

# Practical Problems in Voltammetry

## 2. Electrode Capacitance

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The charging current required to change the electrode potential can have a significant effect on the current response for linear sweep techniques. This article reviews this problem and discusses the methods used to minimize the effects.

Cyclic voltammetry is one of the most widely used voltammetric techniques. It can provide information on the number and stability of different oxidation states, and can be used for qualitative investigation of the rates of heterogeneous and homogeneous reactions. However, there are limitations to this technique, and some of these are discussed in this series of articles. In the first article, the influence of solution resistance was described (1).

The fundamental process in electrochemistry is the heterogeneous electron exchange between the surface of the electrode and the analyte molecules in the region adjacent to the surface. Various models have been proposed for this interfacial region (2). In the simplest model, the charge on the electrode is balanced by a layer of solvated ions (of opposite charge) held at the electrode surface by Coulombic attraction (more sophisticated models show that Coulombic effects extend beyond a single layer and that the disruptive effect of thermal motion must also be considered). This arrangement is often referred to as the electric double layer (F1).

In this simple model, the interfacial region consists of two layers of charge separated by a dielectric material (the amount of charge on the layers is +Q and -Q). It is therefore equivalent to a capacitor, and its behavior can be approximated by the equation

$$Q = CE$$

where:

E = potential difference between the layers

Q = charge

C = capacitance of the dielectric material

In this case, the capacitance of the interfacial region is often referred to as the double layer capacitance  $C_{dl}$ .

Although the above relationship is only exact for a simple physical capacitor in which C and E are independent, it does show one important property of the interfacial region: a change in the potential across the interfacial region requires that the charge on the electrode also be changed. A change in charge can only be achieved by a flow of electrons, i.e., a current. Therefore, in any voltammetry experiment, a change in the applied potential is accompanied by a current (often called the background or charging current).

The relationship between the current and the rate of change of the potential is shown by differentiating the above equation

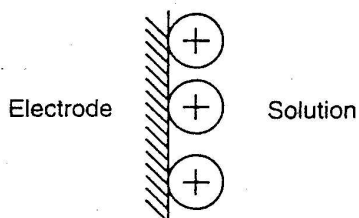
$$i = dQ/dt = CdE/dt$$

If the potential across a pure capacitor is changed instantly, then the charging current is a delta function (F2). However, the charging current of an electrode is affected by the solution resistance  $R_u$ , i.e., the charging current decay is exponentially dependent on the product  $R_u C_{dl}$  (F3b), and approaches zero at a time ca.  $5R_u C_{dl}$  after the potential change. A consequence of this is that the potential change does not occur instantaneously, but also depends on  $R_u C_{dl}$  (F3c) (this product is characteristic of a system, and is often referred to as the cell time constant).

The charging current is particularly important for cyclic voltammetry. In this technique, the poten-

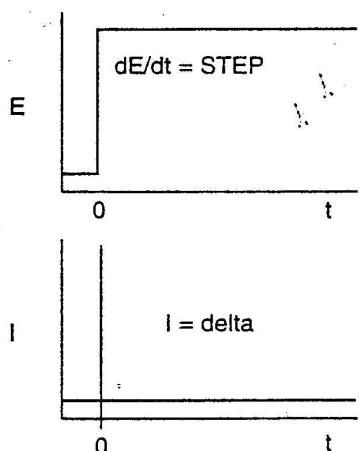
F1

Simple double layer model of the interfacial region



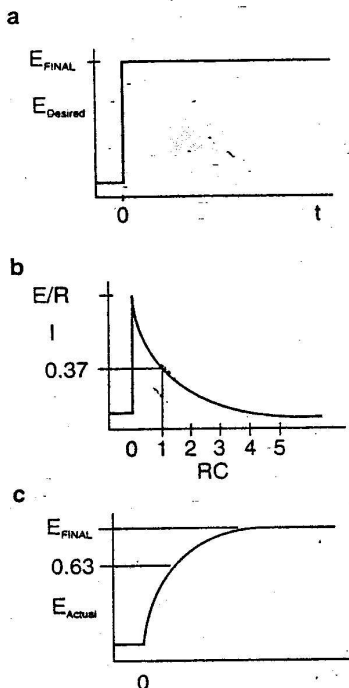
F2

Current response of a capacitor to a potential step



**F3**

Current response of a series capacitor and resistor combination to a potential step



tial is constantly varying with time, so there is a charging current  $i_c$  throughout the experiment of magnitude  $vC_{dl}$  (where  $v$  is the scan rate, i.e.,  $dE/dt$ ).  $i_c$  is not constant throughout the experiment since the value of  $C$  varies with the applied potential. The presence of  $i_c$  places limitations on this technique:

