Practical Problems in Voltammetry: 4. Preparation of Working Electrodes

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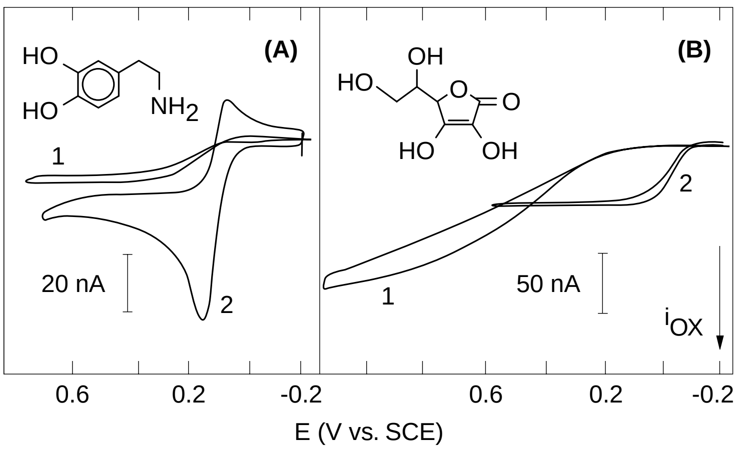
The condition of the surface of the working electrode can have a significant effect on the current response in both voltammetric and amperometric experiments. The methods most commonly used for the preparation of working electrodes (polishing, electrochemical pretreatment, and heat pretreatment) are discussed in this article.

The fundamental process in electrochemical reactions is the transfer of electrons between the electrode surface and molecules in the interfacial region (either in solution or immobilized at the electrode surface). The kinetics of this heterogeneous process can be significantly affected by the microstructure and roughness of the electrode surface, the blocking of active sites on the electrode surface by adsorbed materials, and the nature of the functional groups (e.g., oxides) present on the surface (1, 2). Therefore, there has been considerable effort devoted to finding methods that remove adsorbed species from the electrode and produce an electrode surface that generates reproducible results. Some of these methods have also resulted in the activation of the electrode surface (as judged by an increase in the rate of electron transfer). These methods are the subject of this paper, and include mechanical polishing, heat pretreatment, and electrochemical pretreatment.

The most common method for surface preparation is mechanical polishing. The protocol used for polishing depends on the application for which the electrode is being used and the state of the electrode surface. There are a variety of different materials available (e.g., diamond, alumina, silicon carbide), with different particle sizes suspended in solution (BAS supplies 0.05 µm alumina polish and 1, 3, 6, and 15 µm diamond polishes). The pad used for polishing also depends on the material being used for polishing—Texmet pads are used with alumina polish, and nylon pads should be used with diamond polish. Working electrodes supplied by BAS have first been lapped to produce a flat surface, and have then been extensively polished to a smooth, mirror-like finish at the factory. Therefore, they typically only require repolishing with 0.05 µm or 1 µm diamond polish by the user in between experiments. Materials that have a rougher surface (e.g., electrodes which have been scratched) must first be polished using a larger-particle polish in order to remove the surface defects. After the defects have been removed, the polishing should continue with successively smaller-particle-size polish (e.g., 15 µm, then 6 µm, then 3 µm, and then 1 µm).

Once polishing has been completed (this can require from 30 s to several minutes, depending upon the state of the electrode), the electrode surface must be rinsed thoroughly with an appropriate solvent to remove all traces of the polishing material (since its presence can affect the electron transfer kinetics). Alumina polishes should be rinsed with distilled water and diamond polishes with methanol or ethanol. The rinsing solution should be sprayed directly onto the electrode surface. After the surface has been rinsed, electrodes polished with alumina should also be sonicated in distilled water for a few minutes to ensure complete removal of the alumina particles. If more than one type of polish is used, then the electrode surface should be thoroughly rinsed between the different polishes.

