CARBON PASTE ELECTRODE CHEMICALLY MODIFIED WITH TRIS-4,7-DIPHENYL-1,10-PHENANTHROLINE Fe(II)

By

CHRISTOPHER J. HYNES

Bachelor of Science

Cameron University

Lawton, Oklahoma

1985

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
DOCTOR OF PHILOSOPHY
May, 1991

CARBON PASTE ELECTRODE CHEMICALLY MODIFIED WITH TRIS-4,7-DIPHENYL-1,10-PHENANTHROLINE Fe(II)

Thesis Approved:

Horacio A Mottola
Thesis Adviser

Richard A. Bruce

John F. Fellows

Timothy Wilson

Vernon N Dunbar
Dean of the Graduate College

ACKNOWLEDGMENTS

These few paragraphs will give me a chance to express my appreciation in my own way to those who have stuck with me through better and worse and I would like to think that I haven't disappointed them.

When I enrolled at Cameron University to major in chemistry, I still wasn't totally convinced that I was pursuing the right field. As I progressed under the guidance of Dr. Nalley, Dr. Snider, and Dr. Stanton, I felt that I was headed in the right direction. The enthusiasm and knowledge with which they taught made chemistry much easier and enjoyable. To them I am very thankful.

Upon arriving at Oklahoma State, I was thinking of pursuing Inorganic chemistry. Fortunately, I went Analytical under the direction of Dr. Mottola. I figured that someone who could keep the good disposition about life and chemistry for as long as he has would be the one to work for. Dr. Mottola I want to thank you for the knowledge and wisdom you have given me not only in chemistry but in other aspects of life. I really appreciated your patience, frankness and honesty.

I want to thank my committee members Dr. Bunce, Dr. Gelder, and Dr. Wilson for giving their time to serve on my committee. The reason I chose them was because I felt they

were the most down to earth professors.

There are several "co-workers" in our research group that I would like to thank for showing me the ropes and making graduate school bearable when I felt like it wasn't: Matt (a.k.a. Mr. Excitement), Ricky, Sudah (you're a real sweetheart), Albahadily, Moji (the Iranian godfather), Sun, Jianbo, Paul, Patricia, and Dale (you'll be the only one left when we're gone). I want to give a special thanks to Zachariah for the studying support, big brotherly advice, and opening his home to me. You and your family are welcome at my humble accomodations anytime.

As far as non-academics goes there are some special friends I want to thank for keeping me out of the ruts. Nelson, Kendall, Sly, Janet, Larry, Holly and the rest of the O'Rama crew. I probably would have finished sooner and with a higher G.P.A. if I had not associated with you guys so much, but what the hell, school isn't everything. You've given me a lot of good memories. A special thanks to Tinker Hulen for putting up with me as a roommate and being one of my best friends. A special thanks to Laura, the things you have taught me are yet to be shown.

Last but by no means the least, I would like to thank my mother, father, brothers, and sister for the support they have given me. After five years of being at OSU and wondering what I have been doing, you now have something concrete to put your hands on and read as to what I have been doing. I love you all.

TABLE OF CONTENTS

Chapter Page

LIST OF TABLES

LIST OF FIGURES

Figure Page

CHAPTER I

REVIEW OF CHEMICALLY MODIFIED ELECTRODES

Introduction

The aim of this review is to provide sources of information about the advantages of chemically modifiying electrodes and the different methods available for modification. It will also familiarize the reader with the concept of chemically modified electrodes (CME).

The focus will be directed toward chemically modified electrodes (CME), their characteristics and applications. Research interests in this field are quite broad and rapidly expanding. To cover all aspects involved is beyond the scope of this work and so only a brief rationale will be provided for the merits of chemically modifying an electrode. The coverage will be further narrowed to carbon based electrodes since this is more closely related to the material presented in this thesis. It must be noted that some of these modifications can be and have been applied to electrodes made of other materials.

Electrochemical methods of detection are generally considered to be quite sensitive. Selectivity is realized when we consider that each chemical species has its own

unique oxidation/reduction potential. As with all analytical techniques shortcomings are encountered which must be overcome. Adsorption, precipitation at the electrode surface, high background signal, and slow electron transfer rates are some of the more common problems that can be encountered with electrochemical methods and can result in the loss of sensitivity and/or selectivity. In an attempt to overcome these problems it was realized that perhaps the electrode could be modified in some manner to minimize these obstacles and thus the idea of chemically modified electrodes (CME) was conceived.

By chemically modifying the electrode surface, it is hoped that the electrode will show the desirable characteristics of the modifying species. Enhancement of sensitivity and/or selectivity by minimizing the undesirable electrode processes that were previously mentioned are but two of the ultimate goals. For further reading on the broad scope of chemically modified electrodes, the following reference is recommended (1).

As mentioned before, this review will be focusing on carbon based electrodes. This type of electrode has some advantages that make it well-suited for electrochemical use: 1) it has a larger range of working potentials compared to conventional electrode materials, 2) it is composed of relatively inexpensive materials, and 3) it generally shows lower residual currents due to double layer capacitance as compared to electrodes of conventional materials. When

comparing carbon-based electrodes with the more conventional electrode materials such as Pt or Hg (Fig. 1), it is found that carbon electrodes are capable of operating at strong oxidizing potentials, where Pt is usually employed, as well as strong reducing potentials, where Hg is typically used (2,3). Thus carbon-based electrodes are capable of bridging both regions and therefore have a greater utility.

The earliest form of a carbon based electrode was the graphite rod electrode (4). This electrode required a 1-2 h pretreatment with a wax material such as ceresin to fill the micropores in the graphite rod. Absorption of the wax into the pores prevents unwanted adsorption, and thus greatly reduces the residual current. Since then, the use of carbon material has expanded to include graphite particles, highly ordered graphite rods and discs, pyrolytic graphite, carbon black, glassy carbon, and carbon paste electrodes. This review will be broken up into two sections, one section focusing solely on modified carbon paste electrodes and the other section briefly describing modification of the other forms of carbon-based electrodes.

Carbon Paste Electrodes

Carbon paste electrodes (CPE's) originally devised by Adams (5) provide the same characteristics as the graphite rod but with much easier preparation. Adam's electrode was constructed by mixing graphite with a liquid binder,

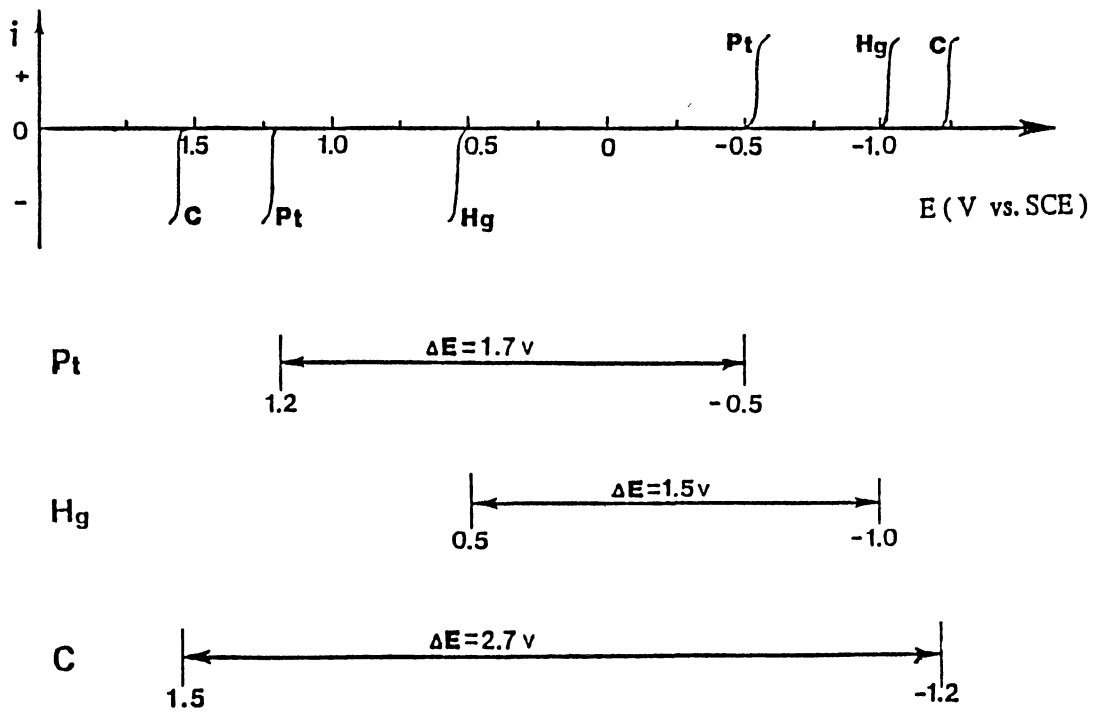


Figure 1. Potential windows of different electrode materials in 0.10 M H_2SO_4. Pt - platinum, Hg - mercury, C - carbon

bromoform. When mixed together the electrode material had the consistency of a paste which could be packed into the well of a capillary tube thus forming an electrode. Electrical contact was made by using a copper wire that was in contact with the paste. The advantage here is that since the electrode has the consistency of a paste, the surface can be easily renewed by polishing. Currently CPE's are constructed with graphite and a Nujol, silicone grease, or mineral oil binder. We will see later that there are advantages to preparing the electrode in this manner.

Although CPE's have great utility in aqueous solvents, nonaqueous solvents are sometimes encountered in electrochemical methods and a problem arises due to the solubility of the binder in the solvent used. Typical binders such as Nujol or mineral oil have an appreciable solubility in nonaqueous solvents such as acetonitrile. Partial success has been accomplished by incorporating a surface active agent, sodium lauryl sulfate, into the carbon paste (6). This prevents paste decomposition in acetonitrile, nitromethane, and propylene carbonate but not in other solvents such as dimethylformamide, dimethylsulfoxide, benzonitrile, and acetic acid. It is also noted that the use of this electrode in an aqueous solvent is detrimental to the electrode. Ceresin wax can be used in organic solvents that are polar to medium polar. In this case it is beneficial to pretreat the electrode surface with a surfactant to improve electron transfer rates (7).

Other binders such as polyethylene (8), Kel-F (9-11), teflon (12), and paraffin wax (18) show promise in nonaqueous solvents like acetonitrile and methanol which are common effluents in liquid chromatography and high performance liquid chromatography. It is noted, however, that these electrodes may require an electrochemical pretreatment (18) for sufficient electron transfer rates. They also show much less paste consistency and more of a solid, hard consistency that resembles that of a glassy carbon or pyrolytic graphite electrode. Although the preparation is still simple and straightforward it is questionable as to how easily the surface can be renewed.

Modification of CPE's

There are basically three methods for modifying CPE's: 1) the modifier can be chemically attached to functional groups on the graphite, 2) it can be chemically attached to the binder, or 3) it can be admixed with the carbon paste. Currently there are no known reports in the literature of modifications of the second type, but research is currently being conducted (13). Hence, comparisons will be made between the first and third types.

Chemical Attachment of the Modifier to the Graphite.

One method to retain the modifier at the electrode surface is to chemically attach it to the graphite particles. This

prevents modifiers that are soluble in the solvent from dissolving into solution which would defeat the purpose of modifying the electrode. This also permits more intimate contact between the modifier and the graphite surface, enhancing electron transfer rates.

In order to chemically attach the modifier, the graphite surface must contain reactive functional groups available for coupling. Graphite exists as carbon sheets sandwiched in a roughly parallel orientation. Oxygen containing functional groups such as carboxylic, phenolic, quinones, and lactones are believed to exist on the edges of these stacked layers (14). The type and distribution of these groups depends on the previous history of the material, i.e. manufacturing and pretreatment processes (15). In order to obtain a higher loading of modifier onto the graphite particles it is advantageous to further oxidize the graphite surface thus increasing the amount of oxygen functionalities such as carboxylic, phenolic, lactones, and quinones.

More oxygen functionalities can be introduced by chemically oxidizing the graphite (16) or electrochemically oxidizing the CPE at sufficiently high potentials i.e. 1.1 volt (16). Cyclic voltammetry experiments (using the $Fe(CN)_6^{-3}/Fe(CN)_6^{-4}$ system) provide evidence that chemical modification occurs under these conditions. An increase in reversibility is shown by a decrease in ΔE_p and at least a one order of magnitude increase in the electron transfer

rate coefficient has been observed. Heating of graphite in an oxygen atmosphere (16) also seems to produce the same effect as seen by a significant increase in the background current. These oxygen functionalities can then be used for the coupling of chemical modifiers.

The work of Cheek and Nelson (17) shows the advantage of using oxidized graphite ("activated") versus untreated graphite ("unactivated") for chemically attaching a modifier. After oxidizing the graphite with a concentrated HNO_3/H_2SO_4 mixture, the organosilane Z-6020 was refluxed with the "activated" or "unactivated" graphite in benzene for 14 h. The graphites thus obtained were mixed with Nujol to form a paste and packed into the well of the electrode. The organosilane Z-6020 contains an ethylenediamine group which was used to preconcentrate Ag(I) at the electrode surface. After preconcentrating with 1.35×10^{-4} M $AgNO_3$ for 40 minutes, voltammograms showed well defined anodic stripping peaks and very good reproducibility between determinations. Comparison of the two graphites showed that the "activated" had a much higher capacity for Ag(I) than the "unactivated" with the end result being a 50-fold increase in peak current. Another interesting result from this study is that "activated" graphite modified with diethylenetriamine via carbodiimide coupling can be used for determinations at much lower Ag(I) concentrations with better reproducibility than with the Z-6020 modified graphite.

The successful attachment of 5-amino-1,10-phenanthroline and the 5-amino derivative of ferroin, tris(5-amino-1,10-phenanthroline)iron(II), to graphite has been shown by Albahadily (18). "Activation" of the graphite by heating in the prescence of O_2 or by chemical reaction with HNO_3/H_2SO_4 was followed by reaction with $SOCl_2$. The resulting acyl function was reacted with the amine function on the ligand backbone. The electrode modified with 5-amino-1,10-phenanthroline showed two voltammogram peaks upon addition of Fe(II) to the electrolyte solution. One peak at 0.50 V vs. SCE which was due to the presence of free Fe(II) while the other peak at 0.95 V vs. SCE was attributed to the formation of the Fe(II) complex at the electrode surface. The tris(5-amino-1,10-phenanthroline) Fe(II) modified electrode showed a single peak around 1.0 V vs. SCE. The bond between the graphite and the ligand, however, was found to be electrochemically labile as shown by the decrease in peak current upon repeated cycling.

Kamin and Wilson (19) successfully attached the enzyme glucose oxidase to graphitic oxide via carbodiimide coupling. The carbon "paste" was made by admixing with a fine teflon powder. This mixture was then tapped into a rotating ring-disk electrode to study the kinetics of the enzyme catalysis. They found high enzyme loading resulting from simple adsorption of the enzyme. As expected, they observed that the binding material had a significant influence on the enzyme specific activity even though the

enzyme loading on the graphitic oxide was fairly constant. It was observed that a higher specific activity was seen when less modified graphite was mixed with the Teflon 7A. This may be the result of a less congested enzyme layer.

