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Immobilization of Amines at Carbon Fiber Surfaces: Relevance to Interfacial Adhesion in Carbon Fiber/Epoxy Composite Materials

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Abstract - The reaction between amines acting as nucleophiles and the C=C bonds on the carbon fiber surface acting as electrophilic vinyl groups has not yet been explored. In this contribution it is demonstrated that both thermal reactions and electrochemical oxidation of amines at carbon fibers allow the covalent bonding of these molecules directly to the carbon fiber surface, presumably via nucleophilic attack of the amine at electrophilic C=C sites at the surface and subsequent formation of C-N bonds between the surface and the amine. A novel strategy for a quantitative assay of the number of amines attached to the surface is developed in which $Fe(CN)_6^{3-}$ is electrostatically bound to the protonated, cationic amine sites, followed by electrochemical determination of the amount of bound $Fe(CN)_6^{3-}$ as a function of its concentration in solution. Analysis of the isotherm for this electrostatic binding process then provides the number of interfacially immobilized amines. The composition of the amine layer is also probed using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared attenuated total reflection spectroscopy (FTIR-ATR). Mechanisms are discussed by which attachment of amines at the electrophilic vinyl groups of the carbon fibers can occur. The likely influence that this type of reaction has on the interfacial shear strength in carbon fiber/epoxy composite materials is also discussed.

Key Words - Carbon fiber, cyclic voltammetry, 2-aminoanthraquinone, dimethylaminomethyl-ferrocene, 1,6-diaminohexane, atomic force microscopy, X-ray photon spectroscopy, infrared attenuated total reflection spectroscopy, adhesion and composite materials.

1. INTRODUCTION

Developments in the materials chemistry of carbon fibers since the 1960's have had a great impact on many areas of modern technology. One very important area in which carbon fibers have been extensively used is in the fabrication of composite materials[1], especially those based on epoxy matrix materials[2]. When used without any surface treatment, carbon fibers (CF's) produce composites with low interlaminar shear strength (ILSS). This observation led many investigators to develop a number of surface treatments aimed at improving the fiber-matrix interfacial bonding. Several research groups[3-9] have studied various surface treatments, including oxidative and nonoxidative methods. In general, these techniques attempt to modify the interfacial region by increasing the surface roughness to produce better

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mechanical interlocking, or by increasing the chemical reactivity of the interfacial region by forming surface functional groups that provide chemical bonding with the resin matrix.

Several possible types of reactions between CF's and the compounds in the epoxy matrix have been previously investigated by Sherwood[6], Fitzer[10], Waltersson[11], and Pinson[12]. However, there is at least one possible reaction which has relevance to carbon fiber-epoxy interfacial adhesion that has not yet been explored. This is the reaction between amines, acting as nucleophiles, and the vinylic C=C bonds on the carbon fiber surface, acting as electrophiles. It is this type of reaction that is the topic of the present study.

There are several previous reports of the addition of amines to vinyl groups[13-21]. The Michael-like, nucleophilic addition of primary, secondary or tertiary amines on electrophilically activated vinyl groups has been known for some time[13-15]. This reaction, which leads to the formation of a new C-N bond, has been shown to proceed in reasonable yields and at modest temperatures[13]. It is also known to be acid catalyzed[13]. Another type of amine addition occurs with the assistance of a metal complex. In this case, amines can undergo a nucleophilic attack on ordinary (i.e. unactivated) olefins[16]. The ionic route through metal activation of the double bond provides regiospecific and, in some cases, stereospecific reaction. Palladium(II)[17,18] and mercury(II)[19] salts have been commonly used as catalysts for this type of reaction. A third type of amine nucleophilic addition to vinyl-like groups is due to the intrinsic electron deficient character of the "olefinic" compound. For example, Haddon[20] et al. have theoretically calculated that icosahedral C_{60} is capable of accepting up to twelve electrons in solution. Wudl et al.[21] have also demonstrated experimentally that buckminsterfullerene, C_{60}, reacts with both primary and secondary amines to yield adducts thought to be derived from nucleophilic addition, perhaps initiated by a single-electron transfer step. While C_{60} clearly has different chemical reactivity than do CF's, observation of this type of reactivity under such mild conditions (Wudl's reaction occurs at room temperature) lends at least some support to the notion of similar reactivity in CF-epoxy composites. Finally, the immobilization of amines onto carbon fibers via electrooxidation of the amine at the fiber surface has also been described[12,22]. In this case, the mechanism is thought to involve the electrochemical production of amine cation radicals which then add to functional groups at the CF surface. All of these previous results suggest that direct addition of amines at CF surfaces may be occur in CF-epoxy composites, with a possible mechanism involving the C=C bonds on the fiber surface serving as the electrophiles and the diamine hardeners in the matrix acting as the nucleophiles. If this is true, then this type of reactivity likely plays an important role in adhesion in these materials. A representation of a possible mechanism for the nucleophilic addition of an amine to an activated vinylic group on a carbon fiber is shown in Figure 1.

Several approaches to the detection of immobilized amines at CF surfaces are explored here. Both XPS and FTIR-ATR are demonstrated to be useful in this regard. We also introduce two electrochemical methods for assaying the yield of the immobilization reactions. In the first, the amines are "tagged" with a redox group, so the yield of the interfacial reaction can be easily measured from the charge associated with these immobilized redox groups. The second method is a relatively unique approach to assaying surface reactivity that allows one to measure the yield of reactions of non-electroactive amines. In this method the amines are protonated in low pH aqueous solutions, then the electrostatic binding of $Fe(CN)_6^{3-}$ to the protonated amine groups is used as an indirect measure of the number of interfacial amines.

Using the methods described above, the data in this contribution present clear evidence that amines do, indeed, add to the vinyl groups of carbon fibers at both room and elevated temperatures. Since, the ultimate goal of this study was to explore the relevance of this type of chemical reactivity to the ILSS in CF-epoxy composite materials, the relevance of the amine immobilization chemistry described here is discussed in the context of previous notions of the origins of adhesion in these materials.

2. EXPERIMENTAL

A. Chemicals and Reactions. The chemical compounds used in this study, 2-aminoanthraquinone, dimethylaminomethyl-ferrocene, didecylamine and 1,6-diaminohexane, were obtained from Aldrich. 2-aminoanthraquinone and dimethylaminomethyl-ferrocene were used as received. 1,6-diaminohexane and didecylamine were purified by distillation before use. The general approach for attaching these amine derivatives to carbon fiber surfaces involved prolonged contact of either the neat amine liquid or a concentrated solution of the amine in tetrahydrofuran (THF) with the carbon fibers either at room temperature or at elevated temperatures. Reactions were run under N_2 on a vacuum line to prevent exposure of both the CF's and the reagents to atmospheric oxygen during the reactions. Unless otherwise specified, prior to these reactions the carbon fibers were first rinsed with THF, then heat-treated at 350 °C under dynamic vacuum to remove as many desorbable impurities as possible. Then, while still under vacuum, the neat amine or THF solution was transferred onto the carbon fibers for the immobilization reaction. After reaction, the CF's were rinsed repeatedly with water, methanol and acetone, Soxlet extracted with THF for at least two days, and dried in a vacuum oven at ca. 70 °C. This procedure was used to reduce the probability of adventitious adsorption or entrapment (as opposed to the desired covalent attachment) of the amine derivatives on the surface or in cracks at the surface. Figure 2 shows representations of the structures thought to be produced by this procedure.

Two types of carbon fibers were used in this study. Most experiments were done with Tonen HMU pitch-based carbon fibers (Tonen Corporation, Japan, HMU type, high-modulus untreated fiber (i.e. with no prior surface treatment)). For purposes of comparison with previous CF studies, some experiments wewre done with Hercules AS-4, polyacrylonitrile-based carbon fibers (Hercules Inc., AS-4 type, surface treated fiber (i.e. with a prior, proprietary oxidative surface treatment applied by the manufacturer). The diameters of these fibers are 10 μm and 7 μm, respectively.

Structure I as shown in Figure 2 was produced by adding 8 g of 1,6-diaminohexane to 2 g of Tonen carbon fibers. The reaction vessel was then held at the reflux temperature for 15 hours. Structure IV was produced using the same conditions, but with didecylamine rather than 1,6-diaminohexane. In this case, the reaction mixture was held at 120 °C for 15 hours. Structure II as shown in Figure 2 was produced by adding 5 g of neat, liquid dimethylaminomethyl-ferrocene to 2 g of pitch- or PAN-based carbon fibers in a reaction vessel. In some cases, water or dilute acid (0.1M, 0.1 mL) was added to act as a catalyst. The reaction was allowed to proceed at room temperature for five days. Structure III was produced by adding 2-aminoanthraquinone (5 g in 10 mL of THF) to pitch- or PAN-based carbon fibers in a reaction vessel. Again, in some cases, water or dilute acid (0.1M, 0.1 mL) was added act as a catalyst. The reaction vessel was then held at the reflux temperature for four days.

The immobilization of amines at carbon fiber surfaces via electrochemical oxidation of the amine[12,22], using the fiber as the working electrode, was also investigated. In these experiments, the fiber electrode was held at 0.9 V versus SCE for 40 seconds in a 0.05 mM solution of 2-aminoanthraquinone in dry, Ar-purged acetonitrile (ACN) containing 0.1 M $NaClO_4$ was electrodeposited at 0.9V vs. SCE for 40 seconds on PAN-based carbon fiber surface in 0.1M $NaClO_4$. Following the immobilization, the fibers were rinsed and dried as described above for the thermal reactions.

B. Instrumentation. Electrochemical experiments employed a PAR 273 potentiostat, a Pt counter electrode, and a saturated calomel reference electrode (SCE), against which all potentials are reported. The carbon fibers were cut into 3 cm lengths, which were then used as the working electrode in a conventional electrochemical cell. All solutions were purged with Ar prior to electrochemical experiments.

