + n\,e^- \longrightarrow R$$

linear sweep and CV lead to the same voltammetric profile, no inverse peak appears on inversing the scan direction

Reduction as an example

$$nFD_O \left.\frac{\partial c_{ox}}{\partial x}\right|_{x=0} = nFk^0 c_{ox}^s \exp\left(-\frac{\left(1-\alpha^c\right)F\left(E-E^0\right)}{RT}\right)$$

$$= nFk^0 c_{ox}^s \exp\left(-\frac{\left(1-\alpha^c\right)F\left(E_i-E^0\right)}{RT}\right) \mathbf{x} \exp\left(-\beta t\right)$$

where $E = E_i - vt$ and $\beta = \frac{\left(1-\alpha_c\right)F}{RT}v$

Peak potential:

$$E_{\text{p}}(\text{irrev}) = E^0 - \frac{RT}{(1-\alpha_{\text{C}})F}\left[0.780 + \frac{1}{2}\ln\left(\frac{(1-\alpha_{\text{C}})FD_{\text{O}}}{RT\left(k^0\right)^2}\right)\right] + \frac{1}{2}\ln v$$

i.e. depends on $\ln v$

Peak current density:

$$j_{\text{p,c}}(\text{irrev}) = -2.99\cdot 10^5\, n(1-\alpha_{\text{C}})c_{\text{ox}}^{\text{b}} D_{\text{O}}{}^{1/2} v^{1/2}$$

$$\left[\frac{\text{A}}{\text{cm}^2}\right] \qquad \left[\frac{\text{mol}}{\text{cm}^3}\right] \quad \left[\frac{\text{cm}^2}{\text{s}}\right] \quad \left[\frac{\text{V}}{\text{s}}\right]$$

e.g.: $\alpha_{\text{C}} = 0,\ n = 1,\ \ D_{\text{O}} = 2.0\cdot 10^{-5}\,\text{cm}^2\text{s}^{-1},\ \ c_{\text{ox}}^{\text{b}} = 10^{-4}\,\text{mol cm}^{-3}$

$$j_{\text{p}}(\text{irrev}) = -0.134\ \text{A cm}^{-2}\ v^{1/2}[\text{in V s}^{-1}]$$

Alternative expression for $j_{\text{p,c}}(\text{irrev})$:

$$j_{p,c}(irrev) = -\underline{0.227}\,nFk^0 c_{\text{ox}}^{\text{s}} \exp\left(-\frac{(1-\alpha^{\text{C}})F\left(E_p(\text{irrev}) - E^0\right)}{RT}\right)$$

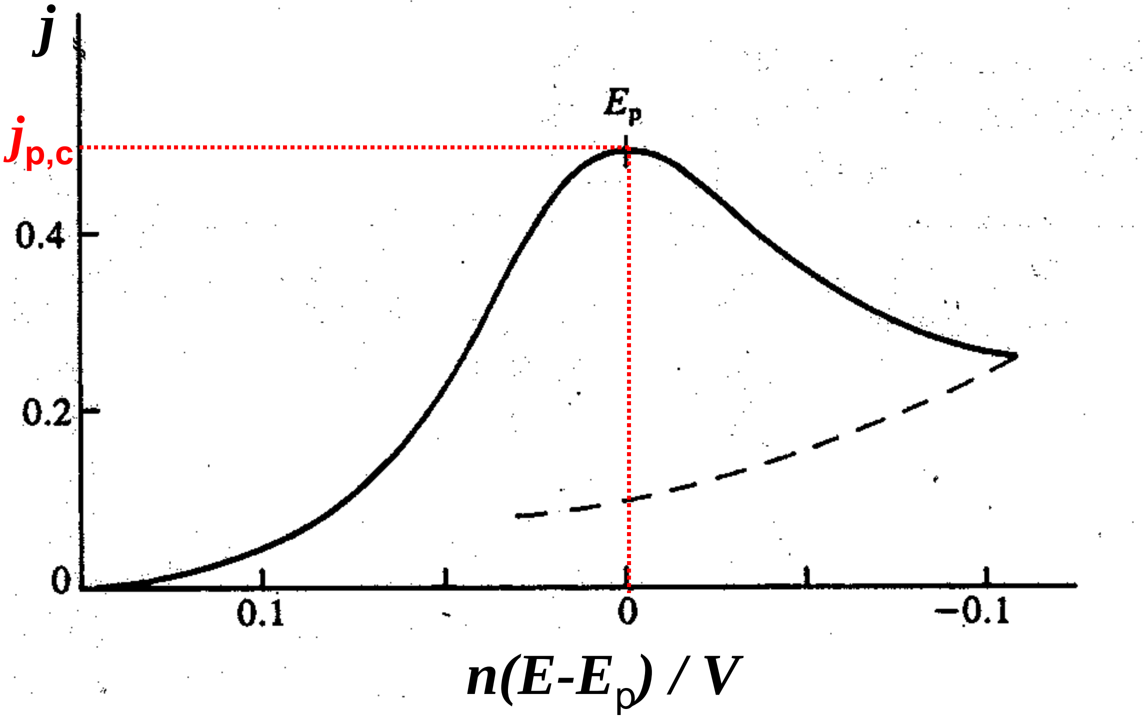
effect of mass transport!

Ratio of peak current densities (simple ET)

$$\left|\frac{j_{\text{p}}(\text{irrev})}{j_{\text{p}}(\text{rev})}\right| = 1.107\left(\frac{1-\alpha_{\text{C}}}{n}\right)^{1/2}$$

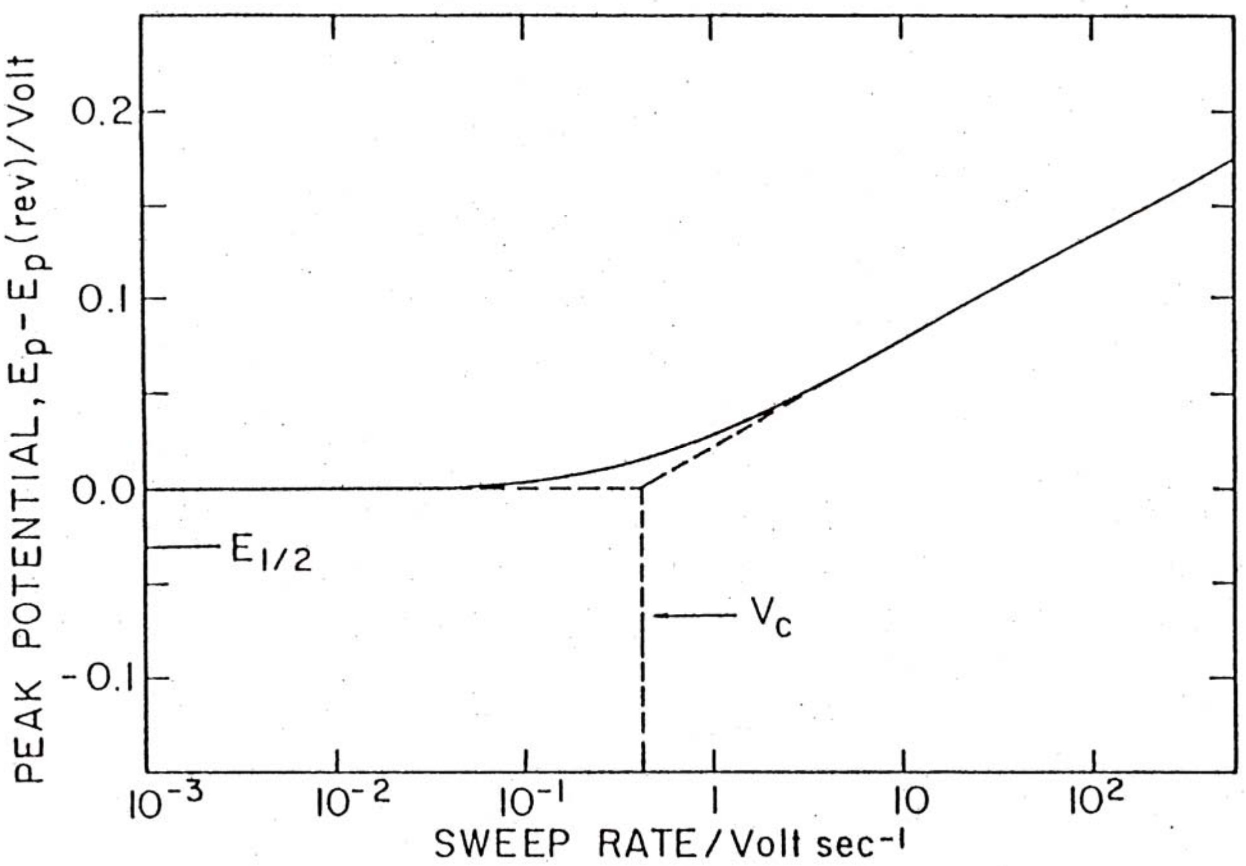
e.g. $\alpha_{\text{C}} = 0.5,\ n = 1 \Rightarrow \left|\frac{j_{\text{p}}(\text{irrev})}{j_{\text{p}}(\text{rev})}\right| = 0.78$ (usually < 1)

Linear sweep voltammogram for irreversible system



- well-separated anodic and cathodic peak (independent)
- current decay upon inverting sweep direction
- peaks at larger (over)potentials compared to reversible system
- E_p (irrev) depends on sweep rate
- larger v → broader and lower peaks, i.e. more irreversible

Peak potential as a function of sweep rate



Reversibility is controlled by sweep rate v !

Quasi-reversible systems

General rule: "irreversibility" increases with increasing sweep rate v

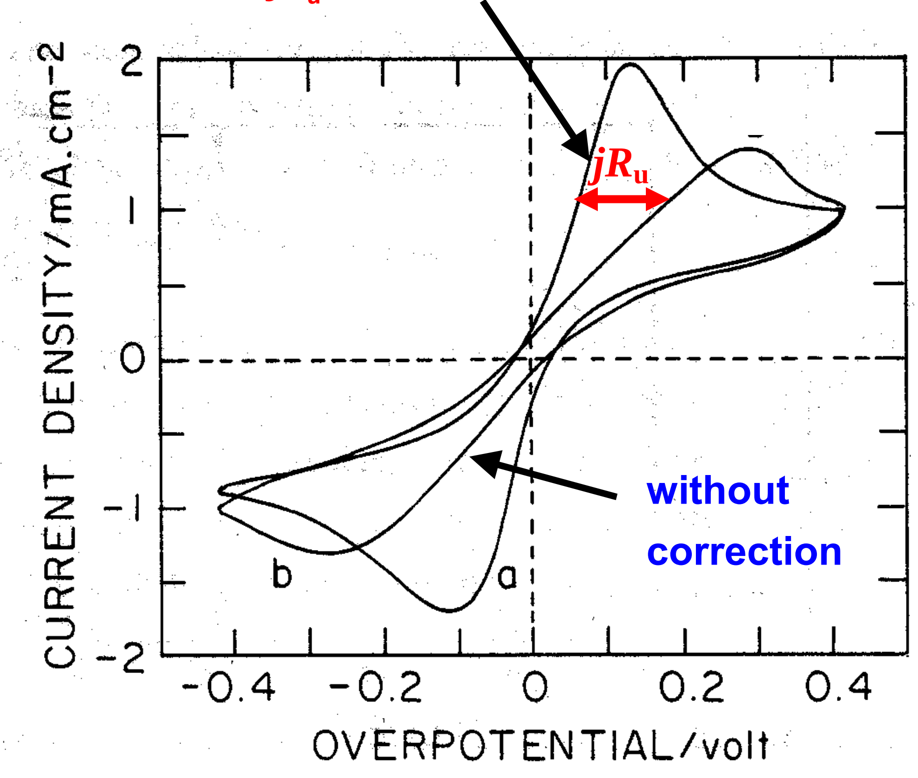
Extent of "irreversibility":

- large sweep rates
- widely separated anodic and cathodic peaks
- decrease in peak current relative to the reversible case

CV: technique with potential control!!! – Problematic!

