

Chemical Modification of Electrodes

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When an electrode, such as a piece of platinum or carbon, is dipped into a solution, its surface becomes covered with a layer of water molecules. Sometimes species present in the solution that have been purposely added or are present as impurities will also attach to the electrode surface. The presence of such adsorbed species will often modify the electrochemical behavior of the electrode. For example, they may cause the current observed for a given electrochemical process to be much smaller, because they block access to the electrode surface. Such effects, with electrode surfaces modified by adsorption of species from solution, often accidentally, have been studied extensively by electrochemists for many years. In recent times electrochemists have become interested in purposely modifying an electrode by adsorbing, coating, or attaching specific molecules to the surface. This deliberate and controlled modification of the electrode surface can produce electrodes with new and interesting properties that may form the basis of new applications of electrochemistry and novel devices. Fundamental studies of such modified electrodes have also provided a better insight into the nature of charge transfer and charge transport processes in thin films. In this paper the methods of preparing and characterizing such electrodes are outlined, and several applications are described. More detailed discussions of these topics and the growing literature in the field are contained in review articles.^{1,2}

How are Electrodes Modified?

Modified electrodes can be prepared by several different techniques and are, therefore, often referred to by such names as *derivatized*, *polymer-coated*, *functionalized*, and *electrostatically-bound* electrodes. Most frequently the layer or coating on the electrode surface is electroactive, i.e., it can exchange electrons with the underlying substrate material and be oxidized or reduced, although some applications of nonelectroactive films have also been discussed.

Strong Chemisorption. Some species find the surface of the electrode much more hospitable than the bulk solution and so attach spontaneously to the surface. For example organic species, such as those containing double bonds, are often hydrophobic and strongly adsorb from aqueous solutions on carbon or platinum surfaces. In these cases the amount adsorbed on the electrode surface, usually written as Γ , is at most a monolayer, i.e., about 1×10^{-10} mol cm⁻², or 6×10^{13} molecules cm⁻².

Covalent Attachment. Chemical reactions can be carried out to form bonds between the substrate and a molecule of interest (Fig. 1). For example, a metal or carbon can be oxidized so that the surface can be considered as consisting of hydroxyl groups. Such a surface can be "silanized" by reaction with an organosilane and then reacted with another molecule of interest. In this case the silane is a kind of glue for fixing the

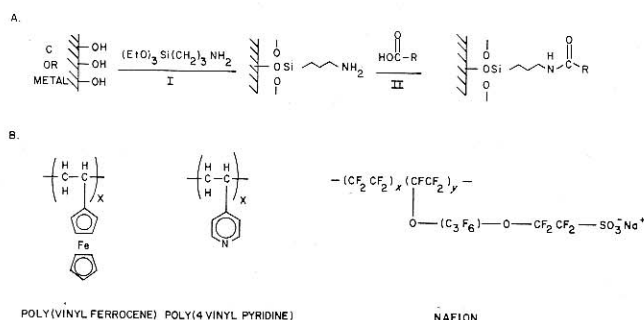


Figure 1. (A) General reaction scheme for covalent attachment to an electrode surface to produce a chemically modified electrode. Treatment I: oxidized carbon or metal electrode is treated with γ -aminopropyltriethoxysilane. Treatment II: the silanized electrode is treated with compound containing desired group to be attached, R. (B) Structures of some of the compounds mentioned in text.

molecule to the surface. One would expect that this technique would also only form a monolayer on the electrode. Frequently, however, the silanization reaction causes polymerization to take place and thicker layers, equivalent to several monolayers, form.

Polymer Layers. By dipping the electrode into a solution containing a dissolved polymer, e.g., poly(vinylferrocene), and allowing the solvent to evaporate, one forms a thin (0.1–10 μ m) film on the surface. A somewhat better method than "dip-coating" for producing more uniform films is "spin-coating" (which is also widely used in the production of semiconductor chips). Polymer layers can also be produced by electrodeposition or by inducing the polymerization of monomers at the electrode surface by electrochemical or other (rf plasma) means. Several types of polymer electrodes have been studied. In some, the polymer itself is electroactive and can undergo redox reactions. In others the polymer is a polyelectrolyte, that is, a material which contains ionic groups, which can extract charged ions from the solution and hold them by electrostatic binding (e.g., poly(vinylpyridine) or Nafion).