XPS data were obtained in the Department of Materials Engineering, Virginia Polytechnic Institute and State University, using a Kratos X-ray photoelectron spectrometer with a Mg K_α X-ray source. Atomic ratios were obtained from these spectra using standard methods.

FTIR-ATR was used to spectroscopically characterize the CF surfaces after their modification with the various amine reagents. A Mattson CYGNUS 100 spectrometer with a liquid nitrogen cooled, mercury cadmium telluride (MCT) detector was used. Spectra were collected at a resolution of 4 cm^{-1} using 1024 scans. A SPECTRA-BENCH ATR attachment and a germanium internal reflection element (SPECTRA-TECH, Inc.) with dimensions of 50 x 20 x 2 mm and with end face angle of 45° were used. To obtain these spectra, the fiber samples were placed with the long axis of the fibers along the long axis of the ATR element. Careful sample placement was critical to obtaining reproducible results in these experiments.

3. RESULTS AND DISCUSSION

A. Characterization of untreated fibers.

It is known that voltammetry at untreated carbon fibers usually shows slow electron transfer (ET) rates and often very poorly defined waves[23]. The rate of electron transfer at carbon fiber electrodes in aqueous solution is affected by several factors, many of which are poorly understood. However, many chemical and electrochemical pretreatments are known to significantly modify the observed reaction rates[23]. To briefly examine these effects for our fiber samples, the electrochemical response of an outer-sphere redox couple, $Fe(CN)_6^{-3/-4}$, on bare Tonen HMU pitch carbon fiber was studied. The electrochemical response of $Fe(CN)_6^{-3/-4}$ on a bare Tonen HMU carbon fiber electrode is not detectable in pH=3.45 acetic acid/sodium acetate, or in pH=6.8 potassium dihydrogen phosphate/NaOH buffered 0.1 M $NaCl_{(aq)}$ electrolyte. However, in pH=1.25 KCl/HCl buffered electrolyte, an electrochemical response is observed. The k_s is calculated to be 2.3×10^{-2} cm/sec from the variation of the peak separation with scan rate[24]. The data clearly show a distinct dependence of the heterogeneous electron transfer rate constant on solution pH for the $Fe(CN)_6^{-3/-4}$ redox couple at these carbon fiber electrodes. Similar results were observed on glassy carbon electrodes by Wightman et al.[24]. They observed a dependence of the k_s of $Fe(CN)_6^{-3/-4}$ on pH at glassy carbon electrodes, but not at platinum or gold electrodes. Thus, it is clear that the pH dependence on carbon fiber electrodes is a property of the electrode itself, not the electroactive species. It has been speculated[23,24] that the increase in k_s at low pH is due to the protonation of interfacial functional groups at the carbon surface. These results suggest that, while there may be some subtle differences between Tonen HMU fibers and other carbon electrode materials studied in the past, their overall behavior as an electrode material is quite similar to that of these other materials.

The double layer capacitance of the bare Tonen HMU carbon fiber electrode was calculated from cyclic voltammograms at several scan rates (50 mV/s - 400 mV/s) and different pH values (3.5 - 6.5). The double layer capacitance, C_{dl}, was determined from $i_c = C_{dl}\, dE/dt$, where dE/dt is the scan rate and i_c is the charging current. The values of C_{dl} obtained from these experiments are between 6.5 and 7.5 $\mu F/cm^2$. Adams and coworkers[25] compared the capacitance of the end of a carbon fiber (as a disk electrode, i.e. a single fiber sealed into a glass capillary) with that of the exposed cylinder. Their untreated fiber had a double layer capacitance of 23 $\mu F/cm^2$ on its end and 6.8 $\mu F/cm^2$ on the cylindrical surface. They claimed that this difference is caused by increased roughness on the fiber end and/or by a higher fraction of basal plane on the cylindrical surface. Since the capacitance[26] of the basal plane of HOPG is 2-3 $\mu F/cm^2$ and the pure edge plane capacitance[26] of HOPG is about 70 $\mu F/cm^2$, the double layer capacitance values we obtained suggest that both edge and basal plane surfaces are exposed on the cylindrical surface of the Tonen HMU fibers. Most importantly, these results unambiguously demonstrate that the cylindrical surface is <u>not</u> predominantly basal plane, even on these high-modulus fibers, and, therefore that edge plane must be exposed. As will be seen below, we believe these must be sites at which the amine attachment chemistry occurs.

B. Characterization of treated fibers.

1. Alkylamines.

1,6-diaminohexane, a primary amine, was reacted with Tonen HMU pitch-based carbon fibers as described in the *Experimental* section. Following reaction, FTIR-ATR was used to characterize the interfacial adducts produced by the reaction. This method has been shown to be a versatile technique that is very useful in the characterization of chemical functionalities and orientation of molecules at surfaces or in thin films[27]. Fourier transform infrared spectroscopy (FTIR) in transmission mode has not been applied successfully to study carbon fiber materials due to the severe scattering characteristics and the high absorptivity of these materials. However, the limited penetration depth of the ATR method allows one to obtain spectra of acceptable quality. This method has been used previously on the analysis of carbon fiber-epoxy prepregs[28-30] with some success.

A criterion for using ATR on samples such as these is that n_1 and n_2, the refractive indices of the optical element and the sample, respectively, must obey the condition $n_1 > n_2$ in order to obtain adequate reflection of the incident light within the ATR element. Also, the incident angle has to be larger than the critical angle Θ_c ($\sin \Theta_c = n_2 / n_1$). These conditions can be satisfied by using a germanium element, because it has the highest refractive index of the commonly used ATR materials ($n_{Ge} = 4.0$, $n_{ZnSe} = 2.4$, $n_{KRS\text{-}5} = 2.4$). This results in total reflection of the incident light even for a sample such as graphite, with a refractive index of 3.3[31]. Note that the ATR configuration maximizes interaction of the IR source radiation with the sample surface, rather than its bulk, which leads to a relative enhancement in the contribution of species at the surface to the spectrum.

In Figure 3, the C-H stretching regions of the ATR spectra of 1,6-diaminohexane derivatized HMU fibers and bare HMU fibers are shown. As can be seen in curve B, there are no C-H stretching peaks detected on the bare pitch-based carbon fiber samples[29]. However, the asymmetrical (υ_{as},CH_2) and symmetrical (υ_s,CH_2) C-H stretches[32] of diaminohexane, near 2930 cm^{-1} and 2852 cm^{-1}, are observed clearly in curve A. Given that these samples were exposed to prolonged solvent extraction, rinses, and vacuum drying, these data are strongly suggestive of the permanent, covalent immobilization of the amine-derived adducts at the CF surface following the reaction. However, they do not provide information on the type of linkage to the surface. Attempts to observe the C-N stretch of the adduct proposed in Fig. 2I were unsuccessful due to interference from residual atmospheric moisture in the spectrometer. Also, quantitative analysis of these data is not possible because the precise surface area probed in this FTIR-ATR sampling configuration is not known.

Because of this inability to determine the amine surface coverage from the FTIR-ATR spectral data, an electrochemical method was developed to assay the yield of amines immobilized at the surface. This method uses the electrostatic binding of $Fe(CN)_6^{3-}$ (present at very low concentrations in solution) to the protonated, cationically charged interfacial amine groups as a way of "marking" these cationic groups. Then, an electrochemical measurement is used to determine the number of interfacial metal complexes, from which the number of amine groups can be calculated. These experiments were done as a function of both pH and concentration of $Fe(CN)_6^{3-}$ in solution. Then, plots of the surface coverage of $Fe(CN)_6^{3-}$ versus concentration can be used to extract the binding constant for the metal complex to the cationic amine groups at the interface and the saturation coverage of the metal complex (which is proportional to the amine surface coverage.

Figure 4A shows a set of CV data typical of the response of amine-derivatized carbon fibers at a variety of concentrations of the metal complex in solution. Figure 4B shows the control experiments for the bare (untreated) carbon fiber. The curves in Fig. 4A clearly show the accumulation of excess $Fe(CN)_6^{3-}$ at the surface as its concentration in solution is raised, as evidenced by the considerably larger peak current for its reduction at the derivatized fiber (at ca. 0.22 V) than at the bare fiber. Note also that the reoxidation of $Fe(CN)_6^{4-}$ back to $Fe(CN)_6^{3-}$ is also enhanced relative to the purely solution phase response shown by the control experiments in Fig. 4B, but not so much as for the reduction process. This is most likely due to a lower binding constant for $Fe(CN)_6^{4-}$ compared to $Fe(CN)_6^{3-}$. The reason for this is not entirely clear at this time, but it may be due to ion pairing between $Fe(CN)_6^{4-}$ and the cations from the supporting electrolyte. This phenomenon is known, at least for K^+ ion[33]. Another possibility is that the spatial distribution of the cationic amine groups hinders adsorption of the more highly charged species. In other words, it is possible that the amine groups are sufficiently far apart so that adequate neutralization of the 4- charged $Fe(CN)_6^{4-}$ species is not possible. Finally, it is also possible that the radial diffusion that is responsible for the sigmoidally-shaped $Fe(CN)_6^{3-}$ CV response at the bare electrode leads to sufficient perturbation of the interfacial concentrations of the relevant species that an equilibrium situation does not prevail at reducing potentials. At any rate, because of these possible complications for the $Fe(CN)_6^{4-}$ case, it was decided to use the $Fe(CN)_6^{3-}$ reductive charge to assay the amine groups.