- **Problem:** potential drop jR_u due to **uncompensated solution resistance**
- Actual **interfacial potential** is smaller than controlled potential (between -WE and CE), $|E_{int}| = |E_f| - jR_u$
- Effect: **reduced current peak** (flattened CV) at apparently higher potential

with dynamic jR_u correction



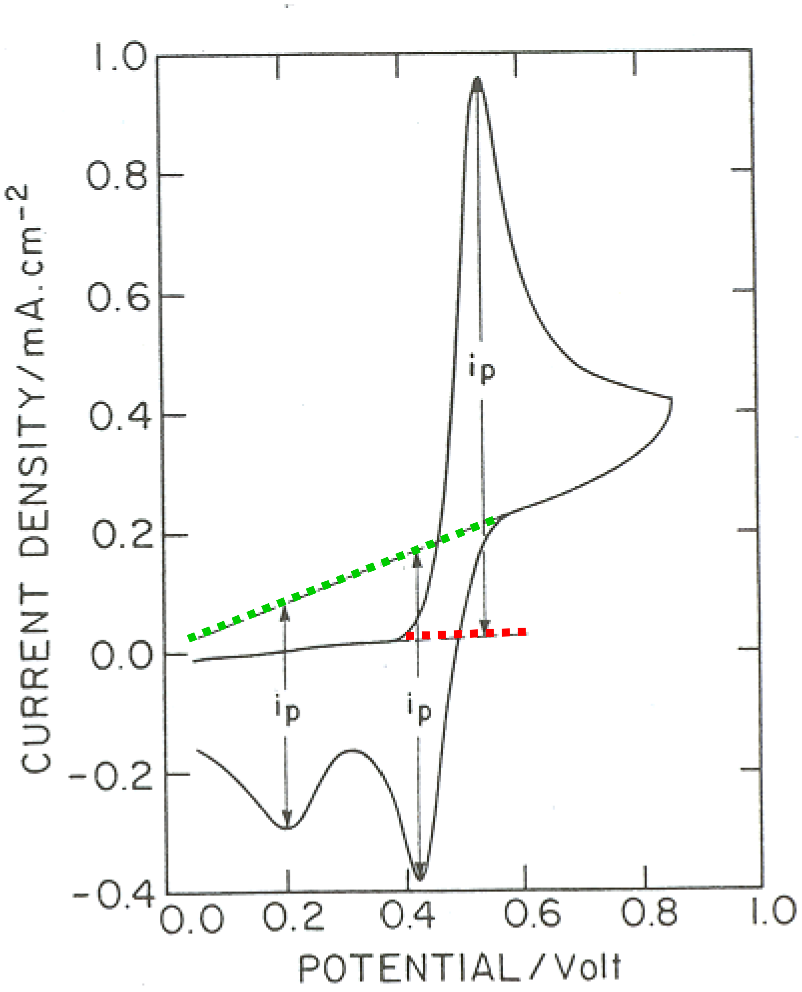
without correction

Quinhydrone (5 mM) in 1 mM H2SO4, $\nu = 75$ mV s^{-1}

Distorted shape of CV in particular in vicinity of peak: effectively reduced sweep rate at the interface near peak!

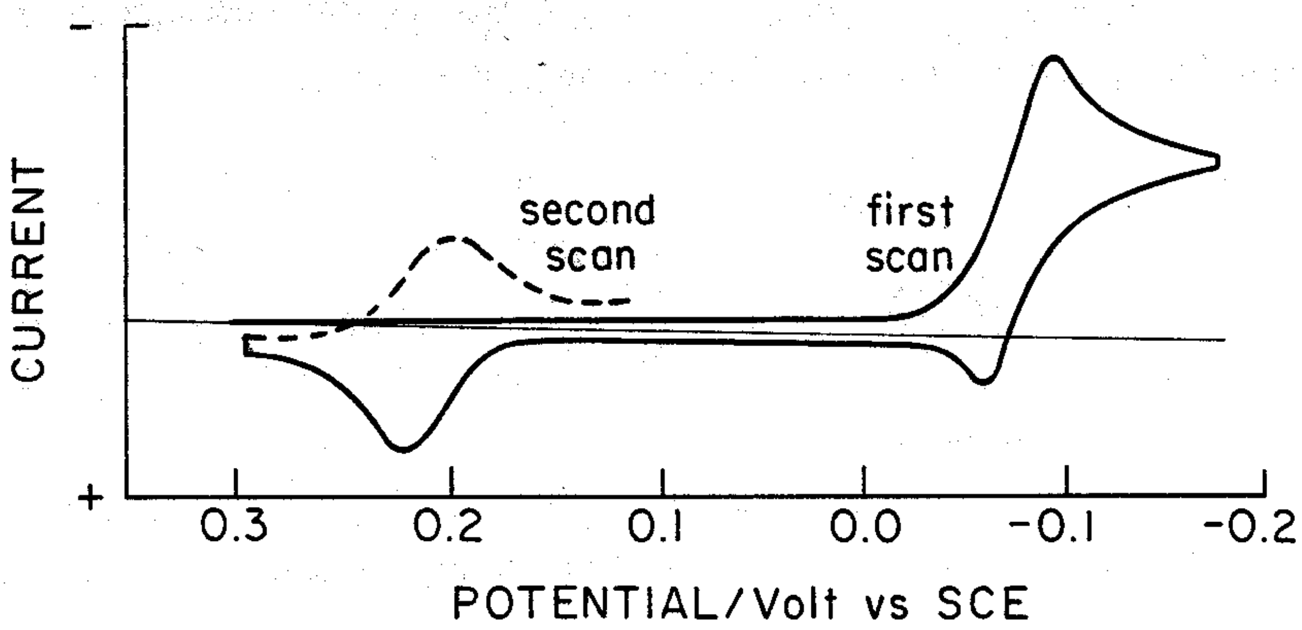
Determine peak current density in CV

- ❑ **extrapolate baseline** (no theoretical basis for this – imaginative extrapolation)
- ❑ **weakness of CV** when used as a **quantitative** tool



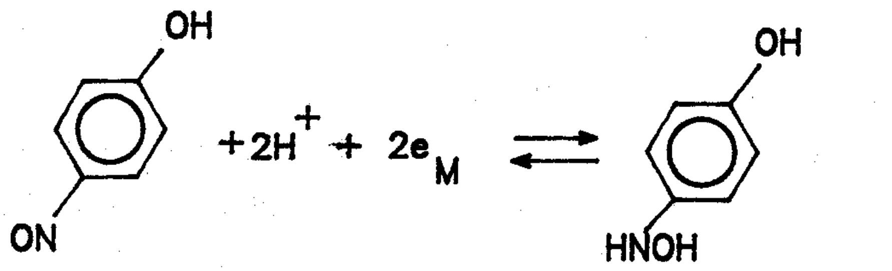
Use of CV: qualitative studies of reactions in certain potential range

Example 1: **CV of dropping mercury electrode (DME) in solution of p-nitrosphenol in acetate buffer**



- ☐ **Start at 0.3 V vs. SCE in cathodic direction:**

  first reduction peak at -0.1 V



p-nitrosphenol **p-phenolhydoxylamine**

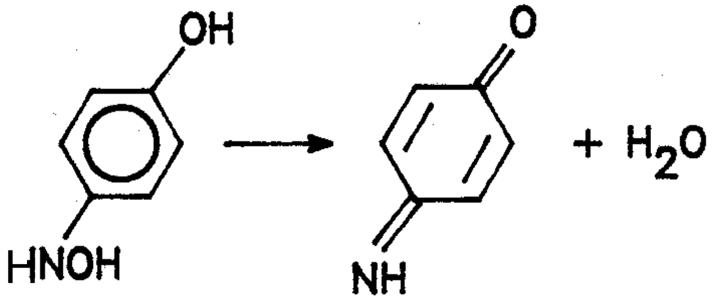
- anodic return sweep: reverse reaction → peak at -0.05 V, position as expected, but suppressed
- another unexpected anodic peak at +0.22V, corresponds to cathodic peak not seen in first scan!

What is going on?

Chemical reaction following charge transfer

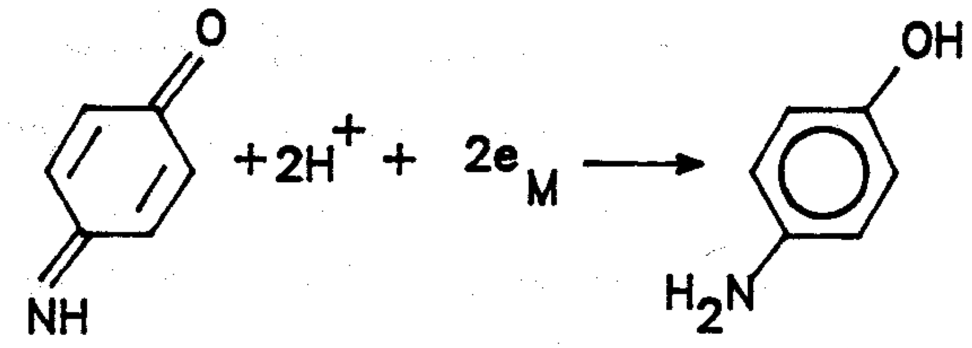
Producing new redox couple!

