

2,4,6-Triphenylpyrylium Ion Encapsulated into Zeolite Y as a Selective Electrode for the Electrochemical Determination of Dopamine in the Presence of Ascorbic Acid

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2,4,6-Triphenylpyrylium ion immobilized inside the supercages of zeolite Y enhances by 1–2 orders of magnitude the response of electrochemical oxidation of dopamine in neutral aqueous media accompanied by a remarkable inhibition of post-electron-transfer reactions. The negative charge of the zeolite framework in which the 2,4,6-triphenylpyrylium ion is incorporated blocks the electrochemical oxidation of the negative ascorbate ion, enabling the determination of micromolar concentrations of dopamine in the presence of a large excess (10^3 – 10^4 times) of ascorbate in phosphate buffer (pH 7.4). Under optimized conditions, linear calibration plots were obtained for a differential pulse detection mode over the range 250–1 μ M dopamine with a sensitivity of 62 nA/ μ M and a detection limit (S/N = 3) of 0.2 μ M in the presence of 1.0 mM ascorbate.

Dopamine plays an important physiological role as an extracellular chemical messenger. Because the loss of neurotransmitter-containing neurons may result in some serious diseases such as Parkinson's, the determination of such compounds in real biological samples is an obvious target in neurochemical studies.¹ Because dopamine and the other neurotransmitter catecholamines are easily oxidized, electrochemical methods based on anodic oxidation have been used to monitor its concentration.^{1–4}

Apart from the need to reach low detection limits, the electrochemical determination of dopamine is complicated by the coexistence of many interfering compounds. Among them, ascorbic acid is of particular importance, because this species is oxidized at a potential close to that of dopamine at almost all electrode materials. Ascorbic acid accompanies dopamine in

biological samples; for instance, in the extracellular fluid of the central nervous system, ascorbic acid is present at the 100–500 μ M concentration level, whereas the concentration of dopamine is less than 100 nM.⁵

To increase selectivity for catecholamine oxidation, different methods of electrode pretreatment and electrode modification have been reported: electrochemical preanodization,⁶ high-speed polishing,⁷ heat treatment,⁸ and laser activation.⁹ Electrode modification includes the use of permselective polymer coatings,¹⁰ polymer coatings covering an electroactive material exhibiting catalytic activity toward dopamine oxidation,^{11–13} and electropolymerized films.^{14–19} The use of zeolites²⁰ and nontronite clays²¹ has also been reported.

A promising strategy consists of the use of inorganic microporous solids to host an electroactive guest to increase selectivity and sensitivity of the modified electrode. In this context, we have already reported that the zeolite-Y-encapsulated 2,4,6-triphenylpyrylium ion (TP⁺) exerts a significant electrocatalytic effect on the electrode oxidation of neurotransmitter catecholamines.²²

Encapsulation of metal complexes and organic molecules within the supercages of zeolites has been a topic of intense research as a result of the remarkable catalytic properties of the resulting materials. Zeolites are a family of crystalline aluminosilicates whose structure defines strictly uniform channels and cavities of molecular dimensions. Confinement of elusive organic

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guests into the rigid framework of zeolites produces a remarkable increase of the persistence of these reactive species when there is a tight fit of the guest inside the restricted reaction cavity defined by the host.^{23–26} However, the guest molecule can interact with smaller molecules through the cavity windows, provided that the probe molecules can diffuse through the zeolite framework.

In particular, the pore structure of zeolite Y consists of almost spherical 1.4-nm cavities interconnected tetrahedrally through smaller apertures of 0.74-nm diameter. The TP⁺ ion can be prepared inside the zeolite Y supercages through a “ship-in-a-bottle” methodology that relies on the diffusion of much smaller synthetic precursors.²⁷ Recently one of us showed that TP⁺ ions are stabilized inside the rigid zeolite matrix (TPY).²⁸

Because the negative zeolite matrix is able to incorporate cationic species and repel anionic ones, it combines size-exclusion and charge-exclusion properties. Taking into account that at physiological pHs, the ascorbate ion (pK_a = 4.2) and protonated catecholamines (pK_a ca. 10.6) exist in solution, the zeolite host can act as a charge-selective membrane. Thus, it can be expected that the zeolite matrix increases selectivity in the determination of dopamine in the presence of ascorbate ions, whereas the electrocatalytic effect on dopamine oxidation displayed by TP⁺ ions enhances the sensitivity of such determinations.

In this work, we report on the use of TPY as a modifier on polymer film electrodes (PFEs) deposited over glassy carbon and graphite/polyester composite electrodes for selective detection of dopamine in the presence of ascorbic acid.