How are Modified Electrodes Characterized?

After the surface of an electrode has been subjected to one of the above treatments, one must prove that the surface has indeed been modified and find out about the properties and nature of the layer. Since one is dealing with a very small amount of material on the surface, rather sensitive analytical techniques are required. Generally one wants to learn about the amount of material on the surface, how easy it is to oxidize or reduce this material, what is its composition and structure, and what are its other chemical and physical properties.

Electrochemical Methods. Even monolayer amounts of material can be analyzed electrochemically, since small currents can be measured quite readily and, by Faraday's law, 10^{-10} moles of material is equivalent to about 10 microcoulombs ($n = 1$). Thus, the cyclic voltammetry of a monolayer of material (Fig. 2) will show a peak with an integrated area equivalent to that amount of material on the electrode surface.

¹ Murray, R. W., in "Electroanalytical Chemistry," Bard, A. J., (Editor), Marcel Dekker, Inc., New York, Volume 13, 1983 (in press).

² Murray, R. W., *Accts. Chem. Res.*, **13**, 135–141 (1980).

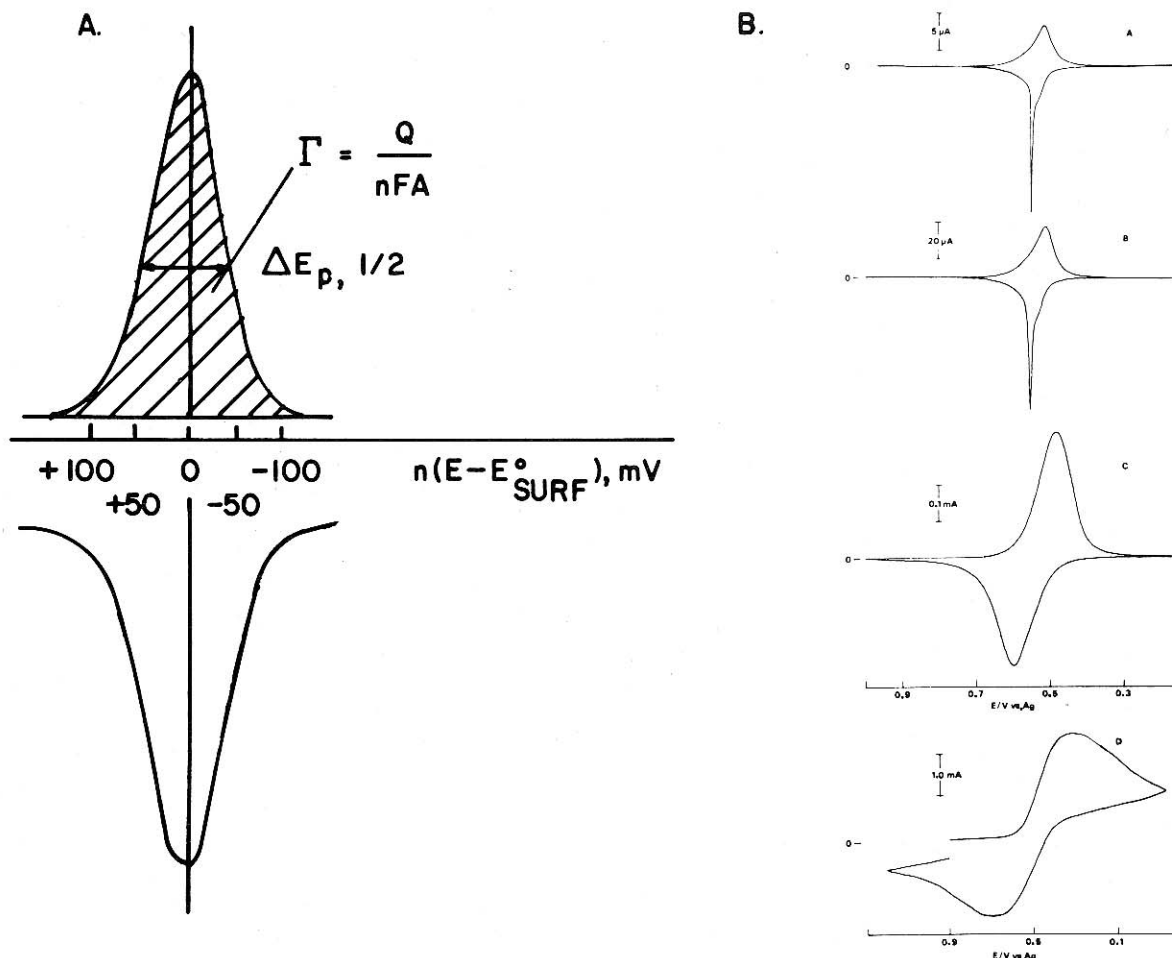


Figure 2. (A) Ideal cyclic voltammogram for a surface layer on an electrode. The amount of material on the electrode, Γ , can be obtained from the area under the wave, Q (in coulombs) (n is the number of electrons in the electrode reaction, F is the Faraday, and A is the electrode area). Such ideal behavior is only approached for slow scan rates for films that show no intermolecular interactions and rapid electron transfers. In most cases the cyclic voltammogram behavior is less ideal, as shown in B. (B) Experimental cyclic voltammograms for a poly(vinylferrocene) film on a platinum electrode in acetonitrile solution at scan rates of (a) 2 mV s^{-1} ; (b) 10 mV s^{-1} ; (c) 0.2 V s^{-1} ; (d) 10 V s^{-1} . [From Pearce, P. J., and Bard, A. J., *J. Electroanal. Chem.*, **114**, 89–115 (1980).]