Quantitative measurement of the relevant reductive charge was accomplished by measuring the area under the peak and subtracting the area under the matching curve for the control experiment. these data are shown as a reciprocal Langmuir plot[34] in Fig. 4. The linearity of this plot shows that the behavior of the "adsorbing" $Fe(CN)_6^{3-}$ species is reasonably well approximated by the Langmuir approximation. The deviation of the plotted points toward higher coverage at the higher concentrations is most likely due to difficulties in properly subtracting the charge from the control experiments. A linear least squares fit through the data gives a saturation surface coverage for $Fe(CN)_6^{3-}$ of 3.3×10^{-11} mol cm^{-2}. Assuming a 3:2 ratio for amine groups to $Fe(CN)_6^{3-}$, this gives approximately 5×10^{-11} mol cm^{-2} for the amine coverage. Note that we assume here that both the amine group near to the CF surface and that at the far end of the chain (i.e. on the solution side) are protonated and participate in the electrostatic neutralization of $Fe(CN)_6^{3-}$. This assumption seems reasonable since these experiments were done at a pH of 1.25 where the primary alkyl amine would certainly be protonated and so should the amine involved in bonding to the carbon fiber surface. The slope of this plot gives a binding constant for adsorption of the $Fe(CN)_6^{3-}$ to the surface of ca. 1.35×10^6 M^{-1}, which is reasonable given the concentration range over which binding and saturation occur.

Examination of the redox behavior of this same system at different pH values yielded the data given in Table 1. These data show that the apparent formal potential of the $Fe(CN)_6^{3-/4-}$ complex shifts positive as pH is lowered. This is consistent with the known acid-base behavior of this couple, and is due specifically to protonation of $Fe(CN)_6^{4-}$.[35] The data also show that the peak separation for the anodic and cathodic peak currents increases as pH is raised. This is consistent with Wightman's observations[24] that the heterogeneous electron transfer kinetics of this redox couple are strongly pH dependent at carbon electrodes, with much lower rates observed at higher pH's. Attempts to use the assay procedure at the higher pH values were unsuccessful due to the fact that the currents due to the adsorbed metal complex were considerably smaller, so that unambiguous separation of the interfacial and bulk responses was not possible.

Finally, we examined the uptake of $Fe(CN)_6^{3-}$ at didecylamine-derivatized carbon fiber surfaces. Interestingly, these experiments did not show significant uptake, even though the FTIR-ATR experiments clearly showed the presence of the amine adduct at the surface. This is most likely due to a considerably lower binding constant for $Fe(CN)_6^{3-}$ at this surface. The origin of this effect is not clear at this time, but possibilities include the spatial distribution of the cationic charges and a lower dielectric constant at the interface due to the presence of the long alkyl chains of this amine derivative.

2. Ferrocene derivatives.

The results given above demonstrate the attachment of amine derivatives to the carbon fiber surface, and are consistent with the proposed Michael-like chemistry discussed above. However, they do not unequivocally exclude the possibility of amine reaction with oxygen-containing groups at the carbon fiber surface (which would not be eliminated in the vacuum heat treatment described in the experimental section[36]) to produce amide adducts[6]. To test whether tertiary amines are also capable of immobilization at the surface via these thermal reactions, the attachment of dimethylaminomethylferrocene (DMAFc) was investigated. For tertiary amines, nucleophilic attack of the amine at the vinyl groups of the carbon fiber would produce a quaternized nitrogen. Importantly, for this case amide formation via attack at the oxygen-containing functionalities is not possible, so any permanent attachment must occur by some other mechanism, such as the Michael-like chemistry discussed above[13,14].

The cyclic voltammogram of a Tonen HMU CF after thermal reaction with DMAFc is shown in Figure 6A. The response of the ferrocene redox group is clearly observed by the presence of the wave centered at 0.45 V. The relatively large peak separation is not unusual for such immobilized species, and may have many possible explanations. However, for the present purpose of exploring the attachment chemistry of these amines reagents, this issue is not important. The surface coverage of ferrocene groups at this CF is 5 x 10^{-11} moles/cm^2, as determined by integration of the current for the peak centered at 0.45 V. This represents about 25% of the expected saturation surface coverage[37] for this compound of ca. (2-3) x 10^{-10} mole/cm^2. Figure 6B shows the CV of a DMAFc-derivatized AS-4 (PAN-based) carbon fiber, which was reacted under the same conditions as the pitch carbon fiber. In this case, the surface coverage is 1 x 10^{-11} moles/cm^2, ca. 5% monolayer coverage. Control experiments were done in which both pitch and PAN carbon fibers were refluxed with ferrocene (1M) in toluene for six days. The products were rinsed in methanol and THF for three days. As can be seen in Fig. 7, there is no detectable surface coverage of ferrocene for either type of fiber.

In addition to the reaction of neat DMAFc with the CF's, the use of water or dilute acid as catalyst[13] was also investigated as described in the *Experimental* section. The ferrocene surface coverages (Γ_{Fc}) obtained from five replicate experiments were: pitch CF (dilute acid as catalyst) > pitch CF (DI-water as catalyst) > pitch CF (neat DMAFc without catalyst) (Γ_{Fc} = (5.1±0.3) x 10^{-11} moles/cm^2 > (3.9±0.2) x 10^{-11} moles/cm^2 > (2.7±0.2) x 10^{-11} moles/cm^2, respectively). Thus, the reaction is clearly aided by the availability of protons, which is consistent with the Michael-like mechanism described above[13]. Taken in total, these results demonstrate that DMAFc is irreversibly attached to both PAN- and pitch-based CF surfaces via the thermal reaction procedures described. The surface coverages observed are quite high, representing significant fractions of a monolayer. The ability to irreversibly attach **tertiary** amines to the surface under the conditions described strongly suggests that the linkage is not via amide bond formation, but rather may be due to covalent bond formation via the Michael-like mechanism described above.

If attachment of DMAFc occurs by nucleophilic addition, then the charge on the DMAFc interfacial adduct should be cationic due to the formation of a quaternary nitrogen center after the Michael-like reaction. The presence of a cationic charge so near to the ferrocene center in the interfacial adduct should have a significant influence on the formal potential of the ferrocene moiety, shifting it positive with respect to the uncharged case. Thus, one way to investigate the possible presence of charge on the DMAFc interfacial adduct is to compare its formal potential with that of its parent complex in solution. Figure 8 shows such a comparison. Curve A shows a CV of a DMAFc-derivatized Tonen HMU carbon fiber in acetonitrile solution. Under these conditions, the ferrocene center exhibits a formal potential of ca. 0.5 V. Curve B shows a CV of bulk DMAFc dissolved in acetonitrile solution, where it exhibits a formal potential of 0.3 V. These results show that in the interfacial adduct, the ferrocene center is fully 0.2 V more difficult to oxidize. This result is consistent with the presence of cationic charge on the DMAFc species immobilized at the surface and is difficult to reconcile with other possibilities.

3. Anthraquinone.

To test the generality of the reaction scheme described above, we also investigated the immobilization of 2-aminoanthraquinone at CF surfaces. This species also bears an amine group, so it should be capable of undergoing the same type of coupling chemistry as the compounds described above. However, because the amine group is conjugated with an aromatic ring system, it should probably exhibit considerably lower reactivity as a nucleophile. Figure 9A shows the cyclic voltammogram of a Tonen HMU CF after the immobilization reaction with 2-aminoanthraquinone. The large cathodic and anodic current peaks centered at -0.22 V are consistent with the electrochemistry expected for immobilized anthraquinone[38]. Integration of the current for the cathodic peak gives a surface coverage of 6×10^{-11} moles/cm^2, ca. 1/4 monolayer coverage. Note that this is only an approximate measure of Γ because of the difficulty in obtaining a proper background subtration. The appropriate control reactions with anthraquinone demonstrate that the amine group is essential to the attachment of the anthraquinone moiety. These results show that 2-aminoanthraquinone is capable of reaction to give fairly high surface coverages, despite expectations of lower nucleophilic reactivity.

We also studied the reactivity of the deprotonated form of 2-aminoanthraquinone which was produced *in situ* by addition of the very strong, hindered base sodium bis(trimethylsilyl)amide. The objective here was to test the hypothesis that the deprotonated form of 2-aminoanthraquinone would serve as a much more potent nucleophile in the Michael-like reaction. Figure 9B shows the CV of the fibers that were treated in this way. The surface coverage of anthraquinone resulting fromthis reaction 1.3×10^{-10} moles/cm^2. This is a promising result, showing about twice the surface coverage as the reaction of 2-aminoanthraquinone without deprotonation. It is unclear whether this result occurs due to a rate enhancement for the amide species, or from reaction pathways that are not available to the parent species (i.e. access to different types of immobilization sites).

The electrooxidative production of amine cation radicals near the electrode surface[12,22] was also briefly examined as a method to immobilize 2-aminoanthraquinone. As shown in Figure 10, after a PAN carbon fiber was held at 0.9V vs. SCE for 40 seconds in an ACN solution containing 0.05 mM 2-aminoanthraquinone and 0.1 M $NaClO_4$ under Ar, the cyclic voltammogram of that CF after transfer to pure supporting electrolyte clearly shows that the anthraquinone redox moiety has been electrodeposited by virtue of the peaks centered at -0.25 V. The surface coverage, 5×10^{-11} moles/cm^2, is essentially the same as that for the amine reaction. It is interesting to note that there is no immobilization when the electrooxidation is done at higher concentrations of 2-aminoanthraquinone (> 0.5 mM). The most probable reason for this observation is the formation of dimers from coupling of the aminoanthraquinone radical cations near the electrode surface, a process that should become more important at high concentration.

There are several previous reports[23] of redox waves from interfacial species on "bare" carbon electrodes that have a pH dependence consistent with quinone-like electrochemistry. For example, Anson et al.[39] observed a redox peak on an edge-plane pyrolytic graphite electrode, and attributed it to the presence of quinone-like functional groups on the edge plane of the graphite surface. However, there is still some controversy about this assignment[23,40]. To verify that the waves we observed were actually due to immobilization of 2-aminoanthraquinone and not to such a background process, we conducted several control experiments in which untreated carbon fibers were examined at various pH values. These experiments showed that no such peaks are observed in either acidic or basic solutions for the untreated fibers, suggesting that the residual level of such "quinone-like" species on these CF's must be quite low. Thus, the redox responses described above are clearly a result of the reaction of 2-aminoanthraquinone with the CF surface.