EXPERIMENTAL SECTION

Materials and Chemicals. The synthesis of the 2,4,6-triphenylpyrylium ions in the intracrystalline cages of zeolite Y was carried out as previously reported. TPY samples contained a 4.8 wt % of TP⁺.²⁷

Dopamine (Fluka) and ascorbic acid (Fluka) were of analytical reagent grade and were used as received. For electrochemical experiments in MeCN, Et₄NClO₄ (Aldrich) and (TBA)PF₆ (Aldrich) were used as supporting electrolytes, both at a concentration of 0.10 M. Experiments in aqueous media were conducted in phosphate buffer (pH 7.4); NaCl, 0.15 M; and NaClO₄, 0.15 M.

Electrode Preparation. Paraloid B72, an ethyl methacrylate (70%)/methyl acrylate (30%) copolymer (P[EMA/MA]), and Elvacite 2044, a *n*-butyl methacrylate homopolymer (PnBMA), were selected for PFE preparation because of their ability to form uniform thin films, insolubility in water, and chemical and mechanical stability. Graphite/polyester composite electrodes were prepared using Estratil AL-100, a polyester prepolymer dissolved in styrene (33 wt %) acting as a reactive monomer. A copolymerization reaction was catalyzed by cobalt octanoate incorporated into the initial prepolymer solution (0.07 wt %). The reaction was initiated by adding ethylmethyl ketone peroxide (2 wt %). The

viscosity of the initial prepolymer solution at 298 K was 5 dPa.s. The polymerization reaction was produced at room temperature (298 K), and the curing time was 45 min. The graphite/polymer composite was prepared by adding 45 wt % of graphite powder (Fluka 2 μm) to 55 wt % of polyester resin that was freshly prepared. This composition provided to the paste the fluidity necessary for pouring the polymer into the mold. A rubber mold (2-cm height, 0.5-cm length, 0.3-cm width) was used.

Polymer film electrodes were prepared on the basis of the methods devised by several authors^{29–37} by transferring a few microliters of a dispersion of the zeolite (10 mg) in acetone (5 mL) to the surface of a freshly polished glassy carbon electrode or a graphite/polyester composite electrode and allowing the coating to dry in air. As previously described,^{33,34} Paraloid B72 PFEs form porous coatings (pore diameter, 1–2 μm) that enable the electrochemistry of electrode-attached microparticles, and a composite electrode provides an excellent adherence of such microparticles. After the electrode surface was air-dried, one drop of a solution of the acrylic resin (1 wt %) in acetone was added, and the modified electrode was air-dried. Self-supported zeolite-modified electrodes were prepared by powdering 10 mg of the zeolite in an agate mortar and pressing a portion onto the surface of the composite electrode with a hard spatula to produce a spot of finely dispersed material. The coatings that were examined contained 0.2–1.5 mg cm^{−2} of the dry zeolite.

Electrochemical Measurements. Electrochemical measurements were performed at 298 K in a conventional three-electrode cell. To prevent the aerobic oxidation of ascorbic acid, all of the electrochemical experiments were performed under an argon atmosphere in freshly prepared solutions. Glassy carbon and graphite/polyester composite electrodes were used as the working electrodes. A platinum gauze pseudo-reference electrode was used in the MeCN solution, whereas a saturated calomel electrode (SCE) was used as the reference electrode in experiments in aqueous solution. All potentials in the text are for the aqueous SCE. A platinum-wire auxiliary electrode completed the electrode arrangement.

Prior to electrode modification, the bare glassy carbon or composite electrodes were cleaned and activated. Electrochemical pretreatment was performed in blank solutions by applying +1.50 V vs SCE for 10 min followed by −1.0 V for 1 min. Before each run, the electrodes were polished with an aqueous suspension of alumina on a soft surface, dried, and cleaned.

Instrumentation. Linear scan and differential pulse voltammograms at low scan rates (*v* < 50 mV/s) were performed using a Metrohm E506 Polarecord, whereas cyclic and Osteryoung's square wave voltammograms were carried out using a BAS CV-50W voltammetric analyzer.

Scanning electron micrographs were obtained with a JEOL JSM 6300 scanning electron microscope operating with a Link-

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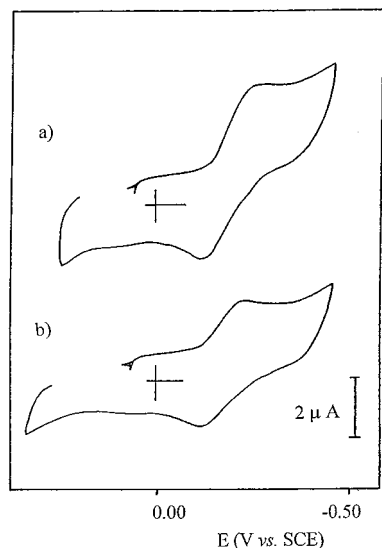


Figure 1. CVs for TPY-modified Paraloid B72 film electrodes immersed into (a) 0.10 M Et₄NClO₄ MeCN or (b) 0.10 M NaClO₄ aqueous solutions. Potential scan rate, 100 mV/s.

