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Chemically Modified Polymer Electrodes: Synthetic Approach Employing Poly(methacryl chloride) Anchors

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SnO_2 electrodes have been chemically modified with poly(methacryl chloride) as an anchor using a silanization technique. Hydroxymethylferrocene was then attached to the polymer chains on the surface of the SnO_2. The modified electrodes were characterized by cyclic voltammetry in acetonitrile and by ESCA. The attached hydroxymethylferrocene gave a highly symmetric oxidation wave at +0.54 V vs. SCE, and reduction wave on scan reversal. The peak currents were proportional to scan rate and the waves persisted upon extended cycling. The surface coverage was about 7×10^{-10} mol/cm^2 demonstrating larger than monolayer coverage. Electrodes prepared by coating (rather than bonding) SnO_2 and Pt electrodes with polymer were also investigated.

Numerous investigations of chemically modified electrodes and schemes for modification of electrode surfaces have been reported recently by several groups (*1–24*). These chemically modified electrodes have been tested for electrocatalytic properties (*9*), as chiral electrodes (*1*), for stabilization of semiconductors (*10*), and for sensitization of solar energy conversion (*14, 15*). Chemically modified surfaces can be produced by covalent bonding of substituent groups to electrodes or by spontaneous irreversible adsorption of organic and biological molecules to platinum, carbon, or mercury electrodes. Recently there have been reports of modified electrodes prepared by coating electrodes with polymers (*25–27*). For example, a recent study from our group has shown that a platinum electrode coated with poly(vinylferrocene) (PVF) from a methylene chloride solution and then transferred to acetonitrile (ACN) behaved like a chemically modified electrode (*25*). We report here a new and versatile technique for the preparation of chemically modified SnO_2 electrodes using covalently bonded poly(methacryl chloride) (PMAC) as an anchor and describe results with hydroxymethylferrocene as an electroactive center.

Electrode Preparation. The procedure is summarized in Figure 1. The silanization step, [I], on SnO_2 followed the general procedure described by the Murray group (*2–7*), and others (*10–16*). The surface modification reaction of γ-aminopropyltriethoxysilane is represented in Figure 1 assuming a three-bond linkage (*5*). A two-bond linkage and partial hydrolysis of the silane reagent, which leads to surface-bonded polymer structures, have also been discussed (*2–7, 10, 11*). However, we found that γ-aminopropyltriethoxysilane is so hygroscopic that solvents, reagents, and even the surface of the SnO_2 had to be rigorously dried to prevent formation of undesired silane polymers. Therefore, all of the reactions described in Figure 1 were carried out under high vacuum (10^{-5} Torr) using break-seal techniques (28). The solvents (benzene, THF, cyclohexane) were stored over Na-K alloy in a vacuum-tight flask and were distilled directly on the vacuum line to the reaction vessels. Under such rigorously dry conditions, we found that the rate of reaction of γ-aminopropyltriethoxysilane with the SnO_2 electrode surface was not very high and it was necessary to heat the benzene solution to 70 °C for more than 12 h to obtain sufficient reactivity. The PMAC was synthesized in benzene–cyclohexane (1:9 by volume) also using a vacuum technique following a literature method (*29*); a THF solution of PMAC was then prepared and stored in glass tubes with break-seals. After treatment III, the electrode was removed from the vacuum, thoroughly washed with THF, benzene, and ethanol, and was kept in an inert atmosphere glove box until use.