Admixing. This method of modification is becoming more popular than the previously mentioned method for several reasons: 1) the amount of modification can be easily controlled as a weight percentage of the paste, 2) a wide range of modifiers can be incorporated provided that they are compatible with the solvent and the binding material, and 3) the modified carbon paste electrode (MCPE) is extremely easy to prepare because neither chemical reactions nor special equipment is required. As mentioned in the beginning of the previous section, one of the criteria for our MCPE is that we want the modifier to be insoluble or, in the worst case, minimally soluble in the electrolyte solution. This can be accomplished by using the modifier in the form of a reasonably insoluble salt, by chemically derivatizing to decrease solubility, or by using a binding material such as wax. The effect of modifier solubility on the usefulness of the electrode was exemplified in the paper by Ravichandran and Baldwin (20). CPE's modified with phenylenediamine or N,N,N',N'-tetramethylphenylenediamine showed loss of activity after prolonged standing in the electrolyte solution. This was due to the dissolution of the oxidized form of the modifier.

The first use of MCPE's prepared by admixing was the classical work of Kuwana and French (21). They realized that the acquisition of electrochemical data on organic compounds was limited by to the insolubility of most organic compounds in aqueous solution. Although some of these compounds can exist as water-soluble salts , oxidation or reduction may render it electrostatically neutral and thus insoluble. To circumvent this problem, they separately dissolved several organic compounds in the binder used to prepare the CPE. The rationale was that when the compound was a neutral species the electrochemistry would take place in the binder phase. After electrolysis the charged species would then dissolve into the aqueous phase where other electrochemical processes could occur. Thus the species under study could diffuse in and out of the organic binder and hopefully produce some meaningful results. The study involved ferrocene, anthraquinone, and 4-aminobenzophenone and it was observed that ferrocene and anthraquinone both produced well defined anodic and cathodic peaks which were reversible and irreversible, respectively. 5-Aminobenzophenone, on the other hand, produced an ill-defined peak that was completely irreversible. Further studies by Schultz and Kuwana (22) showed that these processes were diffusion controlled.

Practical applications of these MCPE's were shown in the works of Baldwin et al. (23-27). With the hope of being used as liquid chromatographic electrochemical detectors,

CPE's were modified with cobalt phthalocyanine (CoPC), which is known to catalyze the oxidation of several organic compounds. These electrodes have the advantages of increasing the rate of electron transfer as compared to an unmodified CPE as well as allowing the detector to operate at lower potentials which minimizes interferences. This electrode was used successfully in the determination of hydrazine (23) and of various saccharides (24,25). CPE's modified with dimethylglyoxime have been characterized and successfully used for preconcentrating and determining trace nickel(II) (26,27).

The modification of CPE's is left up to the creativity of the user. To show the wide variety of modifications that have been done a brief mention of other works is made. Besides cobalt phthalocyanine, other metal complexes admixed in carbon pastes show promise as electrocatalytic detectors (28,29). In some cases a modifier is admixed so that other modifiers can be attached to the electrode surface as in the case of attaching NAD^+ (30) or glucose oxidase (19,31). Glucose oxidase also has been directly admixed into carbon paste (32) but unfortunately a clear comparison cannot be made with the other references (19,31) with respect to enzyme loading or efficiency. What is evident though is that both preparations have comparable lifetimes and that direct admixing is less time consuming.

Ion-exchange resins, clays, and chelating agents have been incorporated into pastes for preconcentrating various

metal ions (33-36) and organic compounds (37) for subsequent determination. This can enhance the sensitivity and lower the limit of detection of a given method. The resin can also act as a carrier for metal catalysts (38,39). The work of Baldwin et al. (38) showed that poly(4-vinylpyridine) incorporated into a carbon paste electrode bound $Fe(CN)_6^{-4}$ under acidic conditions. The modifier was shown to catalyze the oxidation of ascorbic acid and allowed the electrochemical reaction to take place at less extreme potentials.

Selectivity of the analyte over interferents especially in biological matrices is a major concern. An example of how chemical modification can minimize interference problems can be found in the work of Lane (40) where stearic acid was found to act as an electrostatic inhibitor toward ascorbic acid, an interferent, but not dopamine, the analyte of interest.

Another interesting modification is the admixing of plant or animal tissues or whole cells to take advantage of naturally immobilized reagents. Naturally immobilized enzymes in mushroom, banana, and yeast have been used for just that purpose (41,42). Incorporation of these tissues or cells into a CPE is shown to significantly simplify LC chromatograms of complex samples such as urine (42). The simplification of the chromatograms is due to the fact that the enzymes in the tissues are very selective. These types of CME's have a promising future but have the drawback that

they usually will have a high background current due to other chemical species in the tissue. These interferents must be removed before suitable electrochemical behavior can be attained.

As shown in the above examples, a simple modification process can result in a very powerful tool. The wide utility of MCPE's, ease of preparation, and enhancement of sensitivity and selectivity make them useful as electrochemical detectors and/or reactors. Their utilization is rapidly expanding because of these favorable characteristics and no doubt their presence will be felt for some time.

Solid Carbon Electrodes

Solid carbon electrodes come in many different forms, but the more popular forms used in electrochemical methods are glassy carbon, pyrolytic graphite, and graphite rods. Glassy carbon can be visualized as graphite strips that are randomly entangled. Because of this structure, a given surface will contain a mixture of basal and edge plane characteristics (43). Pyrolytic graphite can be visualized as a crude single crystal of graphite with the electrode surface being a basal edge plane (43). Graphite rods can be thought of as graphite micro-particles pressed together to form a solid rod. The particles can be either randomly oriented characterized by an equal amount of basal and edge

planes at the electrode surface or highly ordered so as to have a predominance of basal planes or edge planes at the electrode surface.

Modification of Solid Carbon Electrodes

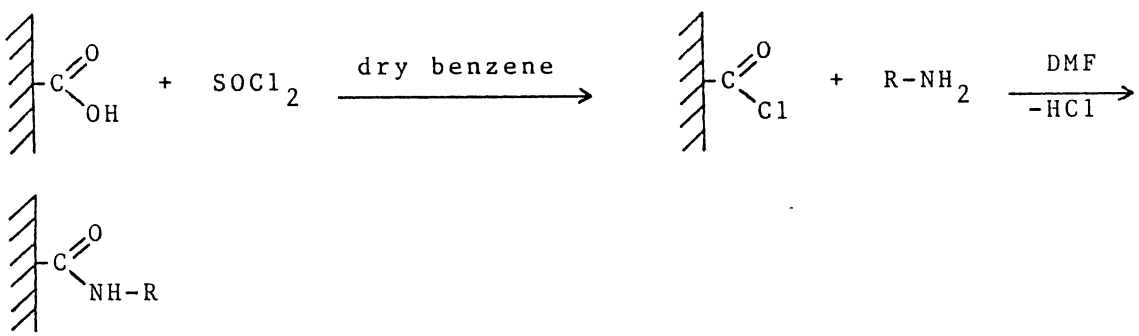
Three different methods for chemical modification of the electrode surface will be dealt with in the following paragraphs: 1) covalent coupling, 2) adsorption, and 3) polymer films. As expected, each form of modification has its advantages and disadvantages and so it is up to the user's discretion to decide what is most important.

Covalent Coupling For chemical attachment of the modifier it is generally believed that the edge plane sites are primarily responsible for providing oxygen containing functionalities that can be used for coupling (14,51). The amount and types of functional groups on the electrode surface depends on the history of the material, i.e. manufacturing, handling, and pre-treatment processes (44). Even though the surface contains oxygen functionalities, further oxidation of the surface is usually carried out by wet chemical (45), O_2/plasma (46,47), or electrochemical treatments (48) to provide more oxygen sites for coupling. There appear to be no reports in the literature that compare the relative merits of these methods as to which is the best way of oxidizing the electrode surface. Wet chemical and

electrochemical treatments would appear to be the easiest to carry out but, with wet chemical methods, care must be taken to prevent contamination by the oxidizing reagents (55). The O_2/plasma treatment would require more elaborate equipment compared to the other methods. The electrochemical treatment would be the easiest method for pretreatment.

In reviewing the literature, three coupling reactions appear to be the most commonly used: $SOCl_2$, carbodiimides, and cyanuric chloride. Although all three methods have been used extensively with good success, the latter two methods are more convenient because much milder reaction conditions are employed. A fourth coupling reaction worth mentioning is the organosilane-type coupling of the modifier but this reaction has seen limited use. Further details of the modifications and some practical applications of each are given below.

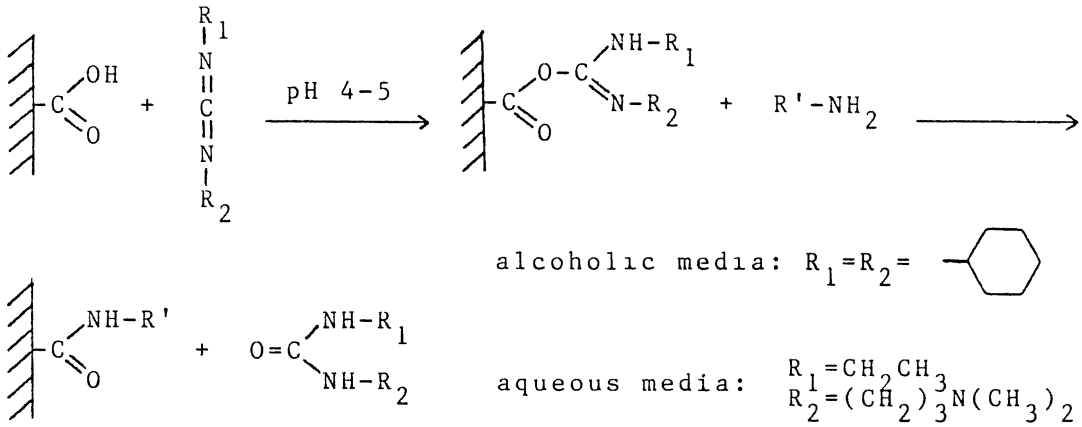
Thionyl Chloride Activation. The general reaction scheme for the reaction of $SOCl_2$ and the subsequent attachment of the modifier is as follows:



This reaction works quite well if some minor pitfalls can be avoided. Thionyl chloride adsorbs on the surface and hence it must be thoroughly washed to remove any adsorbed reagent from the surface. Secondly, the acyl chloride activated surface may not be as reactive as the acyl chloride in free solution which means that gentle heating and longer reaction times may be required to produce a good yield (43).

The first report of a modifier chemically attached to a carbon electrode used this reaction to produce a "chiral" electrode (49). (S)-Phenylalanine methyl ester was attached to the activated surface to produce an electrode that cathodically converts prochiral ketones to chiral alcohols. ESCA results show nitrogen peaks due to the immobilized amino acid on both the basal and edge plane but the basal was only 20% that of the edge plane (50). Koval and Anson (51) used this coupling procedure to immobilize the 4-aminoethylpyridine ligand for subsequent attachment of a ruthenium complex. Several interesting observations were made in this report. One is that the reaction of the ligand directly with the oxidized surface seems to have as much "activity" as the reaction with the acyl chloride surface. As previously mentioned, the acyl chloride on the surface may not be as reactive as it is in solution. Secondly, they observed a higher reactivity of the edge plane over the basal plane. Thirdly, they found the amide linkage was unstable as evidenced by loss of electrode activity even upon the addition of fresh Ru(III).

Carbodiimide Activation. The carbodiimide coupling reaction conditions are much milder when compared to the acyl chloride activation. Carbodiimide reactions can be done in aqueous media at room temperature and require fewer procedural steps. The general scheme is as follows:



The attachment of an active enzyme and a ligand are briefly discussed as two examples of the successful use of this coupling procedure.

The enzyme glucose oxidase has been covalently attached to the surface of a reticulated vitreous carbon (RVC) electrode by using the water soluble carbodiimide 1-cyclohexyl-3-(2-morpholinoethyl)-carbo-metho-p-toluene sulfonate as the coupling reagent (52). Glucose can be determined by monitoring hydrogen peroxide produced in the enzymatic reaction. Because the enzyme is in more intimate

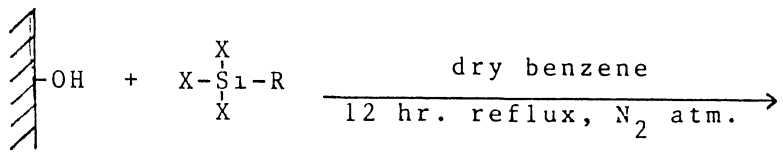
proximity with the electrode surface, the response time is much shorter compared to enzyme electrodes prepared by membrane attachment. Attaching the enzyme to the surface stabilizes the protein as shown by the longer lifetime compared to free enzyme in solution.

Oyama et al. (53) used dicyclohexylcarbodiimide to attach nicotinic acid to the surface of pyrolytic graphite. The pyridine ring on the nicotinic acid was used as a ligand to complex with Ru(II). This modification has a different twist in that the electrode surface was modified to contain amine functions rather than oxygen functions while the modifier contained the carboxylic group. The purpose of this study was to see if there would be any advantage to having an amine activated surface versus an oxygen activated surface. The only conclusion that was drawn was that this "reversing" of functionalities works just as well as the conventional method with no clear advantage. The only difference would be the types of coupling chemistry that could be done with the amine group versus the hydroxyl.

Organosilane Activation. Organosilanes can also be used for coupling the modifier to the surface (54,55) but this has not gained much popularity. This may be due to the ease with which cyanuric chloride and carbodiimide attachments can be carried out. Nevertheless, this approach has been used successfully for the attachment of amines, ethylenediamine, pyridine, and alkyl chloride functions

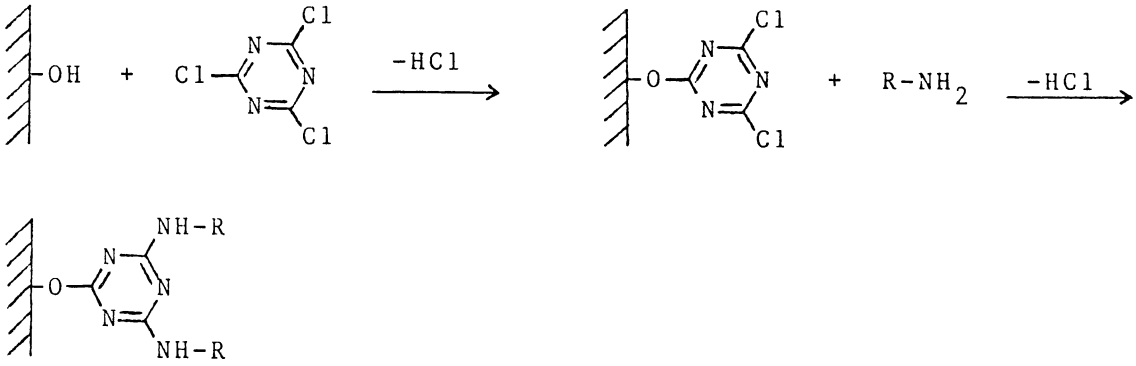
(54).