Oxford-Isis microanalysis system. The analytical conditions were accelerating voltage, 20 kV; beam current, 2 nA.

RESULTS AND DISCUSSION

Electrochemistry of TPY-Modified Electrodes. The electrochemistry of pyrylium ions in solution is complicated by post-electron transfer reactions. In aprotic solvents, pyrylium ions are reduced to the corresponding bipyranilidene together with pyrane, the transient reduction process being controlled kinetically by the irreversible dimerization of the radical formed in the first electron-transfer step.^{38,39} Then bipyranilidene and pyrane are formed by the reversible reduction of the dimer.⁴⁰ In contrast, in protic solvents, pyrylium ions exhibit a one-electron reduction. Controlled potential electrolysis produces dipyran which, in turn, can be reoxidized back to TP⁺.⁴¹

Upon encapsulation in zeolite Y, however, the electrochemistry of TP⁺ becomes more simple. As depicted in Figure 1, both in nonaqueous and neutral aqueous media, CVs of self-supported finely ground TPY pressed onto glassy carbon electrodes exhibit only one cathodic peak at -0.34 V vs SCE coupled with an anodic peak at -0.23 V. The voltammetric response remains stable upon repetitive cycling, and no additional voltammetric peaks are observed. Similar features were obtained in neutral aqueous media using TPY-modified polymer-film electrodes. Thus, despite the relatively large peak potential separation attributable to uncompensated ohmic drops associated with the particular electrode configuration, the electrode process can be considered as an

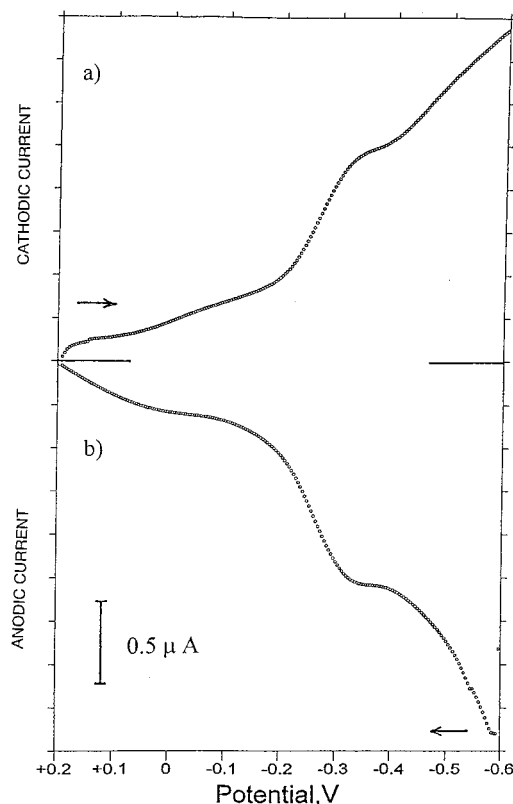
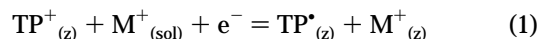


Figure 2. Osteryoung's square wave voltammograms at a TPY-modified electrode in phosphate buffer (pH 7.4): (a) cathodic and (b) anodic. Frequency, 15 Hz; potential step, 10 mV; square-wave amplitude set, 100 mV.

almost reversible one-electron couple at an equilibrium potential of -0.28 V vs SCE. The absence of secondary electrochemical processes can be clearly seen using Osteryoung's square wave voltammetry, a more sensitive technique. As depicted in Figure 2, only one well-defined cathodic peak and only one well-defined anodic peak are recorded.

In light of current ideas on the electrochemistry of zeolite-attached species,^{32,42} the observed voltammetry corresponds to electron-transfer processes affecting pyrylium ions located at the boundary regions of the zeolite grains. The overall electrochemical process can be represented as



involving the incorporation of charge-balancing positive ions M⁺ from the supporting electrolyte to the zeolite boundary sites. Immobilization of TP⁺ as well as its corresponding reduction product, TP[•], in the restricted space of the zeolite supercages impedes their diffusion, and consequently, post-electron-transfer reactions, such as radical coupling or nucleophilic attack of water, are inhibited. Similar compartmentalization effects appear to be involved in the electrochemistry of zeolite-encapsulated anthracene and thianthrene radical ions.⁴³

Blank controls were undertaken to prove that the observed electrochemical response corresponds to guest ions located on

