

Monitoring the Ejection and Incorporation of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ Counterions at Protonated Poly(4-vinylpyridine) Coatings on Electrodes with the Scanning Electrochemical Microscope

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The precise positioning of microtip electrodes close to the surface of substrate electrodes, as practiced in scanning electrochemical microscopy, was exploited to monitor the concentrations of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ anions at the surfaces of protonated poly(4-vinylpyridine) coatings on glassy-carbon electrodes. Positive feedback, which enhanced the magnitude of currents at the monitoring tip electrode, gave way to negative feedback when reactant concentrations were increased to the point that electron propagation through the polyelectrolyte coatings became the current-limiting step. The ejection of counterions when cathodic currents were passed through coatings which were saturated with $\text{Fe}(\text{CN})_6^{3-}$ was readily detected, especially when current steps were applied to the coated substrate electrode. Delayed arrival of counterions at the monitoring tip could be associated with the time required for the ions to traverse the coatings before they were ejected. Reincorporation of multiply-charged counterions immediately following their ejection appeared to be favored over the incorporation of singly charged anions present at much higher concentrations.

Microelectrodes positioned very close to the surfaces of working electrodes provide a sensitive means for monitoring the concentrations of electroactive reagents within diffusion layers at electrodes. This capability was utilized by Engstrom and co-workers (1-3) and has been extended and elaborated by Bard and co-workers (4-10) who added the possibility of scanning the monitoring microelectrode over the surface of a substrate to produce scanning electrochemical microscopic images (7). The precise control of the distance between the monitoring microelectrode and the substrate electrode provided by the piezoelectric positioning devices employed in the scanning electrochemical microscope (7) led us to try to utilize the apparatus to monitor the concentrations of electroactive ions near the surfaces of polyelectrolyte coatings on electrodes. In such applications the *x-y* scanning capability of the electrochemical microscope is utilized only to position the microelectrode tip over the center of a substrate electrode. Thereafter, only the separation between the two electrodes is varied and the resulting changes in the current flowing at the tip electrode are measured. When the coated substrate electrode behaves as a conductor, the tip current increases as the separation between the tip and substrate surface is decreased to one or two tip diameters. This phenomenon has been termed "positive feedback" by Kwak and Bard (6) because it results from the reactant generated at the substrate

electrode diffusing back to the tip electrode where its reaction enhances the tip current. If the coated electrode behaves as an insulator, the tip current decreases under the same conditions. This phenomenon has been termed "negative feedback" (6) although its origin is not the simple inverse of the phenomenon responsible for positive feedback.

The tip electrode can be maintained at a fixed position near the substrate surface to detect electroactive species emanating from the substrate. In the present study this tactic was employed to monitor the concentrations of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ counterions at the surface of coatings of poly(4-vinylpyridine) (PVP) in aqueous acid where the pyridine groups of the PVP are protonated to produce a polycationic coating (PVPH⁺). The multiply-charged counteranions are spontaneously incorporated into the polyelectrolyte coatings by ion exchange (11). As cathodic current is passed through the coatings, some of the incorporated anions are ejected from the coatings in order to satisfy ionic electroneutrality within the coating. The relative quantities of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ that depart from the coating and the timing of their ejections can be measured. The results of experiments of this type are described in this report.

EXPERIMENTAL SECTION

Materials. Poly(4-vinylpyridine) from Polysciences, Inc., was dissolved in methanol and used to prepare electrode coatings. Inorganic chemicals were analytical grade and used as received. Solutions of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ were freshly prepared before each experiment. The microtip electrodes employed consisted of a carbon fiber with a diameter of ca. 11 μm sealed in glass and conically tapered as described in ref 7. The substrate electrode was a polished glassy-carbon disk with a diameter of 5 mm.

Apparatus and Procedures. The instrument for performing scanning electrochemical microscopy was constructed in this laboratory on the basis of the original design of Kwak and Bard (7). The instrument was designed and constructed so as to obtain a high sensitivity for the measurement of both tip and substrate currents. Precise arrangement of circuit elements and careful soldering of connections produced a sensitivity of 1 V/nA in both current amplifiers of the bipotentiostat. The micropositioning system employed three IW-711-00 Inchworm motors with 0.5- μm encoders and a 6000 Series motor controller, all from Burleigh Instruments, Inc. A Gateway 2000 (80386 CPU system) microcomputer was utilized to control all experimental operations and to acquire data. A Model 660 interface board (Burleigh Instruments, Inc.) served to connect the computer with the Motor Controller. An A/D and D/A interface board (DT 2821-F-8DI from Data Translation, Inc.) was interposed between the computer and the bipotentiostat. All experimental operations and data acquisition were under computer control. The software was written in C language and compiled with the Microsoft C Optimizing Compiler (Version 6.00, Microsoft Corp.).

Coatings of poly(4-vinylpyridine) were prepared by transferring 10 μL of a methanol solution containing 0.5 mg/mL of PVP and 0.12 mg/mL of 1,12-dibromododecane to the surface of the

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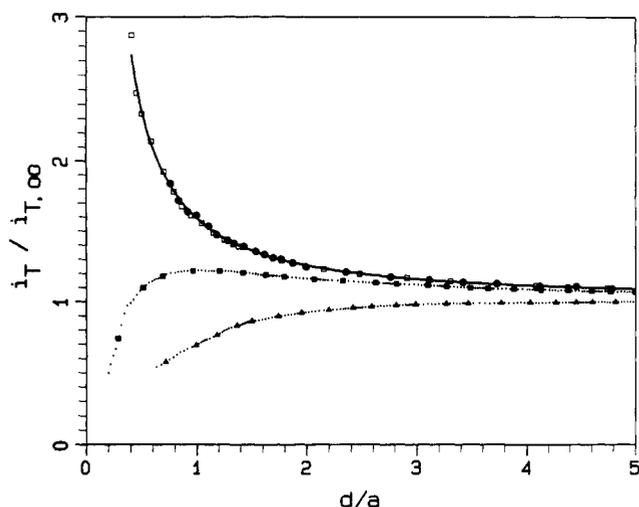