Decomposition of p-phenohydroxlamine



p-phenolhydroxylamine p-imidequinone

New redox couple:



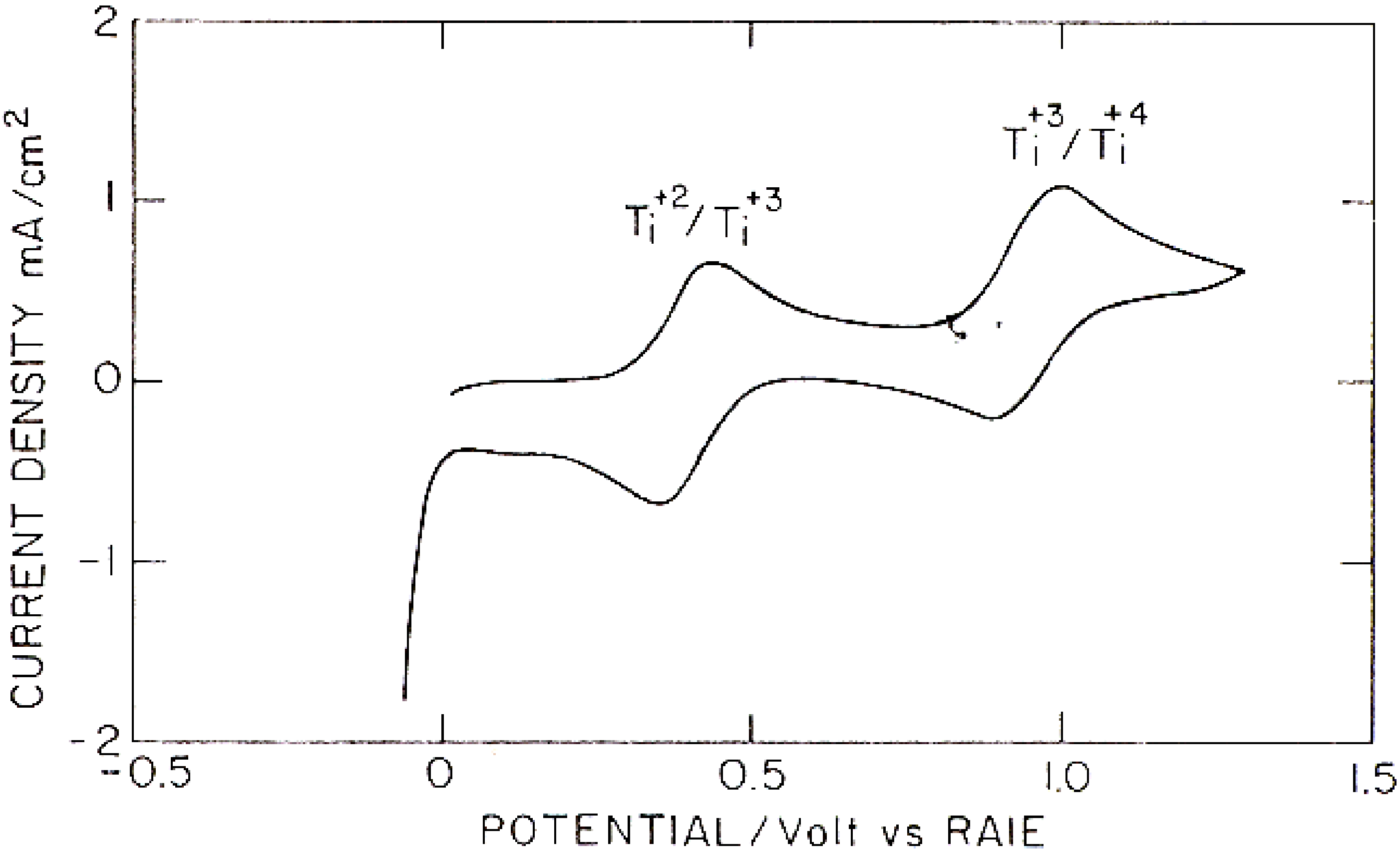
p-aminophenol

Reaction sequence: ECE mechanism

(electrochemical – chemical – electrochemical)

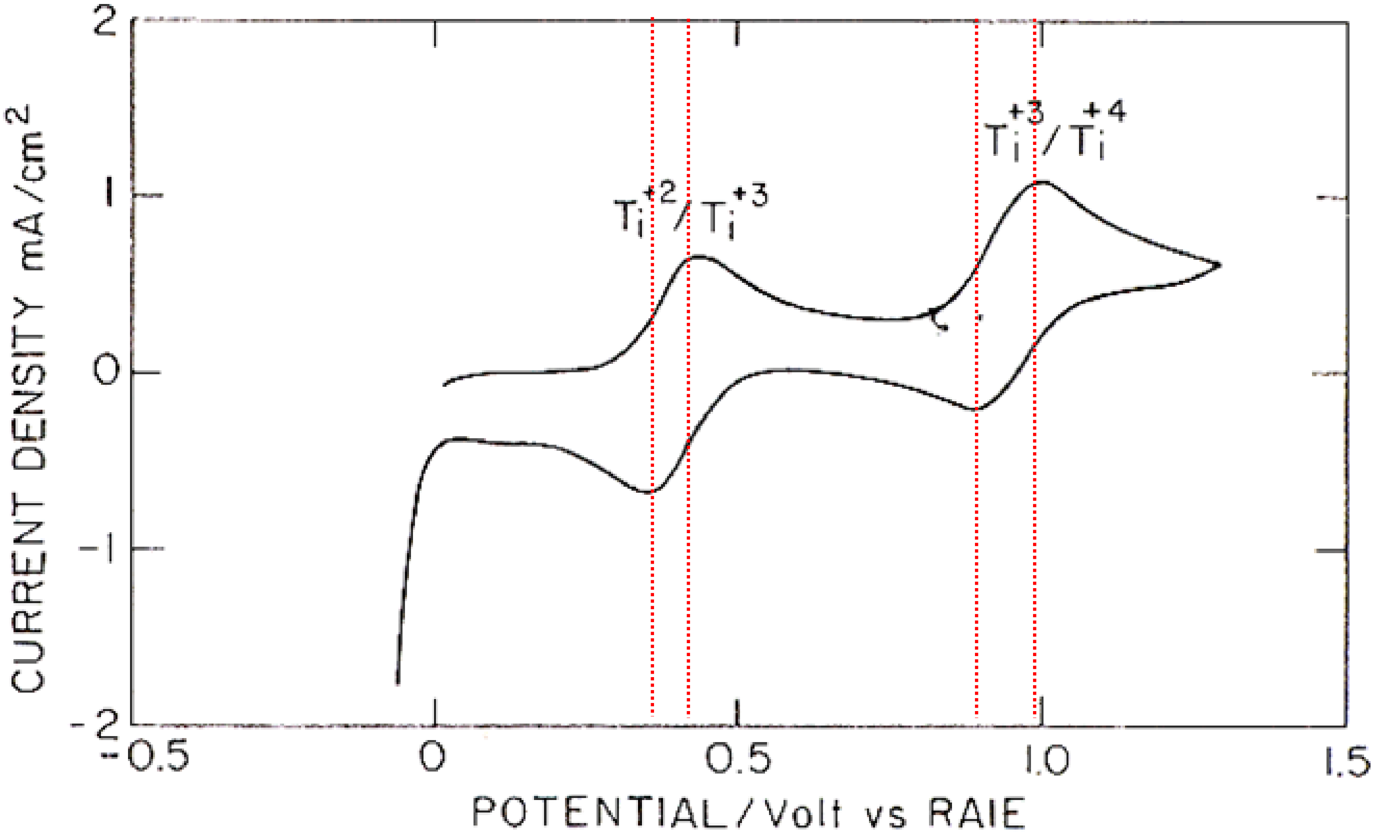
Example 2: reduction of Ti^{4+} in 1:2 NaCl/$AlCl_3$, Ti^{2+} from anodic dissolution of Ti, Al-wire as reference electrode (separate compartment)

Sweep rate (or scan rate): $v = 100$ mV s^{-1}



Two reduction steps, separated by ~0.5 V.

Reversibe or irreversible steps? Which step has the higher rate constant?



CURRENT DENSITY mA/cm2
2
1
0
-1
-2
-0.5
0
0.5
1.0
1.5
POTENTIAL / Volt vs RAIE
Ti+2/Ti+3
Ti+3/Ti+4

~ 60 mV

Introduction to Electrochemical Impedance Spectroscopy

Gamry Instruments

Impedance

- The term *impedance* refers to the frequency dependant resistance to current flow of a circuit element (resistor, capacitor, inductor,etc.)
- *Impedance* assumes an AC current of a specific frequency in Hertz (cycles/s).
- *Impedance*: $Z_\omega = E_\omega / I_\omega$
    - $E_\omega =$ Frequency-dependent potential
    - $I_\omega =$ Frequency-dependent current
- Ohm’s Law: $R = E/I$
    - R = impedance at the limit of zero frequency

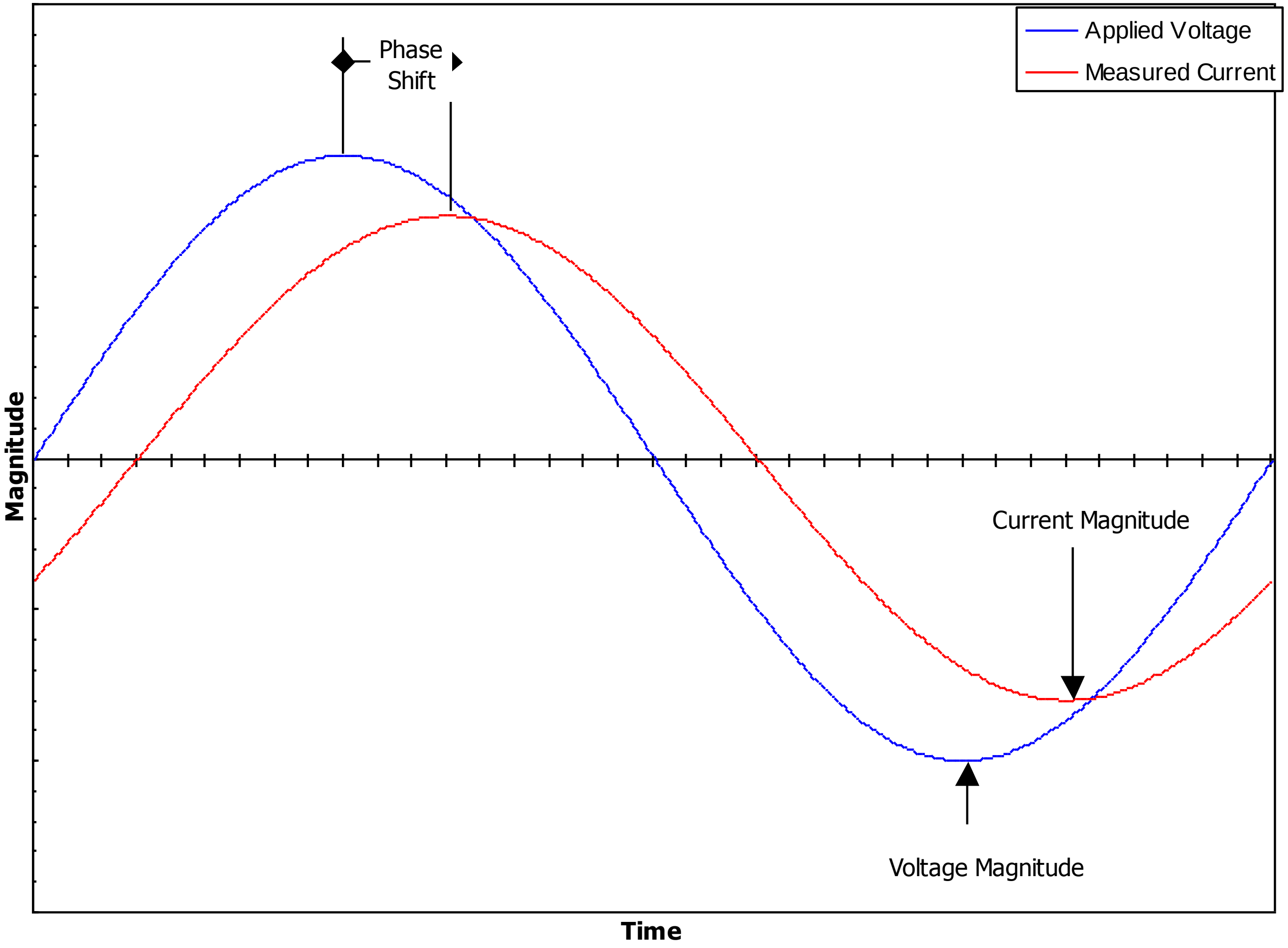
Reasons To Run EIS

- EIS is theoretically complex (and can be expensive) – why bother?
    - The information content of EIS is <u>much</u> higher than DC techniques or single frequency measurements.
    - EIS may be able to distinguish between two or more electrochemical reactions taking place.
    - EIS can identify diffusion-limited reactions, e.g., diffusion through a passive film.
    - EIS provides information on the capacitive behavior of the system.
    - EIS can test components within an assembled device using the device’s own electrodes.

