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A Stable Surface Modified Platinum Electrode Prepared by Coating with Electroactive Polymer

Sir:

Recent studies have demonstrated that solutions of polymers containing noninteracting electroactive centers along the polymer chain in some aprotic solvents show multielectron voltammetric waves with the same wave shape as anticipated for reversible one-electron oxidation/reduction reactions.¹ While in some solvents the polymers show ideal cyclic voltammetric behavior characteristic of both reduced and oxidized forms being dissolved, in many solvent-supporting electrolyte systems the cyclic voltammograms showed sharp surface peaks apparently caused by strong adsorption or precipitation of either the reduced or oxidized form of the polymer on the electrode surface. In a solvent in which both the oxidized and reduced forms of a polymer are insoluble or strongly adsorbed on the electrode, the electrode should closely resemble a chemically modified electrode, several types of which have been recently described (see ref 2-8 and references therein). We report here the preparation of polyvinylferrocene (PVF)-coated platinum electrodes and their electrochemical behavior in acetonitrile (ACN) solutions. The PVF used had an average molecular weight of 15 750, corresponding to a degree of polymerization of 74.3 and the electrochemical behavior of solutions of PVF has been previously described.^{1b,9}

In a typical experiment, a clean, polished 0.07-cm² platinum disk surface sealed in soft glass was coated from an $\sim 10^{-5}$ M solution of PVF in dichloromethane containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). The cyclic voltammogram of this system (Figure 1a) was similar to that found in THF^{1b} and consisted of a broad anodic peak at +0.30 V and, on reversal, a sharp cathodic peak at +0.13 V (vs. a silver wire pseudo reference electrode),¹⁰ indicating adsorption or precipitation of the oxidized polymer. Continuous cyclic scans of the potential between -0.3 and +0.7 V resulted in an increase in the heights of both peaks to give a steady-state voltammogram with an integrated peak current of 570 $\mu\text{C}/\text{cm}^2$ or 0.80×10^{-8} Faradays/cm². The working electrode was held at a potential of +0.7 V for a period of 2 min and was removed from the dichloromethane solution, and the adherent excess solution was removed immediately with a soft tissue. Upon immersion into an ACN solution containing 0.1 M TBAP, this pretreated electrode gave a cyclic voltammogram with sharp anodic and cathodic peaks at +0.365 and +0.345 V, respectively (Figure 1b). The peak shapes (with a half-height width of ~ 80 mV at a scan rate of 20 mV/s) as well as the integrated peak areas ($1.2 (\pm 0.2) \times 10^{-8}$ Faradays/cm² at scan rates ≤ 200 mV/s) were very reproducible for different trials. The results were essentially the same for a platinum disk sealed in glass elec-

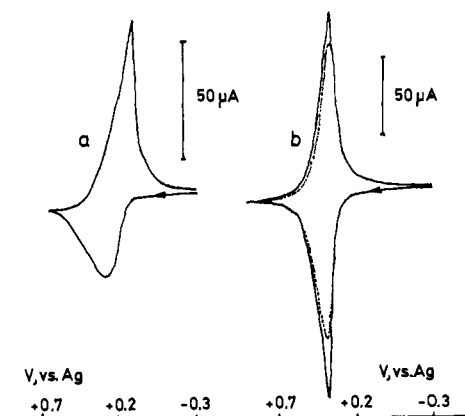


Figure 1. Cyclic voltammograms of polyvinylferrocene at a 0.07-cm² platinum disk (scan rate, 200 mV/s): (a) 10^{-5} M solution in $\text{CH}_2\text{Cl}_2/0.1$ M TBAP; (b) coated on the same electrode in acetonitrile/0.1 M TBAP; —, first cycle; ---, 250th cycle.

trode or a platinum wire electrode positioned with the wire-glass seal out of contact with the solution. This latter experiment shows that the observed results do not arise from trapping of solution in microscopic cracks at the platinum-glass seal giving rise to "thin layer effects".¹¹

With slow scan rates (≤ 0.2 V/s) the peak-to-peak separation, ΔE_p , remained nearly constant at values of 20 mV or less and the peak currents, i_{pc} and i_{pa} , were directly proportional to the scan rate, v , consistent with the confinement of both oxidized and reduced forms to the electrode surface.¹² However, the cathodic peak, at these scan rates, was somewhat broader than the anodic peak, so that i_{pc}/i_{pa} was 0.6 to 0.8, although the integrated currents of both peaks were equal. At higher scan rates ΔE_p increased to 400 mV at 100 V/s, symmetrically with respect to the original peak-to-peak center, while the peak current ratio i_{pc}/i_{pa} approached unity and the integrated peak current dropped to $\sim 20\%$ of its value at low scan rates.

If we assume, as found in solution studies,^{1b} that the number of electrons transferred per molecule of PVF is the same as the degree of polymerization, and that the PVF is distributed uniformly on the Pt surface, then the integrated peak area at slow scans corresponds to $\sim 2.1 \mu\text{g}$ of PVF/cm². Assuming a density of $\sim 1 \text{ g}/\text{cm}^3$ for the polymer, this represents a film thickness of $\sim 210 \text{ \AA}$. This corresponds to a layer containing at least 20 (and probably more) monolayers of individual ferrocene units. The decrease in peak area observed with increasing v could represent electron-transfer rate limitations to outer portions of the film.