Figure 1. Normalized, steady-state tip currents as a carbon tip electrode is moved at $0.5 \mu\text{m s}^{-1}$ toward a glassy-carbon substrate electrode (radius = 2.5 mm) in a solution containing $\text{Fe}(\text{CN})_6^{3-}$: (\square) bare substrate electrode [radius of tip = $4.9 \mu\text{m}$; $[\text{Fe}(\text{CN})_6^{3-}] = 1 \text{ mM}$; supporting electrolyte $0.1 \text{ M KCl} + 5 \text{ mM HCl}$]; (\bullet) PVP-coated substrate electrode [radius of tip = $5.9 \mu\text{m}$; $[\text{Fe}(\text{CN})_6^{3-}] = 0.21 \text{ mM}$; supporting electrolyte $0.1 \text{ M KCl} + 10 \text{ mM HCl}$]; (\blacktriangle) repeat with $[\text{Fe}(\text{CN})_6^{3-}] = 1 \text{ mM}$; (\blacktriangle) repeat with $[\text{Fe}(\text{CN})_6^{3-}] = 5 \text{ mM}$. The potentials of the tip and substrate electrodes were maintained at -0.2 and 0.6 V , respectively. The ordinate is the measured tip current divided by its value when the tip is positioned far away from the substrate electrode. The abscissa gives the ratio of the separation between tip and substrate electrodes, d , to the radius of the tip, a , calculated from $i_{T,\infty} = 4FDCa$. The solid line is the response obtained from Table II of ref 6. The abscissa values for the 1 and 5 mM solutions of $\text{Fe}(\text{CN})_6^{3-}$ are uncertain because of the present lack of a sufficiently general theory to calculate the relationship between i_T and d/a in the presence of negative feedback.

glassy-carbon substrate electrode where the solvent was allowed to evaporate in air. The resulting coating was heated overnight at 70°C to introduce cross-linking via the double quaternization of pyridine groups by reaction with the dibromoalkane (12). Coating thicknesses in the dry state were estimated by measurements with a Dektak profilometer to be $0.5 \pm 0.2 \mu\text{m}$. The thicknesses of swollen coatings were doubtless larger but we did not attempt to estimate the extent of swelling.

The electrochemical cell resembled that described in ref 7. The fourth electrode required for the bipotentiostat was a coiled platinum wire. A saturated calomel reference electrode (SCE) was separated from the cell by a salt bridge. All potentials are quoted with respect to this reference electrode. Solutions were prepared from distilled water that had been passed through a purification train (Barnsted Nanopure). Solutions were not deaerated. Cathodic currents are regarded as negative but are plotted upward.

RESULTS AND DISCUSSION

Feedback Currents at Microtip Electrodes. The current response at a tip electrode as it is moved closer and closer to an uncoated glassy-carbon substrate electrode in a solution of $\text{Fe}(\text{CN})_6^{3-}$ is shown in Figure 1. The tip potential was held at -0.2 V where the $\text{Fe}(\text{CN})_6^{3-}$ was reduced to $\text{Fe}(\text{CN})_6^{4-}$ and the substrate electrode was held at 0.6 V where any $\text{Fe}(\text{CN})_6^{4-}$ reaching its surface was oxidized to $\text{Fe}(\text{CN})_6^{3-}$. When the tip is sufficiently far from the substrate (a separation of 2–3 tip radii), the tip current is independent of its position and is given by (13)

$$i_{T,\infty} = 4FDCa \quad (1)$$

where F is Faraday's constant, C and D are the concentration and diffusion coefficient of $\text{Fe}(\text{CN})_6^{3-}$, respectively, and a is the radius of the tip electrode. The effective tip radius, a , can be calculated from the known concentration and diffusion coefficient of $\text{Fe}(\text{CN})_6^{3-}$. As the tip is moved closer to the

substrate electrode, the tip current increases because of the positive feedback effect described by Kwak and Bard (6). The solid line in Figure 1 gives the predicted response as obtained from Table II in ref 6. The agreement with the experimental currents is good.

When a PVPH⁺ coating was applied to the substrate electrode and the experiment repeated with a 0.2 mM solution of $\text{Fe}(\text{CN})_6^{3-}$, the tip currents were again in good agreement with those expected in the presence of positive feedback (Figure 1, solid circles). This result shows that the PVPH⁺ coating, in which $\text{Fe}(\text{CN})_6^{3-}$ anions are extensively incorporated from 0.2 mM solutions of the anion, behaves like an uncoated, conducting substrate at which all $\text{Fe}(\text{CN})_6^{4-}$ anions impinging on the surface are oxidized to $\text{Fe}(\text{CN})_6^{3-}$. As the concentration of $\text{Fe}(\text{CN})_6^{3-}$ in the solution was increased to produce larger values of $i_{T,\infty}$, larger electron-transfer rates were required at the substrate surface in order to maintain the positive feedback that occurs at all concentrations of $\text{Fe}(\text{CN})_6^{3-}$ at bare substrate electrodes. However, the current which can flow through the coated substrate electrode is limited by the rate at which the incorporated $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ anions can diffuse (physically or by electron-hopping) across the PVPH⁺ coating. When the concentration of $\text{Fe}(\text{CN})_6^{3-}$ in solution is increased to the point where $i_{T,\infty}$ for the reduction of $\text{Fe}(\text{CN})_6^{3-}$ at the tip approaches the maximum current that can be passed through the coated substrate electrode in the vicinity of the tip, the full extent of positive feedback is no longer possible. If the concentration of $\text{Fe}(\text{CN})_6^{3-}$ is increased even further so that $i_{T,\infty}$ exceeds the maximum substrate current, negative feedback of the type observed with insulating substrates (6, 8) sets in so that tip currents decrease as the tip is moved closer to the coated substrate electrode. The behavior shown by the solid squares and the triangles in Figure 1 can be understood on this basis. A disadvantage of the behavior shown by the triangles is that the measured dependence of the tip current on the separation distance can no longer be used to estimate the actual separation between the tip and substrate electrodes as is possible when positive feedback prevails (6).