The general reaction scheme is illustrated as follows:



Care should be taken that the reaction takes place under anhydrous conditions so that the tri-substituted silane does not form an oligomeric silicic acid. If this results, the electrode surface will be covered with what can be described as a multilayer rather than a monolayer. Electrodes modified in this manner (54) are characterized by electrochemically stable linkages and a porous surface coverage that allows ferrocyanide to access the surface of the electrode. The attached silane showed the distinctive property (eg. protonation or Cu(II) coordination) of the functional group.

Cyanuric Chloride Activation. The use of cyanuric chloride (CC) as a linking agent is becoming quite popular because of the mild reaction conditions and its predictable reaction mechanism. As a coupling spacer it provides a short rigid arm for the attachment of the modifier and supplies more than one active site for coupling. It will react with amines or hydroxyl groups in the following manner:



One of the earliest feasibility studies for using CC as a linking agent was done by Lin and coworkers (56). In this report it was shown that hydroxymethylferrocene or 1,1'-bis(hydroxymethyl)ferrocene can be successfully attached as shown by the electrochemical response of the attached iron complexes on the electrode surface. It appears that the linkages are quite stable and that more than one linking configuration occurs as seen by broad voltammogram peaks (57).

Because of the mild reaction conditions, this coupling procedure should be well-suited for the immobilization of enzymes on the electrode surface. Ianiello and coworkers (58) used cyanuric chloride to immobilize glucose oxidase and L-amino acid oxidase on graphite electrodes for characterization studies. The respective electrodes displayed relatively rapid response times and expanded linear ranges as compared to previously reported amperometric enzyme electrodes.

Attachment by Adsorption. All of the previous attachments involve the formation of a chemical bond between the modifier and the electrode surface. Attachment is not limited by chemical bonding only, other binding processes such as adsorption are possible. Adsorption could occur through electrostatic or chemical interaction between the modifier and the electrode surface. Although this type of attachment is considered to be less physically stable compared to covalent binding, it may have the advantages of easy modification and renewal. Koval and Anson (51) have provided a comparison between attachment by covalent binding and adsorption. From this report, several interesting observations are made: 1) attachment by adsorption yields more electroactive modifier on the surface compared to the covalent attachment of the modifier, 2) as expected, the covalently bound modifier persists on the surface much longer than the adsorbed modifier but, 3) readsorption (renewal) can be very easily done compared to the lengthier process of chemical attachment. The major drawback is that this type of modified electrode would not be as well suited for use under flow conditions such as liquid chromatography. Nevertheless, there are reports of practical usage of these kinds of electrodes.

Izutsu and coworkers (59) have used a trioctylphosphine oxide (TOPO) coated glassy carbon electrode for preconcentrating and subsequent determination of uranyl

ions. TOPO is applied as an ethanolic solution to the tip of the electrode and the solvent is allowed to evaporate. The deposited film is then further melted onto the surface by using an infrared lamp. The film shows a slow dissolution into the electrolyte solution but the authors report that the electrode has several hours of usefulness. The film is capable of preconcentrating UO_2^{+2} and some organic compounds. The TOPO layer itself is somewhat porous allowing some species such as Mo(IV) and O_2 to penetrate and access the electrode surface. Other species such as Pb^{+2} and Tl^{+1} are electrochemically "masked". With a 10 minute preconcentration time, 10^{-7} $\underline{M}$ UO_2^{+2} can be determined with 1.8% relative standard deviation (RSD) even in the prescence of several common ions found in seawater.

Cobaltphthalocyanine tetrasulfonate (Co-TSP) readily adsorbs on carbon electrodes and has shown electrocatalytic activity towards N_2H_4 (60) and O_2 (61). There is added interest in that Co-TSP is similar to natural co-enzymes like vitamin B_{12}. This vitamin is involved in several oxidation/reduction reactions that involve -SH and -S-S- functions. Zagal et al. (62) have used Co-TSP adsorbed on graphite to catalyze the oxidation of cysteine to cystine. The oxidation was found to be irreversible and was thought to involve an interaction between the Co(II) center and the sulfur bridge but the mechanism could not be elucidated. The adsorbed catalyst appears to have at least 10 h of stability as shown by controlled potential experiments.

Polymer Film Coatings. The application of a polymer film onto the electrode surface will be briefly discussed. The polymer film can serve several purposes: 1) as a carrier for attaching other modifiers (43), 2) as a protective layer to prevent electrode poisoning or fouling (63,64), and 3) as a layer to entrap the modifier (typically enzymes) within or behind the polymer matrix (65). There are many methods of making polymer films on the electrode surface of which dip coating, droplet evaporation, electrochemical polymerization, and spin coating are the most widely used. A reference by R. W. Murray (43) is an excellent source of information regarding methods of modifying by applying a polymer film.

There are two major limitations of these polymer films: 1) ionic mobility and/or 2) electrical conductance. The polymer film has to allow for the movement of the analyte and/or the counterions in the film for electrochemical activity. If the film is sufficiently conductive this will not be a problem since the polymer-solution interface will act as the electrode surface. Factors such as bulk size, layer thickness, ionic charge, and solvent swelling of the film will greatly affect the electrochemical activity.

As outlined by Murray (43), polymer modified electrodes have three modes of operation: 1) electrocatalysis - redox centers in the polymer matrix act as electron transfer mediators between the electrode and the analyte of interest;

2) intrinsic electroactivity at electrode-film interface - the electroactive species diffuses through the film to the electrode surface where electron exchange may occur (the film may act as a barrier against an interferent or as a reactor); and 3) intrinsic electroactivity at film-solution interface - the polymer film is highly conductive such that the electrode surface is now located at the film-solution interface.

Conclusions

In the given examples we can see the merits of chemical modification of the electrode. To summarize these we can have one or more of the following: 1) sensitivity (23), 2) selectivity (26,42), 3) shortening of response times (52), or 4) prevention of electrode "poisoning". Although these are the major advantages, it should be noted that there are extra benefits such as stabilization and/or conservation of the reagent.

Each of the different forms of modification has its advantages and disadvantages. To choose the method of modification, one has to answer the following questions: What are the circumstances under which the electrode will be operated? Does the electrode surface need to be reproducible? What kind of lifetime and response time are required? How much effort is the user willing to expend to modify the electrode? The answers to these questions and

others should serve as a guide to choose the appropriate method(s).

CHAPTER II

CARBON PASTE PREPARATIONS MODIFIED BY ADMIXING WITH Fe(II)/Fe(III) CHELATES

Among the many methods available for modifying an electrode, admixing with carbon paste seems to offer the most advantages. As mentioned in the review, carbon based electrodes show a wider potential window (Fig. 1) as compared to conventional electrode such as platinum or mercury. The materials used to prepare a carbon paste electrode are relatively inexpensive and they do not have the toxicity as in the case of mercury. Because it is a paste, it allows for easy preparation, easy electrode surface renewal, and incorporation of a wide range of modifiers. Carbon paste electrodes also have sufficient mechanical strength to make them useful sensors under dynamic conditions such as in continuous-flow systems. Because of these advantages, modification by admixing the modifier in a carbon paste matrix was chosen for study.

Before this electrode is used we have to address two limitations encountered when using such an electrode, they both have to deal with solubilities. First of all, we have to consider the solubility of the binding material which is responsible for giving form to the paste. This is not a

problem when aqueous solvents are used, but occasionally non-aqueous solvents such as acetonitrile or methanol are the solvent of choice (especially in HPLC). Conventional binders such as Nujol have an appreciable solubility in these solvents and thus the paste loses its mechanical strength. This problem can be circumvented by the judicious choice of a compatible binder (6,8,9-12). In the following experiments an aqueous solvent will be used so that this is not a major concern.

Secondly, although we could admix any modifier that we choose, we do have to consider the solubility of the modifier in the solvent used in the electrolyte solution. Ideally the modifier would be insoluble or in the worst case would exhibit only slow dissolution. In fact, a slow dissolution may be beneficial if it allows for continual renewal of the active surface of the electrode. As one can imagine, a high rate of dissolution is detrimental because it shortens the useful lifetime of the electrode. This is especially true if the electrode is to be applied in a flow system. Diffusion of the modifier could also be a hindrance to that of the analyte of interest to the electrode surface. As will be shown in a later chapter, the modifier may have an effect on the mechanical stability of the paste material.

Experimental

Reagents

The salts used were of reagent grade unless otherwise noted. $NaClO_4$ (G. F. Smith Chemical Co., Columbus, OH), KNO_3 (Fisher Scientific, Fairlawn, NJ), KCl (J. T. Baker, Phillipsburg, NJ) were used to prepare 1.0 M electrolyte solutions for use in cyclic voltammetric studies. Adjustment of the pH to 4.00 was accomplished by dropwise addition of 3.0 M H_2SO_4.

Apparatus

A BAS-100 electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN) was used for electrochemical studies (cyclic voltammetry). A three electrode electrochemical cell was employed with the modified carbon paste electrode (MCPE) as the working electrode, a platinum wire as counter electrode, and a Ag/AgCl, 3.0 M KCl reference electrode (Bioanalytical Systems).

De-ionized water which had been further purified by distillation from an all borosilicate glass still (Wheaton AUTOSTILL 1.5, Wheaton Instruments, Millville, NJ) was used for solution preparation.

Measurements of pH were made with an Orion digital pH meter model 601A (Orion Research Incorporated, Cambridge, MA) equipped with an epoxy-body combination electode

(Sensorex, Westminster, CA).

Spectrophotometric measurements at 512 nm and 543 nm were made with a Perkin-Elmer 3840 UV-Visible diode array spectrophotometer and a 1-cm glass cuvette.

A diagram of the electrode is provided for clarity in (Fig. 2):

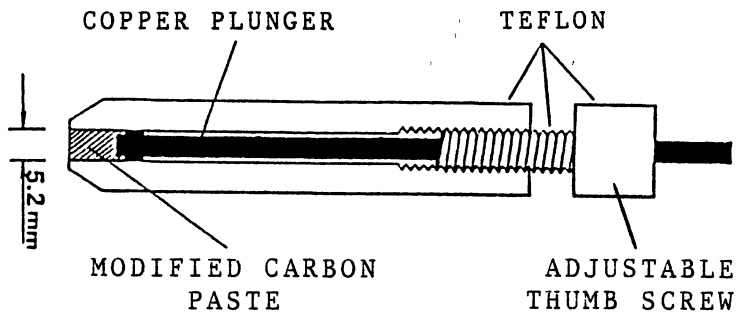


Figure 2. Diagram of modified carbon paste electrode (MCPE)

The electrode body is constructed of Teflon in the form of a cylindrical rod 13.0 mm o.d. An inner bore, 5.2 mm i.d., provides a well for the paste material. A copper plunger inside the bore and connected to an adjustable thumbscrew is in contact with the paste and provides electrical contact. Tightening of the thumbscrew will cause the paste to extrude from the well. The electrode can be wiped smooth and flush on an index card thus creating a new surface.

Preparation of Insoluble Complexes

Ferroin perchlorate, bathophenanthroline, bathocuproine, and 2,4,6-tripyridyl-s-triazine (TPTZ) were of analytical grade (G. F. Smith Chemical Co., Columbus, OH). Ferrous chloride (J. T. Baker, Phillipsburg, NJ) was used for preparation of the Fe(II) complexes or for immersing the electrode surface. The complexes can be prepared by dissolving the appropriate ligand in acetone (technical grade) and then adding an aqueous solution of Fe(II). The ligand is added in slight excess of the stoichiometric 3/1 ratio to insure completeness of Fe(II) complexation. An excess of ligand is not detrimental since it is not electroactive. For initial experiments the complex is precipitated with 1.0 M $NaClO_4$, filtered, rinsed with copious amounts of water, and oven dried overnight at $50^{o}C$. Precipitation for subsequent experiments involved sodium salicylate (Matheson Coleman & Bell, Norwood OH), sodium benzoate (J. T. Baker, Phillipsburg, NJ), or sodium dodecylbenzenesulfonate (K & K Laboratories, Plainview, NY).

Modified Carbon Paste Preparation

The following three equations provide a "recipe" for the amounts of modifier, graphite powder, and mineral oil for preparing the paste:

$$\frac{\text{wt. of modifier}}{\text{desired amount of paste}} \times 100 = \text{desired modification}$$

5/8(amt. of paste - amt. of modifier) = required amount of graphite

3/5(amt. of graphite) = required amt. of mineral oil

Typically, 0.5000 g samples of modified carbon paste were prepared with 2% w/w modifier incorporated. The mineral oil/graphite ratio is 5/3 w/w which seems to be the best compromise. The actual preparation of the paste is accomplished by mixing the graphite powder UCP-1-M (Ultra Carbon, Bay City, MI) and the modifier in a 50-mL beaker. Acetone is added until a fluid slurry is made. This is mixed thoroughly with a Teflon-coated spatula and the acetone is allowed to evaporate. Making an acetone slurry should result in a more homogeneous paste and has a very profound effect as will be shown later. When the mixture becomes dry, it is placed in an oven at 45^{o}C for 30 minutes to achieve a reproducible dry weight. A weighed amount of mineral oil is added and thoroughly mixed with an agate mortar and pestle. The mixture thus obtained has the consistency of a paste and is ready for use.

Surfactant Treatment of Electrodes

A given electrode was soaked in a 0.10 % w/v solution of the anionic surfactant sodium dodecylbenzenesulfonate (K & K Laboratories, Plainview, NY) for 15 minutes, thoroughly

rinsed with deionized distilled water, and then placed in the electrochemical cell to be characterized by cyclic voltammetry.

Results and Discussion

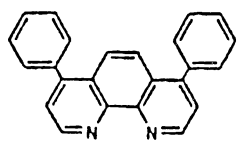
Choice of Modifier

Carbon paste electrodes respond electrochemically to NO_2 but the electrode rapidly becomes poisoned resulting in a decrease in sensitivity and raising the limit of detection. Some ideal characteristics for the modifier would be chemical and electrochemical reversibility, insolubility, mediation of electron transfer (to minimize poisoning) or perhaps to act as a center for electocatalysis.

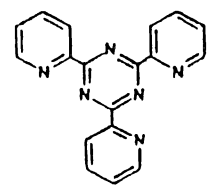
The preliminary choice for the modifier was tris-1,10-phenanthroline iron(II), commonly known as ferroin. It is a well-known redox indicator having several features that make it a favorable candidate for the modifier. It has been characterized under various experimental conditions (66) and shows chemical and electrochemical reversibility under appropriately chosen conditions. It has the unique feature that the organic moiety remains unaffected by the Fe(II)/Fe(III) redox couple. Ferroin has also been used successfully for the amperometric determination of gaseous NO_2 and SO_2 under continuous flow conditions (67,68). In this configuration the ferroin was incorporated as part of the carrier/reactor

stream. This research will focus on the feasibility of incorporating ferroin or ferroin-like derivatives into a carbon paste electrode for the amperometric determination of gaseous NO_2 under continuous flow conditions.

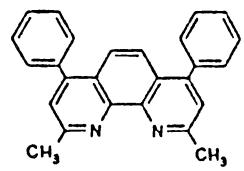
Unfortunately, ferroin is quite soluble in aqueous media. To circumvent this problem various ligands of the 1,10-phenanthroline type, ie. ligands containing -N=C-C=N- coordination sites, as well as different counter anions were studied to ascertain their ability to produce an insoluble complex with Fe(II) and to characterize their electrochemical behavior. Three ligands were chosen as possibilities: 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine), and 2,4,6-tripyridyl-s-triazine (TPTZ). The following structures for each ligand are provided in (Fig. 3):



4,7-diphenyl-1,10-phenanthroline
(bathophenanthroline)



2,4,6-tripyridyl-s-triazine
(TPTZ)



2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline
(bathocuproine)

Although TPTZ is not a member of the phenanthroline family it contains the -N=C-C=N- coordination site which is common to the above ligands.