Electrochemical Results. The electrochemistry of the chemically modified polymer electrode was examined in ACN containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte. A typical cyclic voltammogram is shown in Figure 2. The behavior of the chemically bonded hydroxymethylferrocene was essentially that expected of a surface or an adsorbed species (*21–23*). The peak potential separation ($E_{pa} - E_{pc}$) was practically zero and the wave shape was almost completely symmetrical. The peak potential, +0.54 V vs. SCE, is very close to the potential of dissolved ferrocene in this medium. A plot of the anodic peak current (i_{pa}) for the oxidation of the bound ferrocene moiety vs. the electrode potential scan rate, v, was linear with zero intercept (Figure 3). Moreover, the total charge consumed for the oxidation of the bound ferrocene, (Q_a) (i.e., the integrated current), was independent of v. From the Q_a value, assuming $n = 1$, an average surface coverage equal to 7×10^{-10} mol/cm^2 was found. Since the maximum monolayer coverage on a SnO_2 electrode is usually taken to be of the order of 1 to 2×10^{-10} mol/cm^2 (*4, 5*), the coverage of the electrode is equivalent to 4 to 5 layers. The observed behavior follows closely that described for thin-layer electrochemistry (*30*) except for the broadening of the peaks. The width of the peak at half-height was about 160 mV (independent of v) compared to the theoretical value ($n = 1$) of 90 mV. This behavior, which is shown by many systems (*31*), is probably caused by the existence of the ferrocene moieties at several different sites on the electrode surface of different energy. The surface coverage by our procedure, which is 4 to 5 times larger than a monolayer, suggests that 4 to 5 of the acid chloride functional groups (–COCl) on the attached polymer chain, on the average, remain unsubstituted after treatment II. The average number of the acid chlorides on a polymer chain after treatment II depends upon the degree of polymerization (about 2420 by the present preparation (*29*)), reaction temperature, concentration of polymer and solvent. The actual structures of the polymer chains bound to the surface of the silanized SnO_2 can differ, depending upon the number of points of attachment of the chain to the electrode; this could lead to different spacial distributions and the peak broadening effect shown in Figure 2.

The stability of the chemically modified polymer SnO_2 electrode was excellent. Repeated scanning over the ferrocene waves, between −0.4 V and +1.0 V, caused only a 5% decrease in the peak height after 30 cycles at a slow scan rate (20 mV/s). After standing in ACN solution for at least 3 h without a scan, the shape of the cyclic voltammograms was essentially identical to the initial one.

The oxidation of 10-methylphenothiazine was examined on the chemically modified polymer electrode and showed a reversible cyclic voltammogram, E_{pa} = +0.87 V at v = 50 mV/s, demonstrating that an electrode reaction of a dissolved

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Table I. Relative Intensity Ratios by ESCA

sample	peak intensities[a]						$Sn(3d_{5/2})^b$/$Sn_{untreated}(3d_{5/2})$
	$Sn(3d_{5/2})$	C(1s)	N(1s)	Si(2s)	$Si(2p_{3/2})$	$Fe(2p_{3/2})$	
untreated SnO_2	1	0.034	—	—	—	—	1
γ-aminopropylsilane SnO_2	1	0.17	0.056	0.029	0.046	—	0.74
ferrocene-polymer SnO_2	1	0.38	—	—	—	0.15	0.29

[a] Intensities were normalized to $Sn(3d_{5/2})$. Lines in the table mean that intensity was practically zero. [b] Attenuation of $Sn(3d_{5/2})$ band normalizing to $Sn_{untreated}(3d_{5/2})$.

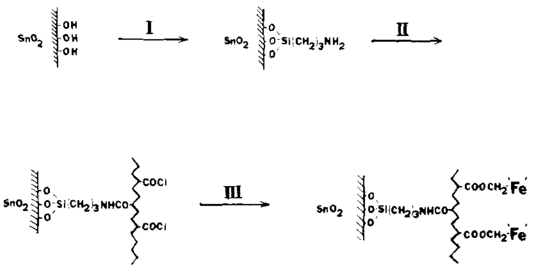

Figure 1. General reaction scheme of the chemically modified polymer SnO_2 electrode employing poly(methacryl chloride) anchors. 'Fe' indicates a ferrocene moiety. Treatment I: SnO_2 electrode reacted with a 5% solution of γ-aminopropyltriethoxysilane in dry benzene at 70 °C for more than 24 h; Treatment II: The silanized SnO_2 electrode is treated with a 5% solution of poly(methacryl chloride) (PMAC) in dry THF at 70 °C for 12 h; Treatment III: The chemically modified polymer electrode reacted with a 5% solution of hydroxymethylferrocene in dry THF at 70 °C for 12 h