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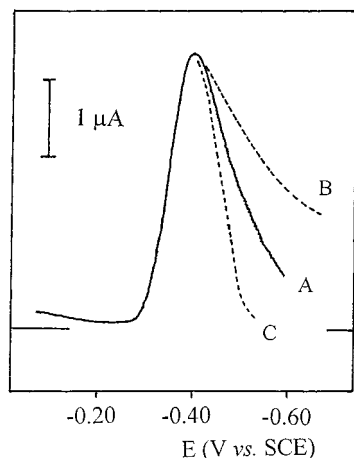


Figure 3. Comparison of an experimental LSV (A, continuous curve) for a self-supported TPY-modified electrode in 0.15 M NaClO₄ ($\nu = 2$ mV/s) and theoretical curves (dotted lines) for a reversible electron-transfer process involving diffusive control in solution (B) and strongly electrode-attached species (C). Theoretical curves calculated to provide identical peak potential and peak current as the experimental voltammetric peak.

the zeolite particles and not to species that could have migrated to the solution or remain adsorbed on the electrode surface. Thus, contacting the material with acetonitrile or water yields no evidence of leaching, and no electrochemical response was obtained at bare GC or composite electrodes immersed in stirred suspensions of the zeolite (1 mg/mL in the electrolyte solution) and their resulting electrolyte solutions previously filtered. Additionally, demodified electrodes obtained by repetitive rinsing of self-supported TPY-modified electrodes lose their electrochemical activity as the zeolite modifier is lost.

These considerations are consistent with the observed voltammetric profiles. As shown in Figure 3, the voltammetric peak for the reduction of TPY (curve A) exhibits a sharp profile intermediate between those expected for two extreme models: (i) a diffusion-controlled process, and (ii) an electron transfer between strongly electrode-attached species.⁴⁴ The first case corresponds to an electrode process controlled by the diffusion of the electrolyte counteranion in the channels/windows system of the zeolite matrix, as described by Baker et al.,^{44,45} and may affect the more external zeolite-associated pyrylium centers. The second presumably involves pyrylium ions firmly attached to the zeolite matrix but located on the zeolite boundary. The difference between a diffusion-controlled process and an electron transfer involving strongly electrode-attached species (reagents and products) is illustrated by theoretical curves (dotted lines B and C, respectively) in Figure 3.

Following Bessel and Rolison,³² it can be assumed that electrochemically accessible molecules are confined to the more external layer of the zeolite. To corroborate this assumption, the number of electroactive centers was calculated using Faraday's law by integrating the area under i-E curves in Figure 3. For TPY-modified electrodes typically containing 0.50 mg of zeolite, net amounts of charge of 45 μC were passed, corresponding to $4.5 \times$

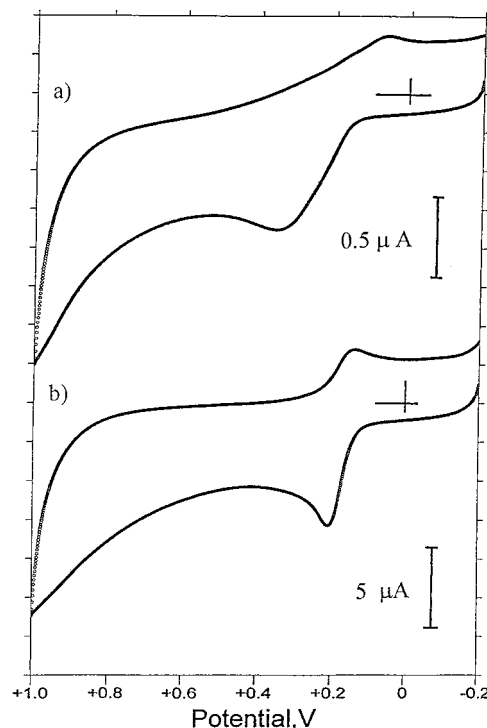


Figure 4. CVs for a dopamine solution (0.12 mM) in phosphate buffer (pH 7.4) at (a) unmodified GCE and (b) TPY-modified PFE. $\nu = 10$ mV/s.

10^{-10} mol. Because the total TP⁺ ion in the zeolite is $\sim 1.6 \times 10^{-7}$ mol mg⁻¹, one finds that only 0.6% of the zeolite-supported TP⁺ is electroactive. This result agrees with the idea that only the population of TP⁺ located in the boundary region of the zeolite grains is electroactive.

