

Controlled Current Techniques

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The *epsilon*TM instruments can perform both controlled potential (potentiostatic) and controlled current (galvanostatic) experiments. Although potentiostatic experiments are much more common, there are some applications for which a galvanostat is advantageous.

The galvanostat uses a three electrode configuration, in which a current is applied between the auxiliary and working electrodes and the potential of the working electrode (measured with respect to the reference electrode) is monitored. The basis of controlled current experiments is that a redox (electron transfer) re-

action must occur at the surface of the working electrode in order to support the applied current. For example, if ferricyanide is present in the solution, then a reducing current will lead to the reduction of ferricyanide to ferrocyanide at the working electrode (note that a balancing oxidation must also occur at the auxiliary electrode). Common applications of the galvanostat include constant current stripping potentiometry and constant current electrolysis (including applications where a constant rate of electrolysis is important, such as electrodeposition and battery studies). One advantage of all constant current techniques is that the ohmic drop due to solution resistance is also constant, as it is equal to the product of the current and the solution resistance. The ohmic distortion can therefore be simply corrected by a constant potential offset. In contrast, in potentiostatic experiments (e.g., cyclic voltammetry), the current, and

hence the ohmic drop, varies with potential, and correction is more complicated.

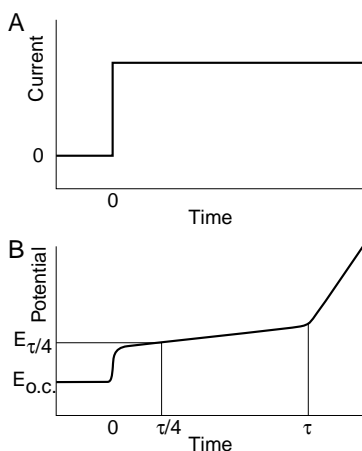
Chronopotentiometry

Chronopotentiometry (CP) is the most basic constant current experiment. In CP, a current step is applied across an electrochemical cell (without stirring). The current excitation signal and potential response are shown as a function of time in **F1**. The nature of the potential response can be rationalized by considering the concentration profiles of the redox species as a function of time.

Let us consider the electron transfer reaction $O + e = R$. Before the current step, the concentration of O at the electrode surface is the same as in the bulk solution (e.g., 5 mM) (**F2**). The initial potential is the rest potential or the open circuit potential ($E_{o.c.}$). Once the (reducing) current step has been applied, O is reduced to R at the electrode surface in order to support the applied current, and the concentration of O at the electrode surface therefore decreases. This sets up a concentration gradient for O between the bulk solution and the electrode surface, and molecules of O diffuse down this concentration gradient to the electrode surface. The potential is close to the redox potential for $O + e = R$, and its precise value depends upon the Nernst equation:

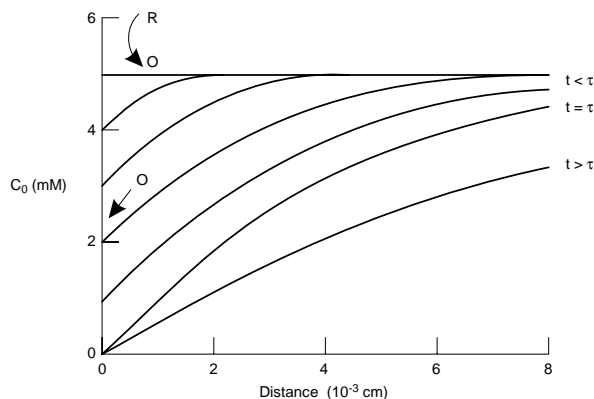
F1

Current excitation (A) and potential response (B) for CP.



F2

Concentration-distance profiles during the reduction of O to R by a current step.



$$E = E^{o'} + \frac{0.059}{n} \log \frac{C_O^s}{C_R^s}$$

where C_O^s and C_R^s are the surface concentrations of O and R, respectively. These concentrations vary with time, so the potential also varies with time, which is reflected in the slope of the potential vs. time plot at this stage. Once the concentration of O at the electrode surface is zero, the applied current can no longer be supported by this electron transfer reaction, so the potential changes to the redox potential of another electron transfer reaction. If no other analyte has been added to the solution, the second electron transfer reaction will involve reduction of the electrolyte; that is, there is a large change in the potential.

