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

Juhyoun Kwak$^1$ and Fred C. Anson$^*$

Arthur Amos Noyes Laboratories, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

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 Fe(CN)$_6^{3-}$ and Fe(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 countertions when cathodic currents were passed through coatings which were saturated with Fe(CN)$_6^{3-}$ was readily detected, especially when current steps were applied to the coated substrate electrode. Delayed arrival of countertions 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 countertions 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 Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$ countertions 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 (PVPF$^+$). The multiply-charged countertions 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 Fe(CN)$_6^{3-}$ and Fe(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 K$_2$Fe(CN)$_6$ and K$_3$Fe(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 1W-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
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 Fe(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 Fe(CN)6^3- anions are extensively incorporated from 0.2 mM solutions of the anion, behaves like an uncoated, conducting substrate at which all Fe(CN)6^3- anions impinging on the surface are oxidized to Fe(CN)6^4-. As the concentration of Fe(CN)6^4- in the solution was increased to produce larger values of $i_{r,T}$, larger electron-transfer rates were required at the substrate surface in order to maintain the positive feedback that occurs at all concentrations of Fe(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 Fe(CN)6^3- and Fe(CN)6^4- anions can diffuse (physically or by electron-hopping) across the PVPH+ coating. When the concentration of Fe(CN)6^3- in solution is increased to the point where $i_{r,T}$ for the reduction of Fe(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 Fe(CN)6^3- is increased even further so that $i_{r,T}$ 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 Fe(CN)6^3-/4- couple but were only partially successful, as shown in Figure 2: With a 5 mM solution of Fe(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 Fe(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

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**RESULTS AND DISCUSSION**

**Feedback Currents at Micropipette 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 Fe(CN)6^3- is shown in Figure 1. The tip potential was held at -0.2 V where the Fe(CN)6^3- was reduced to Fe(CN)6^4- and the substrate electrode was held at 0.6 V where any Fe(CN)6^4- reaching its surface was oxidized to Fe(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)

$$i_{T,0} = 4FDCa$$

where $F$ is Faraday's constant, $C$ and $D$ are the concentration and diffusion coefficient of Fe(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 Fe(CN)6^3-. As the tip is moved closer to the 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 dibromomethane (12). Coating thicknesses in the dry state were estimated by measurements with a Dektak profilometer to be 0.5 ± 0.2 μm. 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 bipotentiosat 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.
Electrode is coated with PVPH⁺: The tip current curves for the forward and reverse scan directions become increasingly separated (dotted curves in Figure 3B-F) because of the increasing times required for the Fe(CN)_6³⁻ 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 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 Fe(CN)_6³⁻ is ejected from the PVPH⁺ coating as the remaining Fe(CN)_6⁺ is reduced to Fe(CN)_₆⁴⁻. The PVPH⁺ coatings are saturated with Fe(CN)_₆³⁻ 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 Fe(CN)_₆³⁻ 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 Fe(CN)_₆³⁻ anions from the PVPH⁺ coating begins at the same time as does the reduction of the remaining Fe(CN)_₆⁺ 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
monitor the concentration of Fe(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 Fe(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 Fe(CN)$_6^{4-}$ at the substrate electrode commences and the resulting Fe(CN)$_6^{3-}$ diffuses to the nearby tip electrode (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 Fe(CN)$_6^{3-}$ 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 Fe(CN)$_6^{4-}$ at the tip electrode even at the smallest substrate–tip separation (Figure 4B, solid curves) but eventually the flux of ejected Fe(CN)$_6^{4-}$ anions detected by the tip exceeds the corresponding flux of Fe(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 Fe(CN)$_6^{4-}$ ejected from the coated substrate. The coating is the only source of Fe(CN)$_6^{4-}$ which could produce concentrations of this anion that exceed the concentration of Fe(CN)$_6^{3-}$ in solution as measured by the steady initial tip currents in Figure 3B–F. The reason for the extensive ejection of Fe(CN)$_6^{4-}$ from PVPH$^+$ coatings is the much smaller equilibrium affinity of Fe(CN)$_6^{4-}$ for PVPH$^+$ (14). Similar ejection of Fe(CN)$_6^{4-}$ from PVPH$^+$ coatings had been demonstrated by Dobhoff and co-workers by means of transient rotating ring–disk voltammetry (14–16).