Electrochemistry of Dopamine and Ascorbic Acid at TPY-Modified Electrodes. The electrochemical oxidation of catecholamines in aqueous solution proceeds as a two-electron process to form catecholamine *o*-quinones.⁴⁷ When the amine is deprotonated, the molecule can undergo a 1,4 (Michael) addition, which results in a cyclization reaction yielding leucoaminochrome. This species is more easily oxidized than the parent catecholamine and can experience further two-electron oxidation to form the aminochrome (ECE mechanism). The second oxidation process occurs as a homogeneous electron transfer with *o*-quinone in solution, regenerating the catecholamine through a disproportionation reaction (DISP1 mechanism).^{48,49} As a result, the apparent number of electrons consumed during the oxidation of catecholamines varies from two to four electrons, depending on the time scale of the observation. Interestingly, differences in the rate of cyclization reaction have been exploited to distinguish between norepinephrine and epinephrine.^{50,51}

Figure 4 compares typical cyclic voltammograms of a solution of dopamine (0.12 mM) in phosphate buffer (pH 7.4) recorded at

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unmodified (a) and TPY-modified (b) GCEs. At an unmodified electrode, a prominent anodic peak at +0.31 V appears, followed in the subsequent cathodic scan by two ill-defined overlapped reduction peaks near +0.20 V. These peaks agree with those obtained as a well-resolved pair of peaks by Wightman et al.⁵⁰ that are attributed to the electrochemical reduction of *o*-dopaminequinone and dopaminechrome, respectively. At TPY-modified electrodes, this electrochemical response is significantly modified. As shown in Figure 4, the anodic peak is shifted to less positive values, and the current is 10–20 times enhanced. In the cathodic region, only the first reduction peak appears at +0.18 V with a remarkable increased intensity. This response denotes that there is a moderate electrocatalytic effect on dopamine oxidation accompanied by a blocking effect on post-electron-transfer cyclization reactions affecting *o*-dopaminequinone. This second effect is of special interest for analytical purposes, because the final product, dopaminechrome, can undergo polymerization reactions on the electrode surface, yielding melanin-like compounds,⁵² resulting in electrode fouling.¹⁹

The peak potential shift and the increase in reversibility observed for the oxidation of dopamine at TPY-modified electrodes suggest that it is likely that catalyzed dopamine oxidation occurs through the intermediacy of an adduct formed between both the oxidized catalyst and the oxidized substrate.

Because the electrode oxidation of catecholamines involves two consecutive one-electron transfers coupled with deprotonation reactions, an electrochemical pathway involving the formation of an adduct between surface-confined TP⁺ and the intermediate species generated after the first electron-transfer step seems called for. The formation of TP⁺-dopamine adducts and the diffusion of charge-balancing electrolyte cations through the zeolite channel system are possible rate-controlling steps. The possible electrochemical pathway is presented in Scheme 1.

After prior deprotonation, ascorbic acid is oxidized electrochemically to a diketolactone, which is rapidly hydrated to dehydroascorbic acid. This rearranges to another ene-diol, which is further oxidized at higher potentials.^{53–56} Depending on the solution conditions, dehydroascorbic acid undergoes different subsequent reactions; thus, under anaerobic conditions, it degrades to furfural and carbon dioxide, but under aerobic conditions diketogluconic acid, oxalic acid, and other species are the final products.⁵⁷

Figure 5 compares CVs for a solution of ascorbic acid (5.4 mM) in phosphate buffer (pH 7.4) at an unmodified (a) and a TPY-modified (b) composite electrode. At a bare composite electrode, a prominent anodic peak appears at +0.38 V with no coupled cathodic peaks. At a TPY-modified electrode, the oxidation process is significantly inhibited. Because at neutral pHs ascorbic acid is almost entirely in the form of ascorbate ions, this lack of response can be associated with the electrostatic repulsion exerted by the zeolite framework with regard to anionic ascorbate. Accordingly,

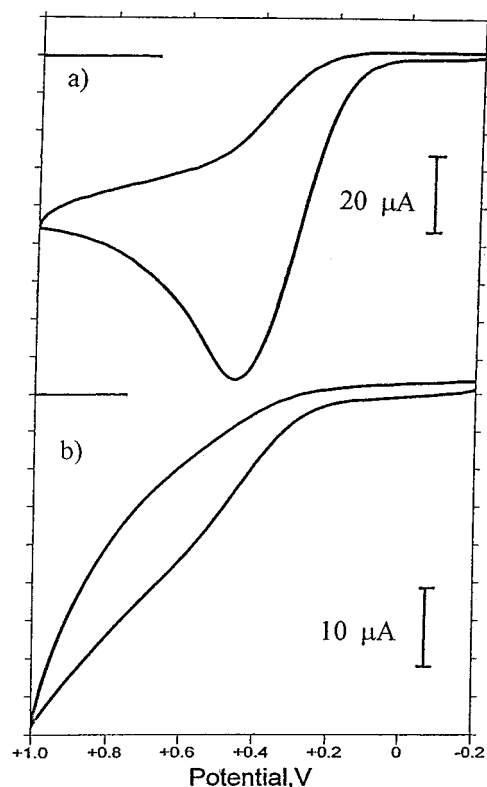
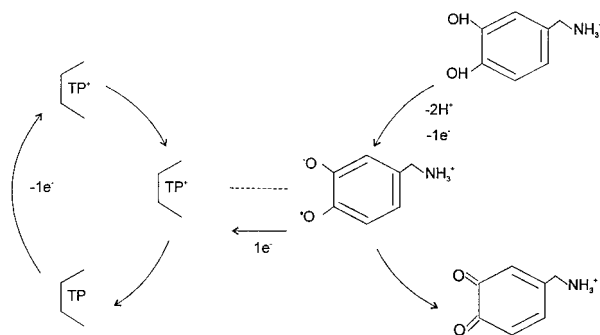