C. XPS characterization of treated carbon fibers.

XPS was used to measure the compositions of the CF's before and after these reactinos. The objective was to gain information as to the approximate atomic composition of the surface region, as well as to attempt to determine the oxidation states of the interfacial species (especially the nitrogen species) via examination of their binding energies. Narrow scan spectra in the N_{1s} region are shown in Figures 11A and 11B for the DMAFc-derivatized and 2-aminoanthraquinone-derivatized Tonen HMU CF's, respectively. Previous work has shown that the binding energy of quaternized nitrogens is between 401 - 402 eV, and non-quaternized nitrogen is about 399 eV[41]. The binding energy of nitrogen bound to oxygen and/or nitrogen bound to a carbonyl group (i.e. an amide group) is about 401.5 eV[41]. The narrow scan of the N_{1s} region for the DMAFc-treated fibers shows a single peak at 401.7 eV. Because this tertiary amine cannot react with interfacial carbonyl or carboxyl functional groups to produce an amide, we attribute this peak to a quaternized nitrogen in the immobilized DMAFc derivative. The N_{1s} binding energy of nitrogen on the 2-aminoanthraquinone-treated pitch carbon fiber is 399.6 eV. This value is inconsistent with an amide nitrogen. Rather, these results are consistent with the notion that 2-aminoanthraquinone reacted at vinylic functionalities on the carbon fibers. Table 2 shows the N_{1s} peak positions observed for these two cases as well as a few relevant atomic percentages, which were obtained using a simple gaussian fit to the peaks. For example, for the DMAFc-treated fibers, the Fe:N ratio is observed to be 3.17:2.05, which is reasonably consistent with the expected 1:1 ratio. Also, for the 2-aminoanthraquinone-treated fibers, the O:N ratio is observed to be 7.34:4.25, which, again, is consistent with the expected ratio of 2:1.

4. CONCLUSIONS

Many research groups have examined the covalent attachment of various types of compounds at carbon fiber surfaces. However, in the majority of cases for which electrochemical applications were the goal of the work, this attachment was done at the tip of a carbon fiber embedded in some type of supporting material[23,24]. Thus, the observations in those studies would have been mostly derived from the chemistry of the edge planes of the carbon fibers[43-46], and therefore their results and conclusions may not have much direct relevance to our studies of the cylindrical surface of the pitch-based, high modulus fibers studied here. In fact, since our focus is on understanding the nature of the adhesive interaction between carbon fibers and epoxy matrix materials, we will direct our attention toward the composite materials application of the type of immobilization chemistry studies here. For some time, researchers have thought that covalent chemical bonding at the interface of carbon fiber-epoxy composites occurs only at the edge plane, at which there is a variety of oxygen-containing functional groups produced after the usual oxidative pretreatments. Adhesion is thought to be controlled by a combination of chemical bonding due to the functional groups at the edge plane and mechanical interlocking due to the surface morphology. Specifically, it is the prevailing wisdom in the area that reaction between oxygen-containing functionalities (produced at the carbon fiber surface by the oxidative pretreatments usually employed) and possible reaction partners in the matrix material, such as epoxy groups or amines (present in the matrix precursor material as so-called hardeners) accounts for the chemical component of interfacial adhesion in these composite materials. These hypotheses have been extensively investigated by several research groups[6,10,11,43-47] in the past few decades. This work has shown that interfacial adhesion is sometimes strongly correlated with the presence of oxygen-containing functionalities at the CF surface. However, direct evidence of the involvement of these functionalities in interfacial bonding remains elusive due to the difficulties associated with spectroscopic observation of the groups at the interface after formation of the composite material.

A reaction type that to our knowledge has been completely ignored in previous investigations of interfacial adhesion in CF-epoxy materials is the nucleophilic attack of amine groups at vinylic functionalities at the CF surface, i.e. the Michael-like addition. The present investigation was initiated in order to elucidate the possible role of this chemistry in CF-epoxy adhesion. The choice of studying attachment of amines on the cylindrical, previously untreated surface of pitch-based, high modulus carbon fibers was made based on an assumption that these surfaces would be less complex and contain fewer oxygen-containing functionalities than the traditional, PAN-based, surface treated CF's. The hope was that this approach would reduce the complexity of the problem of sorting out the many possible interfacial reactions that might occur, and especially that it would eliminate or reduce the likelihood of amine attack at oxygen-containing functionalities to form amide derivatives. The results described above clearly and unambiguously demonstrate that amines can add to carbon fiber surfaces, and that they can do so under conditions where amide formation is not possible. Thus, it is entirely possible that this previously unconsidered reaction makes a significant contribution to interfacial adhesion in CF-epoxy composite materials.

Interestingly, this conclusion is in good agreement with two important, previous studies. Mimeault and McKee[48] studied the interfacial shear strength in CF-epoxy composites produced from carbon fibers that had been oxidatively treated and then used directly or thermally treated at 950 °C under vacuum following the oxidative treatment, where the latter procedure was employed to remove as many of the oxygen-containing surface functional groups as possible. Their results showed that the interfacial shear strength was not sensitive to the removal of the oxygen-containing functionalities. In a later study that employed more sophisticated surface analytical techniques that unequivocally demonstrated the reduction of oxygen-containing functionalities after the high temperature, vacuum treatments, Drzal[49] reached the same conclusion, namely that the oxygen-containing functionalities do not play a pivotal role in producing interfacial adhesion in CF-epoxy composites. These results have been widely interpreted as suggesting that mechanical interlocking is the predominant mechanism by which adhesion is achieved in these materials[42,44]. However, an alternative explanation of those results, and one that is entirely consistent with the results of the present investigation, is that the Michael-like addition reaction between nucleophilic amine groups in the matrix and vinylic groups at the CF surface accounts for the adhesion in these materials. It is noteworthy that this hypothesis also accounts for the strong correlation observed between oxidative surface pretreatments and interfacial adhesion[6,10,11,43,45], because the presence of these electron withdrawing functionalities in conjugation with interfacial vinylic groups would be expected to activate those groups toward nucleophilic attack by the amines[13,14].

This proposal of the involvement of Michael-like chemistry in interfacial adhesion is CF-epoxy materials is somewhat speculative at this time. However, we have recently demonstrated[50] that such reactions can be used to exert very fine control over the interfacial adhesion in such materials, as shown by mechanical testing of samples of amine-treated carbon fibers embedded in epoxy matrix materials. These embedded single fiber test results provide direct and compelling evidence for the role of Michael-like chemistry in adhesion of CF-epoxy materials.

Finally, this contribution has also described two electrochemical methods for assaying surface reactions. The first simply involves "tagging" the incoming reagents with redox groups, so the reaction yield can be obtained by measuring the electrochemical charge from these immobilized redox groups. The second method is more novel, using electrostatic binding of a redox probe species and analysis of its isotherm to assay the yield of the interfacial reaction. This method is applicable even for cases in which the immobilized species is not electroactive. However, it does require that the immobilized species bear a charge. This method is conceptually similar to our previous report of the use of redox-active surfactants to assay the surface coverage of self-assembled monolayers of various organothiol species at Au electrodes.[37]

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Electrolyte	E°	ΔE_{peak}
pH = 1.25	0.260 V	0 V
pH = 3.45	0.175 V	0.05 V
pH = 6.80	0.170 V	0.09 V

Table 1. The formal potential and ΔE_{peak} values of the eletrochemical titration experiment of a 50 μM $Fe(CN)_6^{-3}{}_{(aq)}$ titrant with a 1,6-diaminohexane derivatized carbon fiber electrode in different pH electrolytes.

	N_{1s}	Normalized Atomic Percentage
Dimethylaminomethyl-ferrocene treated carbon fiber	401.7 ev	Fe/N = 3.17/2.05
2-aminoanthraquinone treated carbon fiber	399.6 ev	O/N = 7.34/4.25
Untreated Tonen HMU pitch-carbon fiber	—	C/O/N = 95.12/4.35/0.46*

Table 2. Atomic percentages of elements detected by XPS surface analysis for dimethylaminomethyl-ferrocene and 2-aminoanthraquinone treated Tonen HMU pitch-based carbon fibers. (*data from reference 42, p. 151)

Figure Captions

Figure 1. Nucleophilic bonding of amines with the vinyl groups on the carbon fiber surface.

Figure 2. The proposed structures of the interfacial adducts.

Figure 3. FTIR-ATR spectra, (A) 1,6-diaminohexane treated Tonen HMU pitch-based carbon fiber, (B) untreated Tonen HMU pitch-based carbon fiber.

Figure 4. Cyclic voltammograms of a Tonen HMU pitch-based carbon fiber in solutions of various concentrations of $Fe(CN)_6^{-3}$, (A) 1,6-diaminohexane-treated fiber, concentration of $Fe(CN)_6^{-3}$: a=0.5 μM, b=1 μM, c=1.5 μM, d=2 μM, e=2.5 μM, (B) untreated fiber. Geometrical surface area of carbon fiber electrode: 1.3 x 10^{-2} cm^2. Scan rate: 100 mV/s.

Figure 5. Reciprocal Langmuir isotherm of $Fe(CN)_6^{-3}$ adsorbed on 1,6-diaminohexane-derivatized HMU carbon fiber electrode. Electrolyte: 0.1 M $HCl/NaCl_{(aq)}$ (pH=1.25).

Figure 6. Cyclic voltammograms of DMAFc-derivatized carbon fibers, electrolyte: 0.1 M $H_2SO_{4(aq)}$, scan rate: 100 mV/s, (A) Pitch-based, (B) PAN-based carbon fiber. Geometrical surface area of carbon fiber electrode: 9.4 x 10^{-3} cm^2.