As discussed above, the effect of any surface pretreatment can be determined by its effect on the rate of electron transfer. This can be judged qualitatively by examining the separation of the peak potentials in a cyclic voltammogram of a molecule whose electron transfer kinetics are known to be sensitive to the state of the surface; a more quantitative determination can be made by calculating the value of k_s from this peak potential separation. For example, k_s for potassium ferricyanide at glassy carbon surface following a simple polishing protocol was found to lie in the range 0.01 - 0.001 cm s^{-1} (3,4) (this should be compared with the values measured for k_s for a platinum electrode, which are at least one order of magnitude larger). The strong dependence of the electron transfer kinetics of ferricyanide on the state of the electrode surface means that



F1

Voltammetry at a cylindrical carbon fiber electrode (1) before and (2) after electrochemical pretreatment: (A) 0.1 mM dopamine and (B) 1.0 mM ascorbic acid, pH 7 solutions, scan rate = 0.1 v/s. (Adapted from reference 11.)

there can be significant variations in the peak potential separation after each polishing. Polishing alters the microstructure, roughness, and functional groups of the electrode surface in addition to removing adsorbed species (for example, it has been shown that the oxygen-to-carbon ratio is increased by polishing (5)). It has also been reported that materials used for the polishing can affect the value of k_s (1,4,6). For example, the electrode surface can be contaminated by the agglomerating agents required to keep the alumina particles suspended in solution and by the components of the polishing pad. The presence of these species can have a deleterious effect on the electron transfer kinetics by blocking the active sites for the electron transfer reaction. For the most exacting studies, it was suggested that the alumina suspension be freshly made with ultrapure water and that the electrode should be polished on glass (a k_s value of 0.14 cm s^{-1} for ferricyanide was reported following polishing under these stringent conditions (4)). However, it should be noted that such pronounced dependence on the state of the electrode surface is only observed for certain systems (the most well characterized examples are the reduction of ferricyanide, the oxidation of ascorbate, and the adsorption of dopamine). For such systems, polishing is often used in combination with another pretreatment (e.g., heat or electrochemical). However, for many other systems, the simple polishing described above is adequate (for example, when using non-aqueous electrolytes, since blocking of active sites by adsorbed species is less common in such electrolytes than in aqueous solutions).

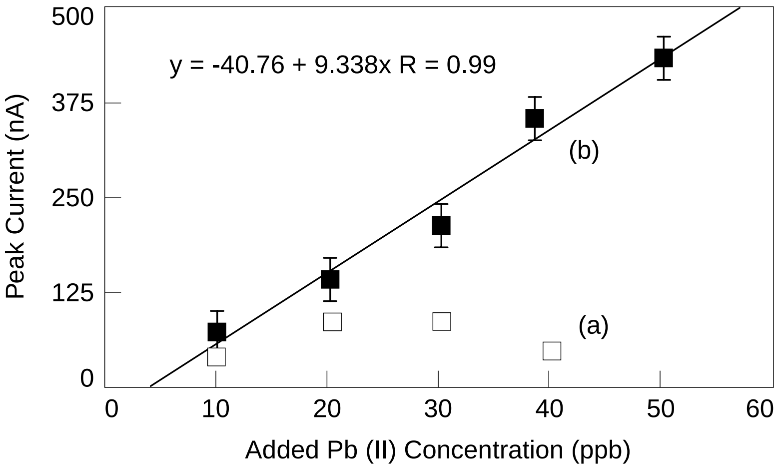
Another method for preparation of the electrode surface that is becoming more widely used is electrochemical pretreatment (ECP), particularly for electrodes which cannot readily be polished (e.g., carbon fiber cylinder electrodes). ECP consists of applying conditioning potentials to the electrode surface before the experiment. As for polishing, this has the effect of removing adsorbed species and altering the microstructure, roughness, and functional groups of the electrode surface. The precise ECP protocol depends upon the application and varies considerably. The potential waveforms typically are held at, or cycle to, a large positive or negative potential, either using steps or sweeps (constant potential (6), potential scan (7,8), triangular wave (9-15) and square wave (16, 17)). Although the development of the preconditioning protocols has been largely empirical, the pretreated electrode surface has been characterizizated in order to elucidate the reasons for the activation of the electrode surface (6,7,17,18). For glassy carbon electrodes, in addition to the removal of adsorbed species, the preconditioning potential leads to the formation of an oxygen-rich layer on the carbon surface. This layer contains oxides as well as other oxygen-containing functional groups which may catalyze electron transfer reactions (the composition of the functional groups in this layer is sensitive to the pretreatment conditions and depends on the solution pH as well as the potentials used for the pretreatment (19)). The oxide layer can also adsorb and/or exchange ions from the solution, which leads to improved detection limits. However, electrochemical pretreatment of electrodes increases the background current of the electrode relative to that of a polished electrode, which may be disadvantageous for some applications.