Making EIS Measurements

- Apply a small sinusoidal perturbation (potential or current) of fixed frequency
- Measure the response and compute the impedance at each frequency.
  - $Z_{\omega} = E_{\omega}/I_{\omega}$
    - $E_{\omega} =$ Frequency-dependent potential
    - I_{ω} = Frequency-dependent current
- Repeat for a wide range of frequencies
- Plot and analyze

Excitation and Response in EIS



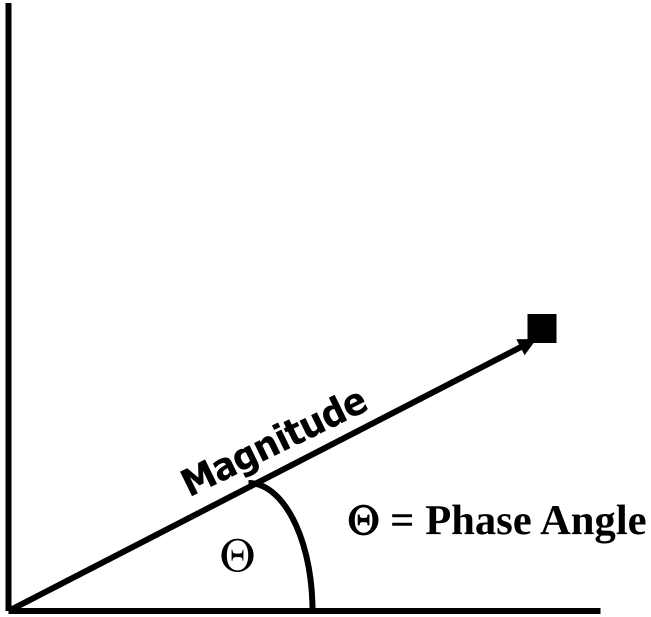
EIS Data Presentation

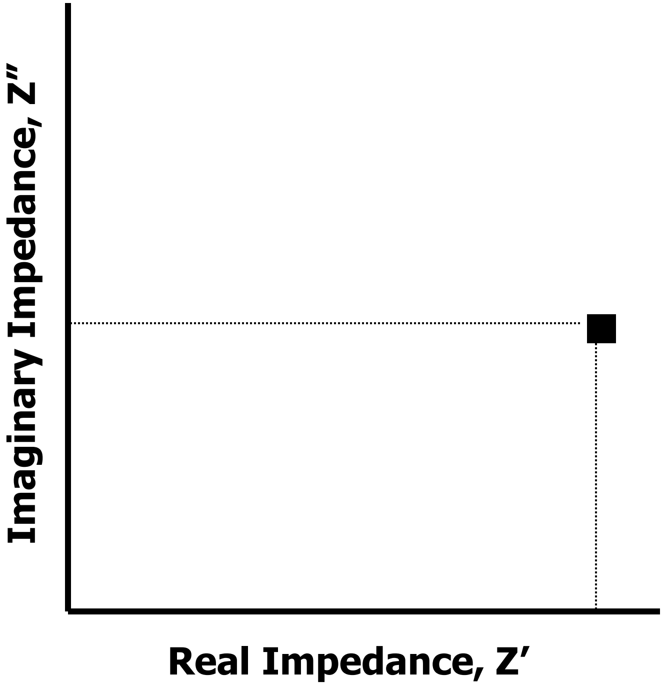
- EIS data may be displayed as either a vector or a complex quantity.
- A vector is defined by the impedance magnitude and the phase angle.
- As a complex quantity, $Z_{total} = Z_{real} + Z_{imag}$
- The vector and the complex quantity are different representations of the impedance and are mathematically equivalent.

Vector and Complex Plane Representations of EIS

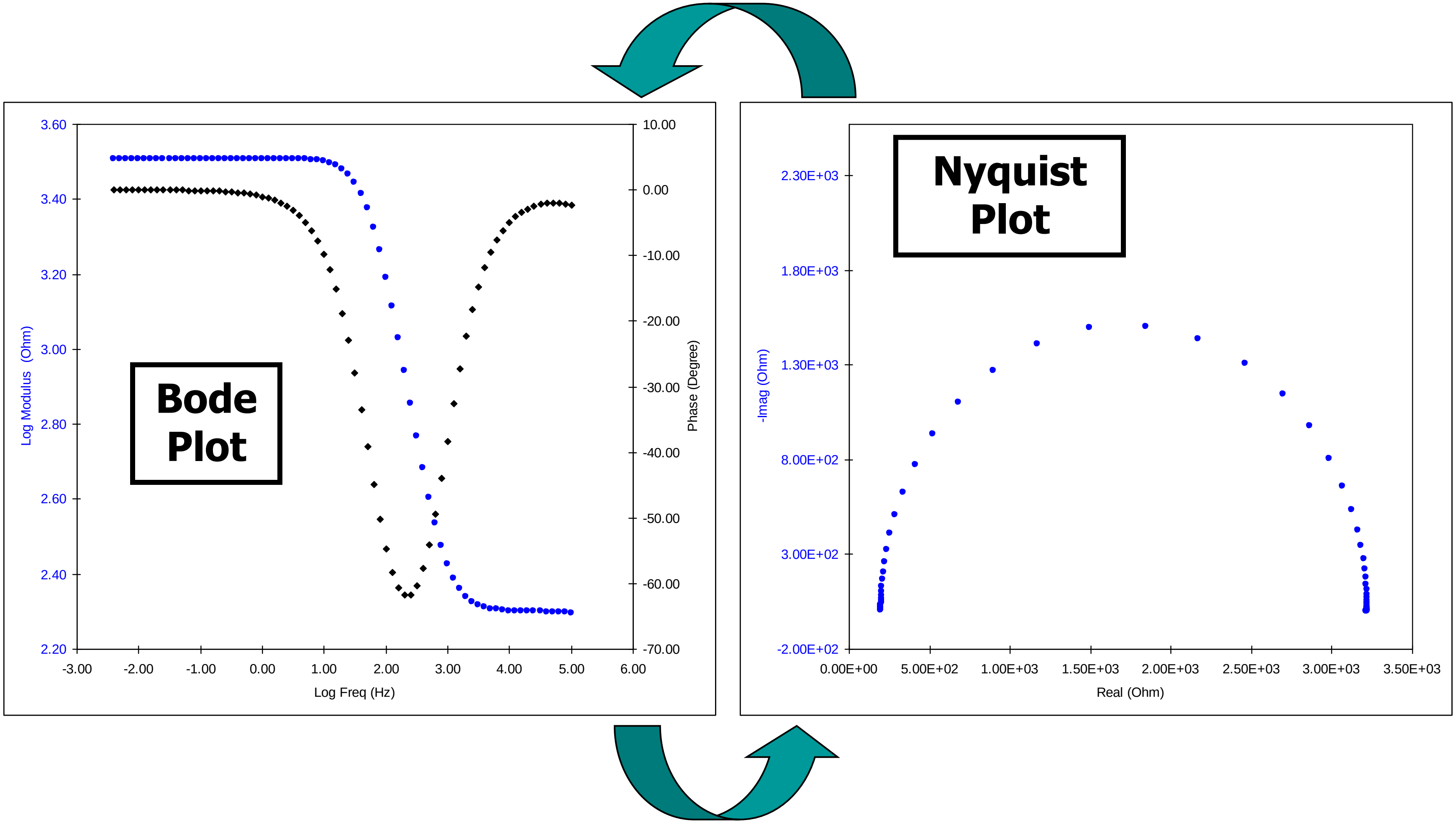
Vector

Complex Plane





EIS data may be presented as a Bode Plot or a Complex Plane (Nyquist) Plot

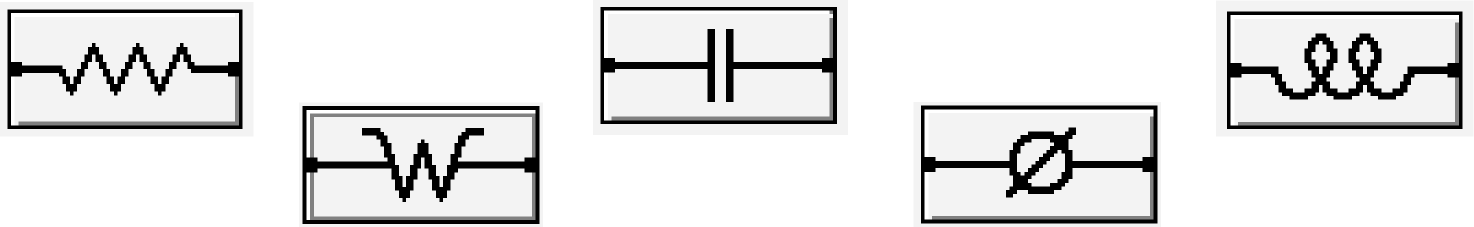


Nyquist vs. Bode Plot

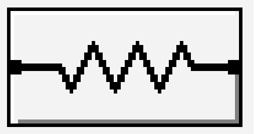
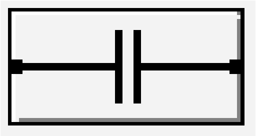
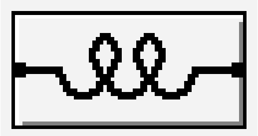
Bode Plot	Nyquist Plot
• Individual charge transfer processes are resolvable.	• Individual charge transfer processes are resolvable.
• Frequency is explicit.	• Frequency is not obvious.
• Small impedances in presence of large impedances can be identified easily.	• Small impedances can be swamped by large impedances.

Analyzing EIS: Modeling

- Electrochemical cells can be modeled as a network of passive electrical circuit elements.
- A network is called an “equivalent circuit”.
- The EIS response of an equivalent circuit can be calculated and compared to the actual EIS response of the electrochemical cell.