To overcome this limitation when solution concentrations which lead to the negative feedback are employed, it should be possible to adjust the potential of the tip electrode to values on the rising part of the wave for the redox couple so that the tip current and the corresponding feedback current at the coated substrate are no larger than those involved when the positive feedback response is obtained. We attempted to employ this strategy with the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple but were only partially successful, as shown in Figure 2: With a 5 mM solution of $\text{Fe}(\text{CN})_6^{3-}$ and the tip potential adjusted so as to limit the tip current to values below the plateau current obtained with a 0.2 mM solution, an initially positive feedback response was obtained (Figure 2B,C). However, when the tip-substrate separation was made even smaller, the tip current began to decrease instead of continuing to increase (Figure 2B,C). These decreasing tip currents were observed even when the tip potential was adjusted so that the tip currents were everywhere smaller than the monotonically increasing currents obtained at tip potentials on the plateau of the $\text{Fe}(\text{CN})_6^{3-}$ reduction wave with a 0.2 mM solution (Figure 2A). The reason for this behavior is unclear. However, the behavior of cross-linked coatings of PVPH⁺ was observed to be somewhat time dependent: Freshly prepared coatings which produced responses with positive feedback (such as in Figure 2A) sometimes exhibited negative feedback under the same conditions after several hours of use. In addition, single coatings sometimes exhibited positive feedback when the tip electrode was positioned over certain regions of the coating but negative feedback when the tip was moved to a position

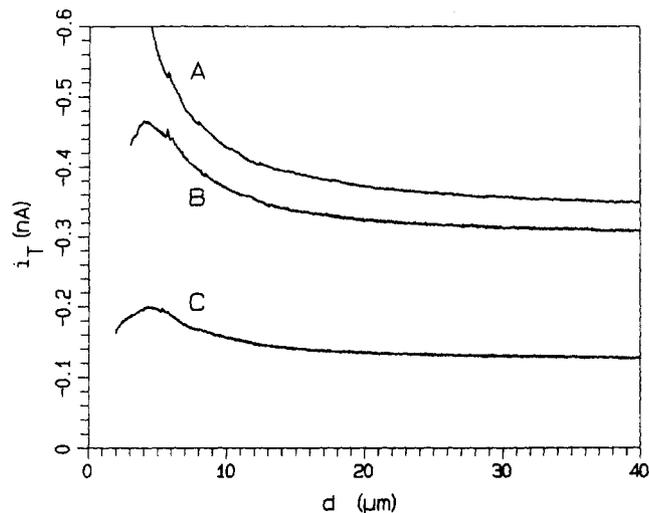


Figure 2. Dependence of tip current on tip-substrate separation as the tip ($a = 5.9 \mu\text{m}$) is moved at $0.5 \mu\text{m s}^{-1}$ toward the substrate electrode coated with PVPH⁺ and maintained at 0.6 V in a solution of $\text{Fe}(\text{CN})_6^{3-}$: (A) $[\text{Fe}(\text{CN})_6^{3-}] = 0.2 \text{ mM}$, tip potential = -0.2 V ; (B) $[\text{Fe}(\text{CN})_6^{3-}] = 5 \text{ mM}$, tip potential = 0.35 V ; (C) repeat of B with tip potential at 0.375 V . Supporting electrolyte: $0.1 \text{ M KCl} + 5 \text{ mM HCl}$.

above other parts of the coating. Despite these difficulties, reasonably reproducible behavior was obtained with freshly prepared coatings and the positive feedback responses obtained in experiments such as the one in Figure 2B were used to provide estimates of tip-substrate separations according to the procedure described by Kwak and Bard (6-8).

Monitoring Fluxes of Electroactive Counterions near the Surface of PVP-Coated Electrodes Employed in Cyclic Voltammetry. Cyclic voltammograms recorded at the bare and PVPH⁺-coated substrate electrode in a solution of $\text{Fe}(\text{CN})_6^{3-}$ are shown in Figure 3A. The larger peak currents obtained when the electrode is coated with PVPH⁺ reflect the incorporation of $\text{Fe}(\text{CN})_6^{3-}$ into the PVPH⁺ coating to produce a much higher concentration on the electrode surface (11). The microtip electrode, maintained at -0.2 V , was positioned at various distances from the substrate electrode and the tip currents were monitored as the potential of the substrate electrode was scanned from $+0.5$ to -0.2 to $+0.5 \text{ V}$. The cyclic voltammogram for the substrate electrode is shown in Figure 3A and the corresponding tip currents are shown in Figure 3B-F. The tip currents at the initial substrate potential (0.5 V) result from the reduction of $\text{Fe}(\text{CN})_6^{3-}$ in the solution as enhanced by positive feedback when the tip is within 10 - $15 \mu\text{m}$ of the substrate. As the potential of the uncoated substrate electrode is scanned to more negative values (dotted line in Figure 3A), the tip current decreases smoothly to essentially zero as the $\text{Fe}(\text{CN})_6^{3-}$ in the vicinity of the substrate is converted to $\text{Fe}(\text{CN})_6^{4-}$ to which the tip (at a potential of -0.2 V) is unresponsive. The tip current rises again as the uncoated substrate electrode is scanned back to more positive potentials, and the tip current returns to its initial value as the substrate electrode reaches its initial potential. The tip current curves for the forward and reverse scans of the substrate potential are essentially coincident when the tip is within $15 \mu\text{m}$ of the substrate (dotted curves in Figure 3B-D). At larger separation distances the curves for the forward and reverse scan directions become increasingly separated (dotted curves in Figure 3E,F) because of the increasing times required for the $\text{Fe}(\text{CN})_6^{3-}$ generated at the surface of the substrate to diffuse to the tip electrode.