Some of the specific effects and applications of electrochemical pretreatment can best be illustrated by a number of examples.

Discrimination Between Ascorbate and Dopamine Using Pretreated Carbon Fiber Electrodes

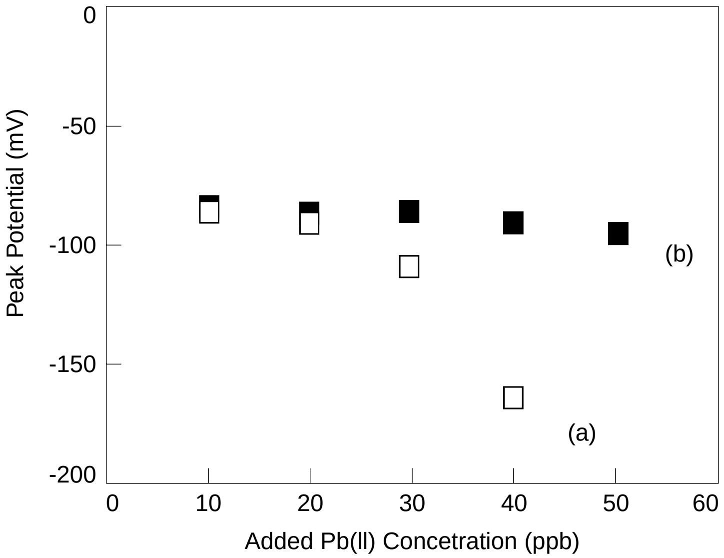
In vivo determination of neurotransmitters such as dopamine is hindered by the ubiquitous presence of ascorbate, since dopamine and ascorbate are oxidized at similar potentials. However, it has been found that pretreatment of carbon fiber electrodes using a triangular waveform (cycling between about 0 V and +3 V at a frequency of 70 Hz for 20 s, followed by holding at a constant potential of +1.5 V for 20 s) increases the rate of electron transfer for both ascorbate and dopamine (***F1***) and changes the sensitivity of the electrode to these two analytes (9-12). The shift in the peak potentials allowed resolution of the peaks due to ascorbate and dopamine measured using differential pulse voltammetry. The relative sensitivities for dopamine and ascorbate for pretreated electrodes were about 1000:1, which provides further discrimination against interference by ascorbate.

The effect of this pretreatment on carbon fiber electrodes was further examined by studying the behavior of a range of molecules at



F2

Peak current variation with increasing concentration, (A) without electrochemical pretreatment and (B) with electrochemical pretreatment. Plating time = 30 sec. Each data point is the average of three repetitions. (Reprinted from reference 21.)