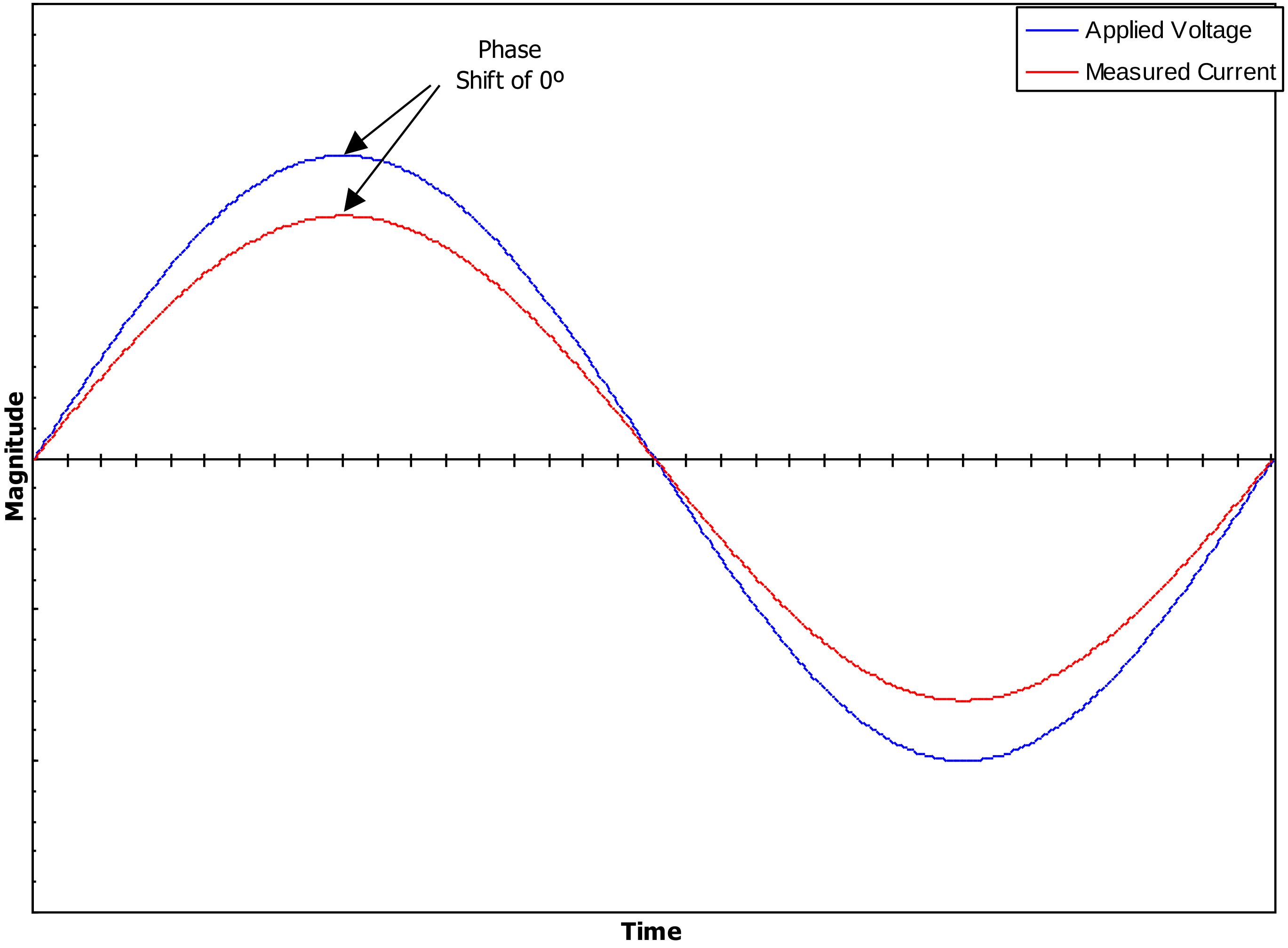


Frequency Response of Electrical Circuit Elements

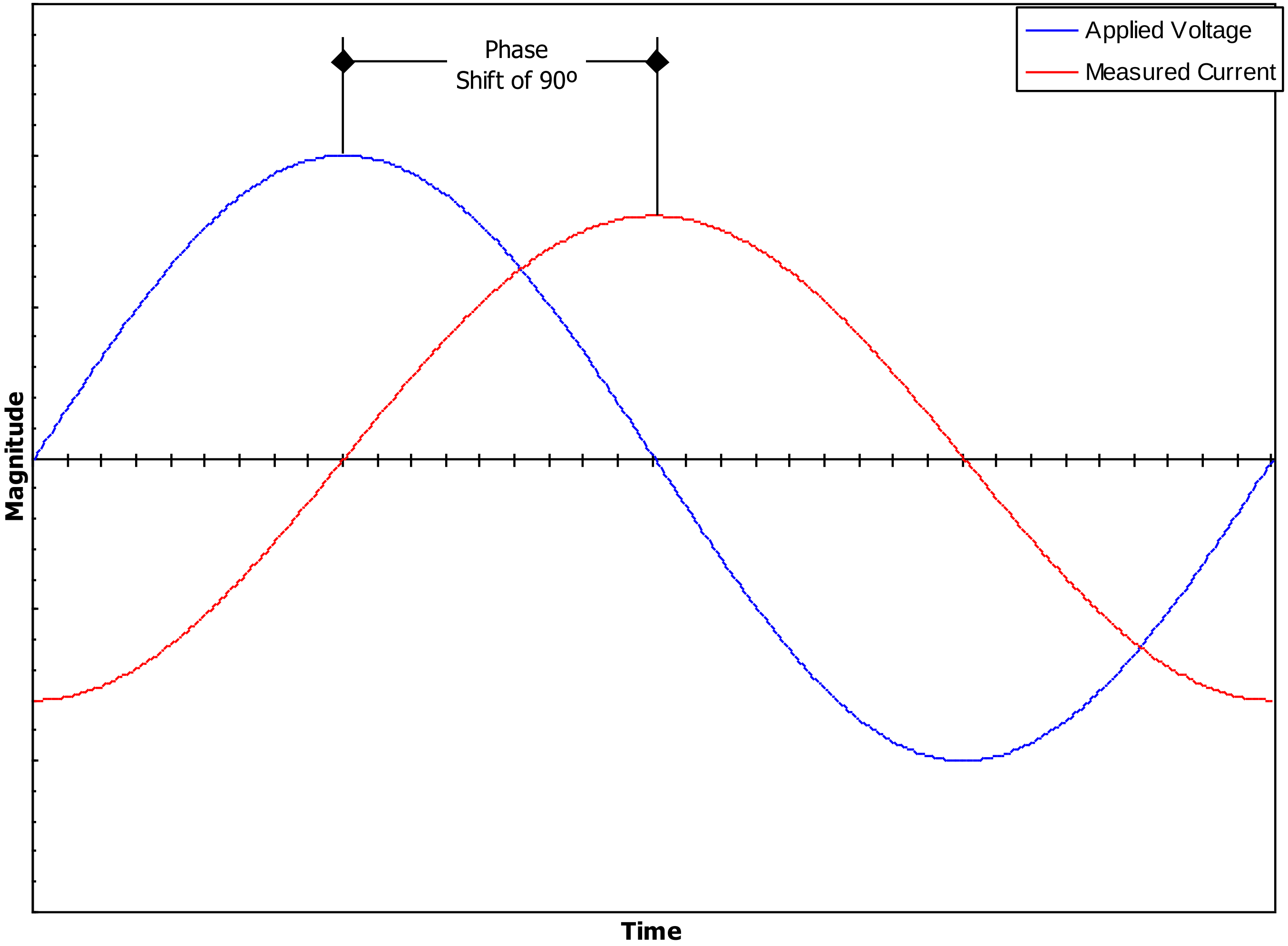
		
Resistor	Capacitor	Inductor
$Z = R$ (Ohms)	$Z = -j/\omega C$ (Farads)	$Z = j\omega L$ (Henrys)
0° Phase Shift	-90° Phase Shift	90° Phase Shift

- $j = \sqrt{-1}$
- $\omega = 2\pi f$ radians/s, f = frequency (Hz or cycles/s)
- A real response is in-phase (0°) with the excitation. An imaginary response is ±90° out-of-phase.

EIS of a Resistor

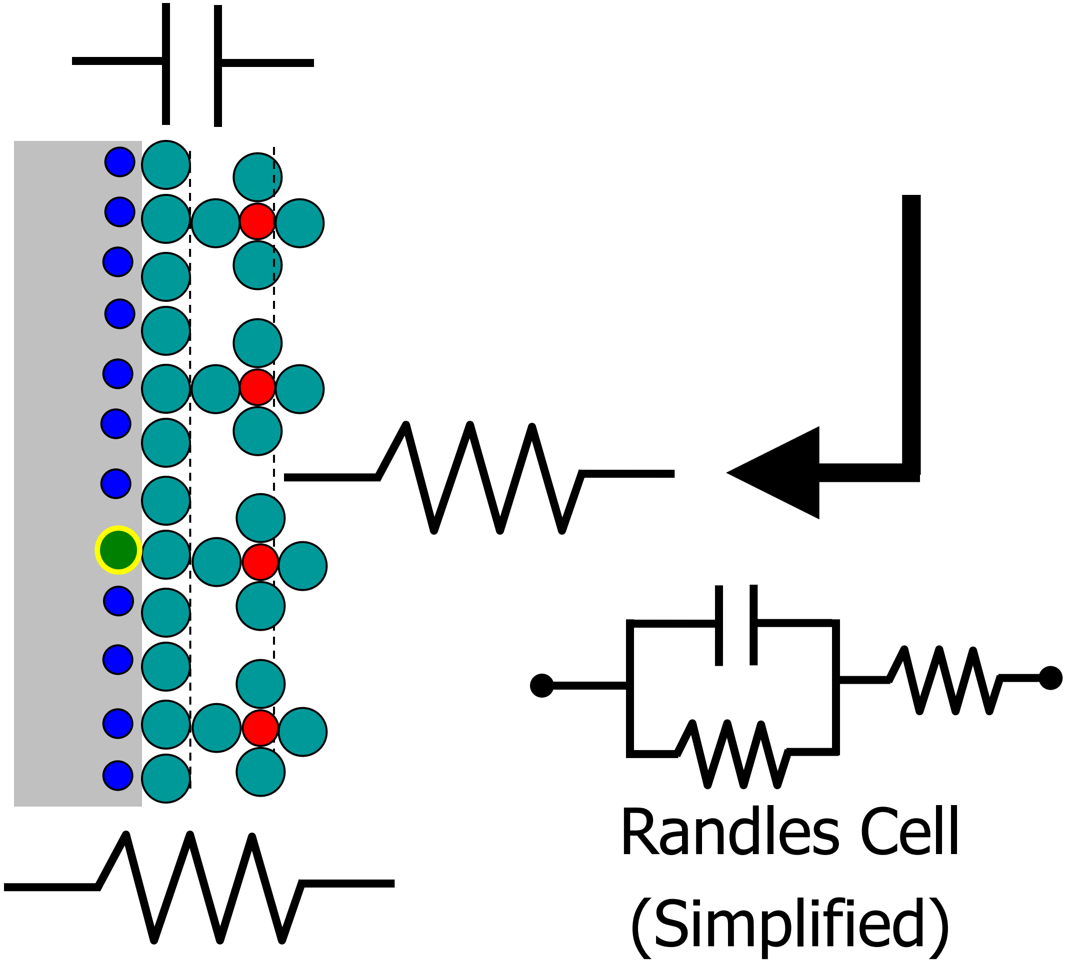


EIS of a Capacitor



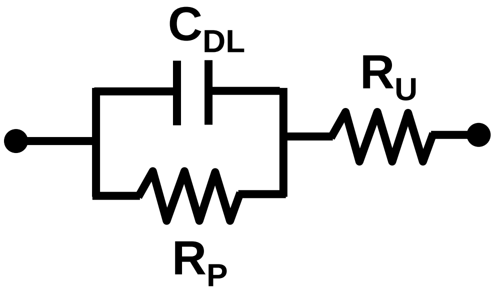
Electrochemistry as a Circuit

- Double Layer Capacitance
- Electron Transfer Resistance
- Uncompensated (electrolyte) Resistance