The behavior is significantly different when the substrate electrode is coated with PVPH⁺: As soon as cathodic current begins to flow at the coated substrate electrode (solid curve in Figure 3A) the tip current increases. It subsequently passes

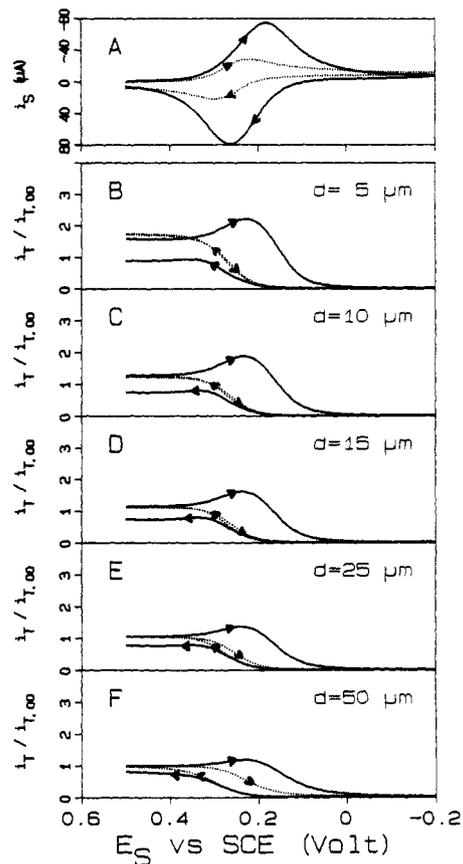


Figure 3. Tip currents recorded during cyclic voltammetry at the substrate electrode in solutions of $\text{Fe}(\text{CN})_6^{3-}$. (A) Cyclic voltammograms obtained with the bare substrate electrode (dotted curve, $[\text{Fe}(\text{CN})_6^{3-}] = 1 \text{ mM}$) or PVPH⁺-coated substrate electrode (solid curve, $[\text{Fe}(\text{CN})_6^{3-}] = 0.2 \text{ mM}$). The electrode potential was scanned at 23 mV s^{-1} from $+0.5$ to -0.2 to $+0.5 \text{ V}$. Supporting electrolyte is as in Figure 2. (B-F) Normalized cathodic tip currents obtained during the recording of the voltammograms in (A) with the tip electrode ($a = 5.9 \mu\text{m}$) maintained at -0.2 V to monitor the concentration of $\text{Fe}(\text{CN})_6^{3-}$ and positioned at various fixed distances from the bare substrate electrode (dotted curves) or coated substrate electrode (solid curves). The separation, d , was calculated from the positive feedback currents measured with the substrate potential at 0.5 V using the treatment of ref 6.

through a maximum before decreasing to zero as the substrate electrode is scanned to more negative potentials (solid curves in Figure 3B-F). This behavior demonstrates that some $\text{Fe}(\text{CN})_6^{3-}$ is ejected from the PVPH⁺ coating as the remaining $\text{Fe}(\text{CN})_6^{3-}$ is reduced to $\text{Fe}(\text{CN})_6^{4-}$. The PVPH⁺ coatings are saturated with $\text{Fe}(\text{CN})_6^{3-}$ in 0.2 mM solutions so that anion ejection (or cation incorporation) is required to maintain electroneutrality when cathodic currents are passed through the coating. The tip current increases again as the substrate electrode is scanned back to more positive potentials, but 1-2 min are required for the tip current to return to its initial value with the substrate potential maintained at 0.5 V . This delay in the restoration of the tip current reflects the time needed for reincorporation of $\text{Fe}(\text{CN})_6^{3-}$ into the PVPH⁺ coating so that the full positive feedback effect is restored. Before this restoration, the tip current is actually slightly smaller than its value at infinite separation, as expected if the coating temporarily acted to depress the tip current because of negative feedback (6, 8). The results summarized in Figure 3 demonstrate that the ejection of some $\text{Fe}(\text{CN})_6^{3-}$ anions from the PVPH⁺ coating begins at the same time as does the reduction of the remaining $\text{Fe}(\text{CN})_6^{3-}$ anions which are retained within the coating.

A similar set of experiments was conducted with the potential of the tip electrode maintained at 0.6 V in order to

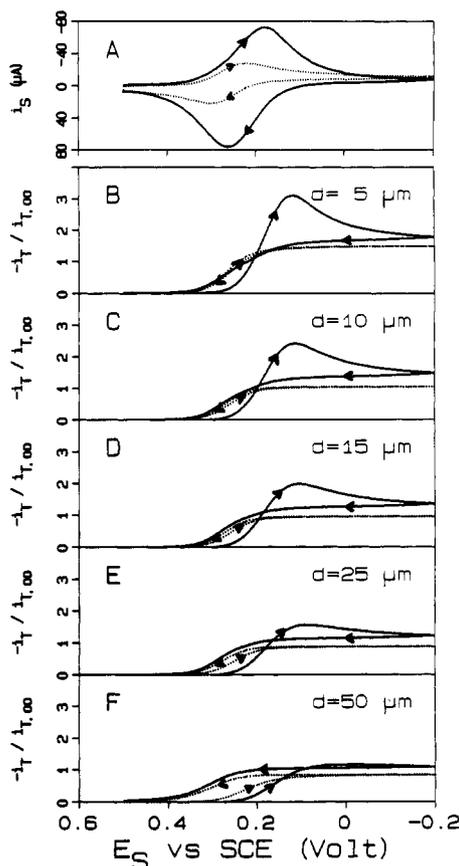


Figure 4. Repeat of Figure 3 with the tip electrode maintained at 0.6 V to monitor the concentration of $\text{Fe}(\text{CN})_6^{4-}$.

monitor the concentration of $\text{Fe}(\text{CN})_6^{4-}$ near the substrate electrode. The results are shown in Figure 4. In these experiments there is no initial tip current because no $\text{Fe}(\text{CN})_6^{4-}$ is present until the substrate electrode is scanned to potentials sufficiently negative to generate it. When the tip electrode is positioned close to the surface of an uncoated substrate electrode, an anodic tip current begins to flow almost as soon as the reduction of $\text{Fe}(\text{CN})_6^{3-}$ at the substrate electrode commences and the resulting $\text{Fe}(\text{CN})_6^{4-}$ diffuses to the nearby tip (Figure 4B–D, dotted curves). When the tip is located farther away from the substrate, a delay in the tip current response is observed (Figure 4E,F, dotted curves) because of the time required for the $\text{Fe}(\text{CN})_6^{4-}$ to diffuse from the substrate to the tip electrode.