Ligand Modified Carbon Paste Electrode

The initial study involved the ability of the different ligands to complex Fe(II) at the electrode surface. A given ligand is admixed into the carbon paste and then the electrode is immersed in a 1.0×10^{-2} M solution containing Fe(II). After 15 minutes of immersion the electrode is thoroughly washed with distilled water. From cyclic voltammograms it was observed that the bathophenanthroline did complex with the Fe(II) while the other two ligands did not. Figure 4 illustrates a typical voltammogram of 10% (w/w) bathophenanthroline admixed in the carbon paste. Curve A clearly shows that the ligand is not electroactive. After immersion in the Fe(II) solution, curve B is the result. The cathodic and anodic peaks are well defined (this will be important for later comparison) with a formal potential $E^{o'}$ = 0.920 V. This is only slightly lower than a reported value of 1.130 V in sulfuric acid (69). The peak ratios suggest chemical reversibility i_{pa}/i_{pc} = 1.06 while the peak separation ΔE_p = 0.143 V suggests electrochemical quasireversibility.

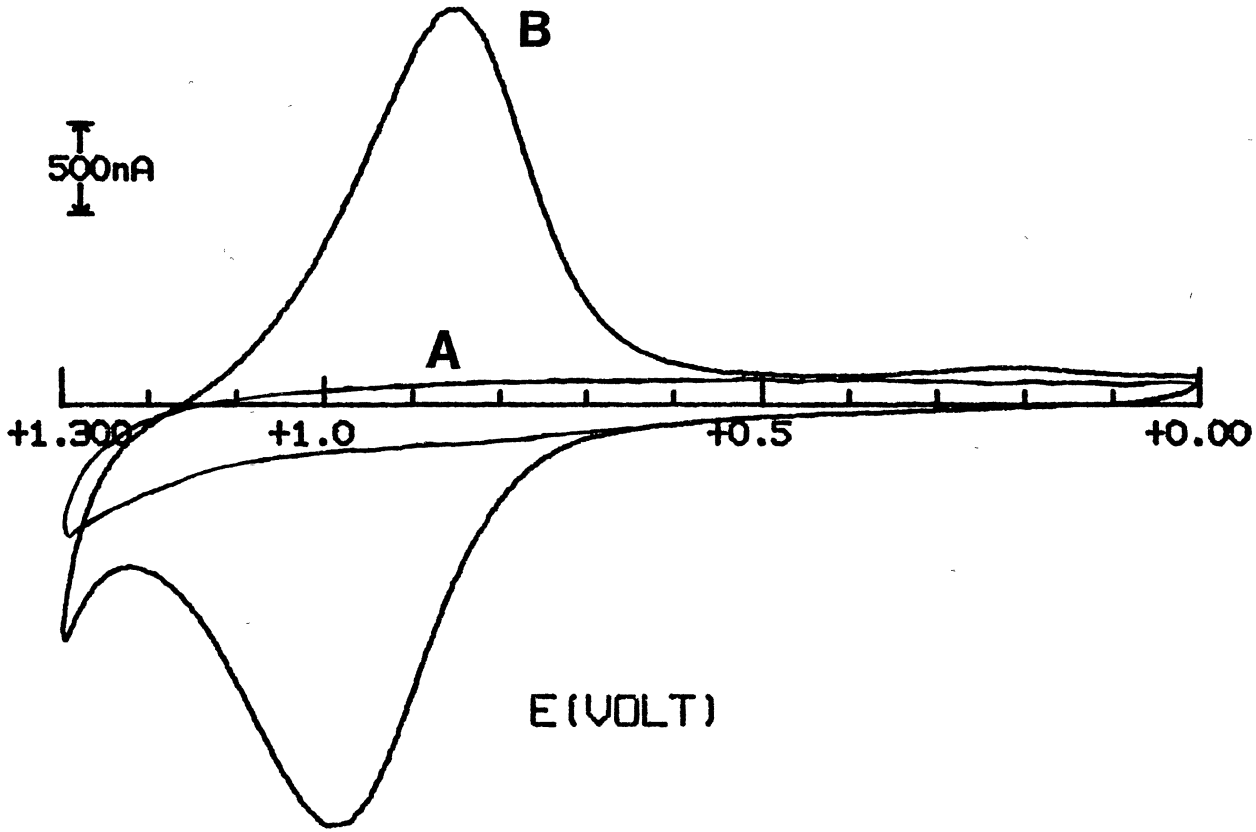


Figure 4. Cyclic voltammogram of bathophenanthroline admixed MCPE; 10% w/w modifier, 1.0 M $NaClO_4$ supporting electrolyte, scan rate 100 mV/sec. Curve A: voltammogram of ligand; Curve B: same surface as in A but after having been immersed in 1.0 x 10^{-2} M $Fe(ClO_4)_2$ for 10 minutes and then thoroughly rinsed

Complex Modified Carbon Paste Electrode

The second approach involves incorporating a given complex as an insoluble perchlorate salt into the carbon paste. Although all the ligands produced their respective iron(II) complexes, only bathophenanthroline and TPTZ could be precipitated successfully. Bathophenanthroline produces a deep red precipitate while the TPTZ produces a deep blue precipitate. Cyclic voltammograms of the tris-TPTZ iron(II) modified electrode in 0.10 M $NaClO_4$ or $NaNO_3$ electrolyte resulted in one cathodic and two anodic peaks (Fig. 5a). In (Fig. 5b) we also see the effect of making the acetone slurry during paste preparation. During the evaporation process the complex probably adsorbs onto the graphite resulting in a more intimate electrochemical communication. This is in contrast to dispersing micro-crystals of complex within the graphite paste where there is probably much less contact.

The effect of different supporting electrolytes on the electrochemical behavior of the electrode is shown by (Fig. 6). Using 1.0 M KCl as supporting electrolyte, one anodic and two cathodic peaks were observed. Iron(II) complexes of 1,10-phenanthroline are known to form mixed ligand complexes with chloride ions (66) and this may be a possible explanation for the multiple voltammetric peaks. It was also noticed that the modified carbon paste would extrude from the electrode well after

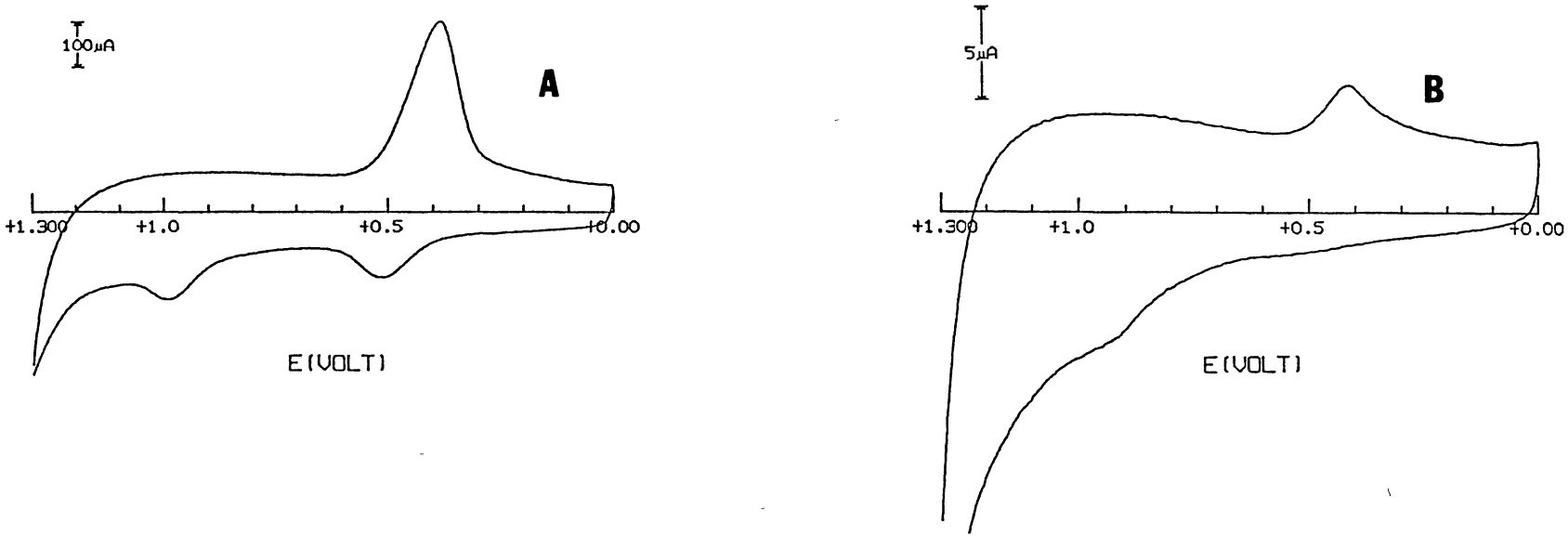


Figure 5. Effect of acetone during MCP preparation; A: using acetone slurry during paste preparation; B: direct admixing of modifier without using an acetone slurry; 2% w/w $Fe(TPTZ)_3^{+2}$, 1.0 M $NaClO_4$ supporting electrolyte, scan rate 250 mV/sec

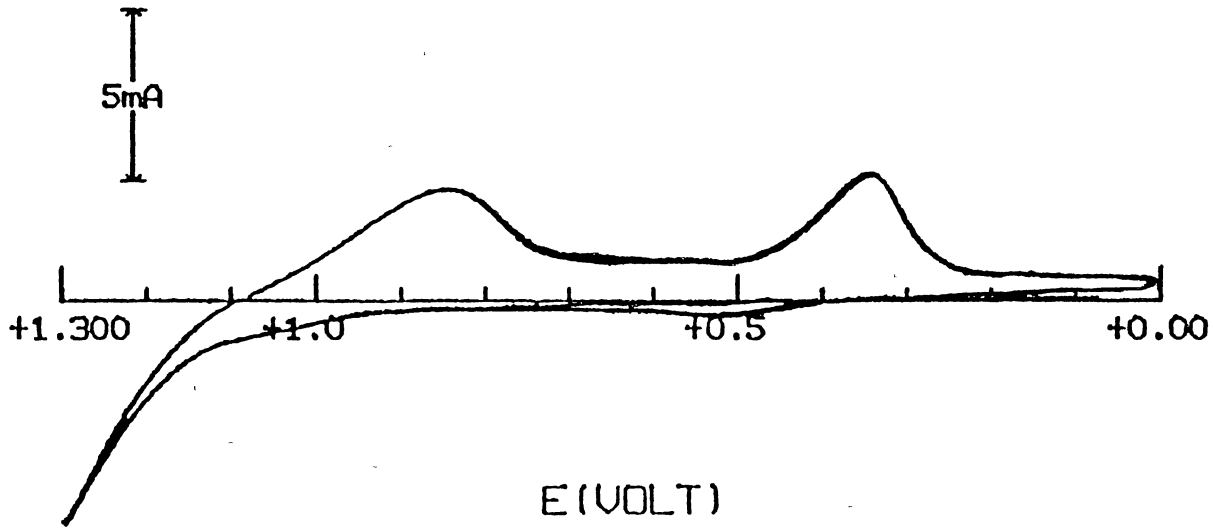


Figure 6. Effect of supporting electrolyte on voltammogram of $Fe(TPTZ)_3^{+2}$ MCPE; 2% w/w modifier, 1.0 M KCl supporting electrolyte, scan rate 250 mV/sec

prolonged contact with the electrolyte solution regardless of whether a potential was applied or not. After a given period of time the face of the electrode would flake off allowing the extrusion process to continue. This effect is clearly visible in (Fig. 7) and was attributed to a surface tension effect between the modified paste and the electrolyte solution. As the paste extrudes, more surface area is exposed and thus an increase in peak currents is obtained with each subsequent scan. This same effect will be observed again in a later experiment.

Figure 8 shows a typical cyclic voltammogram of the tris-bathophenanthroline iron(II) MCPE. The anodic and cathodic peaks are not as well defined as those seen with TPTZ complex. This is probably due to the less soluble nature of the bathophenanthroline complex. It was found that the TPTZ complex is slightly soluble imparting a weak blue color to the solution during precipitation. On the other hand the bathophenanthroline complex appeared to be precipitated quantitatively during preparation. It can be visualized that the TPTZ iron(II) complex diffuses appreciably from the paste forming a solution layer of electroactive species at the electrode surface. This diffusion is also responsible for the observed breakdown of the paste.

The electrolyte effects the cyclic voltammograms of the bathophenanthroline complex in much the same manner as the TPTZ complex. The main difference between the two MCPE's is

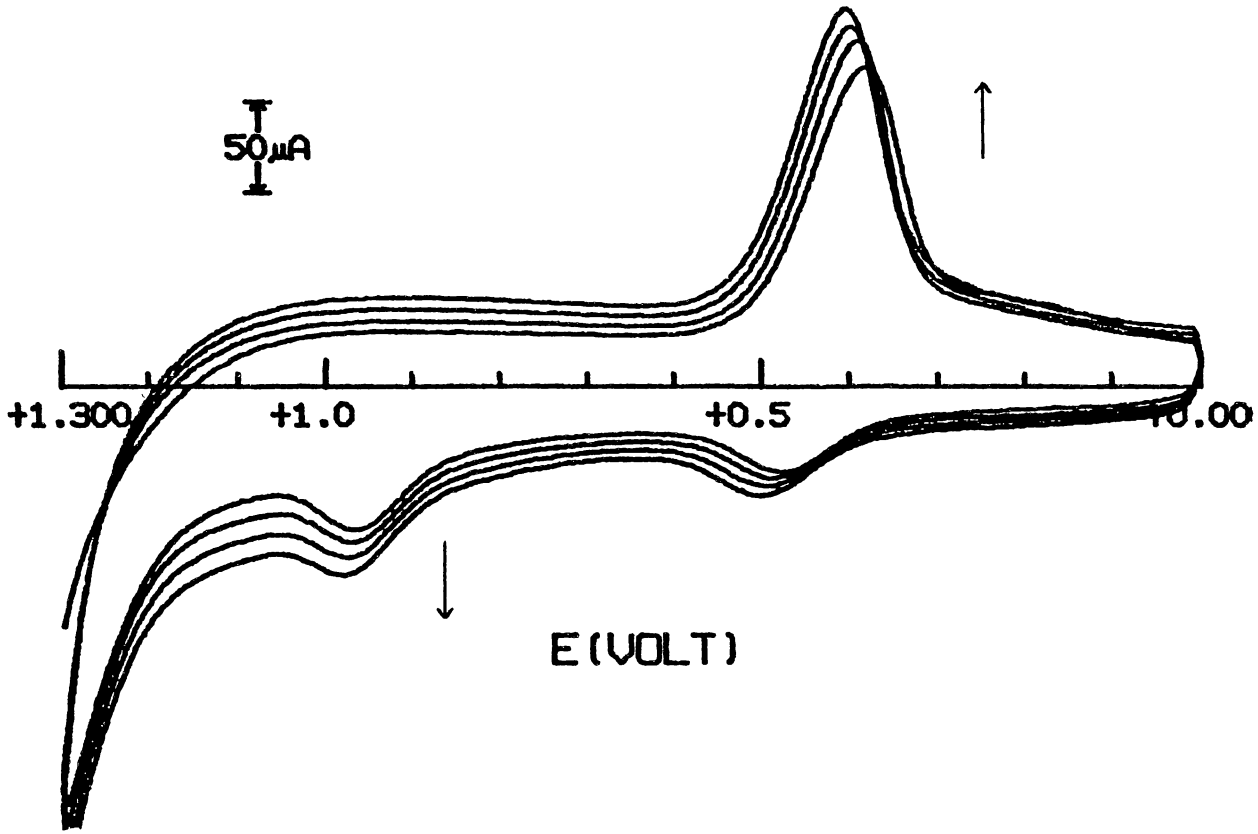


Figure 7. Extrusion of modified paste from electrode well; tris[TPTZ] Fe(II)•$2ClO_4$ 2% w/w, 1.0 M $NaClO_4$ supporting electrolyte, 4 cycles, scan rate 250 mV/sec