The location of the peak on the potential axis is a direct measure of the redox potential of the couple on the surface. Frequently this potential is very near that found for the same or a closely related couple in solution. For thicker layers, the electrochemical response will show larger integrated areas, representing greater amounts of material on the electrode. A detailed inspection of the nature of the response and the shape of the curves can provide information about chemical interactions in the films and the rate and mechanism of charge transport through them.

Spectroscopic Techniques. Electron spectroscopy (such as X-ray photoelectron and Auger electron spectroscopy) can be used for an analysis of the elements present in the surface layers. For example, a nitrobenzene group attached to a tin oxide electrode via a silane bridge will show peaks for Sn, Si, C, and N. Direct optical spectroscopic measurements in the visible, IR, and UV regions are also possible, either by absorption (when the films are on a transparent electrode substrate), or by reflectance (e.g., with metal substrates).

Other Methods. Direct observation of the surface by optical or scanning electron microscopy is often useful for multilayer films to provide information about the texture and porosity of the layers. An important measurement that is surprisingly difficult to make is the determination of the thicknesses of the coating. Techniques for measuring hard, dry, films with thicknesses greater than 100 \AA have been developed for applications in semiconductor technology. There are problems in applying such techniques to the softer films on electrode surfaces. Moreover, such films change dimension when they are immersed in the electrolyte solution, so that measurements

of dry thickness can only be considered as rough estimates for the electrodes as used under actual electrochemical conditions.

Why Modify Electrodes?

Many of the studies of modified electrodes were undertaken simply because electrochemists were curious about how species attached to electrode surfaces behave compared to these species in solution. However, such modified electrodes have possible applications in all kinds of devices; several will be described briefly below.

