

Electrochemistry for the Nonelectrochemist

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Seven Lessons on Finite Current Electrochemistry

1 Electrodes are Surfaces

Electrochemistry is a surface science. Therefore the amount of anything that happens is best treated per unit area as well as per total area. You need to get used to the fact that we are dealing with a surface in contrast to many chemical measurements which *most often* involve homogeneous (uniform) solutions in three dimensions (e.g. NMR, UV, F, conductance). We normally measure *current* in our experiments. Therefore we should recognize that *current density* (amps/cm²) is the more fundamental thing. Without changing anything else, the current encountered at a large electrode will be higher than at small electrodes in direct proportion to the relative surface areas.

When the current results from a chemical substance dissolved in the solution adjacent to an electrode, it is not surprising that the probability of a molecule or ion reacting at the surface is directly related to concentration. Thus current density is directly related to concentration unless the electrode reaction has unusual features (e.g. involves adsorption or dimerization).

A point of nomenclature: It's not useful to say that "current flows." The word current by itself is enough. When water flows or charge flows we have current.

2 Current is Rate

Current is expressed in amperes (coulombs/sec). As the word implies, it is a quantitative expression of how fast something is happening (e.g. water in a garden hose). The differential form of Faraday's Law

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

tells us that the rate at which electricity is moved across the electrode-solution interface is directly related to how fast the chemistry is accomplished at that interface. Thus, when we determine or plot *current*, we are also determining or plotting the rate of a chemical reaction. This is a *unique feature of electrochemistry*. Most other techniques do not give an instantaneous readout of rate.

It is important to understand how the rate is controlled in a process (such as electrochemistry) which involves many steps. How fast does the reactant get to the site of reaction? Is it already there? How fast does the electron transfer itself occur? How fast do reactions coupled to the surface electron transfer occur? In *analytical* electrochemistry of dissolved substances, *usually* the slowest step is transfer of reactant to the surface. There are many cases where this is *not* true and where the rate of the fundamental surface reaction is of interest (e.g. corrosion electrochemistry).

Some things which influence the current signal:

- electrode surface area
- reactant concentration
- temperature
- viscosity
- velocity of solution
- applied potential

We often keep all of these things constant in which case current is proportional to concentration. This is how electrochemistry is used in quantitative analysis. For example, in LCEC the detector can respond linearly to concentration changes over 4-5 orders of magnitude.

Sources of *background current*:
electrolysis of impurities
electrolysis of solvent(s)
electrolysis of the electrode surface material
capacitive currents

These current sources are generally undesirable and attention must be given to minimizing their impact. In some cases, they can safely be subtracted from the total current to leave the signal of interest. In other cases, this is not so easy. In the worst cases, the background and signal currents are combined in a nonlinear fashion making it impossible to reliably estimate the background current in the absence of the sample. Fortunately such cases are rare.

The electrode-solution interface behaves like an electrical capacitor (it can store charge) and to a first approximation obeys the following equation:

$$Q = CV$$

where Q is charge stored, C is capacitance in farads, and V is potential difference.

The differential form of this equation is:

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

where i_c is the capacitance "charging" current.

The total current will therefore be a summation of currents including faradaic currents for the sample, impurities, the electrode material and the medium, as well as charging current.

$$i_{\text{total}} = i_r(\text{sample}) + i(\text{background})$$

$$i_{\text{total}} = i_r(\text{sample}) + i_r(\text{impurities}) + i_r(\text{electrode material}) + i_r(\text{bulk medium}) + i_c$$

All but the first are undesirable and their impact should be minimized. Often the three undesirable faradaic currents can be easily subtracted out and the charging current made negligible by operating the electrode at a fixed potential, $dV/dt = 0$, in a moving solution. This is why LCEC has gained popularity so rapidly. We bring sample to the electrode in the form of a chromatographic peak. Between peaks we have the opportunity to precisely monitor the total background current and therefore can remove it from the signal of interest.

3 Charge is Amount

If we integrate a rate, we get an amount. Look at the integrated form of Faraday's Law.

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

The amount of electricity is called *charge* and the unit of charge is the coulomb. Of course, we all recognize via Faraday's Law that the amount of chemistry done (moles) is proportional to the charge.

$$\text{COULOMBS} = \int_0^t (\text{COULOMBS/s})dt$$

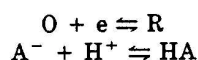
4 Potential controls position of equilibrium between O and R.

Potential is a measure of *electron pressure* just as pH is a measure of *proton pressure*.

more negative potential = higher electron pressure

lower pH = higher proton pressure

Redox reactions respond to electron pressure just as acid base reactions respond to proton pressure. Redox couples and acid base couples have much in common.