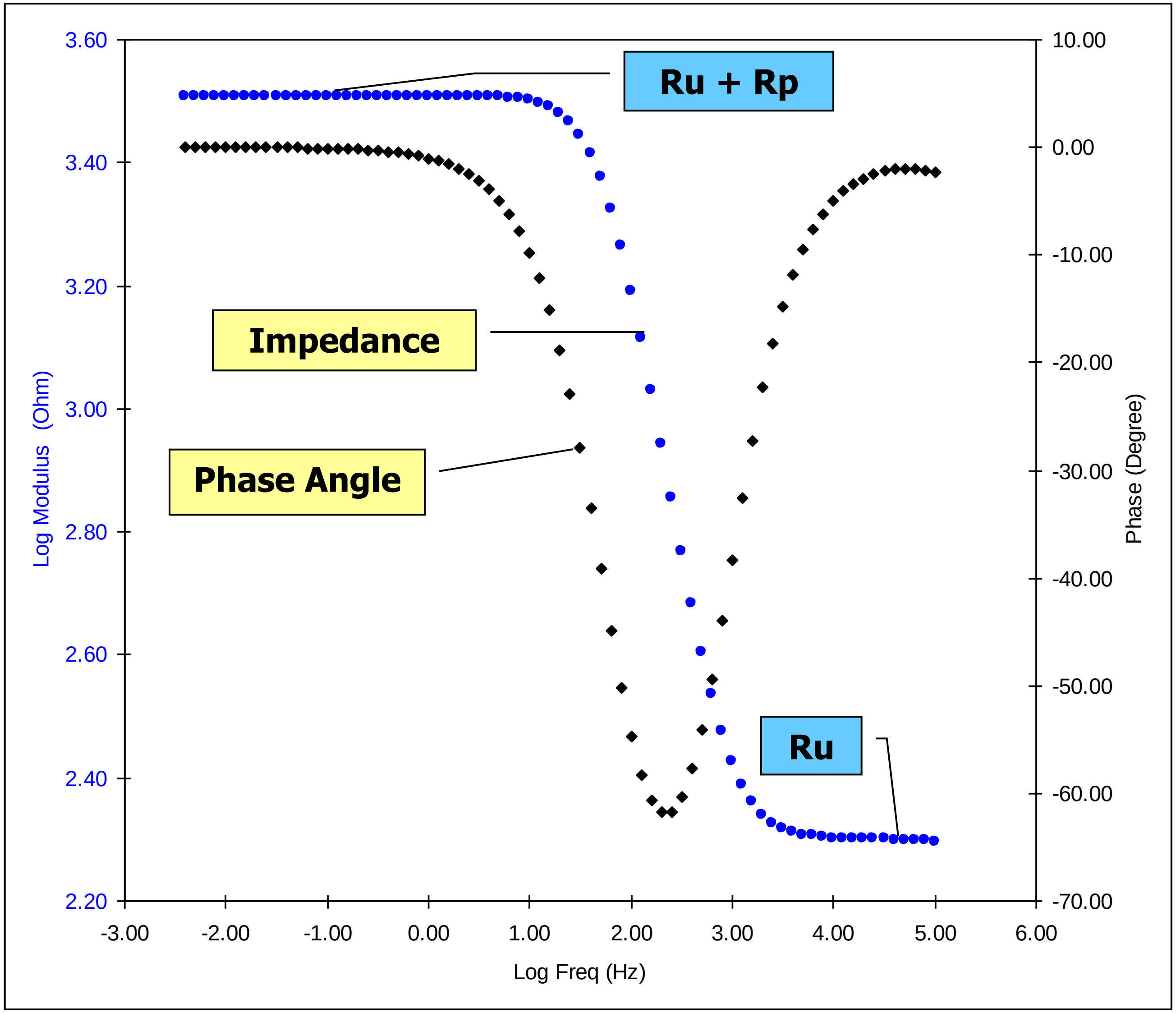


Randles Cell (Simplified)