- a) the detection limit is about  $10^{-5}$  M (below this concentration, the Faradaic current ( $i_f$ ) is less than the charging current).
- b) the peak current for a reversible process varies with  $v^{1/2}$ . Therefore, the  $i_f/i_c$  ratio decreases with increasing scan rate, and this can place an upper limit on the scan rate that can be used (F4) (it should be noted that the scan rate is also limited by the time constant, since this controls how rapidly a potential change can occur).

rent measured at a time  $5R_uC_{dl}$  after the potential step is the Faradaic current, as the charging current has decayed to a negligible level (F5).

Pulse techniques are a combination of potential steps with a linearly varying potential function. These are the commonly used techniques:

a) Staircase voltammetry

The staircase potential consists of a series of small amplitude steps (F6). The current response depends on  $\Delta E$  (the step height),  $\tau$  (the step width) and  $\alpha$  (the current sampling parameter). As  $\Delta E$  and  $\tau$  approach zero, the potential tends towards a linear function; indeed, staircase voltammetry has been proposed as an alternative to linear sweep and cyclic voltammeteries (4). However, although staircase voltammetry does have the apparent advantage of decreased charging current in the current-potential plot, it has more parameters than linear sweep voltammetry and does not work well for adsorbed species (5).

b) Normal pulse voltammetry

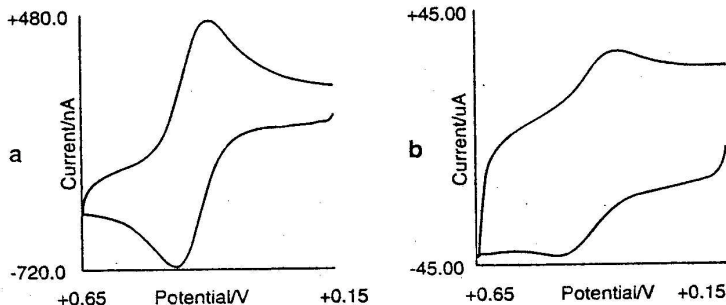
The potential waveform is a series of pulses of increasing amplitude with sufficient time between pulses to allow restoration of the initial conditions at the electrode surface (F7a) (i.e., the concentrations of the oxidized and reduced species at the electrode surface before each pulse does not depend on the effect of previous pulses). The diffusion controlled current is therefore independent of time, giving rise to a sigmoidal current response (F7b).

c) Differential pulse voltammetry

The potential waveform for this technique is the sum of a staircase potential and a series of small pulses of constant amplitude (F8a). The current measurement is different from the previous two techniques in that the current is sampled before and after the potential pulse, and the difference is recorded as a function of the base potential. The current response is therefore a symmetric peak (F8b).

**F4**

Cyclic voltammograms of ferrocene in acetonitrile (0.1 mM), supporting electrolyte 0.1 M  $[t\text{-Bu}_4\text{N}][\text{BF}_4]$ , scan rate = 50 mV/s (a), 50 V/s (b).



There are a number of ways to decrease the impact of the above effects.

Pulse techniques (3)

The basis for these techniques is the potential step experiment. Here the potential is instantaneously changed from an initial potential,  $E_i$ , to a different potential,  $E_s$ , and held there. As discussed above, the charging current for this potential step decays exponentially (the exponent is  $-t/R_uC_{dl}$ ). The Faradaic current also decays with time, but at a much slower rate; for example, if the current is diffusion controlled, then the rate of decay depends on  $t^{1/2}$ . Therefore, the cur-

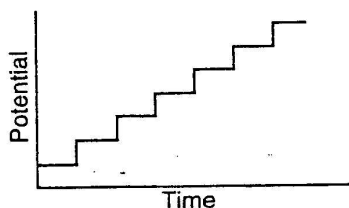
**F5**

Current decay following a potential step of the charging current (a) and the Faradaic current (b).



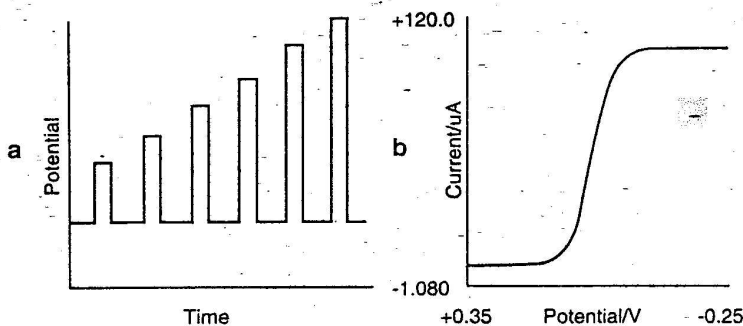
**F6**

Potential waveform for staircase voltammetry.