In both cases, there is a unique situation in which the concentration of each form (O vs R or A^- vs HA) becomes equal. The pressure at which this occurs is in one case $E^{\circ'}$ and in the other case pK_a . These provide a convenient index of the relative strength of an oxidant/reductant or acid/base. In both cases the numbers are medium dependent (i.e. they will differ between various nonaqueous and aqueous solutions).

When proton pressure is higher than the pK_a , an acid will favor its protonated form (HA). When the electron pressure is higher than $E^{\circ'}$, a redox couple will favor the reduced form (R).

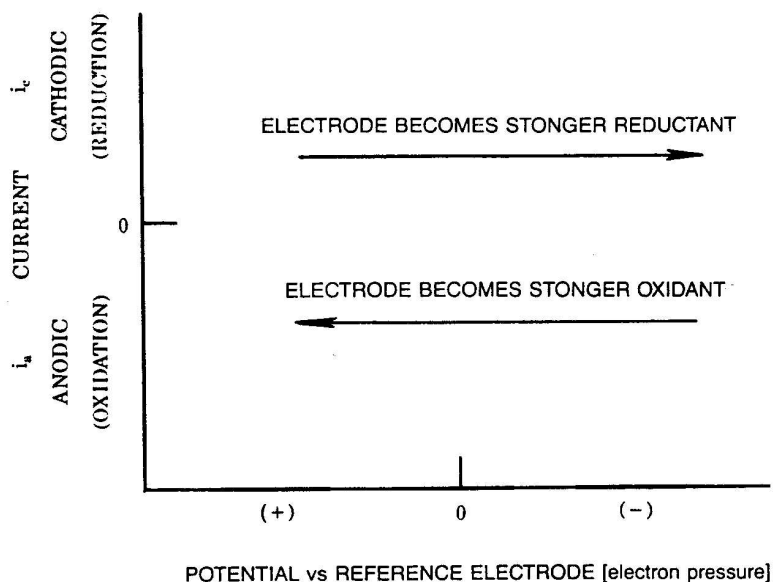
5 Potential Controls Rate

In electrochemistry the potential is very influential on the rate of the reaction. In principle, all electrode reactions occur to some degree at all potentials, but in some cases the rate is too slow to be interesting. The electron transfer rate increases exponentially with applied potential. This is a very powerful tool. It is a unique feature of electrochemistry. We can

tune the rate by changing the applied potential. More positive potentials will speed up all oxidations. More negative potentials will speed up all reductions.

6 The Voltammetric Axes

Current vs. Potential (i vs E) provides the most common format for presentation of electrochemical data. As will be shown in the accompanying article, voltammetric data can be reduced to a convenient one dimensional form when comparing different substances. Voltammetry information is frequently misinterpreted because it is not clear to novices what is being plotted. I caution beginners not to speculate on the chemical interpretation of a voltammogram until the two axes are clearly understood. The role of the reference electrode has been described in previous issues of "Current Separations." Suffice it to say here that the zero on the x-axis is quite arbitrary. The important thing is the relative position of different observations along the potential axis and not the sign (+ or -).



7 *Current, Potential, and Time*

There are only *two* basic presentations of experimental results: current vs E (voltammetry) and current vs t (chronoamperometry). Since E is often related to t by experimental design, the i vs E experiments also contain some features of the i vs t experiments. [Q vs E or Q vs t experiments are simple integral versions of the i vs E and i vs t experiments respectively.]

The large number of electroanalytical techniques can discourage the novice. Don't be alarmed. The vast majority of them are simple combinations of voltammetry and chronoamperometry. We only have E, i, and t to play with. We change either E *or* i as independent variables (we can't control both at the same time) and t takes care of itself. The inverse relationship between time and frequency often plays a role. High frequency experiments relate to short time experiments. The use of both fre-

quency and time domains increases the number of techniques we invent, but not the information about the chemical system under study. The difficulty always comes in data interpretation! For historical reasons, more electrochemical techniques have been developed than are really needed.

It is my contention that you must understand these seven basic areas in order to move on to more advanced topics. In my experience, students often become confused about various issues because these very fundamental ideas are not second nature to them. Another brief article with the same intention as this one was written several years ago by Professor Larry R. Faulkner. I recommend "Understanding Electrochemistry: Some Distinctive Concepts": J. Chem. Educ. 60 (1983) 262-264. Larry takes a slightly different point of view which could help some people cement these critical concepts deep in their central nervous systems.