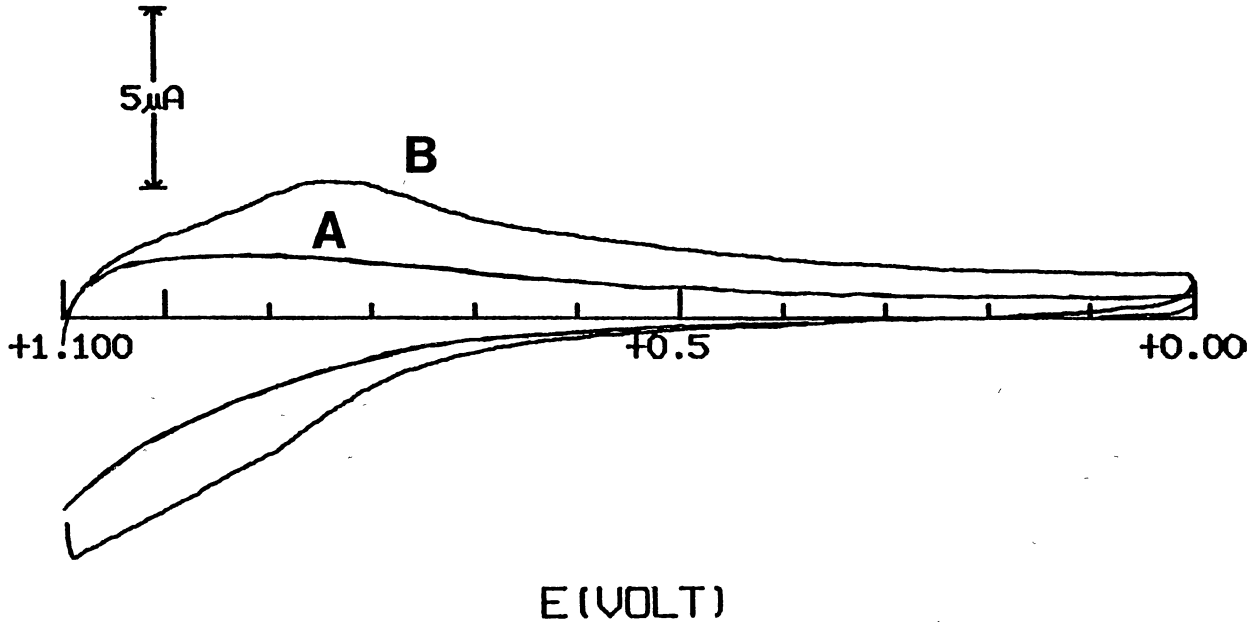


Figure 8. Cyclic voltammogram of tris[bathophenanthroline] Fe(II)·$2ClO_4$ admixed MCPE; 2% w/w modifier, 1.0 M $NaClO_4$ supporting electrolyte, scan rate 250 mV/sec; Curve A: blank CPE; Curve B: MCPE

the absence of the extrusion effect with the bathophenanthroline complex. From these findings it was decided that the bathophenanthroline complex will be further studied mainly because of its physical stability and electrochemical simplicity in 0.10 M $NaClO_4$.

Effect of Precipitating Counterion

Although initially the complexes were precipitated with perchlorate as counterion, other counterions such as benzoate, salicylate, and dodecylbenzenesulfonate (DBS) were examined to see if a decrease in solubility could be effected. Benzoate did not induce precipitation while salicylate was moderately effective. Precipitation with DBS produced a very fine dispersion which had to be centrifuged to obtain a workable salt. The salicylate salt showed sufficient stability when incorporated into the carbon paste and as such its properties will be investigated in parallel with the perchlorate salt. When the DBS was incorporated into the paste, a very pronounced extrusion effect (Fig. 9) occurred which was very similar to that obtained with the TPTZ complex. The extrusion process can be visualized as the squeezing of a tube of toothpaste and was thus coined the "toothpaste" effect. This can be explained by a surface tension effect between the modifier and the electrolyte solution. This occurs regardless of whether a potential is applied or not.

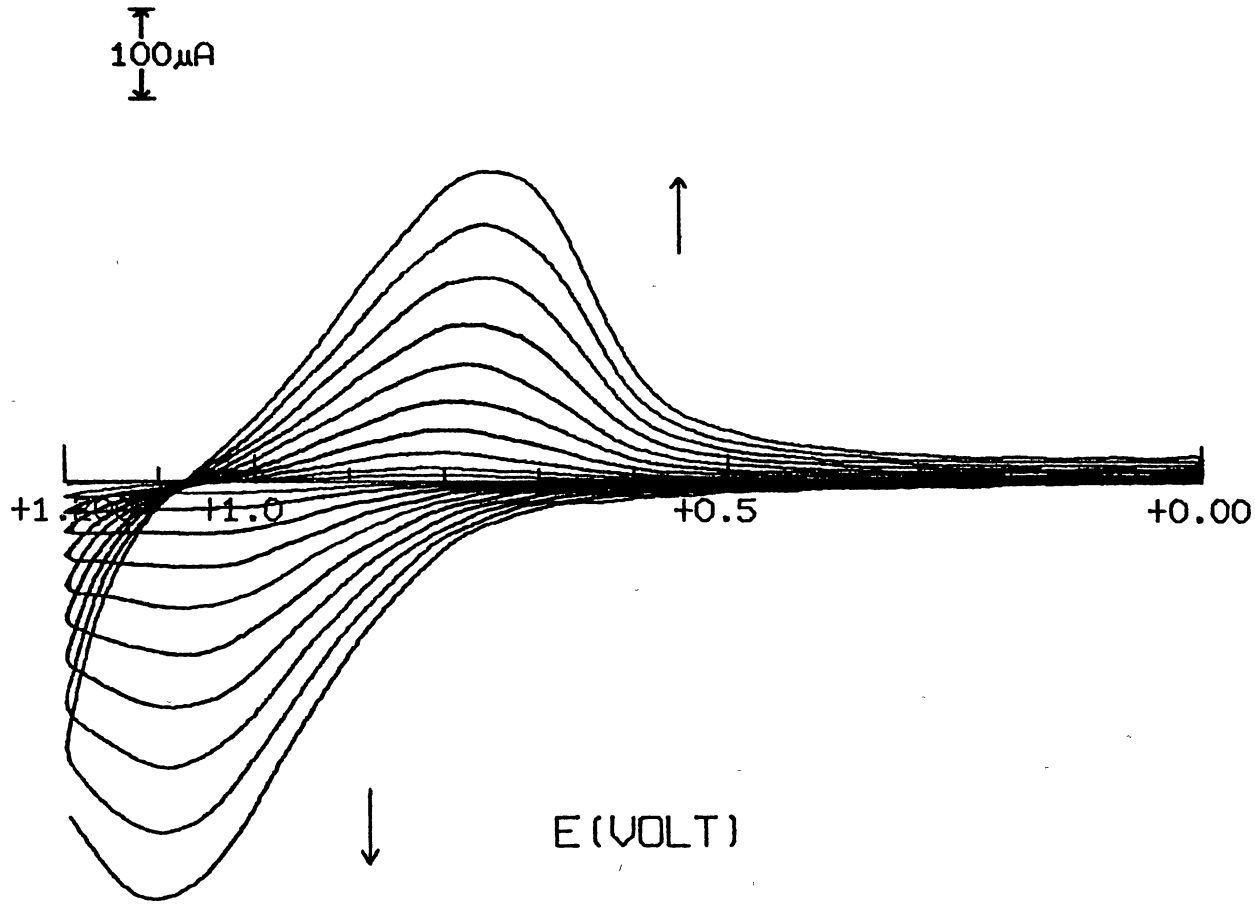


Figure 9. "Tooth paste" effect; Tris-bathophenanthroline Fe(II)•2DBS 2% w/w, 1.0 M $NaClO_4$ supporting electrolyte, scan rate 250 mV/sec, 10 cycles

Spectrophotometric Observation of Leaching

The addition of the two phenyl groups on the 1,10-phenanthroline backbone decreases the solubility of the derivative in due to increasing the molecular weight and augmenting the hydrophobic character of the complex as well as its ability to adsorb on the graphite. The drastic decrease in solubility of the complex is fairly evident as shown in (Fig. 10). A plot of absorbance versus time at the appropriate λ_{max} for each complex shows a relatively high rate of leaching of ferroin from the carbon paste even after 60 minutes. Meanwhile, the bathophenanthroline Fe(II) complex appears to be insoluble at least within the sensitivity limitations of the spectrophotometer. In a later experiment, electrochemical measurements which are inherently more sensitive will show that the derivative appears to leach from the carbon paste but at a very slow rate. For the modifier to be useful for our purposes, ideally it should be insoluble or, in the worst case, only slightly soluble. Otherwise the electrode will have a drastically shortened lifetime.

Surfactant Treatment of Modified Carbon Paste Electrodes

At this point there were two routes by which the carbon paste can be modified to contain Fe(II)/Fe(III) active sites. The ligand can be incorporated into the carbon paste and then subsequently treated with an Fe(II) solution to

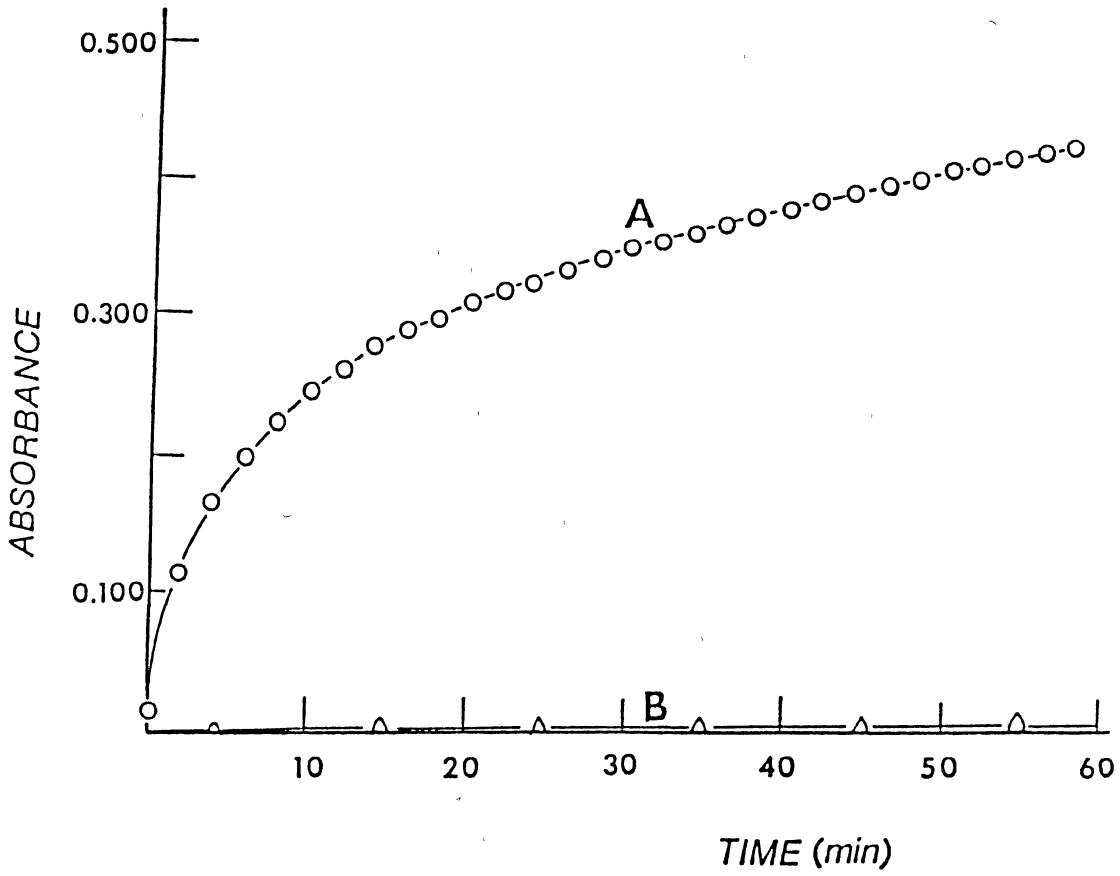


Figure 10. Spectrophotometric observation of leaching; Curve A: ferroin, monitored at 512 nm; Curve B: tris[bathophenanthroline] Fe(II), monitored at 543 nm; 16.8% w/w of appropriate complex, 1.0 M KCl, stirring conditions, no applied potential

produce a suface layer of complex, or the complex can be incorporated as an insoluble salt. Comparing the voltammograms of the two methods it can be seen that the first method produces a more suitable response in terms of well defined peak currents and more active sites. This is probably attributed to a more intimate contact of the active sites with the electrolyte solution compared to the thin film of oil that exists at the complex/solution interface for the latter modification. Indeed the removal of this oil film with a surfactant solution was shown to enhance the response of carbon paste electrodes (7). The following results were obtained from experiments in which a carbon paste, ligand MCPE, and complex MCPE were rinsed in a surfactant solution.

Effect on Carbon Paste Electrode. Comparison of a carbon paste electrode before and after surfactant treatment results in a dramatic increase in background current. A high background current is typical of an electrode that is composed of just graphite without any impregnator or binder (4,70) and seems to indicate that the electrode surface is more graphite-like, meaning an extremely high surface area. The surfactant treatment makes the electrode surface much more wettable, this was observed by placing a droplet of water on the surface of the electrode before and after treatment. Before the treatment, the water droplet will form a spherical shape on the surface, after treatment the

droplet will spread out over the surface, in much the same way it spreads out on a dry graphite surface. Increased wettability will translate into enhanced electrode response.