The time required for the concentration of O at the electrode surface to reach zero is characterized by time τ . The magnitude of τ depends upon the applied current; for example, an increase in the applied current i leads to a decrease in τ . The quantitative relationship between i and t is defined by the Sand equation:

$$i\tau^{1/2} = \frac{nFAC\pi^{1/2}D^{1/2}}{2}$$

where A is the electrode surface area, C is the bulk concentration of the analyte, and D is its diffusion coefficient. The parameter $i\tau^{1/2}$ is a useful diagnostic parameter for CP, as it is constant for redox processes that are not complicated by coupled chemical reactions or adsorption. The characteristic variations of $i\tau^{1/2}$ for more

complicated reactions are discussed below.

One ubiquitous parameter that causes deviations from the ideal behavior represented by the Sand equation is the charging current. Charging current is related to changes in potential, and hence is present throughout all constant current experiments. In addition, since the charging current depends upon the rate of change of potential, the magnitude of the charging current (and hence the fraction of the applied current that is available for the faradaic processes) varies during the experiment.

One advantage of CP is that the Sand equation is appropriate for both planar and spherical electrodes; that is, τ is independent of the form of diffusion to the electrode surface. This should be contrasted with the Cottrell equation, which represents the diffusion-controlled current for a planar electrode at a constant potential. Changing the diffusion from planar to spherical requires a correction term proportional to $1/r$ to be added to the Cottrell equation. Therefore, the diffusion-controlled current can be complicated if the experiment is run under conditions in which both spherical and planar diffusion are significant (e.g., long time and/or small electrodes).

The Sand equation and the Cottrell equation are also related in that they have been used to calculate diffusion coefficients. However, in the Sand equation, the measured parameter (τ) varies linearly with D , whereas the measured parameter (i)

for the Cottrell equation varies with the $D^{1/2}$. Therefore, better precision can be achieved by using CP and the Sand equation.

It is possible to apply more than one current step in a given experiment. Two-step experiments can be useful in characterizing electrode reactions in which the electron transfer reaction is followed by a chemical reaction. Multiple current step experiments are widely used for charging/discharging study of batteries and other energy sources.

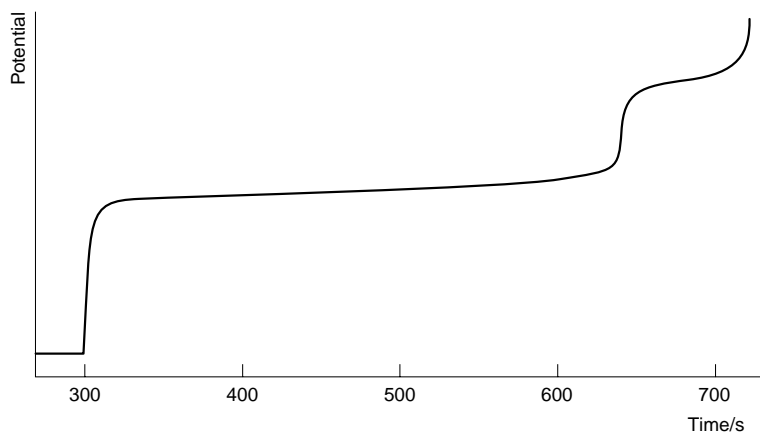
A related technique is the measurement of the open-circuit potential as a function of time (this can be considered as equivalent to a CP measurement with an applied current of zero). This is widely used for the study of corroding systems and for potentiometric stripping analysis.

Constant Current Stripping Potentiometry and Potentiometric Stripping Analysis

These stripping experiments can be used as alternatives to stripping voltammetric techniques for trace analysis (i.e., measurement of ppb concentrations of e.g., metal ions, DNA). As with stripping voltammetric experiments, the first stage involves deposition or preconcentration of metal ions from the solution onto the electrode surface. Once this step has been completed, the metal ions are oxidized (stripped) from the electrode surface either by the addition of a chemical oxidizing agent (potentiometric stripping analysis, PSA) or the application of an oxidizing current (constant current stripping potentiometry, CCSP). The potential is monitored as a function of time. It should be noted that the potential response consists of a series of potential steps, which must be further processed in order to generate the more commonly displayed peak-shaped response. A typical potential response is shown in **F3**.