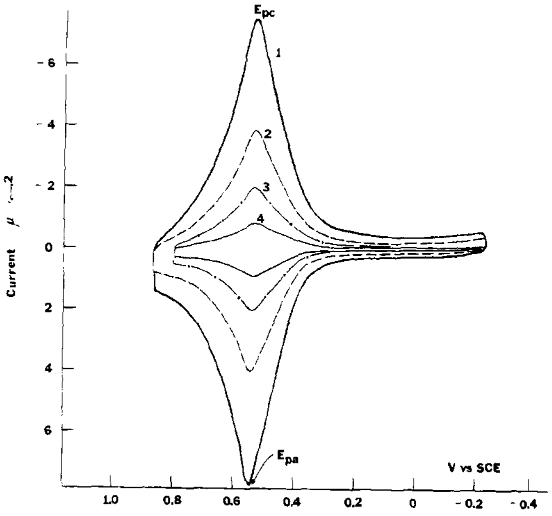

Figure 2. Cyclic voltammetric behavior of the chemically modified polymer electrode substituted with hydroxymethylferrocene at different scan rates. The electrode surface area was about 0.5 cm^2 and the solution was 0.1 M TBAP in ACN at room temperature. (1) 20, (2) 10, (3) 5, (4) 2 mV/s

species can take place on the chemically modified polymer electrode. Studies of other reactions with this electrode are in progress.

ESCA Results. To confirm the surface modification, ESCA analysis of the electrode surface was carried out; results are given in Table I. The absolute intensity of the $Sn(3d_{5/2})$ band was greatly reduced by the chemical modification with the polymer. The increase of the C(1s) band and the appearance of a $Fe(2p_{3/2})$ peak also indicate that the modification reactions have occurred. From the extent of attenuation of the $Sn(3d_{5/2})$ intensity, an average polymer layer thickness can be estimated, assuming a universal escape depth, λ, of 11 Å (*32*), yielding a value of 32 Å. This value roughly agrees with a theoretical length of polymer chain having 4 to 5 ferrocene moieties on the surface. Further work is in progress to obtain more details of the surface structure of the polymer.

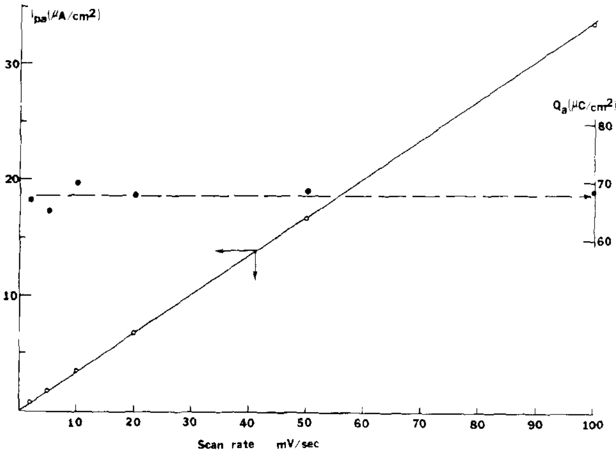

Figure 3. Variations of cyclic voltammetric peak currents (anodic) and surface coverage with scan rates. (●) surface coverage (μC/cm²), (O) peak current (μA/cm²)

Coated Electrodes. Our recent work (*25*) on electrodes coated with PVF by either electrodeposition or dip-coating techniques suggested that similar preparation of poly(hydroxymethylferrocene methacrylate)-coated electrodes would be of interest, especially to contrast their behavior with that of the chemically modified polymer electrode prepared by the covalent bonding technique described above. The polymer, poly(hydroxymethylferrocene methacrylate), was synthesized by the reaction of hydroxymethylferrocene and poly(methacryl chloride) in THF. The polymer-coated electrodes (SnO_2 and Pt) were prepared by an electrochemical anodic deposition of the polymer in THF solution, by a procedure similar to that used for PVF in dichloromethane (*25*). The thickness of the polymer layer was about 400 Å which was one order of magnitude larger than that of the chemically modified electrode. In cyclic voltammetric experiments (Figure 4), and i_{pa} and i_{pc} were again directly proportional to v and E_{pa} was near that of the chemically modified electrode. However, the waves for the coated electrodes were clearly different and less symmetric than those of the chemically modified ones, with the cathodic peak always broader than the anodic peak. Moreover, the peak currents with the coated electrode decreased more during the initial scans, perhaps because of dissolution of some of the polymer, although the peaks persisted after many cycles. The coated electrode could be washed free of polymer in the reduced state with THF while the chemically bonded polymer was stable to extended washing in THF.