Effect on Bathophenanthroline Modified Carbon Paste Electrode. After surfactant treatment, the ligand-MCPE still remains featureless except that the background current shows an approximately 500 fold increase (Fig. 11a). Cyclic voltammograms after subsequent treatment with Fe(II) yield multiple broad peaks (Fig. 11b). During the surfactant treatment it is possible that some of the ligand is removed. When the electrode is subsequently immersed in the Fe(II) solution where there is a stoichiometric excess of Fe(II) compared to the ligand at the electrode surface, the formation of mixed ligand complexes (FeL_2L') or a dimer ($Fe_2L_4L'_2$) could result. This would explain the appearance of the cathodic peak at the lower potential. A cyclic voltammogram of a dimer MCPE indeed does show a cathodic peak in this potential range (Fig. 12).

Effect on Tris-bathophenanthroline Fe(II) Modified Carbon Paste Electrode. Figure 13 is an overlay of typical cyclic voltammograms of the bathophenanthroline Fe(II) MCPE before and after surfactant treatment. As can be seen there is a marked

enhancement in electrode response both in peak definition

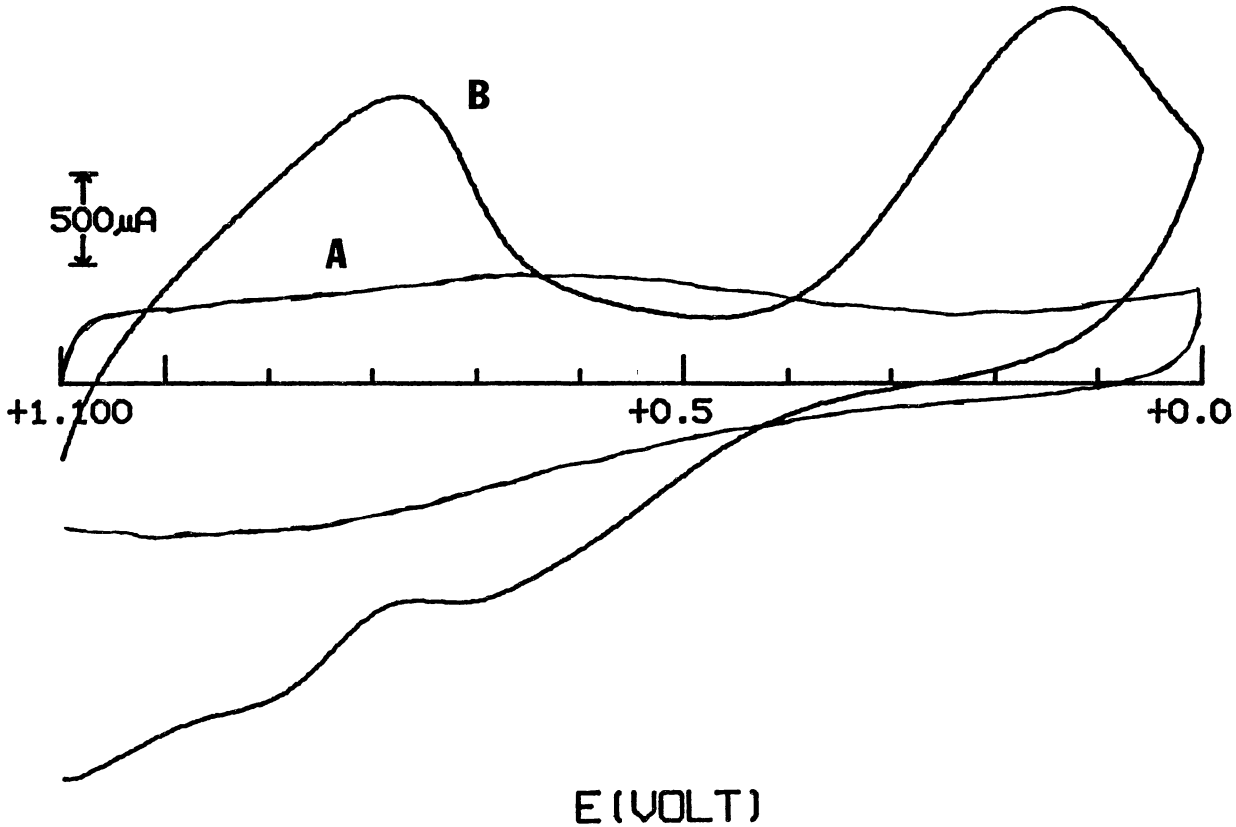


Figure 11. Effect of surfactant treatment on ligand MCPE; Curve A: ligand MCPE after surfactant treatment; Curve B: same surface after Fe(II) treatment; 2% w/w modifier, 1.0 M $NaClO_4$ suporting electrolyte, scan rate 250 mV/sec

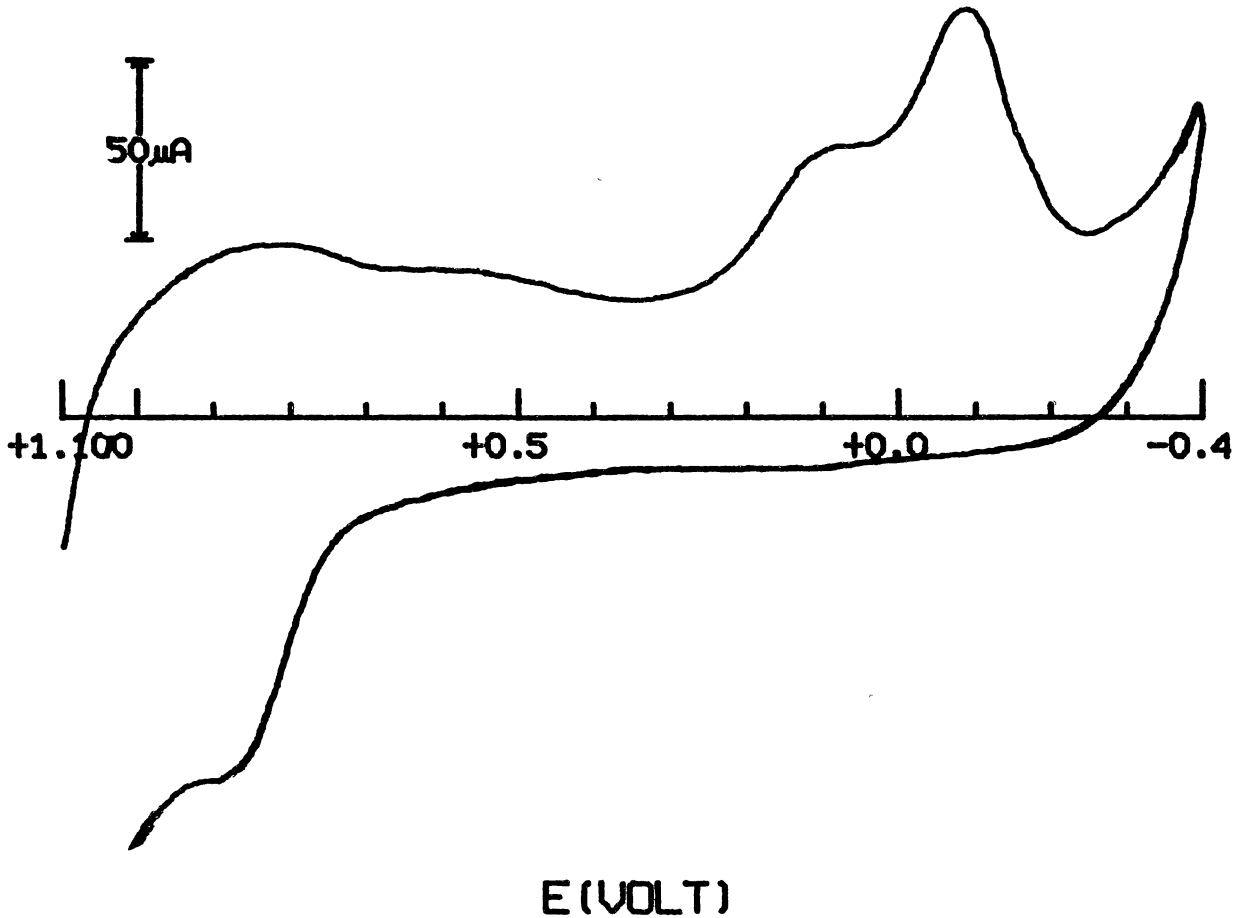


Figure 12. Cyclic voltammogram of dimer, $Fe_2(1,10\text{-phenanthroline})_4(OH)_2^{+4}$; 2% w/w modifier, 1.0 M $NaClO_4$ supporting electrolyte, scan rate 250 mV/sec

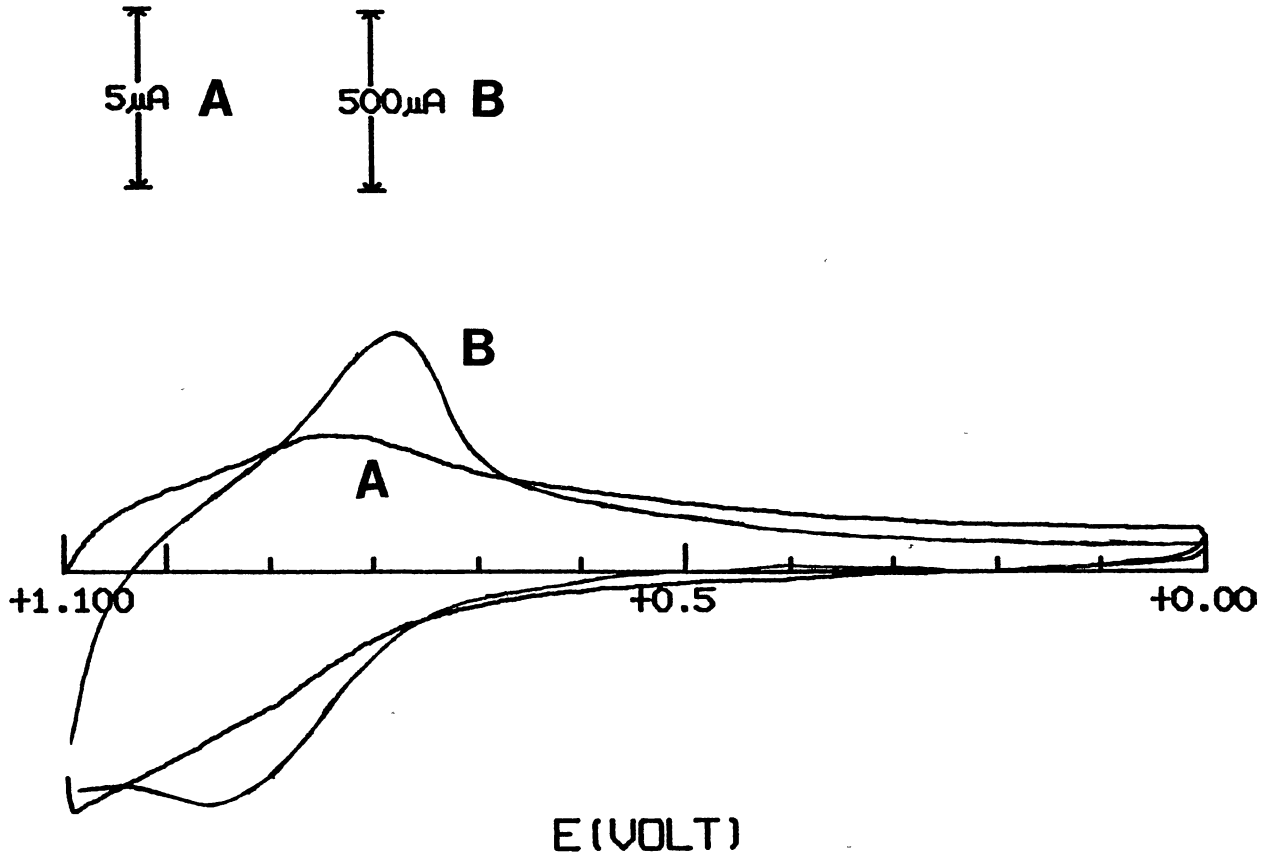


Figure 13. Effect of surfactant treatment; Curve A: before treatment; Curve B: same surface after immersed in 0.10% w/v sodium dodecylbenzenesulfonate and then thoroughly rinsed with distilled water, 2% w/w tris[bathrophenanthroline]Fe(II), 1.0 M $NaClO_4$ supporting electrolyte, 250 mV/sec

and current magnitude. The cathodic peak current has increased 274 fold from 2.1 uA to 576 uA. The peak ratio is 1.13 but the separation is extremely high, ΔE_p = 0.181 V. The $E^{o'}$ = 0.864 V, is slightly lower than the value of 0.920 V calculated from (Fig. 4b) and much lower than the reported 1.130 V (69).

Figure 14 is an scanning electron micrograph of the electrode surface after the surfactant treatment. The topography is far from being smooth and there seems to be a broad distribution of particle sizes. An untreated surface shows the same features as a treated surface so it is assumed that the oil film must be on the order of a few microns thick.

Further experiments revealed that the surfactant treatment shows its maximum effect after 15 minutes. This is illustrated by a plot of cathodic peak current versus length of time of surfactant treatment (Figure 15). After 15 minutes the cathodic peak does not seem to increase appreciably and, therefore, was chosen as the best compromise between treatment time and best response.