Electrocatalysis. Many reactions that one would like to carry out in electrochemical cells, such as the reduction of oxygen to water or the oxidation of natural gas components to CO_2 (for use in fuel cells), do not occur readily at inexpensive electrode materials (e.g., carbon). Thus, it is necessary to catalyze these reactions by introducing suitable, stable, layers to the electrode surface. It is hoped that by applying known chemical principles about structure and reactivity, useful surface layers can be designed for particular reactions of interest. Although practical catalysts of this type have not yet emerged, this remains an important and promising area of research. Perhaps the most successful example of this work is the modification of a graphite surface by irreversible adsorption of a cofacial dicobalt porphyrin dimer which allowed the reduction of oxygen under conditions where reduction was not possible on the substrate itself. More importantly, the path of the reaction was shown to be very sensitive to details of the structure of the attached molecule; these results could be rationalized by how the oxygen molecules "fit" into the

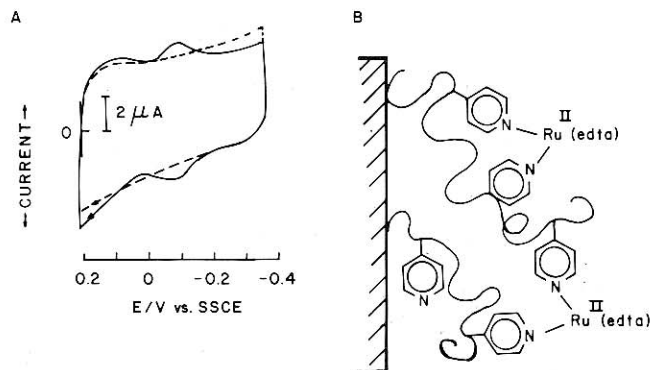


Figure 3. (A) Cyclic voltammogram for a poly(4-vinylpyridine)-coated electrode after immersion in a $5 \times 10^{-8} M$ solution of Ru(II) (EDTA) at scan rate of 200 mV s^{-1} . The dashed curve is the background current obtained in the absence of Ru(II). The area under the small wave represents $6 \times 10^{-11} \text{ mol cm}^{-2}$ of Ru-complex extracted from the solution. (B) Schematic picture of the extraction of the Ru-complex by the polymer film. [From Oyama, N., and Anson, F. C., *J. Amer. Chem. Soc.*, **101**, 3450–3456 (1979).]

structure of the catalyst.

Display Devices. Electrodes in electrochemical cells that change color or emit light when excited electrically are of interest in the production of displays for electronic devices. For example, electrodes modified with polymer layers can change color when they are oxidized or reduced (i.e., show electrochromic behavior). Specially designed polymer electrodes will emit light when electrochemically reduced or oxidized (electrogenenerated chemiluminescence).

Analytical Applications. Molecules may be preferentially extracted into a surface layer and thus be concentrated from a bulk solution. For example, Ru(II) (EDTA) will extract into a poly(4-vinylpyridine) layer from a solution as dilute as $5 \times 10^{-8} M$ and become detectable by electrochemical techniques (Fig. 3). Nonelectroactive polymer layers may also be used to produce a selective electrode that will allow only certain

molecules from solution to reach the electrode surface. For example thick membranes of polyethylene placed on surfaces of gold electrodes will block large protein molecules from reaching the electrode while allowing oxygen to get through. These devices are used to monitor the oxygen concentration in the blood. Similarly designed modified electrodes with even better discriminative properties could find numerous analytical uses.

Photoelectrochemical Applications. Techniques for surface modification are useful in preventing photocorrosion in semiconductor electrodes used in photoelectrochemical cells for solar energy conversion. For example, a silicon electrode in an aqueous solution usually rapidly forms an insulating oxide layer upon immersion that prevents useful operation of the cell. When a layer of the electronically conductive polymer polypyrrole is attached to the electrode surface, the silicon electrode shows much more stable behavior. Modification of semiconductors can also improve the efficiency of operation (in terms of solar energy converted to electrical energy) and can be employed to incorporate catalysts on the electrode to promote desired reactions. Modification techniques also appear useful in attaching dyes to electrode surfaces; these can absorb light and sensitize electron transfer reactions at the electrode.

Conclusions

The study of modified electrodes remains a field of high activity. Many new types of surface structures are being prepared, and electrochemical studies are leading to better insights into the way charge is transported through surface layers and how charge is exchanged between surface species and molecules in solution. While actual practical applications have not yet developed, many promising possibilities lie on the horizon.

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