Bode Plot

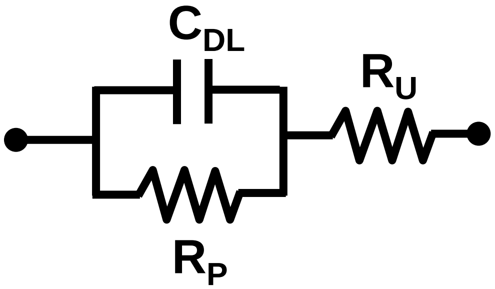


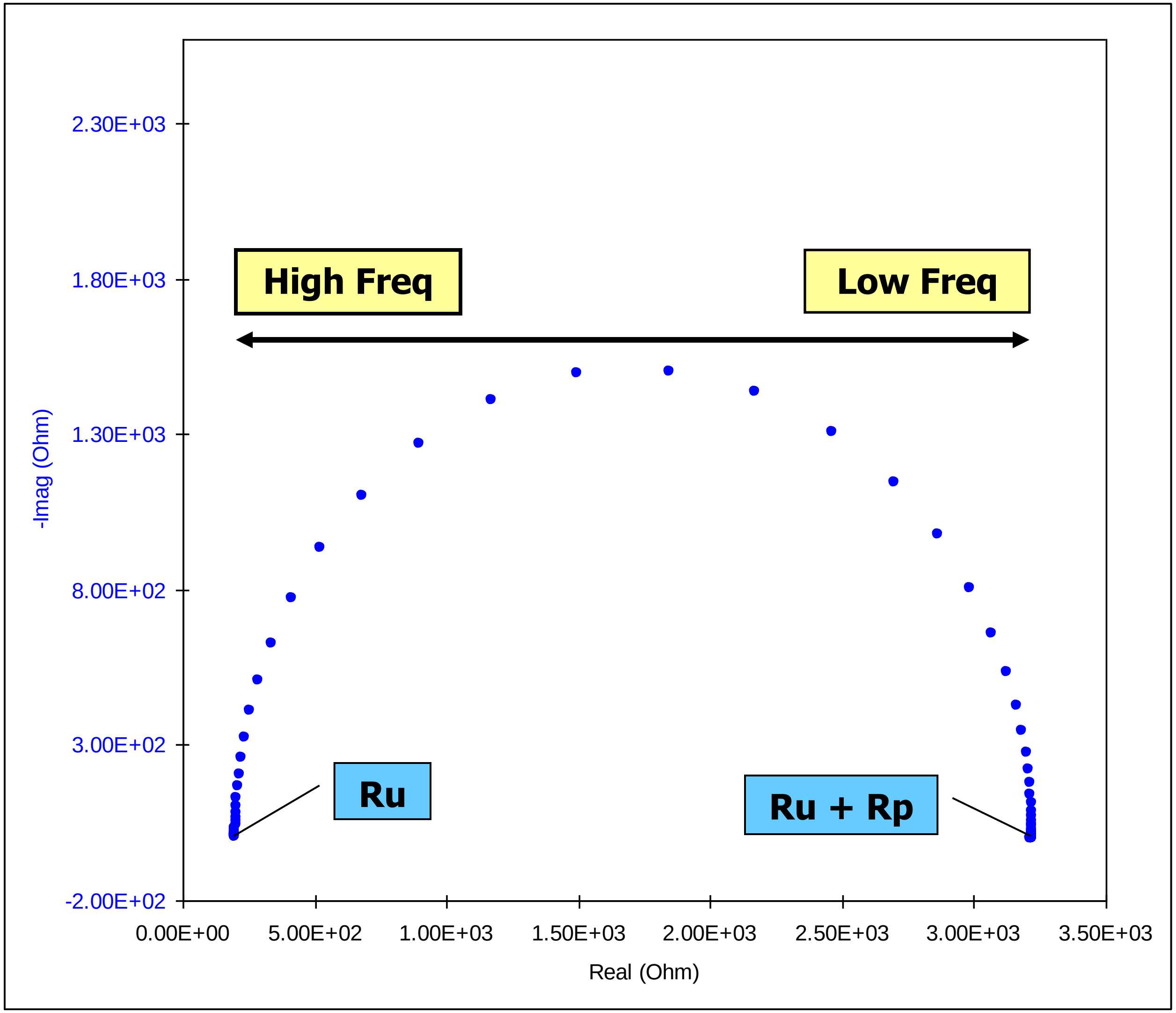
C_{DL}
R_U
R_P



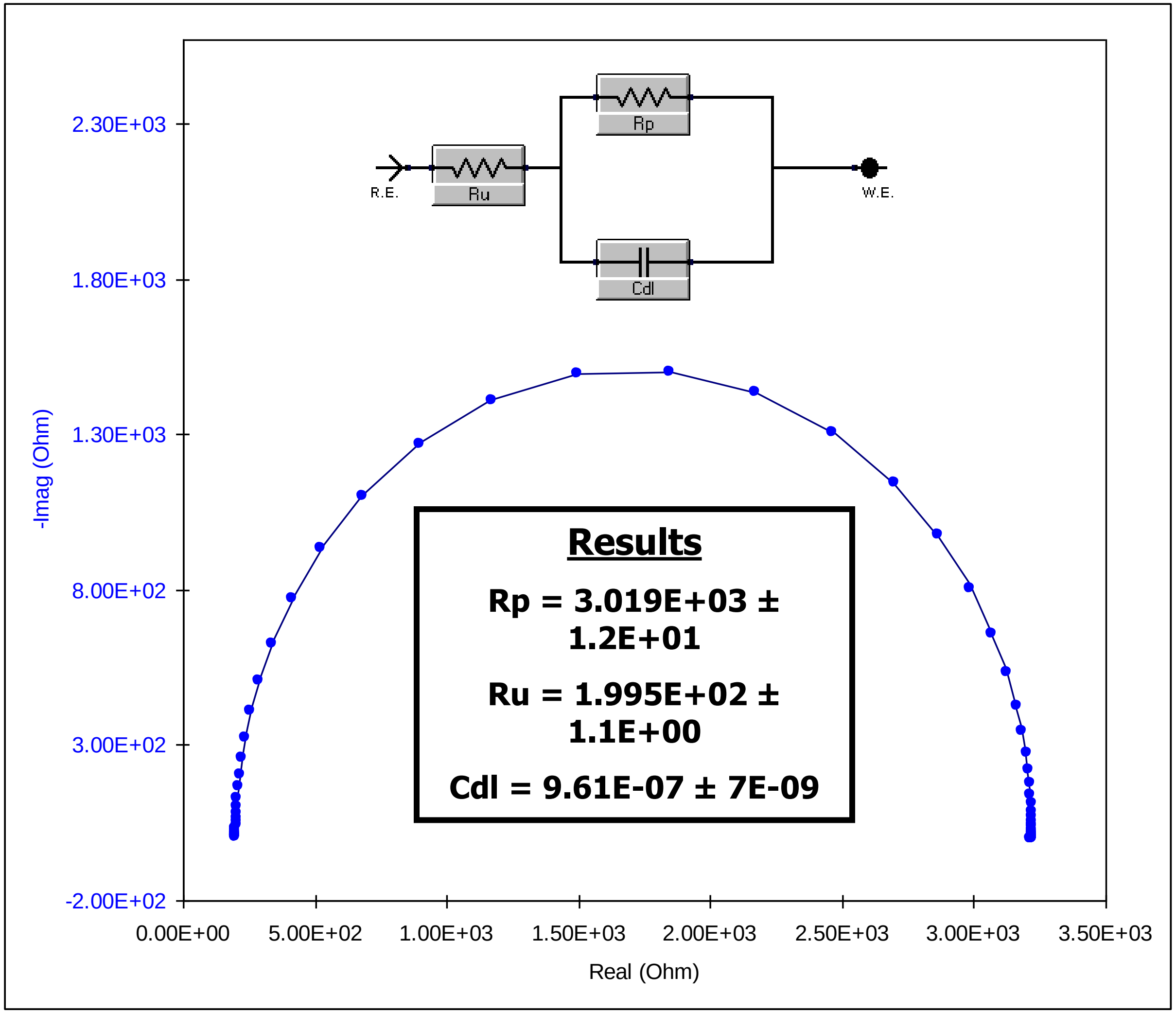
Ru + Rp
Impedance
Phase Angle
Ru
Log Modulus (Ohm)
3.60
3.40
3.20
3.00
2.80
2.60
2.40
2.20
Phase (Degree)
10.00
0.00
-10.00
-20.00
-30.00
-40.00
-50.00
-60.00
-70.00
Log Freq (Hz)
-3.00
-2.00
-1.00
0.00
1.00
2.00
3.00
4.00
5.00
6.00

Complex Plane (Nyquist) Plot





Nyquist Plot with Fit



Results

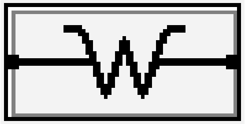
Rp = 3.019E+03 ± 1.2E+01

Ru = 1.995E+02 ± 1.1E+00

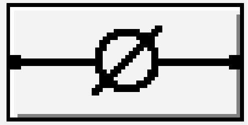
Cdl = 9.61E-07 ± 7E-09

Other Modeling Elements

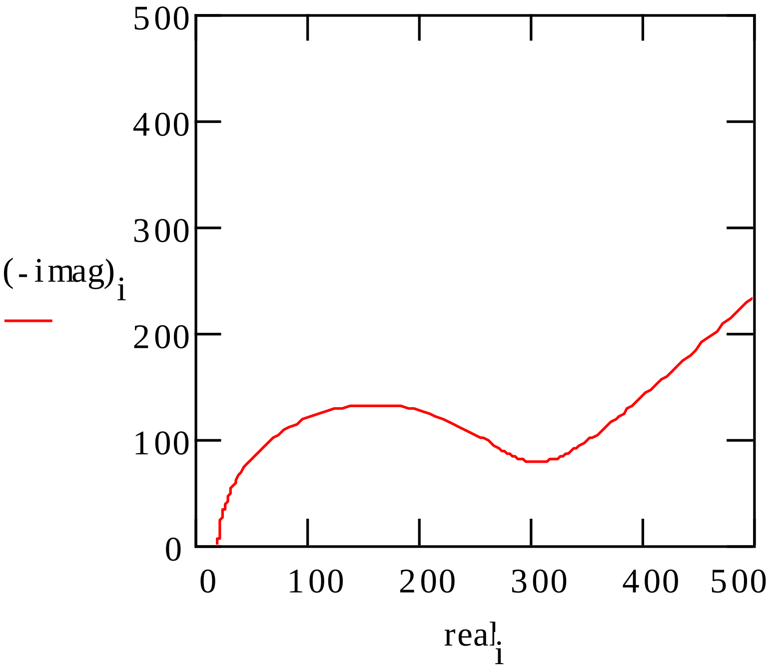
- Warburg Impedance: General impedance which represents a resistance to mass transfer, i.e., diffusion control. A Warburg typically exhibits a 45° phase shift.
  - Open, Bound, Porous Bound

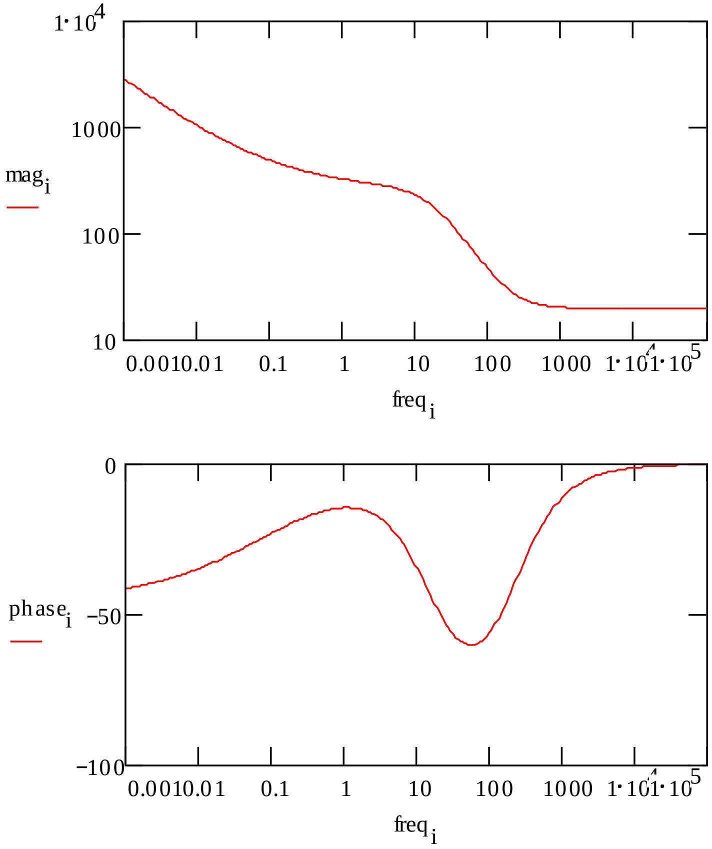


- Constant Phase Element: A very general element used to model “imperfect” capacitors. CPE’s normally exhibit a 80-90° phase shift.



Mass Transfer and Kinetics - Spectra





EIS Modeling

- Complex systems may require complex models.
- Each element in the equivalent circuit should correspond to some specific activity in the electrochemical cell.
- It is not acceptable to simply add elements until a good fit is obtained.
- Use the simplest model that fits the data.

Criteria For Valid EIS

Linear – Stable - Causal

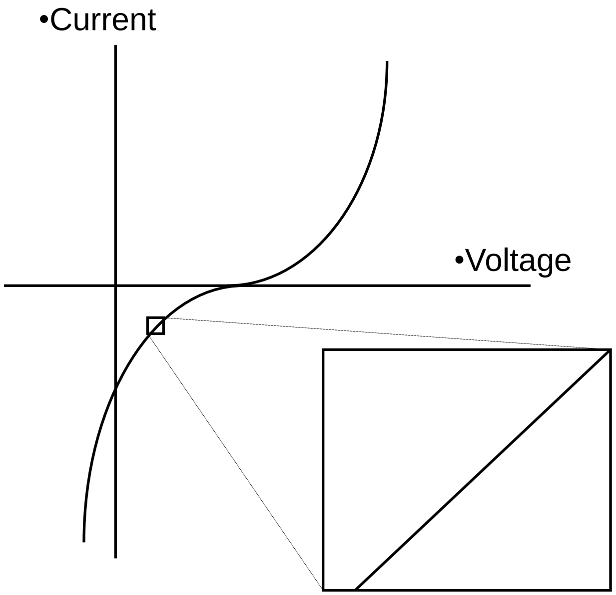
- Linear: The system obeys Ohm's Law, E = iZ. The value of Z is independent of the magnitude of the perturbation. If linear, no harmonics are generated during the experiment.

- Stable: The system does not change with time and returns to its original state after the perturbation is removed.

- Causal: The response of the system is due only to the applied perturbation.

Electrochemistry: A Linear System?

Circuit theory is simplified when the system is “linear”. Z in a linear system is independent of excitation amplitude. The response of a linear system is always at the excitation frequency (no harmonics are generated).



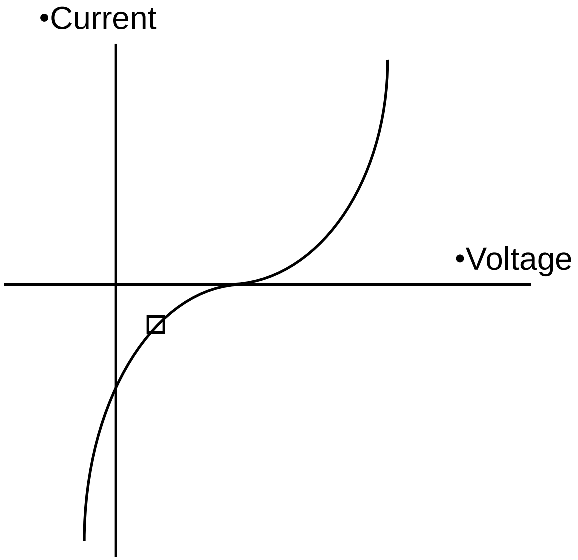
Look at a small enough region of a current versus voltage curve and it becomes linear.

If the excitation is too big, harmonics are generated and EIS modeling does not work.

The non-linear region can be utilized (EFM).

Electrochemistry: A Stable System?

Impedance analysis only works if the system being measured is stable (for the duration of the experiment).



An EIS experiment may take up to several hours to run.

Electrochemical (Corroding) systems may exhibit drift.