When the experiment is repeated with the substrate electrode coated with PVPH⁺, there is a delay in the appearance of $\text{Fe}(\text{CN})_6^{4-}$ at the tip electrode even at the smallest substrate–tip separation (Figure 4B, solid curves) but eventually the flux of ejected $\text{Fe}(\text{CN})_6^{4-}$ anions detected by the tip exceeds the corresponding flux of $\text{Fe}(\text{CN})_6^{3-}$ observed in the experiments of Figure 3. Tip currents in Figure 4 which are larger than the steady current obtained with an uncoated substrate electrode must result from $\text{Fe}(\text{CN})_6^{4-}$ ejected from the coated substrate. The coating is the only source of $\text{Fe}(\text{CN})_6^{4-}$ which could produce concentrations of this anion that exceed the concentration of $\text{Fe}(\text{CN})_6^{3-}$ in solution as measured by the steady initial tip currents in Figure 3B–F. The reason for the extensive ejection of $\text{Fe}(\text{CN})_6^{4-}$ from PVPH⁺ coatings is the much smaller equilibrium affinity of $\text{Fe}(\text{CN})_6^{4-}$ for PVPH⁺ (14). Similar ejection of $\text{Fe}(\text{CN})_6^{4-}$ from PVPH⁺ coatings had been demonstrated by Doblhofer and co-workers by means of transient rotating ring–disk voltammetry (14–16).

The delay in the rise of the tip currents in Figure 4 reflects the time required for $\text{Fe}(\text{CN})_6^{4-}$ anions generated at the coating/electrode interface to diffuse through the coating (by

physical motion or electron-hopping) to reach the coating/solution interface. Until this traverse of the coating has occurred, neither the ejection of $\text{Fe}(\text{CN})_6^{4-}$ from the coating nor the generation of $\text{Fe}(\text{CN})_6^{4-}$ in solution by electron transfer between $\text{Fe}(\text{CN})_6^{3-}$ in solution and $\text{Fe}(\text{CN})_6^{4-}$ at the coating/solution interface can take place. Note that, unlike the behavior seen in Figure 3 for $\text{Fe}(\text{CN})_6^{3-}$ anions, the ejection of $\text{Fe}(\text{CN})_6^{4-}$ anions continues until the potential of the coated substrate electrode is returned to values where $\text{Fe}(\text{CN})_6^{3-}$ is regenerated in the coating. This behavior is a further reflection of the much higher affinity of the coating for the oxidized form of the counterion.

The picture that emerges from the results summarized in Figures 3 and 4 is one in which both $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ are ejected from PVPH⁺ coatings saturated with $\text{Fe}(\text{CN})_6^{3-}$ when the incorporated anions are reduced to $\text{Fe}(\text{CN})_6^{4-}$. The ejection of $\text{Fe}(\text{CN})_6^{3-}$ is immediate and is driven by the maintenance of electroneutrality within the coating. The ejection of $\text{Fe}(\text{CN})_6^{4-}$ is slightly delayed and is the result of reverse ion-exchange in which the $\text{Fe}(\text{CN})_6^{4-}$ anions, more weakly bound than $\text{Fe}(\text{CN})_6^{3-}$ anions, are replaced by anions from the supporting electrolyte, or of electron-exchange between $\text{Fe}(\text{CN})_6^{4-}$ in the coating and $\text{Fe}(\text{CN})_6^{3-}$ in the supporting electrolyte.

Potential-Step Experiments. Microtip electrodes positioned near the surfaces of substrate electrodes while the potentials of the latter were stepped from +0.6 to –0.2 V in solutions of $\text{Fe}(\text{CN})_6^{3-}$ produced the tip current responses shown in Figures 5 and 6 (curves B–F). The chronoamperometric responses from the bare and coated substrate electrode are shown in Figures 5A and 6A. With the tip electrode set at –0.2 V, to detect $\text{Fe}(\text{CN})_6^{3-}$, a steady tip current flows before the potential of the substrate is stepped and its magnitude depends upon the tip–substrate separation because of positive feedback. After the potential of the bare electrode is stepped to –0.2 V, where $\text{Fe}(\text{CN})_6^{3-}$ is reduced to $\text{Fe}(\text{CN})_6^{4-}$, the tip current decays toward zero. The decay is very rapid when the tip is close to the substrate (Figure 5B,C, dotted curves) and less so as the separation is increased. Because of the effect of positive feedback, the tip current provides only a rough estimate of the instantaneous concentration of $\text{Fe}(\text{CN})_6^{3-}$ at various distances from the substrate surface. However, with the bare substrate, the temporal dependence of the tip currents are in qualitative agreement with the expected changes in the concentration of $\text{Fe}(\text{CN})_6^{3-}$. When the potential of the coated substrate electrode is stepped to –0.2 V, increases instead of decreases in the concentration of $\text{Fe}(\text{CN})_6^{3-}$ near the coating surface are observed initially followed by a decay toward zero (Figure 5B–F, solid curves). The ejection of $\text{Fe}(\text{CN})_6^{3-}$ from the coating to maintain electroneutrality is evident as its concentration at the position 5 μm from the coating increases by more than 4-fold (Figure 5B).

Repetition of the potential-step experiments with the tip electrode potential set to monitor the concentration of $\text{Fe}(\text{CN})_6^{4-}$ (Figure 6B–F) showed that, after a delay, this anion is also ejected from the coating. Comparison of Figures 5B and 6B shows that the ejection of $\text{Fe}(\text{CN})_6^{4-}$ commences at about the same time as the ejection of $\text{Fe}(\text{CN})_6^{3-}$ diminishes, suggesting that once the $\text{Fe}(\text{CN})_6^{4-}$ anions have had time to diffuse (by physical motion or electron-hopping) from the electrode surface to the coating/solution interface it is these less strongly bound anions which carry most of the ionic current across the interface.