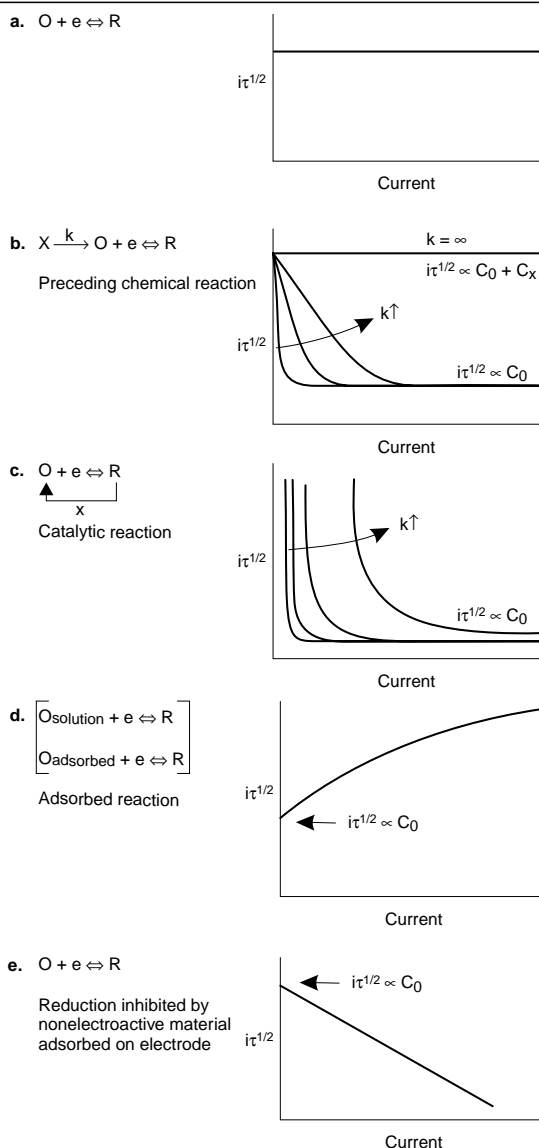
F3

Typical potential response for a PSA or CCSP experiment.



F4

Variation of $i\tau^{1/2}$ with i for various reactions.



Characterization of Electrode Reactions Using Chronopotentiometry

The characterization of electrode reactions using chronopotentiometry involves the study of the variation of $i\tau^{1/2}$ with i (**F4**). If there are no coupled chemical reactions, $i\tau^{1/2}$ does not vary with i (**F4a**). However, for some electrode reactions that involve coupled chemical reactions (e.g., CE and catalytic reactions), $i\tau^{1/2}$ varies with i in a characteristic manner (**F4 b** and **c**). For example, $i\tau^{1/2}$ for a CE reaction depends upon the relative values of i and the rate of the chemical reaction, k . If i is large enough, the chemical reaction cannot have any effect and

$i\tau^{1/2}$ is determined by the equilibrium concentration of O . If i is decreased to a value at which the chemical reaction can have an effect, then $i\tau^{1/2}$ will increase (since O is generated by the chemical reaction), and will continue to increase as i decreases. The value of i at which the chemical reaction will start to have an effect depends on the magnitude of k ; for example, it is smaller for smaller k . The zero current limit of $i\tau^{1/2}$ is related to the sum of concentrations of O and X , since all X is converted to O . The slope of the $i\tau^{1/2}$ vs. current plot at low i is related to k .

The potential responses for reactions that involve adsorption of material to the electrode surface depend upon whether or not the adsorbed

material is electroactive. If it is not electroactive, then $i\tau^{1/2}$ decreases with increasing i (**F4e**), since less time is allowed at higher values i for the electroactive material to penetrate the adsorbed layer. If it is electroactive, then $i\tau^{1/2}$ increases with i (**F4d**). This variation is related to the fact that the Sand equation only considers the contribution to the total current of molecules that diffuse from the bulk solution, and the relative size of this contribution varies with τ .

Constant Current Electrolysis

Constant current electrolysis is based on Faraday's law, which relates the total charge passed in an experiment (Q) to the number of molecules electrolyzed (N) and the number of electrons involved in the electron transfer reaction (n):

$$Q = nFN$$

where F is Faraday's constant. The applications of constant current electrolysis can be analytical (measurement of n) or synthetic. Common synthetic applications include the growth of conducting polymers on electrode surfaces or coulometric titrations (e.g., for the Karl-Fischer determination of water), which involves the *in situ* generation of the titrant by electrolysis. Other applications include the electrodeposition of metals and battery/fuel cell studies (e.g., charging and discharging at constant current).

The aim of this article has been to show that, although constant current techniques are not as widely used as controlled potential techniques, there are some applications for which constant current techniques are advantageous. The inclusion of galvanostatic capabilities on epsilon instruments increases their versatility compared to instruments that have only potentiostatic capabilities.

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