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Electrochemistry for the Non-Electrochemist

This article discusses nine basic concepts in finite current electrochemistry.

1. Electrodes are Surfaces

The fundamental process in electrochemistry is the transfer of electrons between the electrode surface and molecules in the solution adjacent to the electrode surface; that is, it is a *heterogeneous* process, in contrast to many other measurements (e.g., NMR, UV, etc.) that typically involve homogeneous solutions in three dimensions. Therefore, it is often useful to consider quantities per unit area as well as per total area. One quantity that is particularly important in electrochemical experiments is *current* (i), and the current/per unit area is referred to as *current density* (amps/cm^2). Current density is the more fundamental quantity, since it is independent of the electrode surface area, whereas current is proportional to the electrode surface area.

Since current results from a chemical substance dissolved in the solution adjacent to the electrode surface, it is not surprising that the probability of a molecule or ion reacting at the electrode surface is directly related to the concentration. Therefore, current density is directly proportional to the concentration, provided the electrode reaction does not have unusual features, such as adsorption and dimerization.

(A point of nomenclature: It is redundant to say that "current flows." The word *current* is sufficient. When water or a charge flows, we have current.)

2. Current is Rate

Current is expressed in amperes; that is, coulombs/second. As the word implies, it is a quantitative expression of how fast something is happening. The differential form of Faraday's Law

$$i_f = \frac{dQ}{dt} = nF\frac{dN}{dt}$$

shows that the rate at which electrons are moved across the electrode-solution interface (i.e., the *faradaic* current) is directly related to the rate of the reaction occurring at that interface. Therefore, when we measure the faradaic current, we are also measuring the rate of a chemical reaction. This is a *unique feature of electrochemistry.* Most other techniques do not provide an instantaneous measure of rate.

It should be noted that there are multiple steps involved in an electrochemical reaction, such as the electron transfer reaction, transport of molecules from the bulk solution to the electrode surface, and chemical reactions coupled to the electron transfer reaction. As with any multi-step reaction, the rate of the overall reaction is generally determined by the rate of the slowest step (the rate-determining step), and it is important to know which step is the rate-determining step. In analytical electrochemistry of dissolved species, this step is typically the transport of molecules to the electrode surface. However, there are many instances where this is not the case and where the rate of the heterogeneous electron transfer reaction is of interest (e.g., corrosion electrochemistry).

As discussed above, the electrode surface area and reactant concentration affect the current. Other factors that affect the current include the temperature and the viscosity of the solution, and it is important to ensure that these parameters remain constant so the current is proportional to the reactant concentration. This is particularly important for quantitative analysis.

There are some other sources of current in addition to the faradaic current due to the analyte; these are collectively referred to as the *background* current. They include the electrolysis of impurities, the electrolysis of the electrolyte, the electrolysis of the electrode material, and capacitive (or charging) current. The first three are faradaic currents, whereas the last one is a property of the interface between the electrode and the solution. This interface behaves like an electrical capacitor in that it can store charge, and (to a first approximation) it obeys the equation:

$$Q = CV$$

where Q is the charge stored, C is the capacitance (in farads), and V is the potential difference across the interface. An equation for the capacitive current (i$_c$) can be obtained by differentiating

the above equation:

$$i_c = \frac{dQ}{dt} = C\frac{dV}{dt}$$

The total current will therefore be a summation of currents, including the faradaic currents for the analyte, the electrolyte, and the electrode material, as well as the capacitive current. All but the first of these currents are generally undesirable, and attention must be given to minimizing their effects. In some cases, the background current can be subtracted from the total current to leave the signal of interest. However, in other cases, eliminating the background current is not so easy. In the worst cases, the background and signal currents are combined in a non-linear manner, making it impossible to estimate reliably the background current in the absence of the sample. Fortunately, such cases are rare. The capacitive current can be eliminated by operating the electrode at a fixed potential (i.e., dV/dt = 0). One application where the background current can be essentially eliminated is liquid chromatography with electrochemical detection (LC/EC), since a) the fixed potential eliminates the capacitive current and b) the background faradaic currents can be precisely measured between peaks, and then can be subtracted from the analyte signal. However, it is important to note that the capacitive current will change (even at a fixed potential) if the ionic strength or the solvent composition changes the bulk properties of the mobile phase. Such a change can be a transient disturbance; for example, at the "solvent front" or "void volume" on a liquid chromatogram.

3. Charge is Amount

If we integrate a rate, we obtain an amount. From the integrated form of Faraday's Law,

$$\int_0^t idt = Q = nFN$$

we can see the total amount of electricity passed (Q - the charge, measured in units of coulombs) is proportional to the number of moles N of material processed by the electrochemical reaction.

4. Potential Controls the Position of the Equilibrium Between O and R

The fundamental reaction in electrochemistry is the equilibrium between two species (O and R) that are interconverted by the transfer of an electron:

$$O + e^- \quad R$$
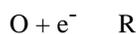
When discussing the effect of the applied potential (E) on this reaction (or *redox couple*), a useful analogy is the acid-base equilibrium:

$$A^- + H^+ \quad HA$$

The position of the acid-base equilibrium is determined by the concentration of protons (i.e., the pH) which can be considered in terms of a *proton pressure* (e.g., increasing the proton pressure [decreasing the pH] moves the equilibrium to the right). When considering the electron transfer equilibrium, we can consider an analogous *electron pressure* which determines the position of the equilibrium between and O and R. The applied potential is a measure of electron pressure in the same way that pH is a measure of proton pressure.