The decay of the rise of the tip currents in Figure 4 reflects the time required for Fe(CN)$_6^{3-}$ 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 Fe(CN)$_6^{4-}$ from the coating nor the generation of Fe(CN)$_6^{4-}$ in solution and Fe(CN)$_6^{3+}$ at the coating/solution interface can take place. Note that, unlike the behavior seen in Figure 3 for Fe(CN)$_6^{3+}$ anions, the ejection of Fe(CN)$_6^{3+}$ anions continues until the potential of the coated substrate electrode is returned to values where Fe(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 Fe(CN)$_6^{3+}$ and Fe(CN)$_6^{4-}$ are ejected from PVPH$^+$ coatings saturated with Fe(CN)$_6^{3-}$ when the incorporated anions are reduced to Fe(CN)$_6^{4-}$. The ejection of Fe(CN)$_6^{3+}$ is immediate and is driven by the maintenance of electroneutrality within the coating. The ejection of Fe(CN)$_6^{4-}$ is slightly delayed and is the result of reverse ion-exchange in which the Fe(CN)$_6^{3-}$ anions, more weakly bound than Fe(CN)$_6^{4-}$ anions, are replaced by anions from the supporting electrolyte, or of electron-exchange between Fe(CN)$_6^{4-}$ in the coating and Fe(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 Fe(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 Fe(CN)$_6^{3-}$, a steady tip current flows, which is then reduced to zero when the potential of the bare electrode is returned to values where Fe(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.

**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.

Figure 4. Repeat of Figure 3 with the tip electrode maintained at 0.6 V to monitor the concentration of Fe(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 Fe(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 Fe(CN)$_6^{4-}$ at the substrate electrode commences and the resulting Fe(CN)$_6^{3-}$ diffuses to the nearby tip electrode (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 Fe(CN)$_6^{3-}$ 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 Fe(CN)$_6^{4-}$ at the tip electrode even at the smallest substrate–tip separation (Figure 4B, solid curves) but eventually the flux of ejected Fe(CN)$_6^{4-}$ anions detected by the tip exceeds the corresponding flux of Fe(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 Fe(CN)$_6^{4-}$ ejected from the coated substrate. The coating is the only source of Fe(CN)$_6^{4-}$ which could produce concentrations of this anion that exceed the concentration of Fe(CN)$_6^{3-}$ in solution as measured by the steady initial tip currents in Figure 3B–F. The reason for the extensive ejection of Fe(CN)$_6^{4-}$ from PVPH$^+$ coatings is the much smaller equilibrium affinity of Fe(CN)$_6^{4-}$ for PVPH$^+$ (14). Similar ejection of Fe(CN)$_6^{4-}$ from PVPH$^+$ coatings had been demonstrated by Dobhoff and co-workers by means of transient rotating ring–disk voltammetry (14–16).
available. At equilibrium, \( \text{Fe(CN)}_{6}^{3-} \) anions are preferentially the much higher concentration of \( \text{Cl}^{-} \) anions which are also.

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crincorporated by PWH\(^+\) coatings from 1 mM solutions of

electrode exposed to a solution of \( \text{Fe(CN)}_{6}^{3-} \) anions for which

PWH\(^+\) coatings have a high affinity. When similar experi-

strate is consistent with expectations based on the analyses of the cyclic voltammetric and potential-step results. The delay in the ejection of \( \text{Fe(CN)}_{6}^{3-} \) anions 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 \( \text{Fe(CN)}_{6}^{3-} \) anions generated at the electrode surface before current reversal are oxidized back to \( \text{Fe(CN)}_{6}^{2+} \) after current reversal. When this current-reversal experiment is carried out with a bare substrate electrode, the cathodic tip currents decay 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 \( \text{Fe(CN)}_{6}^{3-} \) 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 \( \text{Fe(CN)}_{6}^{3-} \) anions present at the coating/solution interface reenter the coating despite the much higher concentration of \( \text{Cl}^{-} \) anions which are also available. At equilibrium, \( \text{Fe(CN)}_{6}^{3-} \) anions are preferentially incorporated by PVP\(^+\) coatings from 1 mM solutions of \( \text{Fe(CN)}_{6}^{3-} \) in 0.1 M KCl. It may be that the three pyH\(^+\) groups