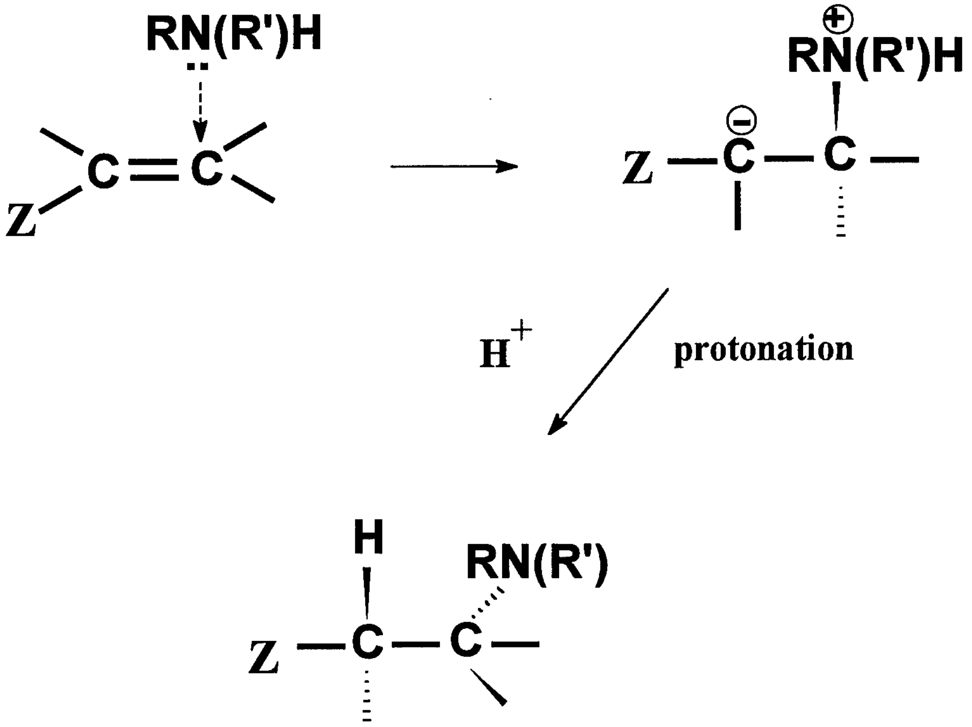
Figure 7. Control experiments ofcarbon fibers exposed to ferrocene in toluene, (A) Pitch-based, (B) PAN-based carbon fiber, electrolyte: 0.1 M $H_2SO_{4(aq)}$, scan rate: 100 mV/s. Geometrical surface area of carbon fiber electrode: 9.5 x 10^{-3} cm^2.

Figure 8. (A) Cyclic voltammogram of DMAFc-treated HMU carbon fiber in ACN, supporting electrolyte: 0.1 M $NaClO_4$, scan rate: 100 mV/s. (B) Cyclic voltammogram of 0.3 mM DMAFc in the same supporting electrolyte at a Pt, solvent: ACN, supporting electrolyte: 0.1 M $NaClO_4$, scan rate: 100 mV/s.

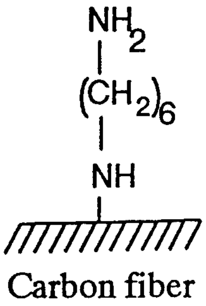
Figure 9. Cyclic voltammograms of 2-aminoanthraquinone-derivatized Tonen HMU carbon fibers, electrolyte: 0.1 M $H_2SO_{4(aq)}$, scan rate: 100 mV/s, (A) after 2-aminoanthraquinone reaction in THF, (B) after 2-aminoanthraquinone and sodium bis(trimethylsilyl)-amide reaction in THF. Geometrical surface area of carbon fiber electrode: 9.5 x 10^{-3} cm^2.

Figure 10. Cyclic voltammogram of carbon fiber (PAN), after electrodeposition of 5 x 10^{-2} mM 2-aminoanthraquinone at potential 0.9 V for 40 sec in ACN, electrolyte: 0.1 M $H_2SO_{4(aq)}$, scan rate: 100 mV/s. Geometrical surface area of carbon fiber electrode: 9.7 x 10^{-3} cm^2.

Figure 11. Narrow scan XPS spectra in the N_{1s} region for (A) DMAFc-treated pitch-based carbon fiber, (B) 2-aminoanthraquinone-treated carbon fiber.



Z = **Electron-withdrawing groups on the carbon fibe surface such as, carboxyl or carbonyl groups**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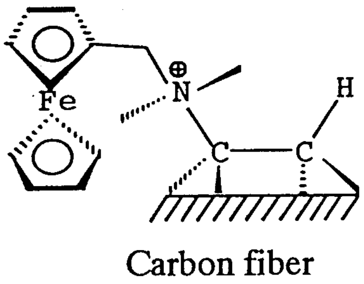
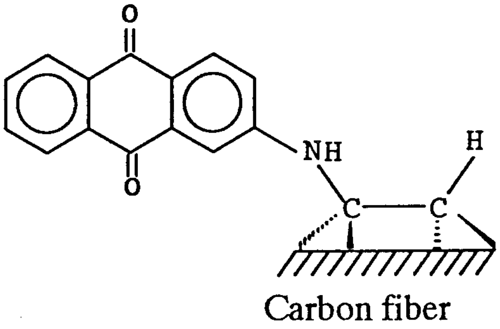
NH
Carbon fiber