Figure 5. CVs for a 5.4 mM solution of ascorbic acid in phosphate buffer (pH 7.4): (a) unmodified composite electrode and (b) TPY-modified PFE. $\nu = 100$ mV/s.

Scheme 1. Scheme of the Electrocatalytic Pathway in Dopamine Oxidation at TPY-Modified Electrodes



the inhibition of the oxidation step decreases on decreasing the acidity of the media below pH 4.

It should be noted that, on comparing with metal electrodes, zeolite-modified electrodes provide (i) a relatively low density of catalytic sites, and (ii) a nonuniform distribution of electrocatalytic centers. This situation is equivalent to that described for metal oxide-based GCEs for which similar electrode coverages have been reported.^{35–37} Figure 6 shows two scanning electron micrographs of a deposit of the zeolite on a glassy carbon surface with different magnifications. In these images, many grains evenly covering the surface are visible, eventually forming aggregates adhered to the electrode surface. As in the case of different metal oxide-based carbon electrodes, the microcrystalline deposit remaining on the electrode surface can be considered as the catalytically active component.^{35–37}

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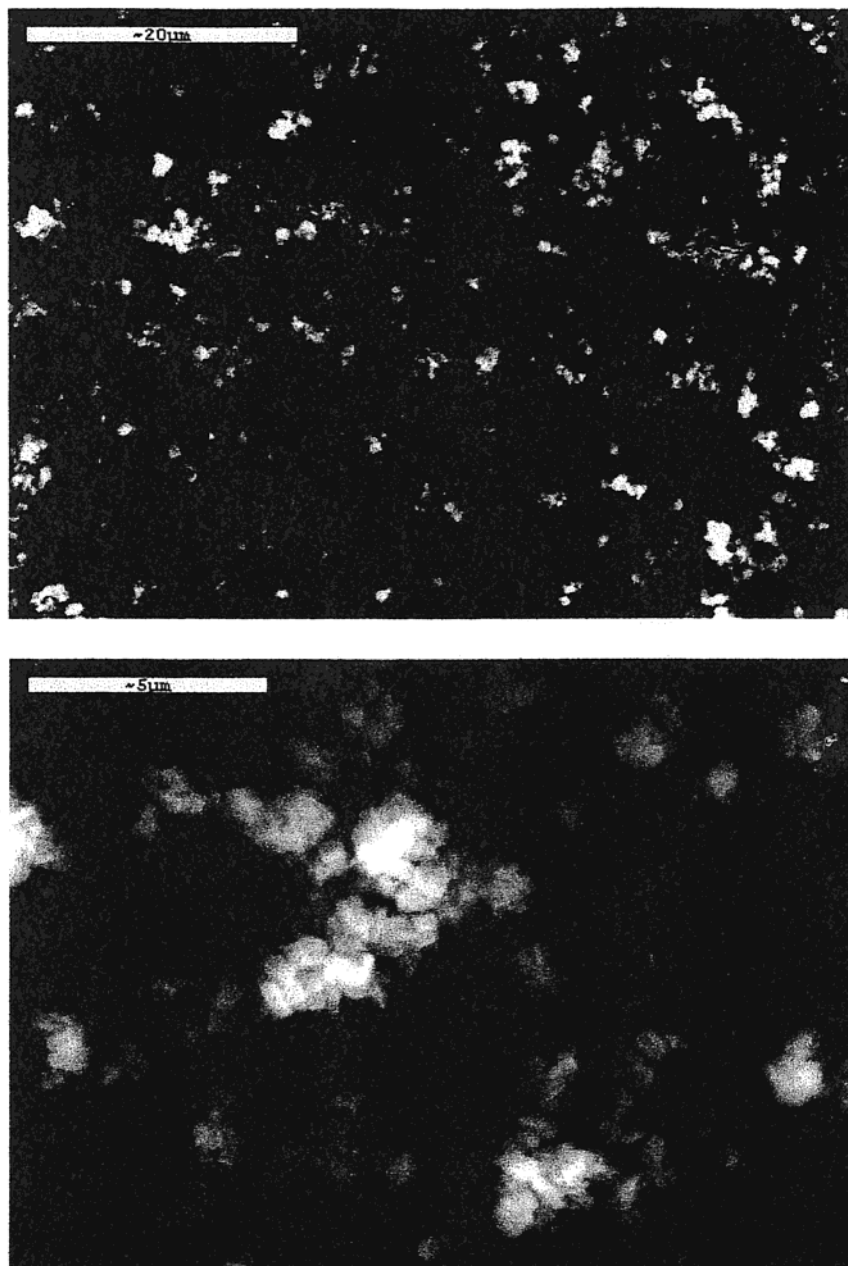


Figure 6. Secondary electron microphotographs using different magnifications of self-supported zeolite-modified GCE.