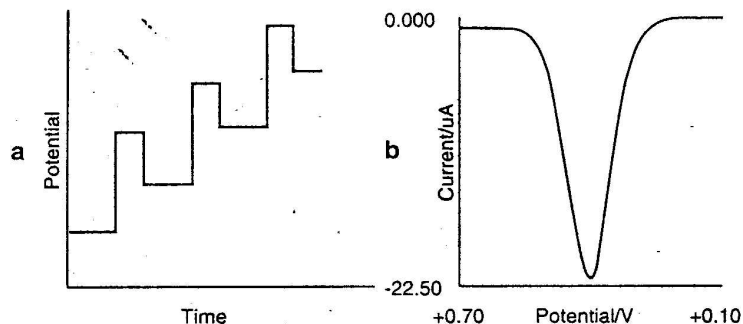


**F7**

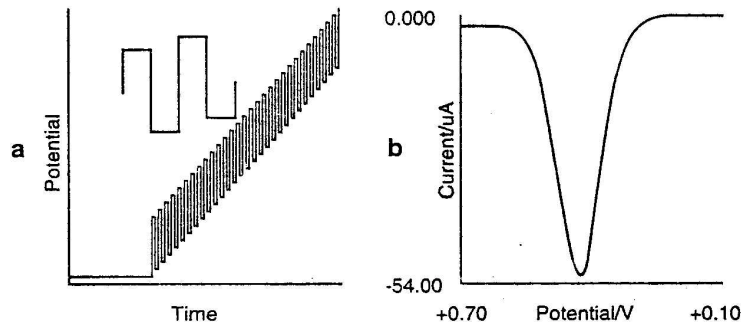
Potential waveform (a) and current response (b) for normal pulse voltammetry.

**F8**

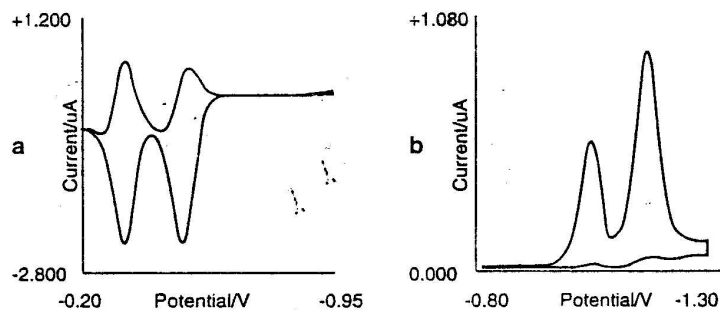
Potential waveform (a) and current response (b) for differential pulse voltammetry.

**F9**

Potential waveform (a) and difference current response (b) for square wave voltammetry.

**F10**

Comparison of reversible (a) and irreversible (b) processes using forward and reverse current responses of square wave stripping voltammetry. a) Lead (50ppb) and cadmium (50ppb) in acetate buffer (pH 4.7) b) Ni(DMG)<sub>2</sub> (20 ppb) and Co(DMG)<sub>2</sub> (40ppb) in NH<sub>3</sub> solution (pH = 9.8).

**d) Square wave voltammetry**

This potential waveform can be considered as the sum of a staircase potential and an alternating square wave (F9a). The current is sampled at the end of each half-cycle of the square wave. In contrast to differential pulse, both the forward and reverse electron transfer reactions are probed, due to the square wave oscillation. Therefore, the difference current is more sensitive for reversible processes than differential pulse (increasing the frequency can further increase the sensitivity, even for irreversible processes). The forward and reverse currents are also recorded, and these can provide information about the reversibility of the redox process (F10).

For all these techniques, ideally only the Faradaic current is measured. This improved discrimination against the charging current (relative to linear techniques) lowers the detection limit (F11). Hence, these techniques are more suited for quantitative analysis than e.g., linear sweep voltammetry. Of the four pulse techniques, differential pulse and square wave have the lowest detection limits, and are the most widely used. Of these two, square wave is often preferred due to its faster speed and greater sensitivity.