The PVF-coated electrode in many respects resembles the Pt electrode modified by chemically bound silylferrocene recently described by Wrighton and coworkers.¹³ It is very durable. After standing in ACN solution for 24 h, the electrode behavior was practically unchanged; when repeated cyclic voltammograms were taken between -0.3 and +0.7 V, only a 12% drop of the integrated peak current was observed after 250 cycles at 200 mV/s (Figure 1b). A total potential range of -3.0 to +1.5 V (vs. Ag) could be scanned without affecting the electrochemical behavior of the coating. Extension of the scan to potentials beyond these limits, even for very short times, caused peak broadening and separation and, after a few repeated scans, total disappearance of the polymer peak into the background. Similar stable, but less reproducible, coatings were obtained by simply dipping a Pt electrode into a PVF solution of CH_2Cl_2 , wiping off the excess solution, and drying in air.

Two substrates, diphenylanthracene (DPA) and anthraquinone (AQ), were chosen to study the behavior of dissolved

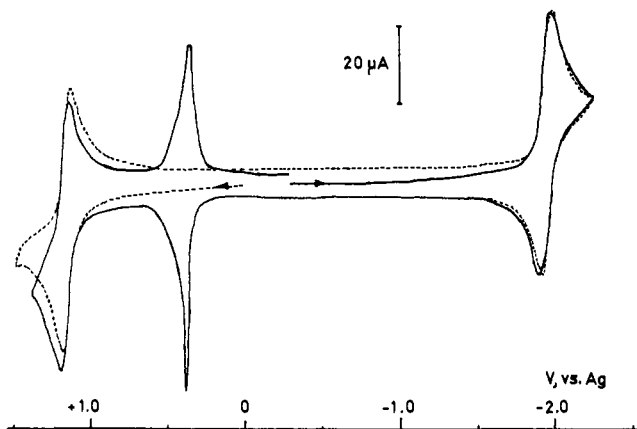


Figure 2. Cyclic voltammograms of 1.33×10^{-3} M 9,10-diphenylanthracene in acetonitrile/0.1 M TBAP at a 0.07-cm^2 platinum disk (scan rate, 200 mV/s): ---, on blank platinum surface; —, after coating the electrode and reimmersing into the same solution.

species at the PVF-coated electrode. Both chemically reversible reduction and oxidation of DPA (Figure 2) and reduction of AQ could be observed at the modified surface in ACN-TBAP solutions. At slow scan rates, the observed peaks occurred at the same potentials and had identical peak current densities as those seen with an uncoated electrode of the same area (Figure 2); however, the peak-to-peak separations of the DPA and AQ waves showed a distinct and scan rate dependent increase on the coated electrode; e.g., at 50 V/s the ΔE_p values for the DPA/DPA⁺ and DPA/DPA⁻ couples were 196 and 600 mV, respectively.¹⁴ In these experiments, the polymer film again was highly stable. Upon continuous potential scanning between -0.3 and -2.5 V the polymer peaks were unchanged after 3 h. When the polymer peaks were included into these scans ($+0.7$ V to -2.5 V), these showed the same decay behavior as described above for the polymer alone. Again, when the potential range was extended to $+1.3$ V, which included the oxidation of DPA, the voltammetric response of the polymer film disappeared within 50 cycles. However, when the electrode potential is scanned only between $+0.8$ and $+1.5$ V, the film remains stable. Since electron transfer through the thick polymer film seems unlikely at potentials where PVF is not reduced, the reduction behavior of DPA and AQ suggests the possibility of pin holes, or channels, in the coating through which the solute species may diffuse to the metal surface. As long as the scan time was such that the diffusion layer thickness was large compared with the film thickness and the spacing between the holes, the voltammetric behavior at such an electrode for a dissolved species would resemble closely that of an uncoated electrode,¹⁵ while a pattern of large coated and uncoated areas on the surface should give rise to a decrease of peak currents which would reflect the reduced active area of the electrode. Oxidations taking place beyond the potential for ferrocene oxidation could occur via the polymer however. The surface of a platinum foil coated as described above was examined by ESCA spectroscopy. Besides the expected signals for carbon and iron the spectrum also showed platinum bands at 71, 74, 100, 314, and 333 eV. Although these were strongly attenuated as compared to blank platinum, this result is inconsistent with a uniform film of the calculated thickness. Further work is in progress to confirm the actual structure of the PVF coating.

In conclusion, a platinum surface coated by adsorption or precipitation of the polymer PVF behaves like a chemically modified electrode. The polymer films are sufficiently stable that the electrochemical behavior of the films and of solute species can be studied over a wide potential range and for an extended period of time. The preparation of our PVF coated

electrode is extremely simple and depends neither on a specific adsorption phenomenon nor on a special pretreatment of the electrode surface. In our case, the electroactive groups linked to the polymer chain provide a convenient monitor for studying the coverage by means of cyclic voltammetry, but their presence does not appear to be essential in the preparation of the film itself. Thus, a more general application of polymer coated electrodes may be envisaged with polymers of special design, e.g., for electrocatalytic properties,¹⁶ for provision of a chiral electrode environment,^{2,7} for protection of semiconductor electrodes,¹³ and in attaching or producing thin layers of dyes for photochemical or photoelectrochemical studies.¹⁷

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A Poly-*p*-nitrostyrene Electrode Surface. Potential Dependent Conductivity and Electrocatalytic Properties

Sir:

We have recently reported a general method for the preparation of organic electrode surfaces involving the strong adsorption of polymers on metals.¹ This approach recalls the results of Hubbard who chemisorbed alkenes on platinum.² Polymer adsorption is, however, relatively nonspecific and this should allow modification of virtually any electrode surface. It should also allow relatively large but controllable amounts of active material to be bound. Recent work has begun to verify this view.^{3,4} These materials are analogous to other chemically modified electrodes in which species are covalently bound to carbon⁵ or metal oxide surfaces⁶ but promise to have unique and especially useful properties. We report here on the electrochemistry of poly-*p*-nitrostyrene (I) adsorbed on platinum. The initial experiments revealed the following results. (1) An adsorbed layer of I could be conveniently prepared by dip