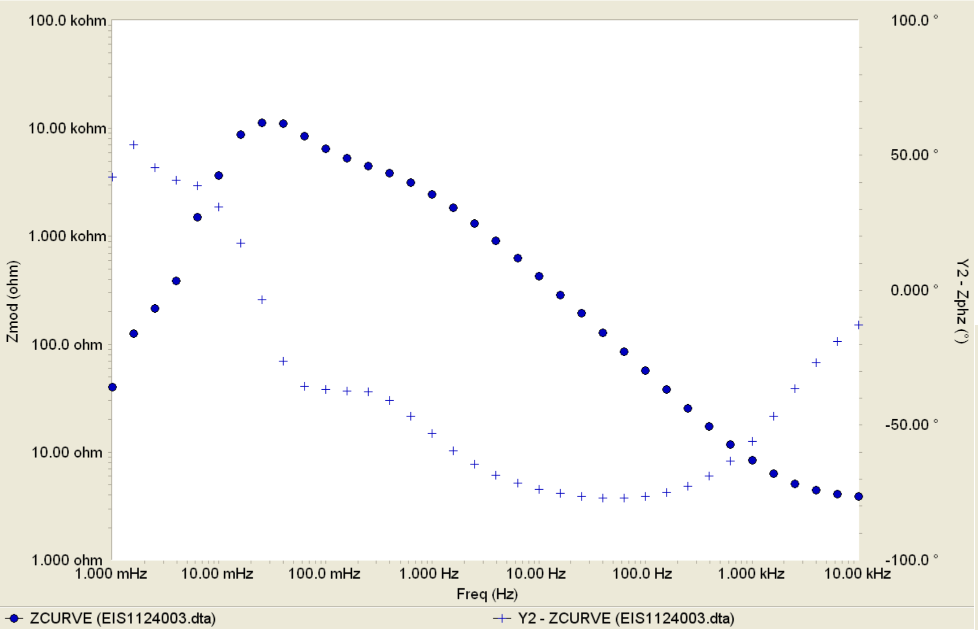
Open circuit potential should be checked at the beginning and end of the experiment.

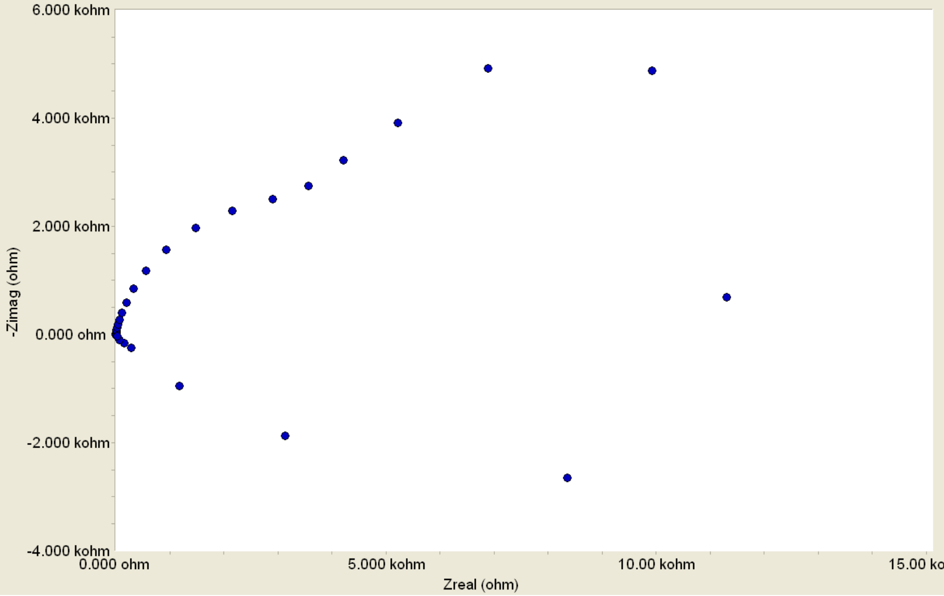
Kramers-Kronig may help.

Kramers-Kronig Transform

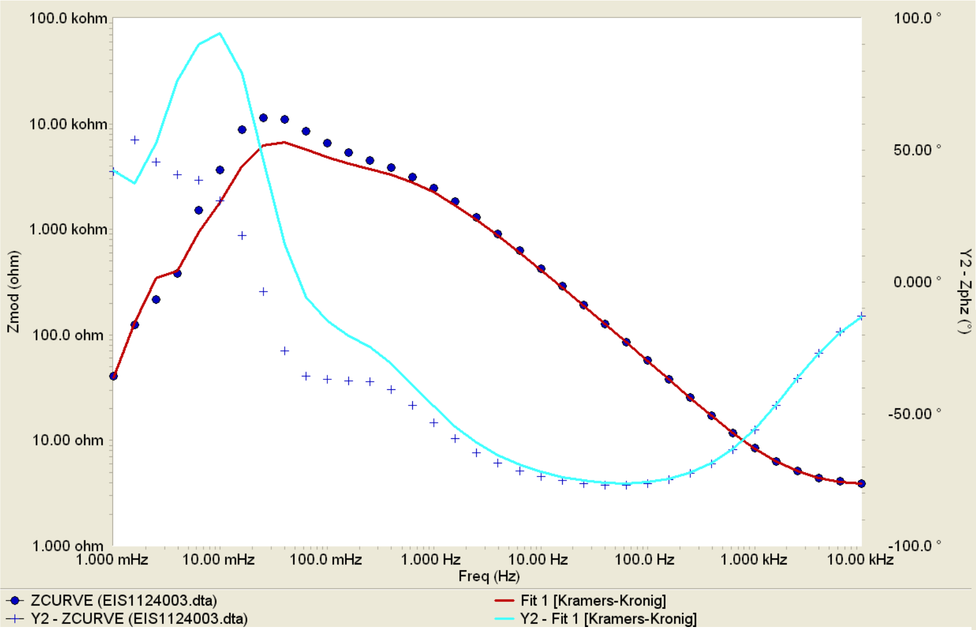
- The K-K Transform states that the phase and magnitude in a real (linear, stable, and causal) system are related.
- Apply the Transform to the EIS data. Calculate the magnitude from the experimental phase. If the calculated magnitudes match the experimental magnitudes, then you can have some confidence in the data. The converse is also true.
- If the values do not match, then the probability is high that your system is not linear, not stable, or not causal.
- The K-K Transform as a validator of the data is not accepted by all of the electrochemical community.

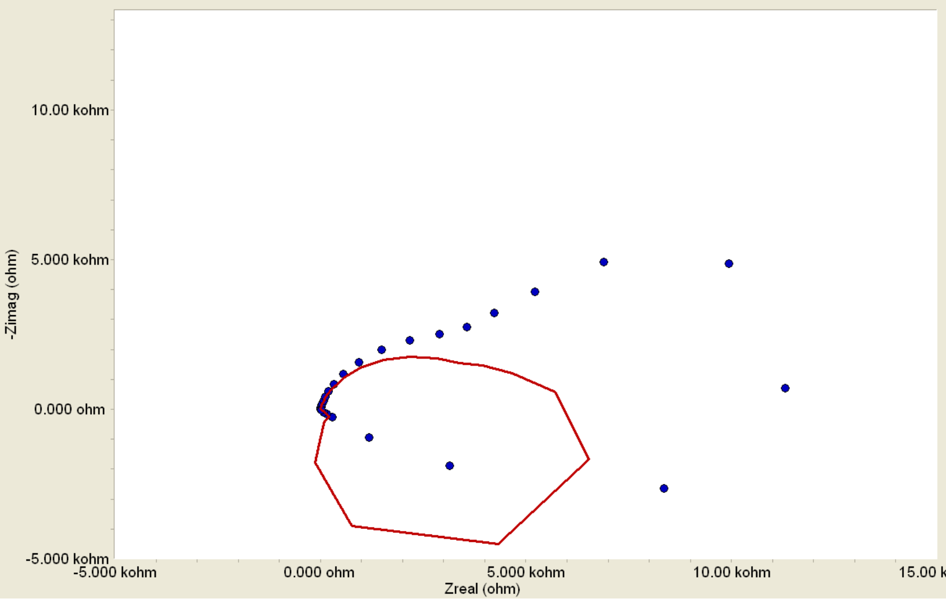
Bad K-K


100.0 kohm
10.00 kohm
1.000 kohm
100.0 ohm
10.00 ohm
1.000 ohm
Zmod (ohm)
100.0 °
50.00 °
0.000 °
-50.00 °
-100.0 °
Y2 - Zphz (°)
1.000 mHz
10.00 mHz
100.0 mHz
1.000 Hz
10.00 Hz
100.0 Hz
1.000 kHz
10.00 kHz
Freq (Hz)
ZCURVE (EIS1124003.dta)
Y2 - ZCURVE (EIS1124003.dta)


6.000 kohm
4.000 kohm
2.000 kohm
0.000 ohm
-2.000 kohm
-4.000 kohm
-Zimag (ohm)
0.000 ohm
5.000 kohm
10.00 kohm
15.00 ko
Zreal (ohm)

Bad K-K


100.0 kohm
10.00 kohm
1.000 kohm
100.0 ohm
10.00 ohm
1.000 ohm
Zmod (ohm)
100.0 °
50.00 °
0.000 °
-50.00 °
-100.0 °
Y2 - Zphz (°)
1.000 mHz
10.00 mHz
100.0 mHz
1.000 Hz
10.00 Hz
100.0 Hz
1.000 kHz
10.00 kHz
Freq (Hz)
ZCURVE (EIS1124003.dta)
Y2 - ZCURVE (EIS1124003.dta)
Fit 1 [Kramers-Kronig]
Y2 - Fit 1 [Kramers-Kronig]


10.00 kohm
5.000 kohm
0.000 ohm
-5.000 kohm
-Zimag (ohm)
-5.000 kohm
0.000 ohm
5.000 kohm
10.00 kohm
15.00 k
Zreal (ohm)

Steps to Doing Analysis

- Look at data
  - Run K-K
  - Determine number of RC loops
  - Figure whether L or W exists
    - If W determine boundary conditions
- Pick/design a model
- Fit it
  - Check to see if CPEs/Transmission Lines needed
- Repeat as necessary
- Extract data

EIS Instrumentation

- Potentiostat/Galvanostat
- Sine wave generator
- Time synchronization (phase locking)
- All-in-ones, Portable & Floating Systems

Things to be aware of…

- Software – Control & Analysis
- Accuracy
- Performance limitations

EIS Take Home

- EIS is a versatile technique
  - Non-destructive
  - High information content
- Running EIS is easy
- EIS modeling analysis is very powerful
  - Simplest working model is best
  - Complex system analysis is possible
  - User expertise can be helpful

References for EIS

- Electrochemical Impedance and Noise, R. Cottis and S. Turgoose, NACE International, 1999. ISBN 1-57590-093-9.

  An excellent tutorial that is highly recommended.
- Electrochemical Techniques in Corrosion Engineering, 1986, NACE International

  Proceedings from a Symposium held in 1986. 36 papers. Covers the basics of the various electrochemical techniques and a wide variety of papers on the application of these techniques. Includes impedance spectroscopy.
- Electrochemical Impedance: Analysis and Interpretation, STP 1188, Edited by Scully, Silverman, and Kendig, ASTM,   ISBN 0-8031-1861-9.

  26 papers covering modeling, corrosion, inhibitors, soil, concrete, and coatings.
- EIS Primer, Gamry Instruments website, www.gamry.com