Conclusions

From the above results, it can be concluded that the ligand of choice is bathophenanthroline with either perchlorate or salicylate as the counterion. This combination seems to produce the more stable MCPE in terms

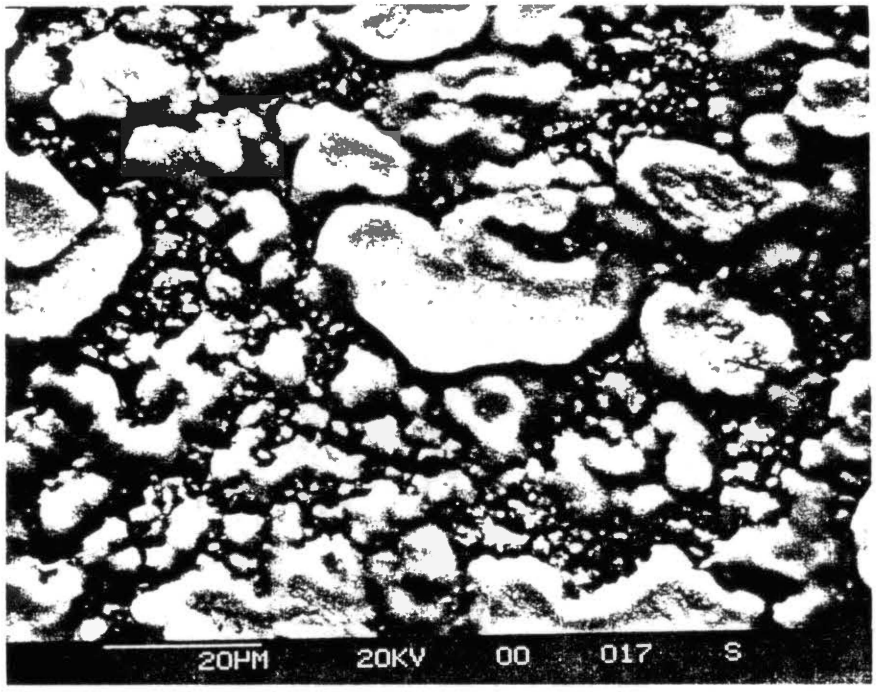


Figure 14. Scanning electron micrograph of electrode surface after surfactant treatment; $Fe(bath)_3^{+2}$ 2% w/w, 1000X

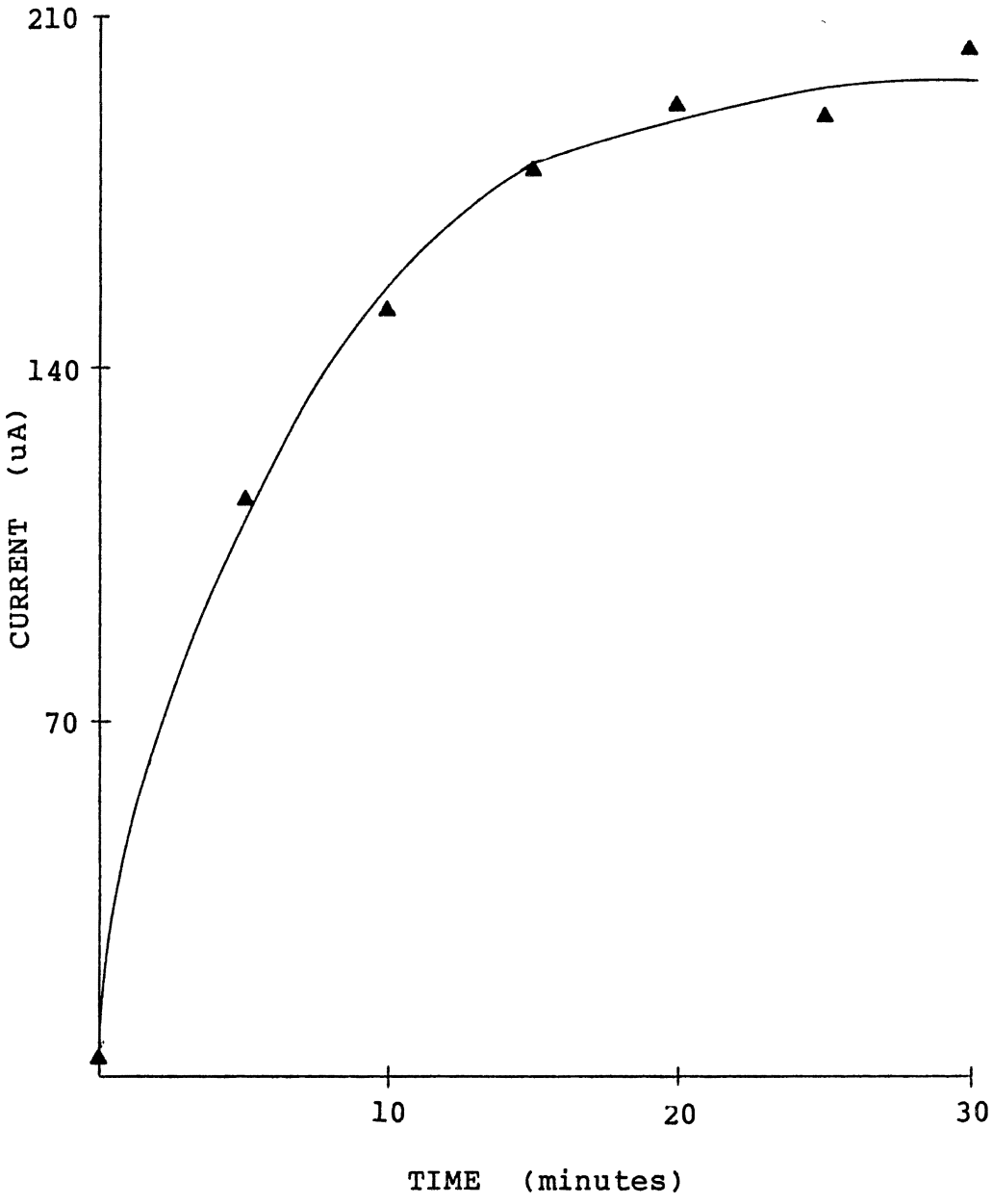


Figure 15. Cathodic peak current versus surfactant treatment time; 10% w/w $Fe(B)_3$ MCPE, surfactant solution: 0.10% w/v dodecylbenzene sodium sulfonate, 0.10 M $NaClO_4$ supporting electrolyte, pH 4.00, scan rate 250 mV/sec

of response and physical characteristics.

Of the two different methods for modifying the carbon paste electrode, the admixing of the complex seems to yield the more satisfactory results in terms of simple voltammograms and higher current response after surfactant treatment. The surfactant treatment results in enhanced electrode response due to an increase in wettability of the electrode surface. This improved response should mean an increase in sensitivity in its final application. Further investigations were conducted on the complex admixed CPE that has been further treated with the surfactant.

CHAPTER III

ELECTROCHEMICAL CHARACTERIZATION

Now that the choice of modifier and mode of modification has been established, the progression of this investigation leads us to the electrochemical characterization of the chemically modified electrode. The following experiments will give a better understanding of the physical and chemical processes that are occuring at the electrode surface. These may provide some insight towards optimum operating conditions in the final application and contribute more knowledge on electrodes modified in this manner.

Experimental

Reagents

All reagents, iron complexes, and paste preparations either commercially obtained or prepared in house are described in Chapter II under the Experimental section.

Apparatus

The instrumentation used throughout has been described previously in Chapter II.

Preparation of Electrodes

The electrodes used contained either the tris-bathophenanthroline iron(II)$\cdot 2ClO_4$ (here after referred to as the perchlorate complex) modified paste or the tris-bathophenanthroline iron(II)$\cdot$2Salicylate (here after referred to as the salicylate complex) modified paste. The electrodes were further treated with surfactant as described in the previous chapter.

Calculation of the Number of Active Sites

The number of active sites at the surface of the electrode was calculated using the area underneath the cathodic peak of a given cyclic voltammogram. Ideally either the cathodic or anodic peak could be used but as it applies here only the cathodic peak was clearly defined. The anodic peak on the other hand suffered interferences from the background making it ill-defined.

The area under the voltammogram peak is proportional to the number of coulombs of charge that are transferred during electrolysis. The following equation relates coulombs to the number of moles of active sites:

$$Q = n F \qquad (1)$$

Q = total amount of charge, coulombs
n = number of moles of active sites
F = Faraday's constant, 9.65×10^4 C/mol

Since the BAS-100 cannot directly integrate the area under the peak, a cut and weigh method was used to obtain the area under the curve.

Results and Discussion

Optimization of Percent Modifier

In the previous experiments a MCPE with 2% w/w modifier was used without any consideration as to whether this amount was optimum. There was also curiosity as to the correlation between % modifier and the peak current obtained in cyclic voltammograms. It is noted here that the number of active sites that were calculated are not absolute because the correction for the background was estimated. However, these values should be useful for comparison purposes.

There are two features to be noted in Figure 16. The first is that for both complexes adding more than 2% modifier does not significantly improve the response of the electrode. It is likely that as the coating of the modifier on the graphite particles becomes thicker the kinetics of electron transfer become more sluggish. The modifier can not be expected to facilitate electron transfer as efficiently as ordinary graphite. This is also seen by the increase in ΔE_p as the amount of modifier increases.

As expected it can be seen that at low percentages the perchlorate complex has a consistently higher response than the salicylate. For a given weight

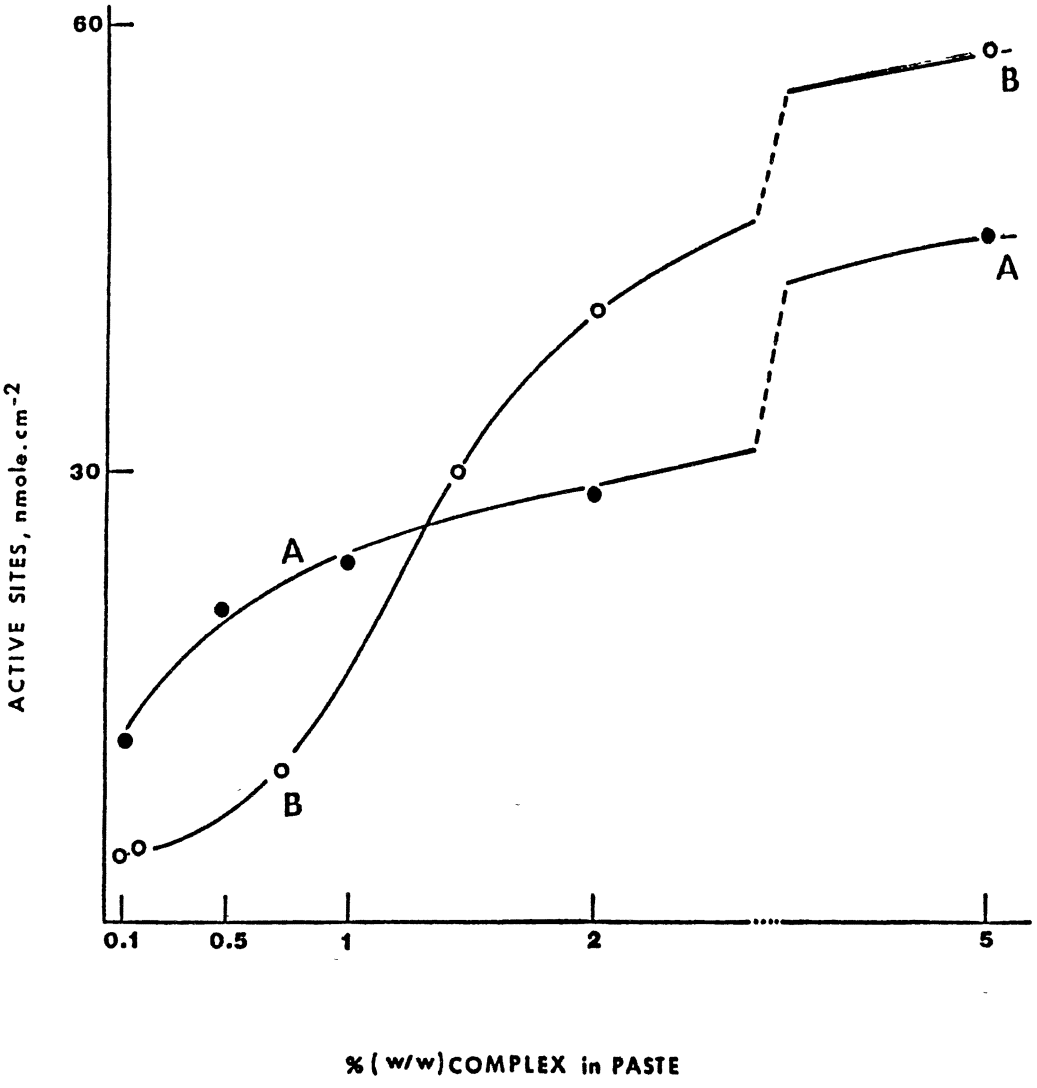


Figure 16. Plot of active sites versus % w/w modifier; A: $Fe(Bath)_3 \cdot 2ClO_4$; B: $Fe(Bath)_3 \cdot 2Salicylate$; 1.0 M $NaClO_4$ supporting electrolyte, scan rate 250 mV/sec

of modifier, the lower molecular weight perchlorate complex should provide more active sites. For a given weight of modifier, the perchlorate complex is calculated to have 6% more active sites than the salicylate complex. However, at higher percentages, it is observed that at higher percentages the salicylate complex has more active sites per unit weight. This phenomenon can be explained by the "tooth paste" effect that was described in the previous chapter, but in this case the effect is not nearly as pronounced. Although the human eye is not sensitive enough to detect this effect, electrochemically it can be detected.

Modifier Leaching, Electrochemical Observation

In Figure 10 from the previous chapter it appeared that the ferroin derivative was quite insoluble from a spectrophotometric viewpoint. Since electrochemical techniques are generally much more sensitive, the rate of modifier bleeding was monitored electrochemically. Figure 17 shows a plot of the cathodic peak currents obtained from cyclic voltammograms with the progression of time. Again it was observed that the cathodic peak currents for the salicylate complex were consistently higher than the perchlorate complex.

Both complexes show an initial increase in cathodic peak current with the salicylate showing the more pronounced effect. This process seems to continue for about 2 hours

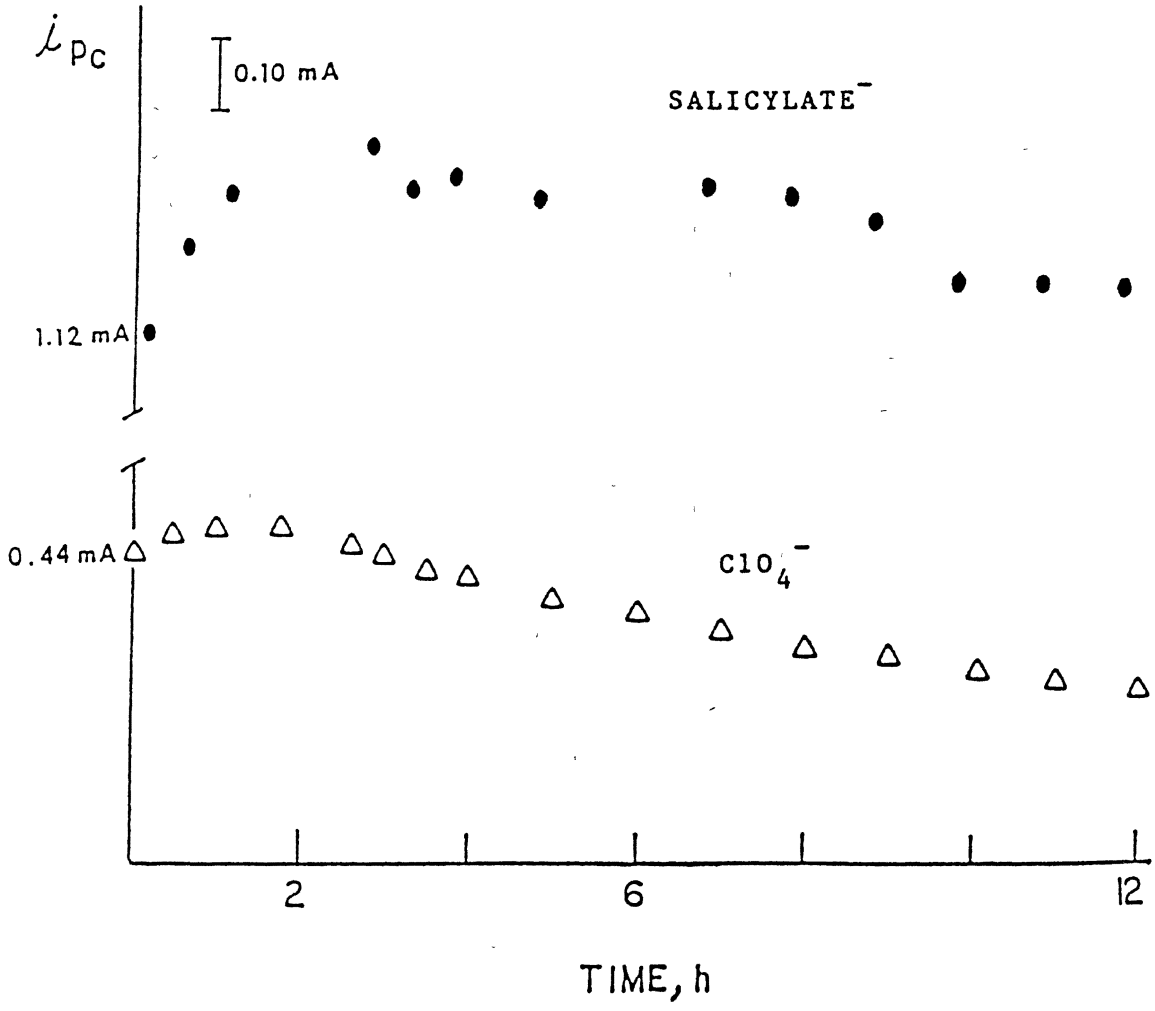


Figure 17. Electrochemical observation of modifier leaching from carbon paste A: $Fe(Bath)_3 \cdot 2ClO_4$; B: $Fe(Bath)_3 \cdot 2Salicylate$; 2% w/w of appropriate modifier, 1.0 M $NaClO_4$ supporting electrolyte, scan rate 250 mV/sec

before the current starts to decay. During the initial stages of the experiment the "tooth paste" effect is the predominating process, but after a given period of time modifier leaching dominates.