**Sinusoidal alternating current (A.C.) techniques**

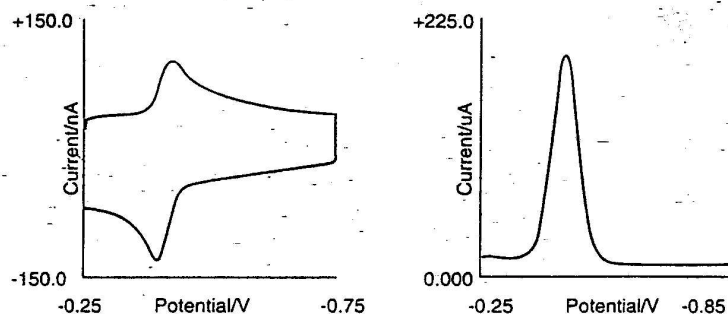
The basis for using A.C. techniques is phase difference between the Faradaic and charging currents. For an ideal reversible redox process, the phase angle of the Faradaic current is  $45^\circ$ , whereas the phase angle of the capacitive charging current is  $90^\circ$ . Therefore, phase selective measurement of the current at  $0^\circ$  should in principle provide good discrimination against the charging current. However, in practice, solution resistance causes a phase shift, so there is a small charging current contribution at  $0^\circ$ .

**Microelectrodes**

$C_{dl}$  is proportional to the surface area of the electrode, so microelectrodes have been used to de-

**F11**

Comparison of a) cyclic voltammetry and b) square wave voltammetry for lead in 0.1M KNO<sub>3</sub> (5ppm).



crease the effects of  $C_{dl}$ . There are two regimes in which microelectrodes are commonly used, and these need to be considered separately (6).

#### a) High-speed voltammetry

As discussed above, the upper limit for the scan rate is determined by the time constant for the system,  $R_u C_{dl}$ . Higher scan rates (greater than 100,000 V/s) can therefore be achieved with microelectrodes due to the faster response time. It is important to note that there is no improvement in the  $i_f/i_c$  ratio when using microelectrodes in this regime.

#### b) Steady state voltammetry

Steady state voltammetry can be achieved with microelectrodes by using slow scan rates (e.g., 20 mV/s). In this regime, the Faradaic current is proportional to the radius of the electrode. Therefore, the  $i_f/i_c$  ratio is proportional to  $r^{-1}$ , i.e., it increases with decreasing electrode size.

In conclusion, the capacitive behavior of the interfacial region has a significant effect on cyclic voltammetry experiments. The contribution of the charging current to the measured current makes this technique unsuitable for quantitative concentration measurements due to the relatively high detection limits.

In addition, the upper limit for the scan-rate is limited by the electrode capacitance. However, these limitations can be circumvented, i.e., by using pulse techniques for quantitative concentration measurements, and microelectrodes for fast scan rate and steady state experiments.

#### References

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## Workshop on In Vivo Sampling: Microdialysis and Ultrafiltration in the Rat

Wednesday, May 19, 1993

Indianapolis, Indiana

Conference Center, Indiana University-Purdue University at Indianapolis

A one-day workshop on in vivo sampling techniques such as microdialysis and ultrafiltration will be offered prior to the 1993 International Symposium on Microdialysis and Allied Analytical Techniques (ISMAAT). The course begins at 9:00 am and ends at 5:00 pm. The cost is \$100 per person and registration is limited to the first 75 participants... Lunch will be provided.

The workshop will be held in the ultra-modern facilities of the University Place conference center. Course participants are comfortably seated in partially reclining chairs with generous desk space for notetaking. Surgical demonstrations taking place in the classroom will be viewed in great detail on a 25 ft projection screen behind the surgeons. Chromatographic instruments will be used for analysis of drugs in both dialysates and ultrafiltrates.

The workshop begins with lectures by researchers experienced in these techniques. Topics covered include an introduction to in vivo sampling, principles of microdialysis and ultrafiltration, applications for pharmacokinetics, neuroscience, pharmacology, and metabolism. The afternoon is devoted solely to demonstrations. Instructors will implant probes into the brain, jugular vein and subcutaneous tissues. Samples will be collected and analyzed. A detailed course notebook will be provided.

To register for the workshop, please use the registration form enclosed with Symposium titles in the center of this journal. Return the completed form with payment of \$100 to the address shown on the application. Hotel reservations must be made prior to May 1 with the University Place Hotel, 850 West Michigan Street, Indianapolis IN 46202. Tel (317)269-9000 or FAX (317)274-3878. Please mention that you are making reservations for the "1993 ISMAAT/IES Symposium" when contacting the hotel. You will then be entitled to the special rate of \$ 95 per night.