Current-Step Experiments. The use of a galvanostatic instead of a potentiostatic perturbation of the substrate electrode produced the set of responses shown in Figures 7 and 8. The behavior of the tip currents when a constant cathodic current was passed through the coating on the sub-

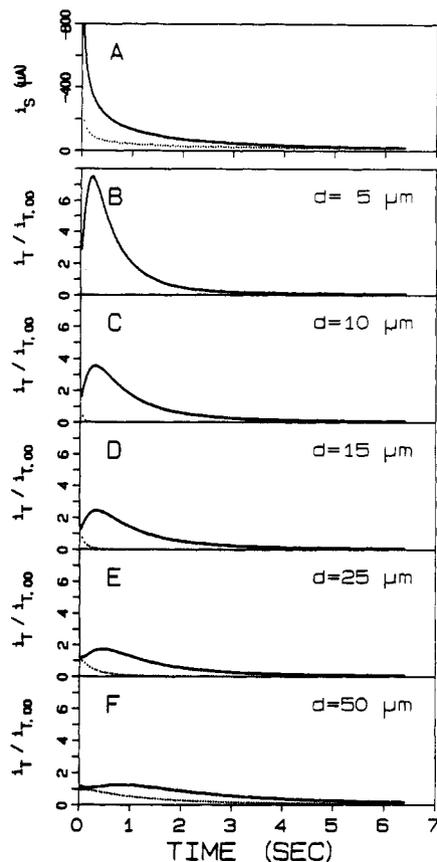


Figure 5. Tip currents resulting from potential steps at the substrate electrode in solutions of $\text{Fe}(\text{CN})_6^{3-}$. (A) Chronoamperometric substrate currents resulting from a potential step from +0.6 to -0.2 V with a bare substrate electrode (dotted curve, $[\text{Fe}(\text{CN})_6^{3-}] = 1 \text{ mM}$) or a PVPH⁺-coated substrate electrode (solid curve, $[\text{Fe}(\text{CN})_6^{3-}] = 0.2 \text{ mM}$). Supporting electrolyte is as in Figure 2. (B-F) Normalized cathodic tip currents obtained during the potential-step experiments in (A) with the tip maintained at -0.2 V to monitor the concentration of $\text{Fe}(\text{CN})_6^{3-}$. The initial tip currents are distorted for 50–100 ms by coupling between the substrate and tip electronic control circuits, especially at the smallest values of d . The tip current corresponding to the bare substrate electrode decayed to zero too quickly to see in Figure 5B. Other conditions are as in Figure 3.

strate is consistent with expectations based on the analyses of the cyclic voltammetric and potential-step results. The delay in the ejection of $\text{Fe}(\text{CN})_6^{4-}$ from the coatings is particularly clear when a current step is employed (Figure 8B–F, solid curves). An interesting phenomenon develops when the current direction is reversed so that the $\text{Fe}(\text{CN})_6^{4-}$ anions generated at the electrode surface before current reversal are oxidized back to $\text{Fe}(\text{CN})_6^{3-}$ after current reversal. When this current-reversal experiment is carried out with a bare substrate electrode, the cathodic tip current decays toward zero, as expected, during the forward current step and increases again immediately after the current reversal (Figure 7B,C, dotted curves). However, with the coated substrate electrode, the cathodic tip current for small tip–substrate separations continues to decrease, and at an enhanced rate, instead of increasing immediately after the current reversal (Figure 7B, solid curve). This unusual behavior is believed to result from the reincorporation of $\text{Fe}(\text{CN})_6^{3-}$ anions by the coating as driven by the anodic current. Anion incorporation by the coating is required to maintain electroneutrality following the current reversal. Apparently, the $\text{Fe}(\text{CN})_6^{3-}$ anions present at the coating/solution interface reenter the coating despite the much higher concentration of Cl^- anions which are also available. At equilibrium, $\text{Fe}(\text{CN})_6^{3-}$ anions are preferentially incorporated by PVPH⁺ coatings from 1 mM solutions of $\text{Fe}(\text{CN})_6^{3-}$ in 0.1 M KCl. It may be that the three pyH⁺ groups

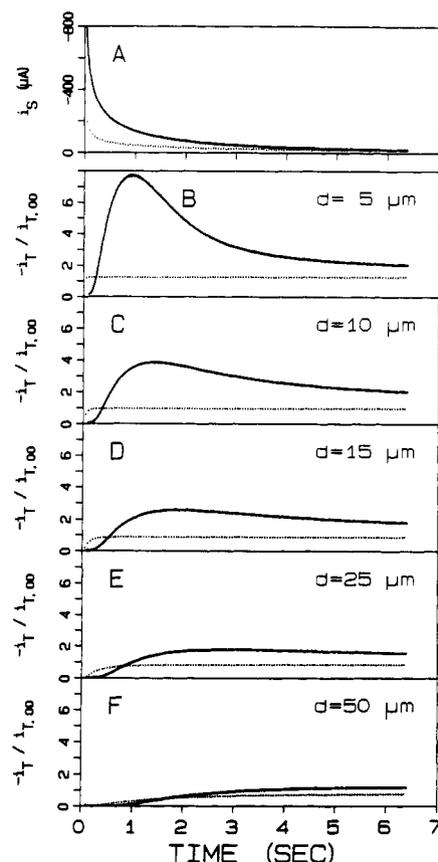


Figure 6. Repeat of Figure 5 with the tip electrode maintained at 0.6 V to monitor the concentration of $\text{Fe}(\text{CN})_6^{4-}$.

in the site within the PVPH⁺ coating from which the $\text{Fe}(\text{CN})_6^{3-}$ anions were ejected, retain a structure which induces the thermodynamically favored reincorporation of the multiply-charged anion over the more abundant singly-charged Cl^- ions. Whatever the origins of this selectivity during reincorporation of $\text{Fe}(\text{CN})_6^{3-}$ anions, the tip current responses in Figure 7B seem clearly to demonstrate its existence.