Optimization. Figure 7 presents the differential pulse voltammogram at an unmodified GCE of a solution containing dopamine (0.70 mM) and ascorbic acid (5.4 mM) at pH 7.4 recorded at unmodified (a) and TPY-modified (b) composite electrodes. At an unmodified electrode, two overlapped but well-defined anodic peaks at +280 and +455 mV vs SCE appear, corresponding to the electrochemical oxidation of dopamine and ascorbate. The sensitivity for ascorbate was considerably less than for catecholamines, in agreement with the literature.⁷ In contrast, at TPY-modified electrodes, the anodic peak corresponding to the oxidation of dopamine is enhanced and shifted toward less positive values, but that corresponding to ascorbate oxidation is lowered.

As shown in Figure 8, the electrocatalytic current increases on prolonging the equilibration time of the modified electrode with the dopamine solution at 0 V. In all detection modes (LSV, DPV, and SQWV), the peak current for dopamine oxidation increases

rapidly in the first few minutes of contact time until it levels off for times longer than 15–20 min (see inset in Figure 8). Blank experiments at PFEs modified with zeolites without encapsulated TP⁺ become electrocatalytically silent.

For TPY-modified electrodes, the electrocatalytic current increases on prolonging the equilibration time of the modified electrode with the dopamine solution at 0 V, as shown in Figure 8. In all detection modes (LSV, DPV, and SQWV) the peak current for dopamine oxidation increases rapidly in the first few minutes of contact time until it levels off for times longer than 15–20 min (see inset in Figure 8). These data are consistent with the idea that the catalytic effect is due to TP⁺ ions that are confined to the more external zeolite surface. Thus, assuming that the observed electrocatalytic effect involves the formation of zeolite-associated TP⁺–dopamine adducts, one can expect that (i) the extent of the electrocatalytic effect progressively increases as the number of

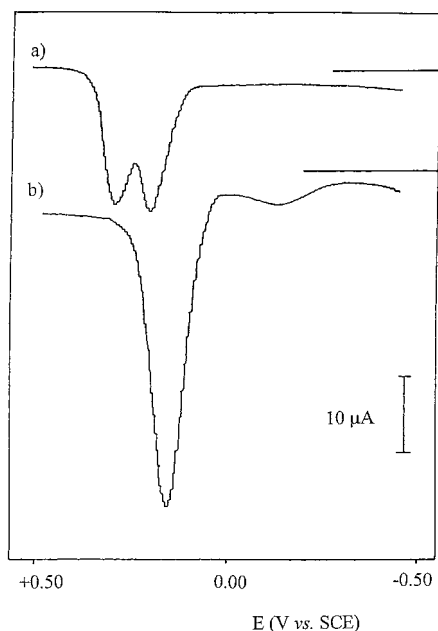


Figure 7. Electrochemical response at an unmodified GCE of a solution (0.15 M NaClO₄) containing a mixture of dopamine (0.70 mM) and ascorbic acid (2.60 mM) in phosphate buffer (pH 7.4). DPV at $\nu = 20$ mV/s; pulse amplitude, 50 mV.

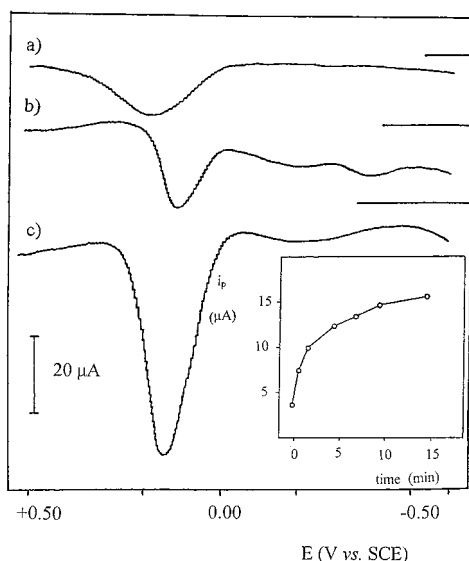


Figure 8. DPVs at a TPY-modified PFE immersed in a 0.53 mM dopamine solution in 0.15 M NaClO₄ after different equilibration times at 0.0 V: (a) 0, (b) 2 min, and (c) 5 min. $\nu = 20$ mV/s; $\Delta U = 50$ mV. Inset: variation of the peak current on the equilibration time.

