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⁶ CHEMICALLY MODIFIED ELECTRODES. XIV.
ATTACHMENT OF REAGENTS TO OXIDE-FREE GLASSY CARBON SURFACES.
Electroactive RF Polymer Films on
Carbon and Platinum Electrodes.

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ABSTRACT

Reactive, deoxygenated glassy carbon surfaces prepared by mechanical abrasion under nitrogen or argon plasma etching react with selected molecules to yield surfaces with immobilized molecular surface states. Vinyl ferrocene and a ruthenium pyridine complex are immobilized on glassy carbon in this way. Introduction of vinyl ferrocene directly into an RF plasma discharge leads to electroactive ferrocene polymer deposition on glassy carbon and Pt surfaces. Surface waves corresponding to 3×10^{-8} moles/cm.² ferrocene are obtained in this way.

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Known attachments of chemical reagents to carbon electrode surfaces can be divided into those depending on chemistry at oxygenated surfaces [1-7] and those based on chemistry at oxide-free surfaces [8-9]. Mazur [8] introduced the concept of electrode modification based on reactivity of the oxide-free graphitic basal plane edge, whose chemistry is schematically represented by Structure I of Figure 1, by binding a variety of unsaturated compounds to thermally deoxygenated carbon fiber. Oyama, et al. [9] showed that the reactive pyrolytic graphite edge binds to amines after argon radiofrequency (RF) plasma etching.

We report here experiments which expand the usefulness of the oxide-free modification approach. Reactive vitreous (glassy) carbon surfaces can be created by mechanical abrasion (an approach not heretofore described)

as well as argon RF plasma cleaning. We illustrate this by reaction of these surfaces with selected olefins (Reaction 2, Reaction 3-4, Figure 1) and amines (Reaction 6-7, Figure 1), respectively, to bind molecular charge transfer states to the carbon surface.

Plasma discharge can also be employed to invoke deposition of polymer films on surfaces [10] and it is known [11,12] that electrochemical reactions of solution species can occur at electrodes coated with such films. We have investigated the RF plasma discharge as a means of depositing a film which is itself electrochemically active, and describe here electrochemically active surfaces produced by Reactions 8 and 9, Figure 1, on glassy carbon and platinum.

OXIDE-FREE CARBON BY MECHANICAL ABRASION

Fracture of a graphitic carbon across its basal plane produces in principle a virgin, unoxxygenated, dangling bond surface. Our approach to this ideal was simple mechanical abrasion of glassy carbon electrodes under a dry nitrogen atmosphere. Furthermore, the generation of fresh surface was carried out in the presence of a large excess of olefinic reagent anticipated to undergo reactions such as cycloaddition analogous to the chemistry proposed by Mazur [8]. The binding represented in Figure 1 follows that suggested by Mazur. In one case, Reaction 2, Figure 1, the olefin vinyl ferrocene, is itself electrochemically active while the second example, Reaction 3, Figure 1, illustrates the binding of a ligand (pyridine), to the surface with subsequent elaboration of the surface by reaction with a labile metal complex (Reaction 4). Preparation and characterization of these surfaces is as follows.

Glassy carbon electrode rods (6 mm, by 3 mm diameter) were polished in air to a shiny finish. The polished ends were gently abraded for 3-5 minutes, in a nitrogen glove box, on the surface of a frosted glass microscope slide in a puddle of either neat, freshly distilled vinyl pyridine or a paste prepared from vinyl ferrocene and dry benzene. The electrodes abraded under vinyl pyridine were after thorough washing reacted with a dimethoxyethane complex of ruthenium(II)bis(2,2'-bipyridine), the preparation of which will be described elsewhere [13]. Control electrodes were prepared by soaking freshly polished glassy carbon electrodes in (i) neat vinyl pyridine or in a concentrated benzene solution of (ii) vinyl ferrocene or (iii) ferrocene, for 20 to 30 minutes in the glove box; (iv) by abrading a glassy carbon electrode with a ferrocene-benzene paste as above; (v) by performing Reaction 4 with a freshly polished glassy carbon electrode, (vi) or by abrading an electrode under neat pyridine before Reaction 4. All electrodes were rinsed with benzene followed by storage in this solvent for 24 hours before use. Both abrasion and rinsing steps were performed in the glove box.

All electrochemical measurements for these and subsequent experiments (unless noted otherwise) were performed in acetonitrile with 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. Electrodes were mounted so that only the cylinder ends were exposed.