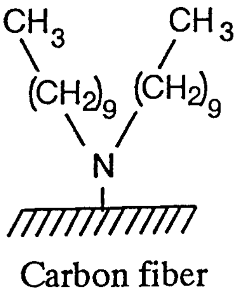
I


Fe
N
H
C
C
Carbon fiber

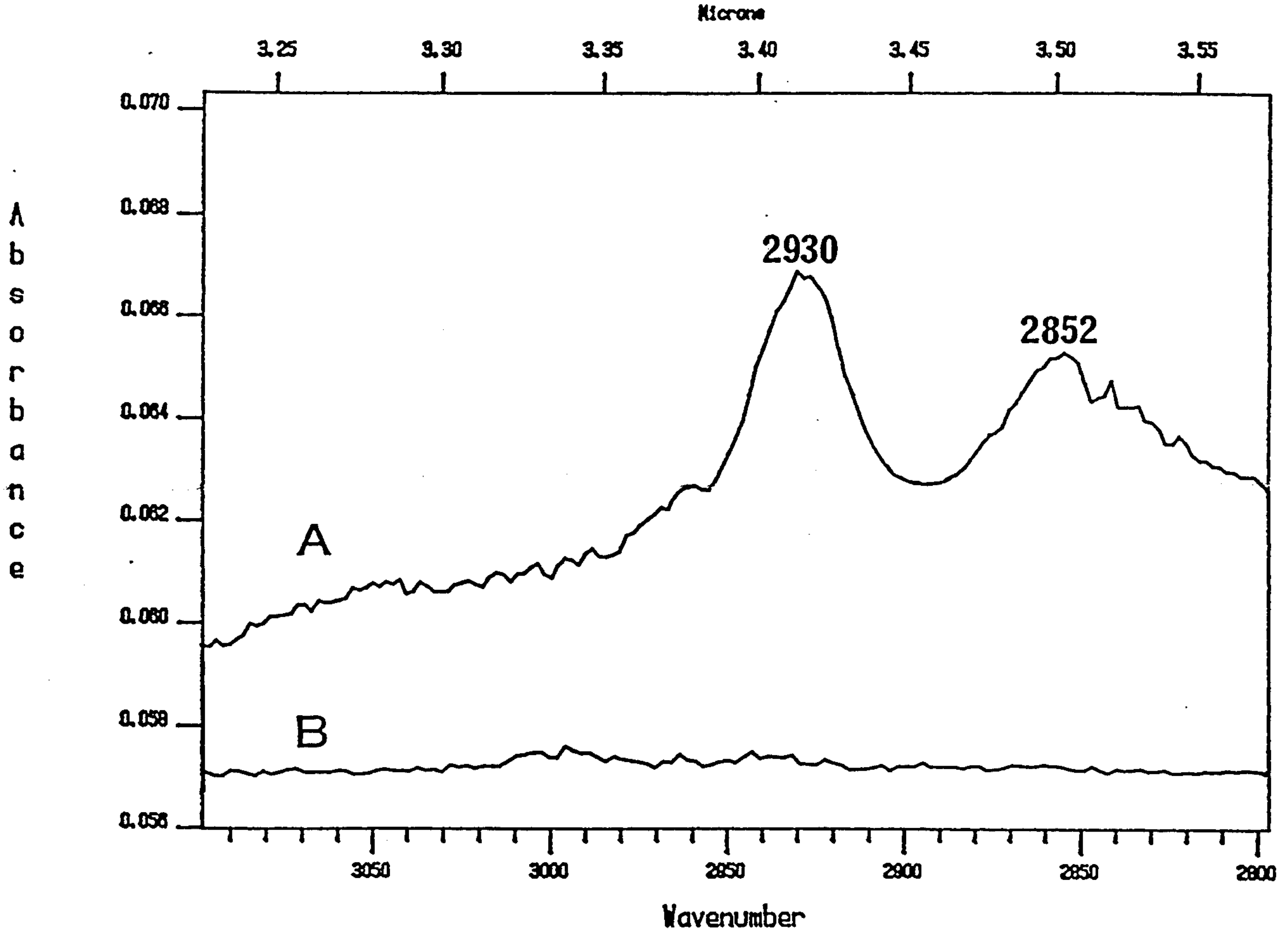
II

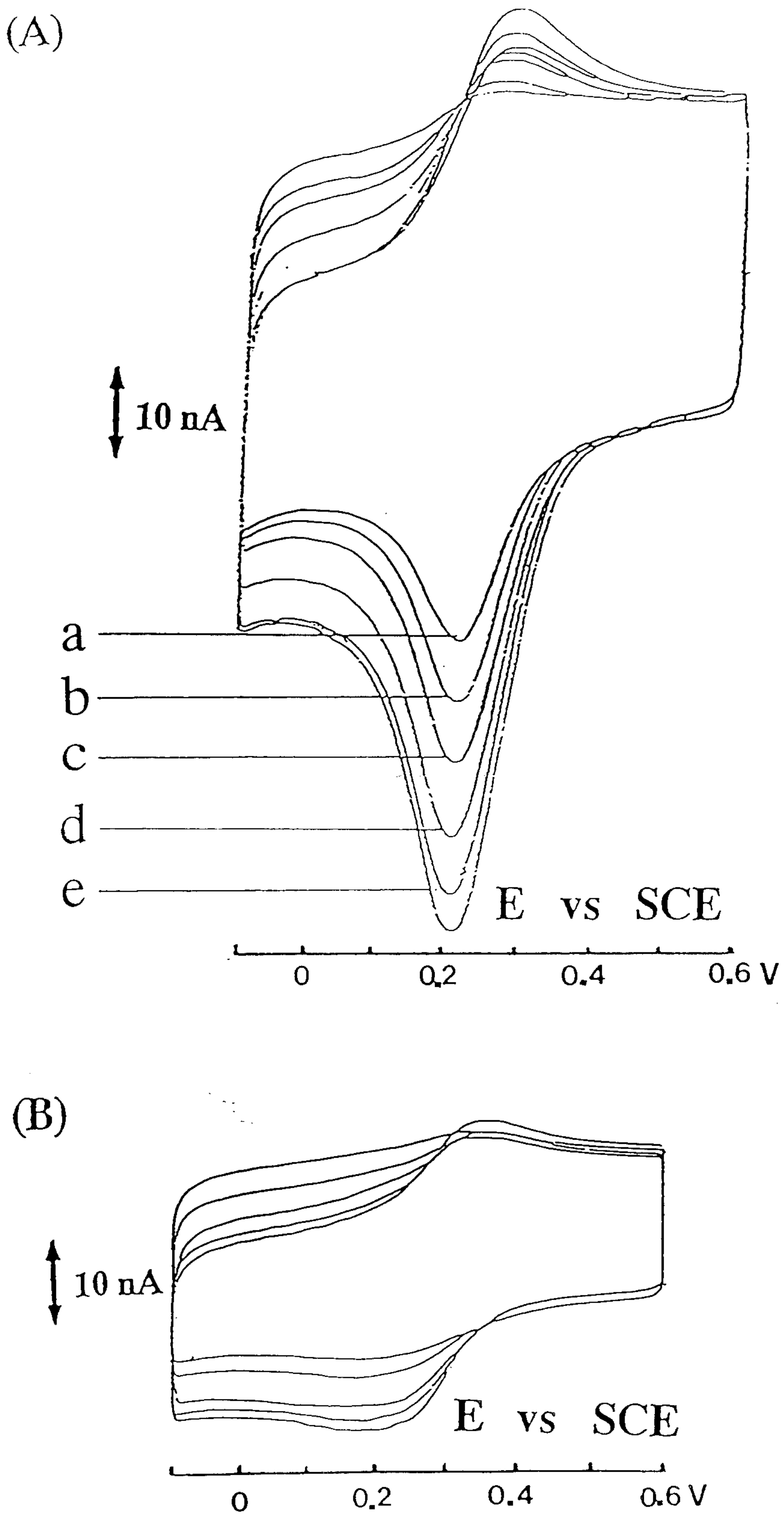

O
O
NH
H
C
C
Carbon fiber

III

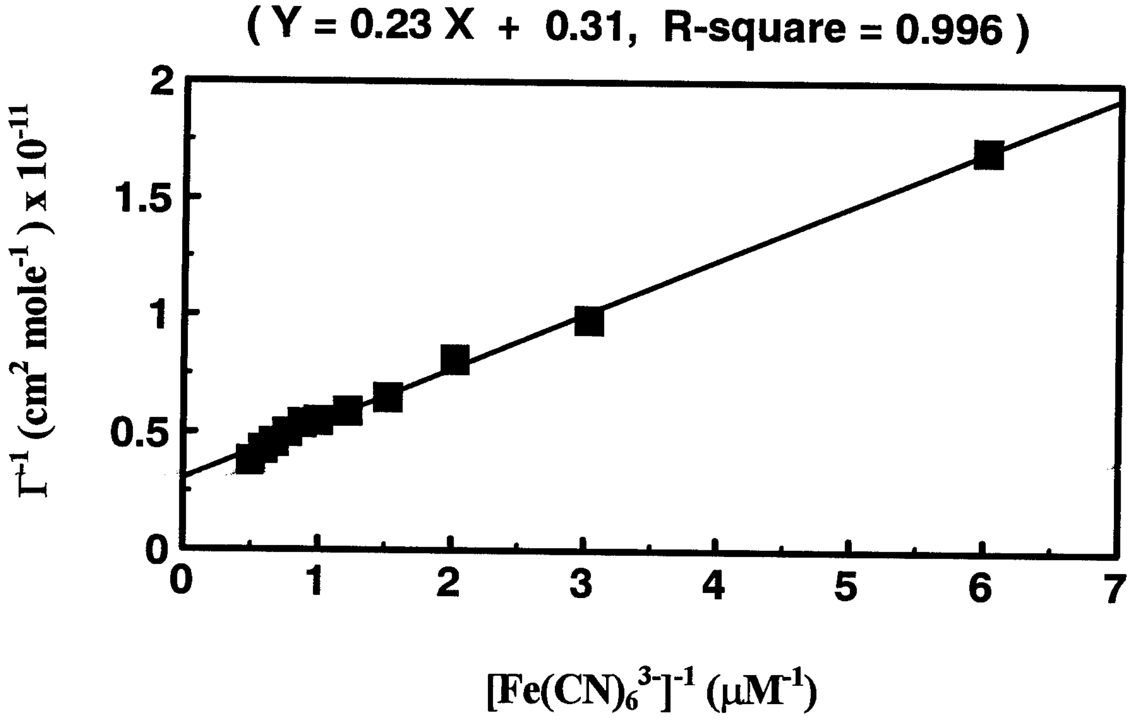

CH3
CH3
(CH2)9
(CH2)9
N
Carbon fiber

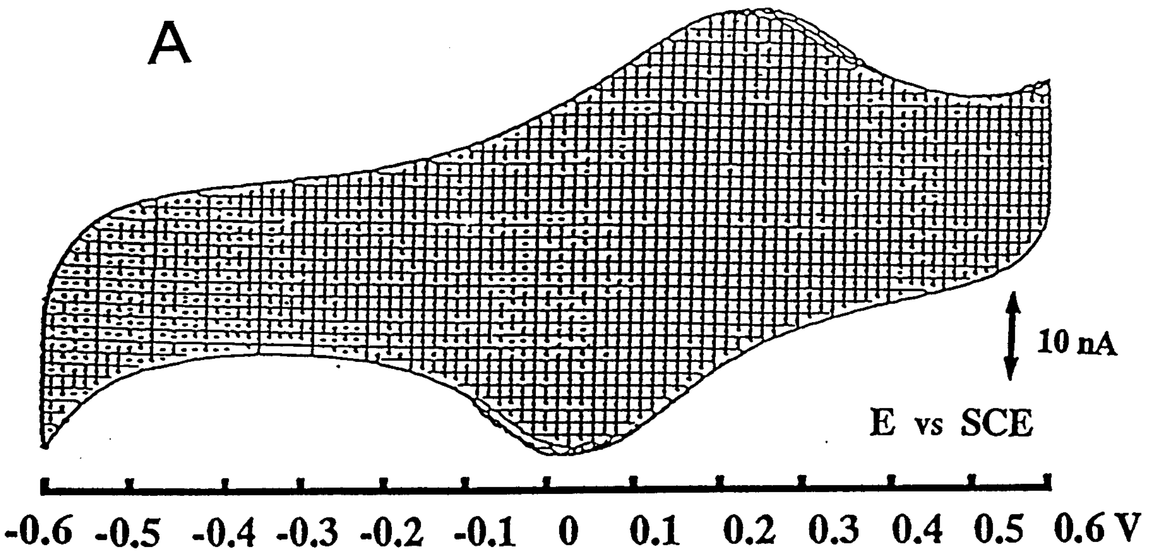
IV

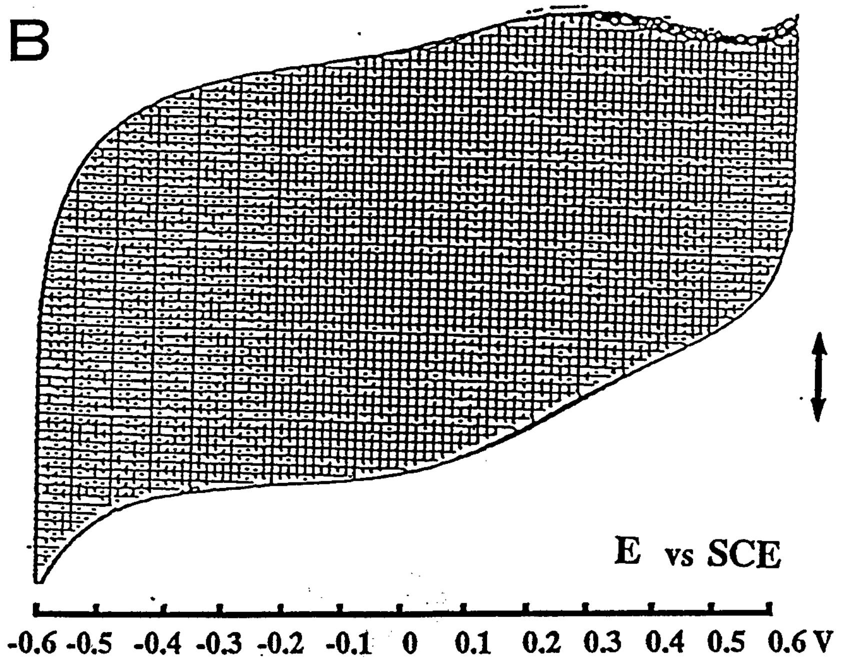

Microns
3.25
3.30
3.35
3.40
3.45
3.50
3.55
Absorbance
0.070
0.068
0.066
0.064
0.062
0.060
0.058
0.056
2930
2852
A
B
3050
3000
2950
2900
2850
2800
Wavenumber