TP⁺–dopamine adducts increases; (ii) the catalytic effect tends to a limiting value when all of the accessible TP⁺ sites on the zeolite boundary are associated to dopamine unities.

Preliminary series of experiments at the micromolar–millimolar concentration range produced satisfactory results for PFEs containing surface concentrations of 0.10–0.30 mg/cm² of TPY sample and 0.20–0.40 mg/cm² of the polymer. An increase in the amount of modifier decreases the mechanical stability of the coating, but an increase in the amount of polymer appears to cause a significant increase in the ohmic resistance of the coating.

Accordingly, optimized conditions were 0.20 mg/cm² of zeolite, 0.30 mg/cm² of polymer, and an equilibration time (0.0 V) of 15

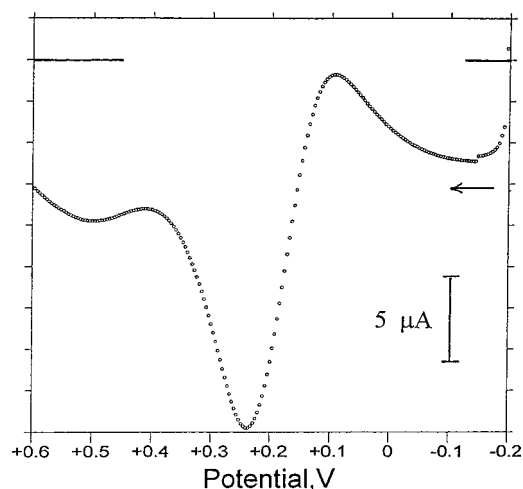


Figure 9. SQWV at a TPY-modified PFE immersed in a 0.24 mM dopamine plus 1.00 mM ascorbate solution in phosphate buffer (pH 7.4). Frequency, 15 Hz; potential step, 10 mV; square-wave amplitude set, 100 mV.

min. DPVs were performed at a potential scan rate of 10 mV/s with a modulating potential of 50 mV. Anodic scans were initiated at -0.6 V vs. SCE. Under these conditions, calibration plots for dopamine in the presence of 0.1 mM ascorbate at pH 7.4 were linear, up 1 μ M to ~ 250 μ M dopamine (slope, 62 nA/ μ M) with a detection limit (S/N = 3) of 0.2 μ M. Similar quantitative results were obtained in unbuffered solutions at neutral pH. As can be seen in Figure 9, SQVs at TPY-modified electrodes also exhibit a well-defined anodic signal for dopamine oxidation in the presence of ascorbate in neutral media. For this detection mode in buffered solutions with optimized conditions (equilibration time, 15 min; frequency, potential step, and square-wave amplitude set at 25 Hz, 10 mV, and 100 mV, respectively) the linearity range was 1–200 μ M dopamine (slope 32 nA/ μ M) with a detection limit (S/N 3) of 0.4 μ M. Interestingly, no interference of chloride and sulfate ions (in both cases, for concentrations 0–0.10 M) was detected. The reproducibility of the results was established for a series of 10 repetitive determinations of 50 μ M solutions of dopamine with comparable results for freshly prepared electrodes and regenerated electrodes. In this second case, successive electrode equilibration steps were performed after each anodic run by applying a regeneration step of 15 min at 0.0 V. The response of regenerated electrodes was stable for at least 10 successive equilibration/measurement steps.

FINAL CONSIDERATIONS

Paraloid B72 film electrodes modified by zeolite Y-encapsulated 2,4,6-triphenylpyrylium ions exert (i) a blocking effect on ascorbate oxidation, (ii) a catalytic effect on the electrochemical oxidation of dopamine, and (iii) an inhibitory effect on post-electron-transfer cyclizations accompanying dopamine oxidation in neutral aqueous media. The first effect can be associated with the well-known reluctance of zeolites with a high Al content to incorporate anions. The electrocatalytic effect exerted on the electrochemical oxidation of dopamine can be attributed to the stabilization of the intermediates via the formation of surface-confined pyrylium–catecholamine adducts.

Under optimized conditions, TPY-modified electrodes are usable for determining low concentrations of dopamine (1–250

μM) in the presence of relatively large concentrations of ascorbate (1 mM) using LSV and DPV modes.

The reported data constitute a further example of the new opportunities offered by zeolite-confined species to be used as electrochemical sensors. The possibility of incorporating different species into the zeolite channel system, the stabilization of reactive intermediates, and the possibility of modulating the electrochemi-

cal properties of the encapsulated species varying the zeolite framework may result in increased sensitivity and selectivity for electrochemical sensing.

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