F3

Variation of peak potentials with increasing concentration, (A) without electrochemical pretreatment and (B) with electrochemical pretreatment. Plating time = 30 sec. Each data point is the average of three repetitions. (Reprinted from reference 21.)

these electrodes (12). Specifically, the current responses measured using cyclic voltammetry were compared with those calculated from theory. Although the electron transfer kinetics for all the systems examined were increased by the pretreatment, the currents measured for cations such as dopamine and transition metal amine complexes were larger than those calculated, whereas currents for anions such as ascorbate and ferricyanide were smaller. The shape of the cyclic voltammograms for the cations were consistent with adsorption, and this was confirmed using chronocoulometry. The model proposed on the basis of these results involved the formation of a multilayer insulating oxide film on the carbon surface, together with fracturing of the surface. The oxide layer can preferentially take up positively charged species, which leads to the larger currents observed for dopamine and the other cations. Anions, such as ascorbate and ferricyanide, can only react at the active sites exposed by the fracturing; that is, they can only react at a small fraction of the electrode surface, which is consistent with the small current response.

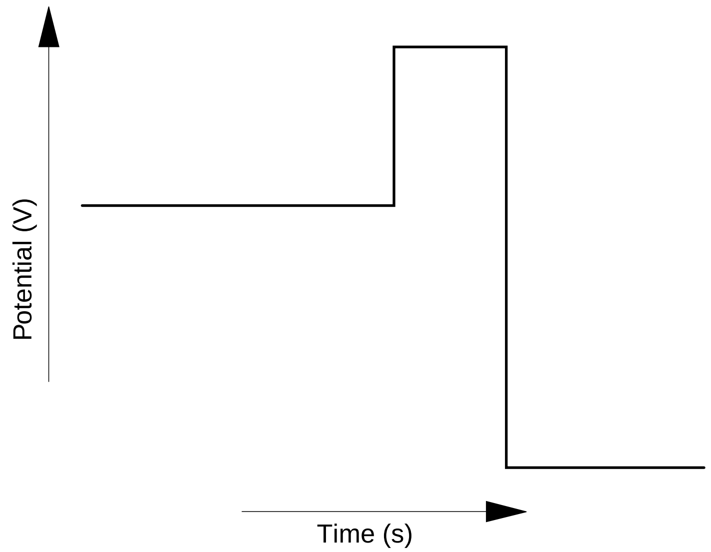
Although the above method does lead to high sensitivity for dopamine, the preconcentration required means that there is delay in the response time. The response time can be improved by using less positive potentials in the pretreatment waveform (about +1 - +2 V) (13-15). A surface oxide layer is still formed at these potentials, but it is thinner, and hence it provides some increase in its sensitivity for dopamine, while maintaining a good response time.

Analysis of Lead(II) by Square Wave Voltammetry Using a Gold Disk Electrode

Mercury electrodes are more commonly used than solid electrodes for the detection of lead by anodic stripping voltammetry, due to the more complex interactions of lead with the surfaces of solid metals. This leads to a non-linear relationship between the current and the lead concentration (***F2A***) and significant variation in the peak potential with increasing lead concentration (***F3A***). These poor data were attributed to accumulation of the plated metal on the gold surface, which leads to variations in the surface condition from one experiment to the next. These variations can be eliminated by holding the electrode at a potential of +0.8 V vs. Ag/AgCl for five minutes before starting the stripping experiments, and then holding the electrode at this potential for 50 s between experiments. The improvements in the linearity of the relationship between the current and the concentration, and in the consistency of the peak potential, are readily apparent from ***F2B*** and ***F3B***, respectively. These data show that this pretreatment restores the electrode surface to a well-defined condition.