Additional evidence of the preferential incorporation of the multiply-charged anions following current reversal can be found in Figure 8B,C where the potential of the tip electrode was set to monitor the concentration of $\text{Fe}(\text{CN})_6^{4-}$ near the coated substrate electrode. As explained above, the delay in the arrival of $\text{Fe}(\text{CN})_6^{4-}$ anions at the tip after the cathodic current step is applied to the substrate reflects the time required for $\text{Fe}(\text{CN})_6^{4-}$ anions generated at the underlying electrode to reach the coating/electrolyte interface. For the same reason, a comparable delay would be expected after current reversal as the $\text{Fe}(\text{CN})_6^{3-}$ anions generated at the electrode move to the coating/solution interface where they can accept electrons from the $\text{Fe}(\text{CN})_6^{4-}$ anions in the solution and diminish the concentration of the latter anion. However, as is clear from the solid curves in Figure 8B,C, the decrease in the concentration of $\text{Fe}(\text{CN})_6^{4-}$ commences immediately after the current reversal and proceeds at a rate somewhat greater than that obtained at the uncoated substrate electrode. This immediate, rapid decrease in the concentration of $\text{Fe}(\text{CN})_6^{4-}$ seems a clear indication that this anion, like $\text{Fe}(\text{CN})_6^{3-}$, is driven into the coating by the anodic current despite the presence of a much greater concentration of Cl^- anions. This feature of the behavior of PVPH⁺ coatings had not been noted in previous studies (14–16) which lacked the sensitivity available with the scanning electrochemical microscope.

The results in Figure 8 were obtained with the substrate electrode exposed to a solution of $\text{Fe}(\text{CN})_6^{3-}$ anions for which PVPH⁺ coatings have a high affinity. When similar experi-

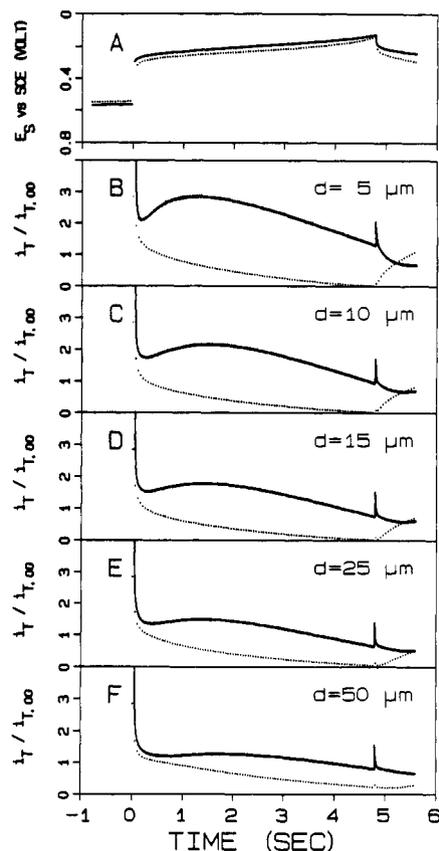


Figure 7. Tip currents resulting from current steps at the substrate electrode in solutions of $\text{Fe}(\text{CN})_6^{3-}$. (A) Chronopotentiograms recorded with a bare substrate electrode (dotted curve, $[\text{Fe}(\text{CN})_6^{3-}] = 1 \text{ mM}$) or a PVPH⁺-coated substrate electrode (solid curve, $[\text{Fe}(\text{CN})_6^{3-}] = 0.2 \text{ mM}$). The cathodic current steps applied were -28 and $-80 \mu\text{A}$ at the bare and coated electrodes, respectively. The current direction was reversed after 4.8 s , which was before the transition time. The electrode was equilibrated at 0.6 V for 2 min and placed at open circuit for 0.8 s before the current step was applied. (B–F) Normalized cathodic tip currents obtained in response to the current steps in (A) with the tip electrode maintained at -0.2 V to monitor the concentration of $\text{Fe}(\text{CN})_6^{3-}$. The tip currents at $t = 0$ are distorted for 50 – 100 ms by electronic coupling. Other conditions are as in Figure 3.

ments were carried out with solutions of $\text{Fe}(\text{CN})_6^{4-}$, which is incorporated less strongly by PVPH⁺, the temporal behavior of the tip currents was different, as shown in Figure 9B,C for one value of the tip–substrate separation. With the tip potential set at 0.6 V , to monitor the concentration of $\text{Fe}(\text{CN})_6^{4-}$, passing a constant anodic current through the coated substrate electrode produced almost no change in tip current for the first 1.5 s (Figure 9B). Since the anodic current step applied to the substrate electrode (Figure 9A) causes anions to be incorporated, not ejected, from the substrate, the absence of a decrease in tip current for 1.5 s indicates that the incorporated anions are primarily the more abundant Cl^- anions. This apparent incorporation of Cl^- instead of $\text{Fe}(\text{CN})_6^{4-}$ in Figure 9B contrasts with the behavior following current reversal shown in Figure 8B,C where recently ejected $\text{Fe}(\text{CN})_6^{4-}$ anions were reincorporated by the PVPH⁺ coating more readily than Cl^- anions. This behavioral difference adds support to the suggestion made in connection with Figures 7 and 8 that PVPH⁺ coatings from which $\text{Fe}(\text{CN})_6^{3-}$ or $\text{Fe}(\text{CN})_6^{4-}$ anions have been ejected are better able to reincorporate these anions than are coatings which have not engaged in an anion ejection–anion incorporation cycle.

At times longer than 2 s in Figure 9B the concentrations of $\text{Fe}(\text{CN})_6^{4-}$ near the substrate decreases as $\text{Fe}(\text{CN})_6^{3-}$ anions generated within the coating reach the coating/solution interface where they can accept electrons from the $\text{Fe}(\text{CN})_6^{4-}$

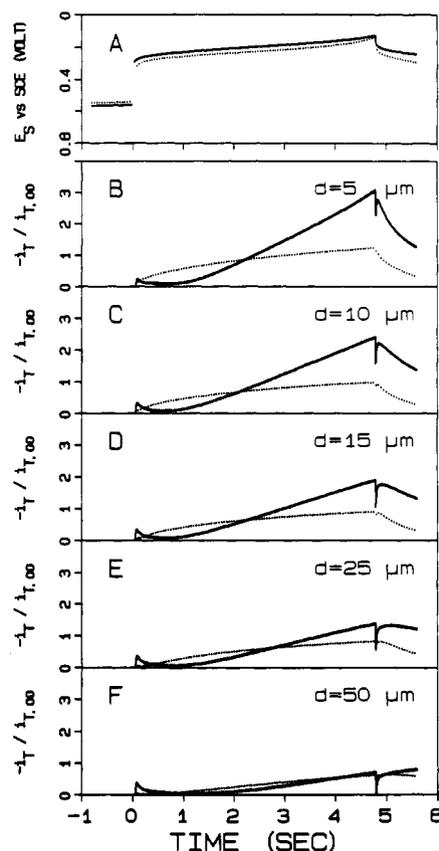


Figure 8. Repeat of Figure 7 with the tip electrode maintained at 0.6 V to monitor the concentration of $\text{Fe}(\text{CN})_6^{4-}$.