Figure 5. Tip currents resulting from potential steps at the substrate electrode in solutions of \( \text{Fe(CN)}_{6}^{3-} \). (A) Chronoamperometric substrate currents resulting from a potential step from +0.6 to -0.2 V with a bare substrate electrode (dotted curve, [\( \text{Fe(CN)}_{6}^{3-} \)] = 1 mM) or a PVP\(^+\)-coated substrate electrode (solid curve, [\( \text{Fe(CN)}_{6}^{3-} \)] = 0.2 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 \( \text{Fe(CN)}_{6}^{3-} \). 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.

in the site within the PVP\(^+\) coating from which the \( \text{Fe(CN)}_{6}^{3-} \) anions were ejected, retain a structure which induces the thermodynamically favored reincorporation of the multiply-charged anion over the more abundant singly-charged \( \text{Cl}^{-} \) ions. Whatever the origins of this selectivity during reincorporation of \( \text{Fe(CN)}_{6}^{3-} \) 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 \( \text{Fe(CN)}_{6}^{3-} \) near the coated substrate electrode. As explained above, the delay in the arrival of \( \text{Fe(CN)}_{6}^{3-} \) anions at the tip after the cathodic current step is applied to the substrate reflects the time required for \( \text{Fe(CN)}_{6}^{3-} \) 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 \( \text{Fe(CN)}_{6}^{3-} \) anions generated at the electrode move to the coating/solution interface where they can accept electrons from the \( \text{Fe(CN)}_{6}^{3-} \) 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 \( \text{Fe(CN)}_{6}^{3-} \) 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 \( \text{Fe(CN)}_{6}^{3-} \) seems a clear indication that this anion, like \( \text{Fe(CN)}_{6}^{3-} \), is driven into the coating by the anodic current despite the presence of a much greater concentration of \( \text{Cl}^{-} \) anions. This feature of the behavior of PVP\(^+\) 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 \( \text{Fe(CN)}_{6}^{3-} \) anions for which PVP\(^+\) coatings have a high affinity. When similar exper-
Figure 7. Tip currents resulting from current steps at the substrate electrode in solutions of Fe(CN)$_6^{3-}$. (A) Chronopotentiograms recorded with a bare substrate electrode (dotted curve, [Fe(CN)$_6^{3-}$] = 1 mM) or a PVPH$^+$-coated substrate electrode (solid curve, [Fe(CN)$_6^{3-}$] = 0.2 mM). The cathodic current steps applied were -28 and -80 μA 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 Fe(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.

Measurements were carried out with solutions of Fe(CN)$_6^{3-}$, 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 Fe(CN)$_6^{3-}$, 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 Fe(CN)$_6^{3-}$ in Figure 9B contrasts with the behavior following current reversal shown in Figure 8B,C where recently ejected Fe(CN)$_6^{3-}$ 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 Fe(CN)$_6^{3-}$ or Fe(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 Fe(CN)$_6^{3-}$ near the substrate decreases as Fe(CN)$_6^{4-}$ anions generated within the coating reach the coating/solution interface where they can accept electrons from the Fe(CN)$_6^{4-}$ 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 Fe(CN)$_6^{3-}$ anions replace Fe(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 Fe(CN)$_6^{4-}$ (along with Fe(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 Fe(CN)$_6^{3-}$ near the substrate electrode. The delay in the appearance of Fe(CN)$_6^{3-}$ at the tip matches the delay in the decrease of the concentration of Fe(CN)$_6^{4-}$ in Figure 9B. It reflects the time required for Fe(CN)$_6^{3-}$ generated at the electrode to reach the coating/solution interface. After current reversal, anion ejection commences and sufficient Fe(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 Fe(CN)$_6^{4-}$ (Figure 9) is consistent with the interpretation offered earlier for the behavior in solutions of Fe(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 PVPH$^+$/Fe(CN)$_6^{3-}$/4$^-$ system. The ejections of both Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$ anions from PVPH$^+$ coatings saturated with Fe(CN)$_6^{3-}$ observed in this study are in accord with the previous results of Dobhalhofer and co-workers who measured transient currents at rotating ring-coated disk electrodes (14–16). In both studies, the ejection of Fe(CN)$_6^{3-}$ was observed to be coincident with the passage of cathodic current through the coating while the ejection of Fe(CN)$_6^{4-}$ was delayed by the time required for the Fe(CN)$_6^{3-}$ to diffuse across the coating (by physical motion or electron-hopping). The apparent preferential reincorporation of the ejected Fe(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. PVPH$^+$ coatings in which Fe(CN)$_6^{3-}$ or Fe(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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