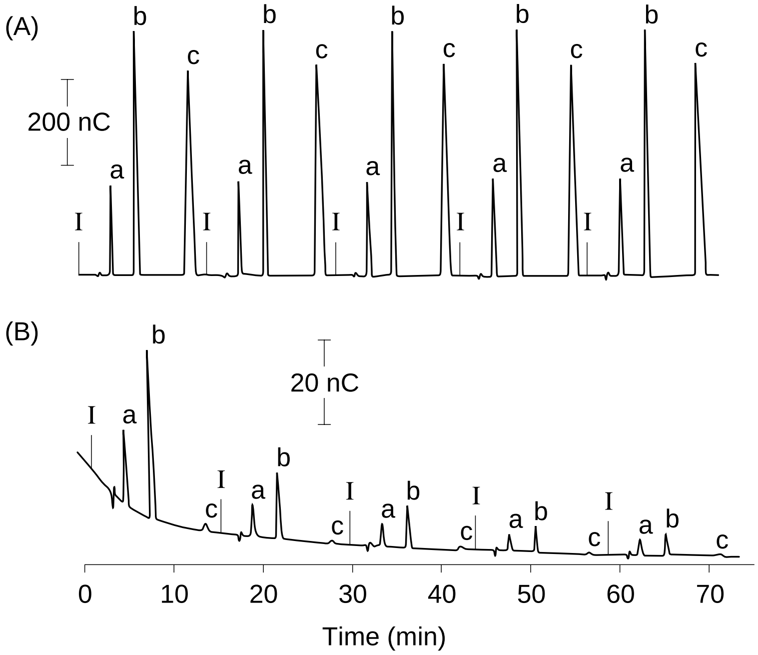
Detection of Sugars, Amines, and Sulfur Compounds Using Pulsed Electrochemical Detection

In the two examples above, the pretreatment potential was applied before each experiment. However, the preconditioning potential can also be incorporated into the experimental waveform to provide electrode cleaning and activation at regular intervals during the experiment. One example of such an experiment is the Pulsed Electrochemical Detection (PED) used for



F4

Potential waveform for PED.



F5

Comparison of current vs. time plots for (A) PED and (B) constant potential amperometry. Solutions: (a) lysine, 30 ppm; (b) glucose, 10 ppm; (c) sucrose, 40 ppm. (Reprinted with permission from reference 23.)

the detection of, for example, sugars, amines, and sulfur compounds at gold and platinum electrodes (22, 23). These molecules can be oxidized at the surface of a platinum or gold metal via an electrocatalytic reaction which is thought to involve adsorption of the analyte and reaction with adsorbed hydroxyl groups (a detailed mechanism has not yet been elucidated). Since the reaction involves adsorption, the electrocatalytic activity of the electrode (and hence the current response) decreases with time. This problem can be solved through the application of a triple potential pulse waveform (***F4***). The first pulse is at a potential at which the electrocatalytic reaction occurs (detection step). Since this step passivates the electrode surface, the next pulse is at a more positive potential. This results in the desorption of the passivating species, concomitant with the formation of an inert oxide layer (cleaning step). The electrode is now reactivated by the removal of the oxide layer using a negative potential (reactivation step). The electrode is now ready for the next detection step. The triple pulse sequence can be used either amperometrically for EC detection following separation by LC, or voltammetrically, by combining the triple pulse with, for example, a staircase potential waveform (both options are available on the BAS 100B/W).

The effect of the cleaning/deactivation potential pulses is illustrated in ***F5***. ***F5A*** shows the current response using a fixed potential for the detection of sugars following chromatographic separation. The decrease of the current response with time is due to the progressive passivation of the electrode surface. In contrast, the current response for the triple pulse sequence does not diminish with time (***F5B***)(23).

Activation of the electrode surface can also be achieved by thermal pretreatment. The electrodes can either by heated under vacuum (24,25) or can be exposed to a laser (26-28). Although such treatments do give rise to enhanced rates of electron transfer, as well as reproducible surfaces, they are not practical for routine use. The activation for these pretreatments was attributed to the removal of adsorbed species from the electrode surface (29,30).

The development of pretreatment methods has been accompanied by the characterization of electrode surfaces before and after such pretreatments in order to elucidate the changes in the surface that lead to activation (4-7,17,18,24-26,29-34). However, for most pretreatments, it is not possible to identify unambiguously any one change in the surface that can be correlated with the activation (for example, the activation in some instances may be due simply to the removal of adsorbed species from active sites, whereas in other instances the changes in the surface functional groups may also be important). The effectiveness of a given pretreatment also depends on the analyte under investigation. Therefore, the optimal pretreatment for a given application can only be found experimentally.

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