Electrodes prepared by the mechanical abrasion experiment, Figure 1, Structures II and IV, yield well defined symmetrical cyclic voltammograms (Figure 2A) having characteristics anticipated for surface attached redox systems [14,15] and with formal potentials, E° , consistent with that of solution analogs of the proposed surface structures. Cyclic voltammetric data are presented in Table I.

The small anodic-cathodic peak potential separation for the vinyl ferrocene abraded electrode, Structure II, (Table I) and the accurate linear relationship between peak current and potential scan rate (0.50 to 0.050 volt/sec, correlation coefficient 0.990) are characteristic of a surface bound moiety [14]. A preliminary indication of good stability of this surface was demonstrated by cycling the electrode between oxidized and reduced forms 150 times which resulted in less than a 3% loss in coverage Γ . The control electrodes (ii), (iii) and (iv), showed no evidence of ferrocene waves in cyclic voltammetric experiments. X-ray photoelectron spectroscopy (XPES) experiments verified the presence and absence of iron on vinyl ferrocene abraded and the control electrodes, respectively.

Similar cyclic voltammetric behavior (Figure 2A) was observed with the vinyl pyridine abraded electrodes to which ruthenium had been attached as in Figure 1, Reaction 4. Plots of i_p vs. scan rate were linear (range 0.50 to 0.020 volt/sec, correlation coefficient 0.999). The particular electrode used for the Figure and Table data had been stored under dimethoxyethane for four weeks before use although electrodes which are used immediately after preparation and rinsing with DME behave similarly. A preliminary test of stability showed a decrease in coverage of less than 5% after 180 scans through the wave. Glassy carbon electrodes (control (v)) reacted directly with the ruthenium complex exhibit no waves although electrodes (controls (i), (vi)) soaked in vinyl pyridine or abraded with pyridine, rinsed, and reacted with this complex exhibit a wave with charge approximately 5% and 10% of the coverage of the vinyl pyridine abraded samples, respectively. Semiquantitative analysis of the XPES results for ruthenium, nitrogen and chlorine is consistent with electrochemical coverage data for the latter three electrodes.

Thus, mechanical abrasion appears to be a suitable means of creating an active carbon surface for attaching substances to glassy carbon electrodes. The demonstration (e.g., control electrodes) of the importance of the vinylic group in producing modified electrodes is supportive of the chemical models proposed for "oxide free" carbon surfaces [8] and suggests many other possible attachments using the wide availability of olefinic compounds. Other functional groups may be equally as suitable and should not be overlooked considering the simplicity of the abrasion method.

SURFACE OXYGEN REMOVAL BY ARGON PLASMA ETCHING

Oyama, et al. [9] have recently described the procedure of etching an edge plane of pyrolytic graphite with a radiofrequency (RF) argon plasma in order to remove some or all of the surface oxides and increase the reactivity of the carbon surface toward amine reagents. We have extended this approach to glassy carbon using the Reactions 5-7, Figure 1.

Polished glassy carbon electrodes were placed in a (Harrick) plasma cleaner and exposed to an argon plasma for 30 minutes after which vapor of freshly distilled diethylenetriamine was differentially pumped through the chamber for an additional 30 minutes. Electrodes prepared in this manner were placed in methylene chloride with $(bpy)_2(\underline{iso-nic})RuCl^{1+}$ and dicyclohexylcarbodiimide [13]. The reaction was allowed to proceed for 30 hours after which the electrodes were rinsed copiously with methylene chloride. Cyclic voltammograms obtained with these electrodes, Figure 1, Structure VI, resemble those obtained with Structure IV electrodes but exhibit larger background currents. A plot of i_p vs. scan rate was linear (correlation coefficient 0.998) over the range 0.50 to 0.050 volt/sec. The coverage loss was less than 5% after 250 scans through the peak. Electrodes reacted

directly according to Figure 1, Reaction 7, without reaction steps 5 and 6, exhibit coverages approximately 10% of the values obtained with electrodes prepared according to Reactions 5 through 7. It is significant that essentially the same electrochemically active surface structure (IV and VI, Figure 1) can be prepared by two quite different synthetic procedures. The results also demonstrate that Reactions 5 and 6 function on glassy carbon surfaces, i.e., they are not dependent on some feature unique to pyrolytic graphite surfaces.