In both cases, there is a unique situation in which the concentration of each form (O and R or A^- and HA) is equal. This occurs at the potential/electron pressure $E^{o'}$ in the former case and in the pH/proton pressure pK_a. These values provide a convenient index of the relative strength of an oxidant/reductant or acid/base. In both cases, the values are medium dependent (i.e., they will differ among

various non-aqueous and aqueous solutions).

When the pH is higher than the pK_a, an acid will favor its protonated form. When the applied potential is more negative than $E^{o'}$, a redox couple will favor the reduced form R.

5. Potential Controls Rate

There are two important parameters that affect the rate of the heterogeneous electron transfer reaction—the intrinsic ability of the molecule to undergo an electron transfer reaction (as reflected in the rate constant k_s) and the applied potential. The rate of electron transfer increases exponentially with the applied potential. Therefore, we can adjust the rate by varying the applied potential; for example, if the intrinsic rate of electron transfer for a given species is slow, it can be accelerated by applying a sufficiently large potential. Relatively more positive potential will speed up oxidations, whereas relatively more negative potentials will speed up reductions. Note that, for example, a "relatively more negative potential" can still be positive; see #6.

6. The Voltammetric Axes

The most common format for presenting electrochemical data is a plot of current vs. potential (i vs. E). However, it is important to note that there are a number of different axis conventions (*F1*). In the classical (or polarographic) convention shown in *F1*, negative potentials are plotted in the positive x direction, and cathodic currents (due to reductions) are positive. In the IUPAC convention, positive potentials are plotted in the positive x direction, and anodic currents (due to oxidations) are positive. (In other conventions, current is plotted along the x axis and/or a logarithmic current scale is used.) It is also vital to realize that the potential values are

quoted *relative to a reference potential,* the value of which is defined by the reference electrode; that is, the zero on the x-axis is quite arbitrary. Therefore, there is no significance in the absolute values. Different values of $E^{o'}$ for a given species under identical conditions are measured for different reference electrodes. It should also be noted that there is no correlation between positive and negative potentials and oxidations and reductions; that is, reductions can occur at positive potentials and oxidations can occur at negative potentials.

7. Current, Potential and Time

There are only two basic formats for displaying experimental data: current vs. potential (i vs. E - voltammetry), and current vs. time (i vs. t - chronoamperometry). (Charge plots are obtained by integrating current plots.) Since potential is often related to time by experimental design, i vs. E experiments also contain some features of the i vs. t experiments.

For historical reasons, more electroanalytical techniques have been developed than are really needed, and the large number of techniques can intimidate the novice. However, it should be noted that the vast majority of these are simple combinations of voltammetry and chronoamperometry. The key experimental variables in a given experiment are E, i, and t. Only one of E and i can be varied independently, and t takes care of itself. The inverse relationship between time and frequency often plays a role (e.g., high frequency experiments can be used to look at fast reactions), although data from frequency domain experiments can be more difficult to interpret.

8. Light

The electrical measures described above are not all inclusive to electrochemical experiments. For example, electrode reactions can result in emission of light (electrochemiluminescence). Likewise, light can also influence the rates and mechanisms of electrochemical reactions (photoelectrochemistry). Phenomena of this sort have been known since the 19th Century. Finally, light is often used to study electrochemical reaction mechanisms.

This falls under the general terminology of spectroelectrochemistry. It ranges from the UV to the IR and includes transmission as well as reflection (off the electrode) methods. Raman spectroscopy of material adsorbed on electrodes is used as well as a variety of high vacuum techniques. The latter require removal of the electrode from solution (and are well beyond the scope of this primer).

9. The Sound of One Hand Clapping

While it is obvious once given some thought, we should not forget that electrochemistry with a single electrode is like the sound of one hand clapping. In other words, it is largely meaningless. One needs a minimum of two electrodes to light a bulb or to do electrochemistry. If a reduction (oxidation) is occurring at the working electrode, then a second electrode must be present and an oxidation (reduction) must be occurring there. The two electrodes are needed to "complete the circuit" (using the language of high school physics). Yes, you can have more than two electrodes. A reference electrode is often the third electrode, but it is also possible to have any number of working electrodes, all operating at different applied potentials in an array. Needless to say, this is not common.

Conclusion

It has been our intent in this article to outline nine of the most basic concepts of electrochemistry, since we have found that these concepts must be thoroughly mastered before more advanced topics can be understood. In our experience, students often become confused about various issues because these very fundamental ideas are not second nature to them.

F1.
The classical (or polarographic) convention for plotting voltammetry data.

ELECTRODE BECOMES STONGER REDUCTANT

ELECTRODE BECOMES STONGER OXIDANT

POTENTIAL vs REFERENCE ELECTRODE [electron pressure]