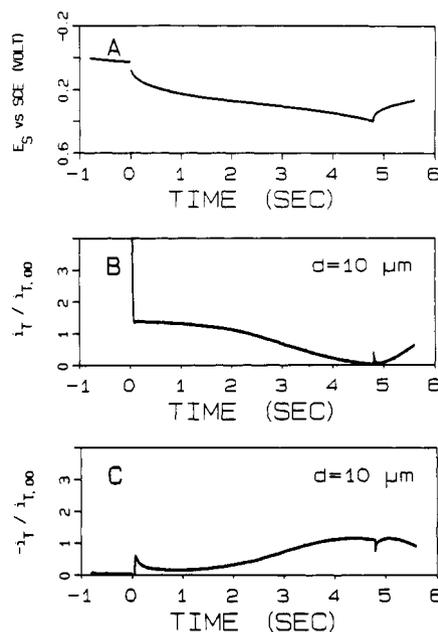


Figure 9. Tip currents resulting from current steps at the substrate electrode in solutions of $\text{Fe}(\text{CN})_6^{4-}$ with a tip–substrate separation of $10 \mu\text{m}$. (A) Chronopotentiogram recorded with a PVPH⁺-coated substrate electrode in $0.2 \text{ mM Fe}(\text{CN})_6^{4-}$. The anodic current step applied was $30 \mu\text{A}$. The current direction was reversed after 4.8 s , which was before the transition time. The electrode was equilibrated at -0.2 V for 2 min and placed at open circuit for 0.8 s before the current step was applied. (B) Normalized anodic tip current obtained in response to the current step in (A) with the tip electrode maintained at 0.6 V to monitor the concentration of $\text{Fe}(\text{CN})_6^{4-}$. (C) Normalized cathodic tip current with the tip electrode maintained at -0.2 V to monitor the concentration of $\text{Fe}(\text{CN})_6^{3-}$.

anions in solution to decrease the concentration of the latter. The positive feedback, which causes the initial normalized tip

current to exceed 1.0, diminishes and becomes negative as $\text{Fe}(\text{CN})_6^{3-}$ anions replace $\text{Fe}(\text{CN})_6^{4-}$ anions within the coating, and this factor produces further decreases in the tip current. Upon current reversal, the likely ejection of some $\text{Fe}(\text{CN})_6^{4-}$ (along with $\text{Fe}(\text{CN})_6^{3-}$) anions and the gradual restoration of positive feedback produce an increase in the tip current.

Shown in Figure 9C is the current response at the tip when it is set at -0.2 V to monitor the concentration of $\text{Fe}(\text{CN})_6^{3-}$ near the substrate electrode. The delay in the appearance of $\text{Fe}(\text{CN})_6^{3-}$ at the tip matches the delay in the decrease of the concentration of $\text{Fe}(\text{CN})_6^{4-}$ in Figure 9B. It reflects the time required for $\text{Fe}(\text{CN})_6^{3-}$ generated at the electrode to reach the coating/solution interface. After current reversal, anion ejection commences and sufficient $\text{Fe}(\text{CN})_6^{3-}$ appears to be ejected to produce a slight increase in its concentration near the substrate before the ultimate decline back to zero ensues. The overall behavior observed when the coated substrate is bathed in $\text{Fe}(\text{CN})_6^{4-}$ (Figure 9) is consistent with the interpretation offered earlier for the behavior in solutions of $\text{Fe}(\text{CN})_6^{3-}$ (Figures 7 and 8).

CONCLUSIONS

The utility of microtip monitoring electrodes in detecting dynamic phenomena which accompany the flow of ionic and electronic current across the coating/solution interface is well illustrated by the $\text{PVP}^{\text{H}^+}/\text{Fe}(\text{CN})_6^{3-/4-}$ system. The ejections of both $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ anions from PVP^{H^+} coatings saturated with $\text{Fe}(\text{CN})_6^{3-}$ observed in this study are in accord with the previous results of Doblhofer and co-workers who measured transient currents at rotating ring-coated disk electrodes (14–16). In both studies, the ejection of $\text{Fe}(\text{CN})_6^{3-}$ was observed to be coincident with the passage of cathodic current through the coating while the ejection of $\text{Fe}(\text{CN})_6^{4-}$ was delayed by the time required for the $\text{Fe}(\text{CN})_6^{4-}$ to diffuse across the coating (by physical motion or electron-hopping). The apparent preferential reincorporation of the ejected $\text{Fe}(\text{CN})_6^{3-}$ anions instead of the more abundant Cl^- anions of the supporting electrolyte was detected for the first time in the present study. PVP^{H^+} coatings in which $\text{Fe}(\text{CN})_6^{3-}$ or $\text{Fe}(\text{CN})_6^{4-}$ anions are incorporated can exhibit either positive

or negative feedback in experiments with microtip electrodes positioned close to the coatings (Figure 2). This behavior requires that the experimental conditions employed be matched to the particular objective. Thus, when the microtip electrode is to be used to monitor concentrations near the coated substrate electrode, positive feedback can be desirable. In that case, conditions (i.e., reactant concentrations) must be chosen so that maximum substrate currents do not exceed the limit imposed by the diffusional rate of the redox couples incorporated in the coatings. In cases where this is not possible, it may be necessary to operate with substrate-tip separation distances large enough to avoid feedback altogether.

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