ARGON PLASMA POLYMERIZATION/DEPOSITION

A trivial change in the experimental procedure of the previous experiment produces a significant difference in the outcome. This variation involves leaving the argon plasma on while a reagent of suitable volatility and functionality is present in the reaction chamber (Figure 1, Reactions 8 and 9). Vinyl ferrocene was chosen for this experiment as it has the possibility of (i) attaching to glassy carbon in a manner analogous to the abrasion experiment and/or (ii) polymerization and forming a deposit on the electrode surface [10]. Both glassy carbon and platinum electrodes have been investigated in order to study the importance of the substrate material. Chamber pressure, geometry, RF intensity and deposition time are important variables [16] in these types of experiments and their details are currently under investigation.

A typical cyclic voltammogram for a glassy carbon electrode exposed to an argon plasma in the presence of vinyl ferrocene vapor is shown in Figure 2B. (The color of the plasma was different from a pure argon plasma.) Plots of i_p vs. scan rate for these electrodes are linear (correlation coefficient 0.999, range 0.50 to 0.050 volt/sec). The stability of these

electrodes is quite remarkable. For example, one electrode showed no significant change in coverage after the following treatment: 1250 cycles through the wave, soaked overnight in acetonitrile, rinsed with water, and rinsed with acetonitrile. Electrochemical ferrocene waves have been obtained with platinum electrodes modified in the same way (Table I). Table I and Figure 3 also illustrate the extraordinary coverage and unusual peak shape observed in 0.1 M HClO_4 for a Pt electrode treated at longer deposition times. The sweep-rate dependent coverage for this electrode is 2×10^{-8} moles/cm². Some platinum electrodes have exhibited coverage as high as 3×10^{-8} moles/cm² which is, to our knowledge, the highest reported coverage of an electrochemically active material on an electrode surface and many times monolayer for ferrocene. A yellowish film is clearly visible on the platinum electrodes as well as on the carbon electrodes at significantly lower coverages. A successful RF polymerization reaction is indicated by such results.

Platinum and glassy carbon electrodes treated in the vacuum simply with vinyl ferrocene vapor (argon plasma off) do not exhibit any electrochemistry other than the usual background behavior for these materials.

Clearly, this new approach to electrode surface modification has numerous possibilities in terms of varying substrate materials, reagents and other parameters mentioned above.

CONCLUSIONS

We have shown that glassy carbon surfaces can be activated for chemical modification by mechanical abrasion and argon RF plasma etching and that the

introduction of reagents directly into the plasma gas can be used for preparation of electrochemically active surface states. To what degree the chemistries in these three attachment procedures are similar remains to be seen but some commonalties seem likely. Ideally, for instance, the ferrocene polymer formed in Reaction 8 is also linked to the carbon [17] in the manner of Reaction 2. The stable coatings we obtained on Pt in Reaction 9 indicate however that such surface linking is not essential for useful surface preparations and this approach is perhaps then a general one for different electrode materials.

The RF plasma polymer films are certainly multilayers of redox sites. The voltammetric shape and scan rate behavior on Pt may reflect kinetic events such as molecular motions or electron or counterion transport limitations.

Further data on the experimental approaches described above will be given in a full paper.

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Table I. Cyclic Voltammetric Data for Modified Electrodes in Acetonitrile.

<u>Electrode</u>	<u>Experiment</u>	<u>volt/ sec</u>	<u>$E_{surf}^{o'}$ vs. S.C.E.</u>	<u>ΔE_p, mv</u>	<u>$\Gamma \times 10^{10}$, mole/cm²</u>
glassy C	Abrasion				
	a. vinyl ferrocene	0.2	0.43 ^a	55	1.1
	b. vinyl pyridine, (bpy) ₂ Ru(DME) ⁺²	0.2	0.80 ^a	50	4.1
glassy C	Ar plasma				
	a. OFF, Dien (bpy) ₂ Ru(iso-nic)Cl ⁺¹	0.2	0.80 ^a	40	1.8
	b. ON, vinyl ferrocene	0.2	0.42 ^a	30	1.6
Pt	Ar plasma				
	a. ON, vinyl ferrocene	0.080	0.42 ^b	30	4.5
	b. ON, vinyl ferrocene (aqueous HClO ₄)	0.016	0.32 ^b	140	200.0