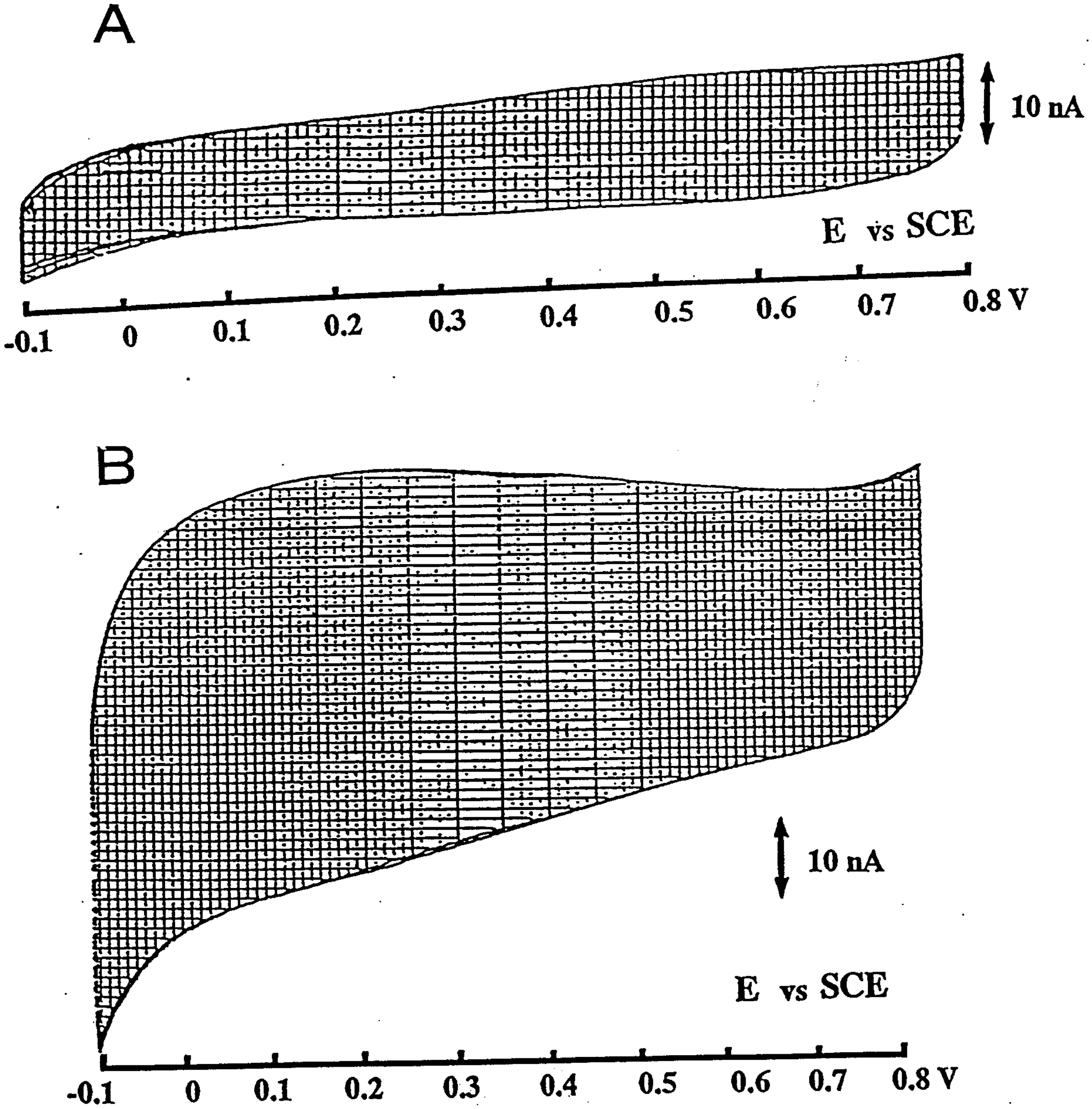


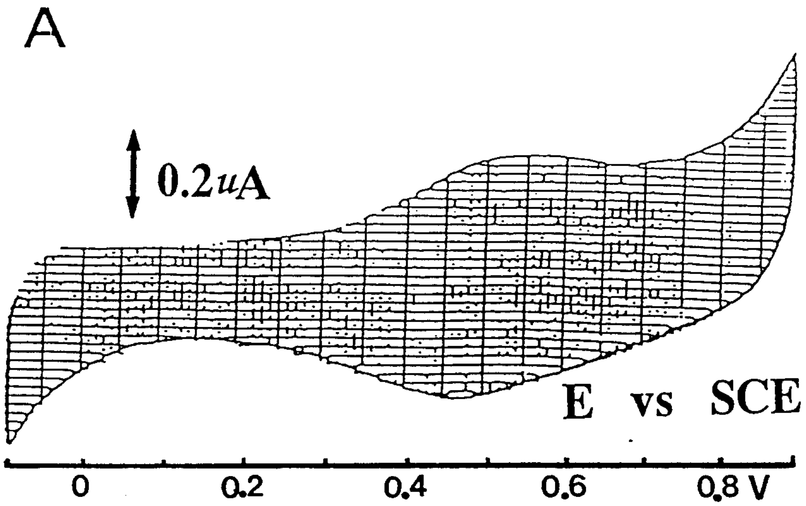
4


(Y = 0.23 X + 0.31, R-square = 0.996)
Γ^{-1} (cm^2 mole^{-1}) x 10^{-11}
0
0.5
1
1.5
2
0
1
2
3
4
5
6
7
$[Fe(CN)_6^{3-}]^{-1}$ (μM^{-1})


A
10 nA
E vs SCE
-0.6 -0.5 -0.4 -0.3 -0.2 -0.1 0 0.1 0.2 0.3 0.4 0.5 0.6 V


B
10 nA
E vs SCE
-0.6 -0.5 -0.4 -0.3 -0.2 -0.1 0 0.1 0.2 0.3 0.4 0.5 0.6 V


A
10 nA
E vs SCE
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8 V
B
10 nA
E vs SCE
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8 V