In conclusion, the chemical modification of electrodes by the method described here is a very useful and general one, because the acid chloride groups on the polymer chain can be reacted quantitatively with many molecules having amino or hydroxy functional groups. An analogous technique was previously described (*1, 7, 21*) for modification of a carbon electrode, treated with thionyl chloride, to yield the acid

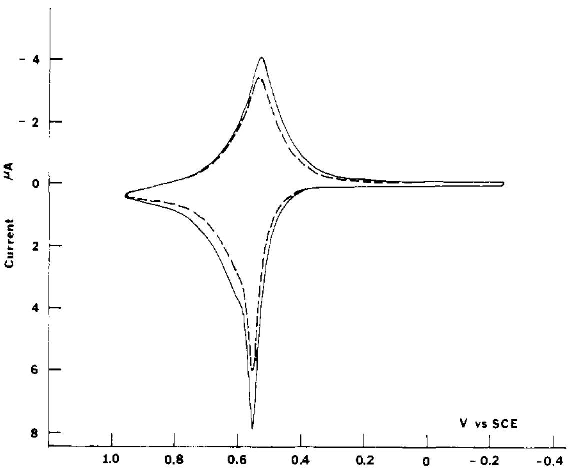

Figure 4. Cyclic voltammetric behavior of the poly(hydroxymethylferrocene methacrylate)-coated Pt electrode. The electrode surface area was about 0.038 cm^2 and the solution was 0.1 M TBAP in ACN at room temperature. Scan rate was 50 mV/s. (—) the first scan, (- - -) after 10 times scans

chloride functional group, which could then be substituted further. The results reported here make this functional group available with SnO_2 and potentially other electrodes through the chemical modification and coating techniques. Further studies concerning substitution of other electroactive groups on the polymer chain are in progress.

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Current–Potential–Time Relationships in Differential Pulse Polarography: Theory of Reversible, Quasireversible, and Irreversible Electrode Processes

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A rigorous theory of differential pulse polarography is developed for reversible electron transfer processes in which drop expansion and the sphericity effect are considered. The theory is extended to include the quasireversible and irreversible cases and a general current–time–potential expression is obtained which can be used to determine kinetic parameters. Methods for the determination of these parameters are suggested.

Pulse polarography has become a widely used electroanalytical technique since its development by Barker and coworkers (*1*, *2*). The two modes of pulse polarography, the differential mode and the integral or normal mode, are based on the measurement of the current response to a potential step, usually referred to as a pulse, which is of short duration, i.e., in the millisecond range. Both methods can be analyzed in terms of a potential perturbation which has the value E_1 immediately before the pulse is applied at some time τ and the value $E_2 = E_1 + \Delta E$ at time $t > \tau$ during the rectangular pulse. The difference between the methods is that ΔE is fixed and E_1 varies from point to point in the differential mode while E_1 is fixed and E_2 varies from point to point in the integral mode. In most experimental setups for the differential mode, the rectangular pulse is superimposed on a slowly varying potential ramp signal so that the potential E_1 is not actually constant but varies slightly in any measurement cycle. In the treatment in this paper, we consider the potential from time $t = 0$ to $t = \tau$ before the pulse is applied to be constant (a very slow scan rate) so that the theory developed for any one measurement cycle is amenable to both differential and integral pulse polarography. However, most of our discussion will be directed toward the differential method.

In previous closed form treatments of differential pulse methods (*3*, *4*) the current response to a potential pulse

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