a. NaSCE

b. KCl-satd SCE

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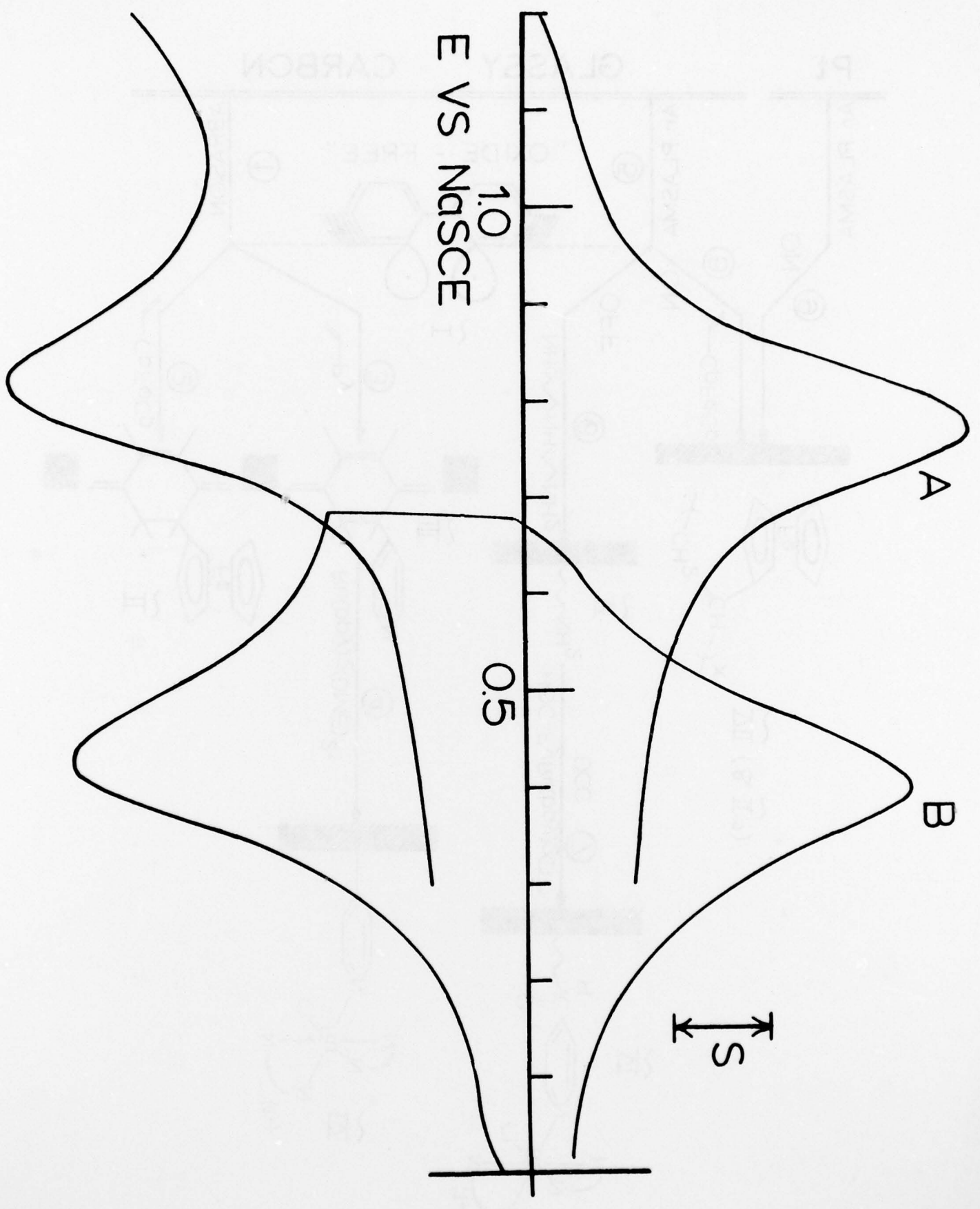
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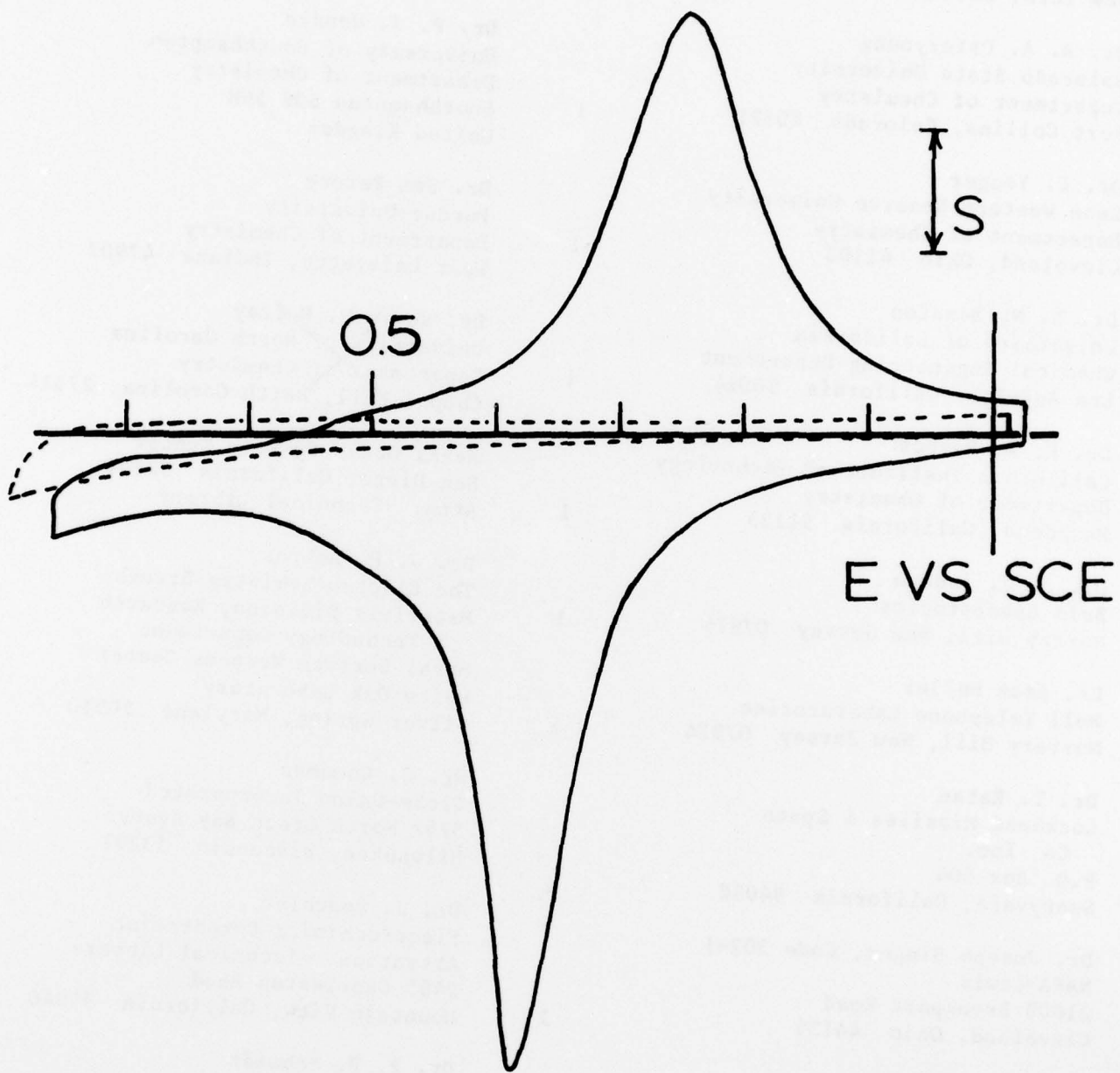
Figure 1. Surface Chemical Reactions with Proposed Surface Structures.

$\begin{matrix} \diagup & \text{C} & \text{FeC} & \diagdown \\ & \text{p} & & \text{p} \end{matrix}$ is vinylferrocene. $\begin{matrix} \diagup & & \diagdown \\ & \text{Py} & \end{matrix}$ is vinylpyridine.

Figure 2. Cyclic Voltammograms in 0.1 M Et_4NClO_4 , CH_3CN (A = 0.2 volt/sec; B = 0.5 volt/sec) of Chemically Modified Glassy Carbon Electrode Prepared According to Abrasion Procedure Reactions 1,3,4 (Curve A) and Plasma Procedure Reaction 8 (Curve B). $S = 0.5 \mu\text{a}/\text{cm}^2$.

Figure 3. Cyclic Voltammogram in 0.1 M HClO_4 (Aqueous) at 0.016 volt/sec of Pt Electrode Coated by Plasma Polymerization According to Reaction 9. $S = 8.6 \mu\text{a}/\text{cm}^2$.





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