A
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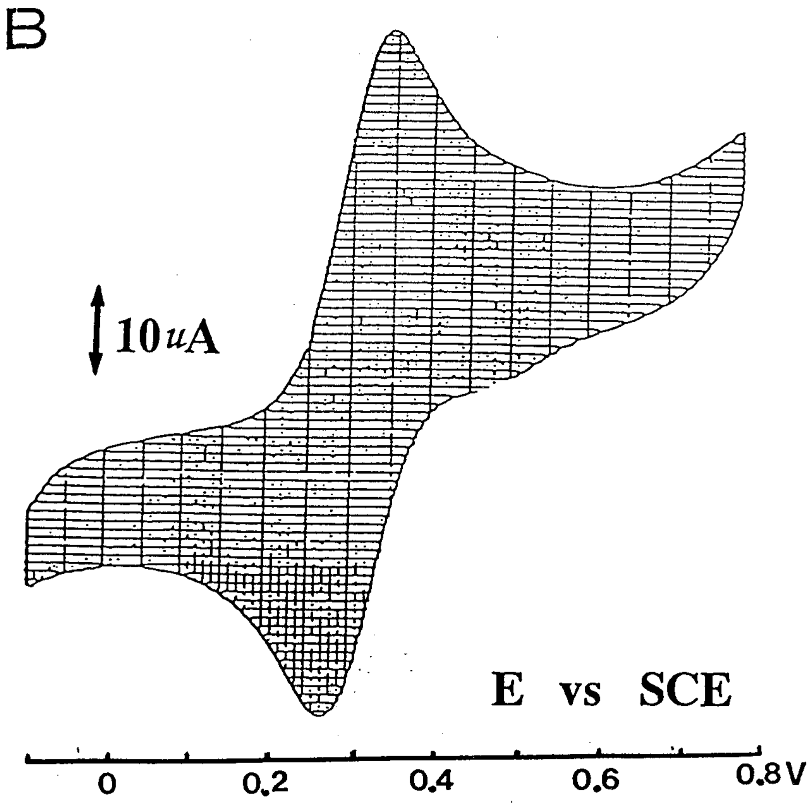
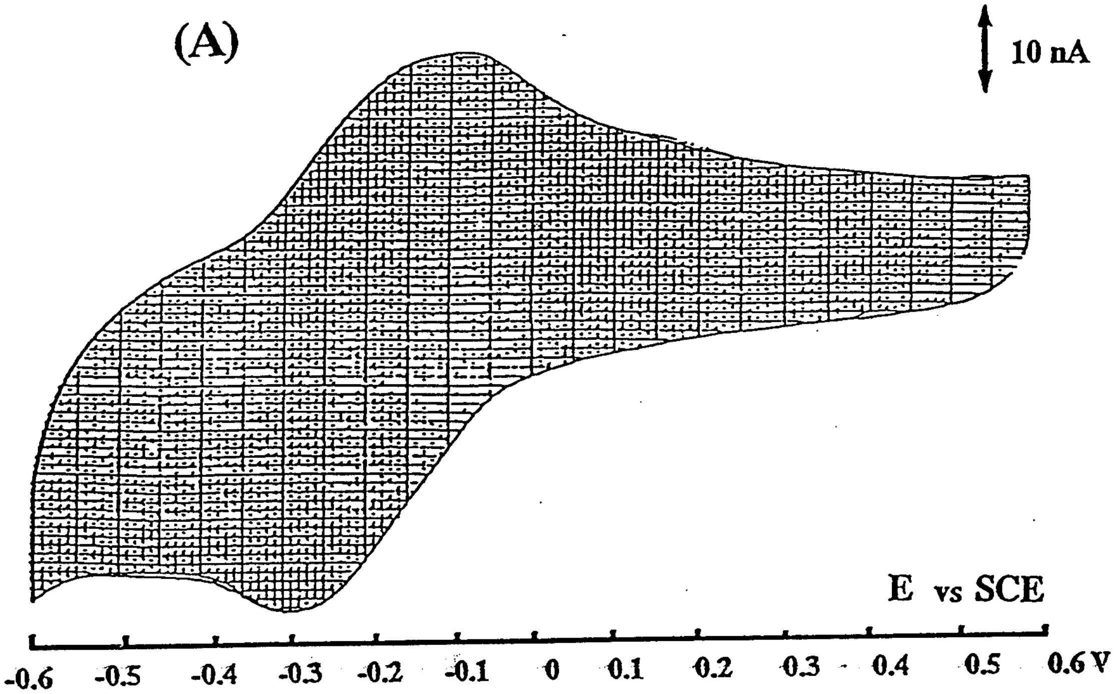
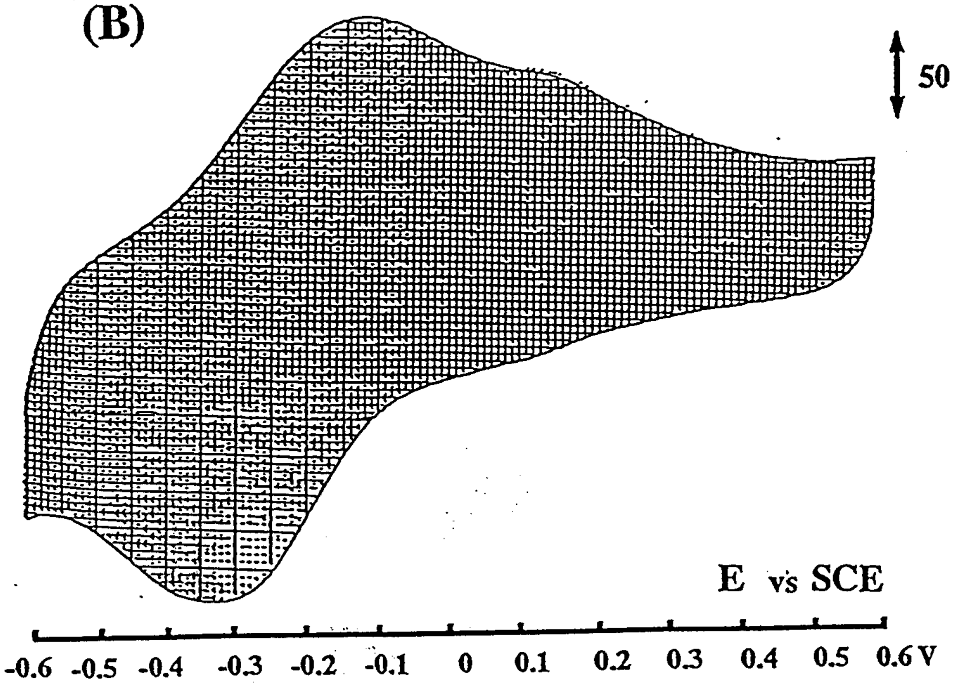
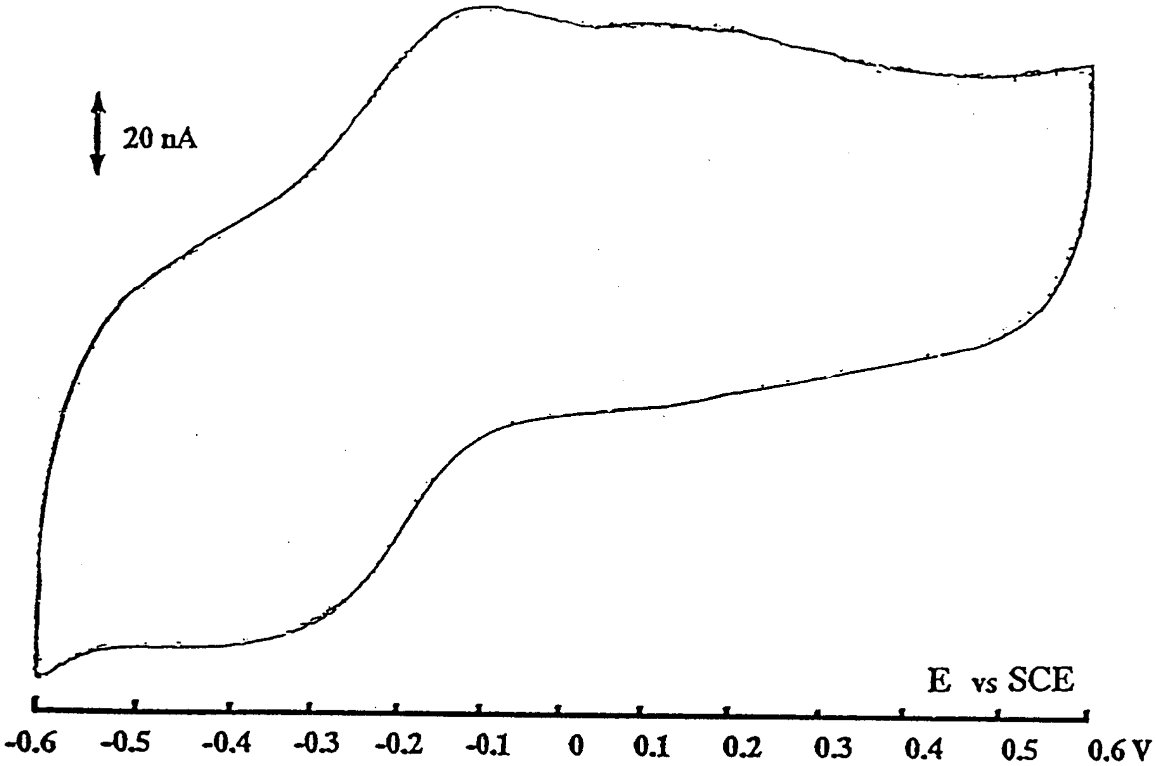
E vs SCE
0
0.2
0.4
0.6
0.8 V

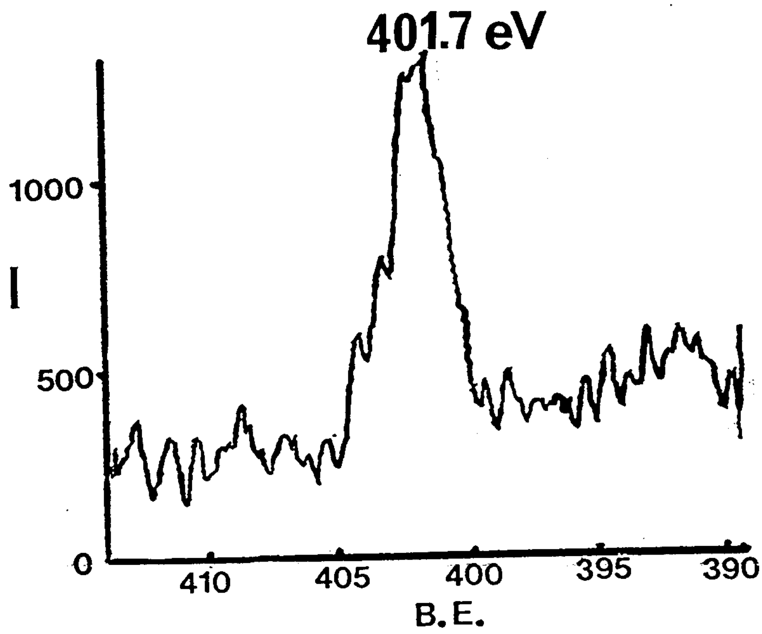

B
10uA
E vs SCE
0
0.2
0.4
0.6
0.8 V


(A)
10 nA
E vs SCE
-0.6
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6 V

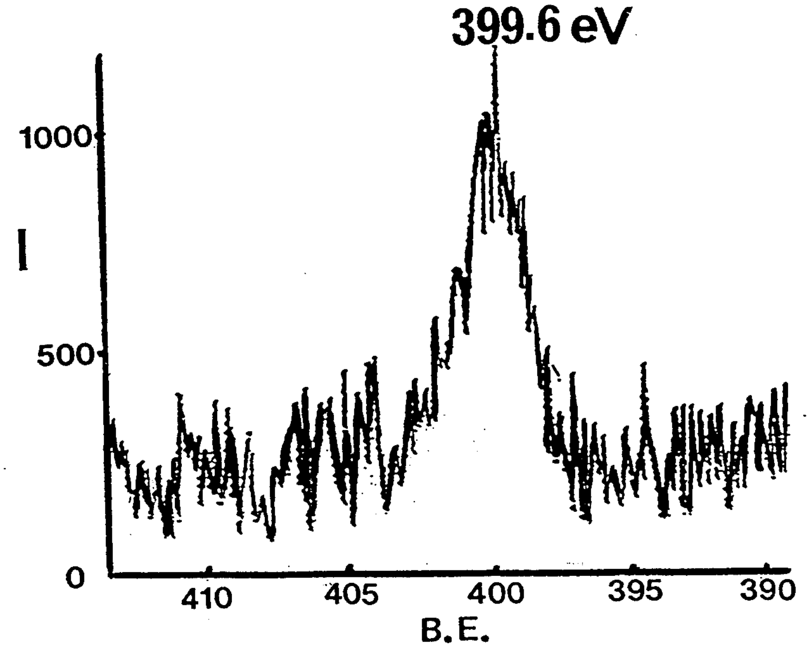

(B)
50 nA
E vs SCE
-0.6
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6 V


20 nA
E vs SCE
-0.6
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6 V

A


401.7 eV
1000
I
500
0
410
405
400
395
390
B.E.

B


399.6 eV
1000
I
500
0
410
405
400
395
390
B.E.