From a practical viewpoint the perchlorate complex shows a 36.9% loss in peak current over an 8 hour period from the point of maximum peak response while the salicylate showed a 13.4% loss over the same period. In both cases the current response was still appreciable even after 10 hours. Even though it has a higher percentage of loss, the perchlorate complex may be the better modifier because the overall smoothness of the curve suggests more physical stability. The decay portion of the salicylate curve was somewhat erratic in that the curve was not smooth. This could be due to the loss of electrode material from the face of electrode.

Scan Rate Study

For a diffusion controlled (from solution to the electrode surface), reversible process the peak currents in cyclic voltammetry can be described by the Randles-Sevcik equation:

$$i_p = k\, n^{3/2}\, D^{1/2}\, A\, C\, v^{1/2} \qquad (2)$$

i_p = peak current, amperes
k = constant, $2.69 \times 10^5\ C^2(mol/sec)^{1/2}J^{-1}$
n = number of electrons transferred, equiv/mol
D = diffusion coefficient, cm^2/sec
A = area of electrode surface, cm^2
C = concentration of analyte, mol/cm^3
v = scan rate, volt/sec

A plot of peak current versus the $v^{1/2}$ should produce a straight line. Non-linearity is an indication of irreversibility or that the electron transfer process is not diffusion controlled. Figure 18 is a plot of cathodic peak current versus $v^{1/2}$ and as can be seen there is a linear relationship. A plot of $\log(i_{pc})$ versus log (v) yields a slope of 0.59 with a correlation coefficient of 0.996. A slope of 0.50 is expected for a diffusion controlled process whereas a slope of 1.0 indicates that the modifier is truly immobilized. The diffusion dependence can be explained by the slow bleeding of the modifier from the paste and forming a stagnant layer at the electrode surface. It is from this layer that the diffusion component arises.

pH effect on Modified Carbon Paste Electrode

Since it was known that ferroin is capable of forming dimers when oxidized at relatively low pH's (66), it was of interest to investigate the chemical properties of the chosen modifier. In the final applications of this CME, low, localized pH's will be encountered due to the nature of the gas that will be dealt with, NO_2. Figure 19 shows an

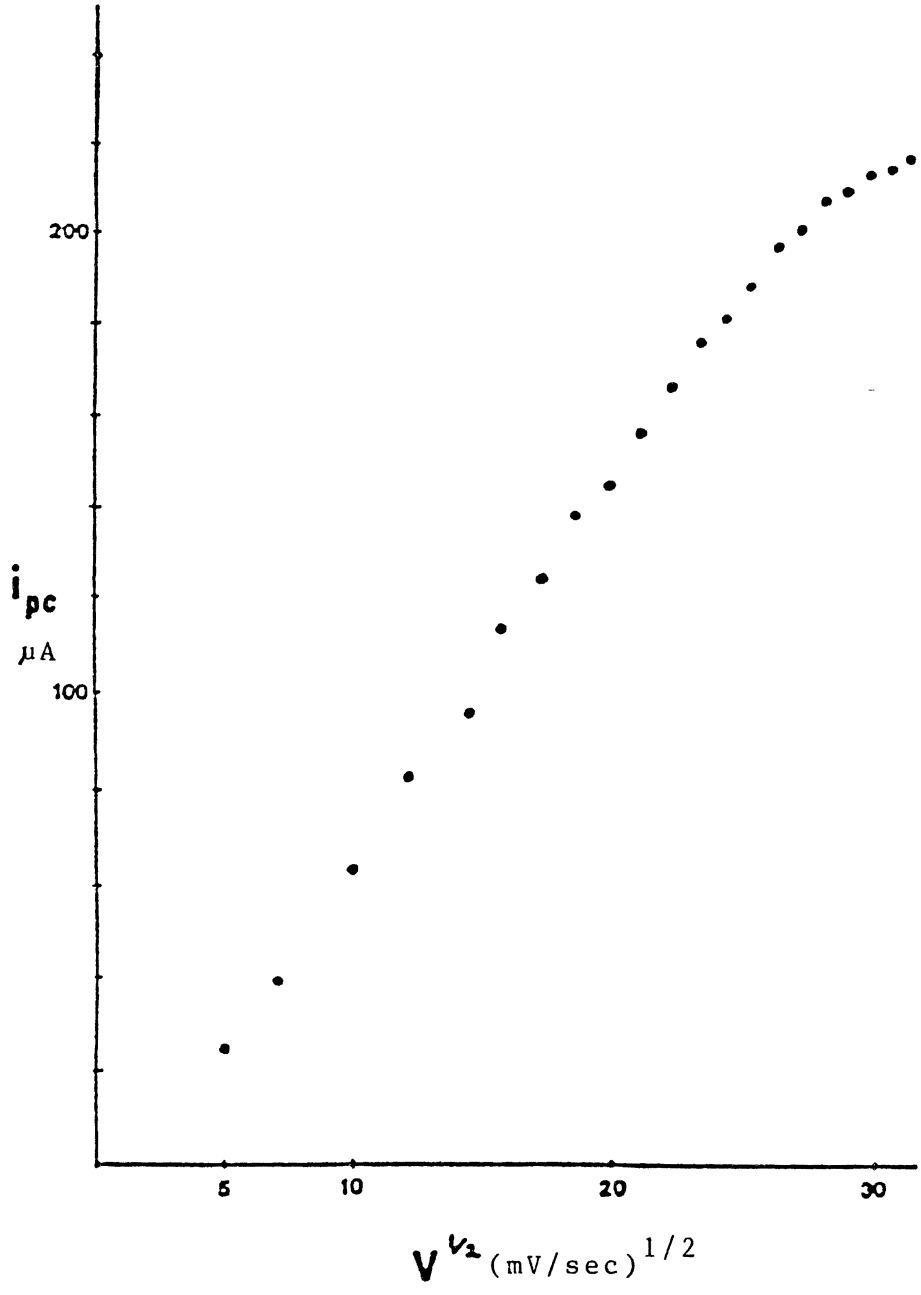


Figure 18. Plot of cathodic peak current versus square root of scan rate; 2% w/w MCPE $Fe(B)_3 \cdot 2ClO_4$, 1.0 M $NaClO_4$, pH 4.00

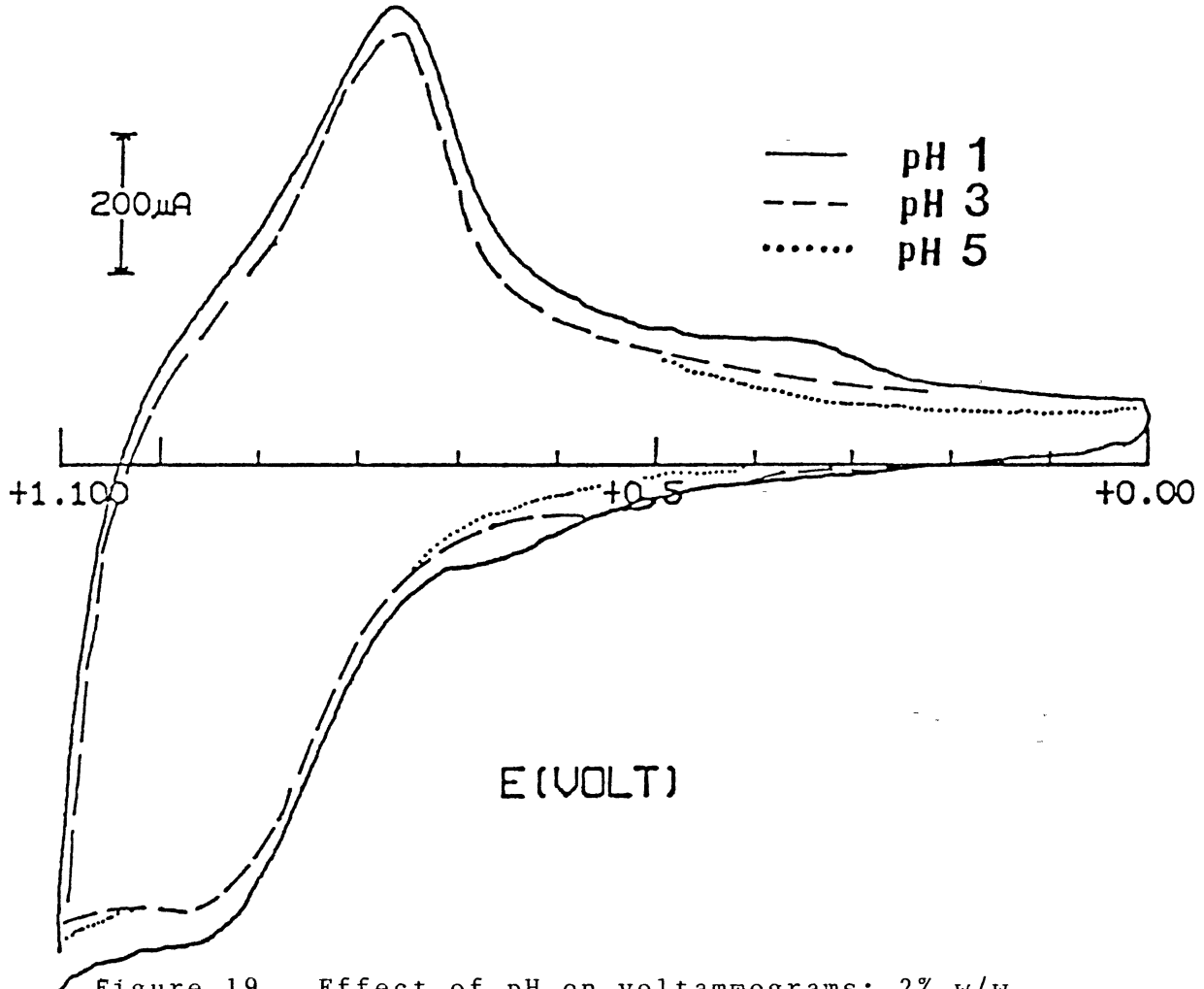


Figure 19. Effect of pH on voltammograms; 2% w/w $Fe(Bath)_3 \cdot 2ClO_4$, 1.0 M $NaClO_4$ supporting electrolyte, acidified with 3.0 M H_2SO_4, scan rate 250 mV/sec

overlay of cyclic voltammograms of the perchlorate complex CME under various low pH conditions. The voltammograms show the same basic qualities from pH 1.00 to 5.00 which indicates that the complex is stable in terms of lack of formation of a dimer. The only observable difference seems to be an approximate 5% increase in peak currents at the lower pH.

Chronocoulometric Studies

Chronocoulometry is an electrochemical technique which can be best described as a "step" technique. Figure 20 provides an illustration of the parameters that are used in a typical chronocoulometric experiment. The response consists of three components: 1) diffusing reactants, 2) electrode double layer, and 3) adsorbed species. Figure 21 shows typical electrode responses and the associated Anson plot for an untreated and treated electrode. The charge produced as the potential is stepped up (or down) can be described by the integrated Cottrell equation:

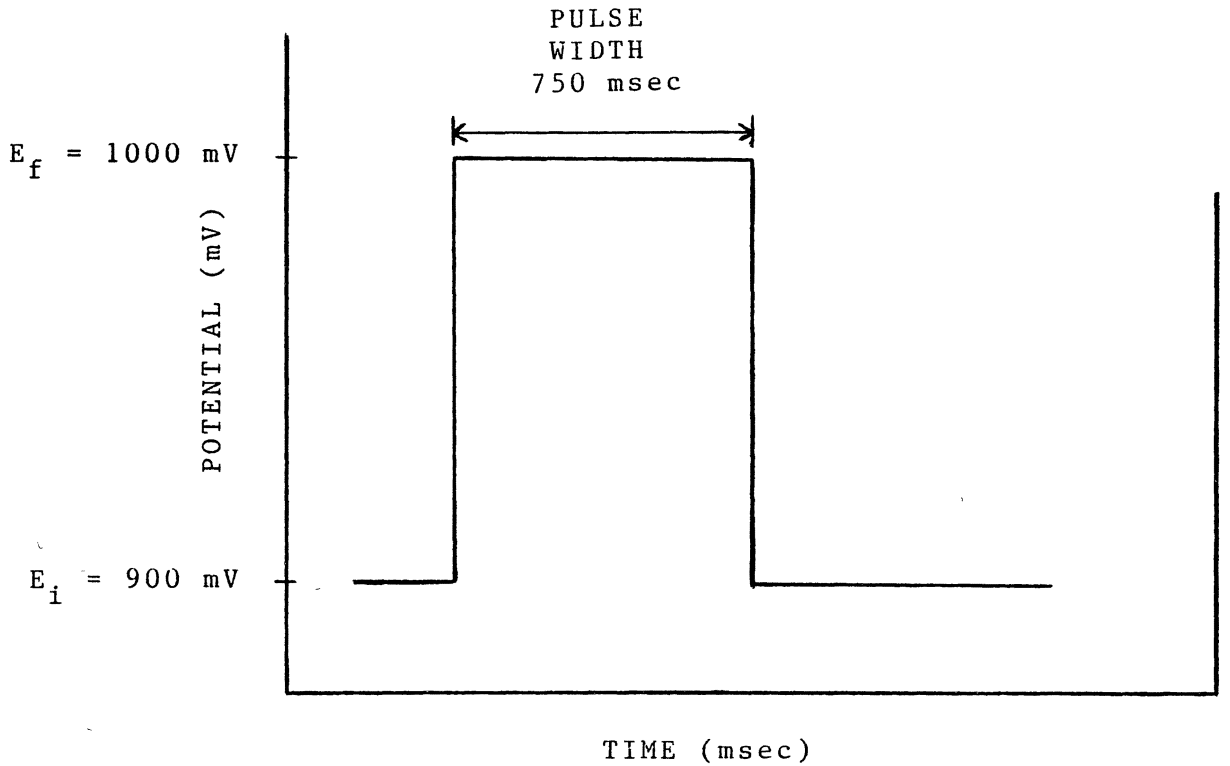


Figure 20. Diagram of the potential step used in the chronocoulometry study

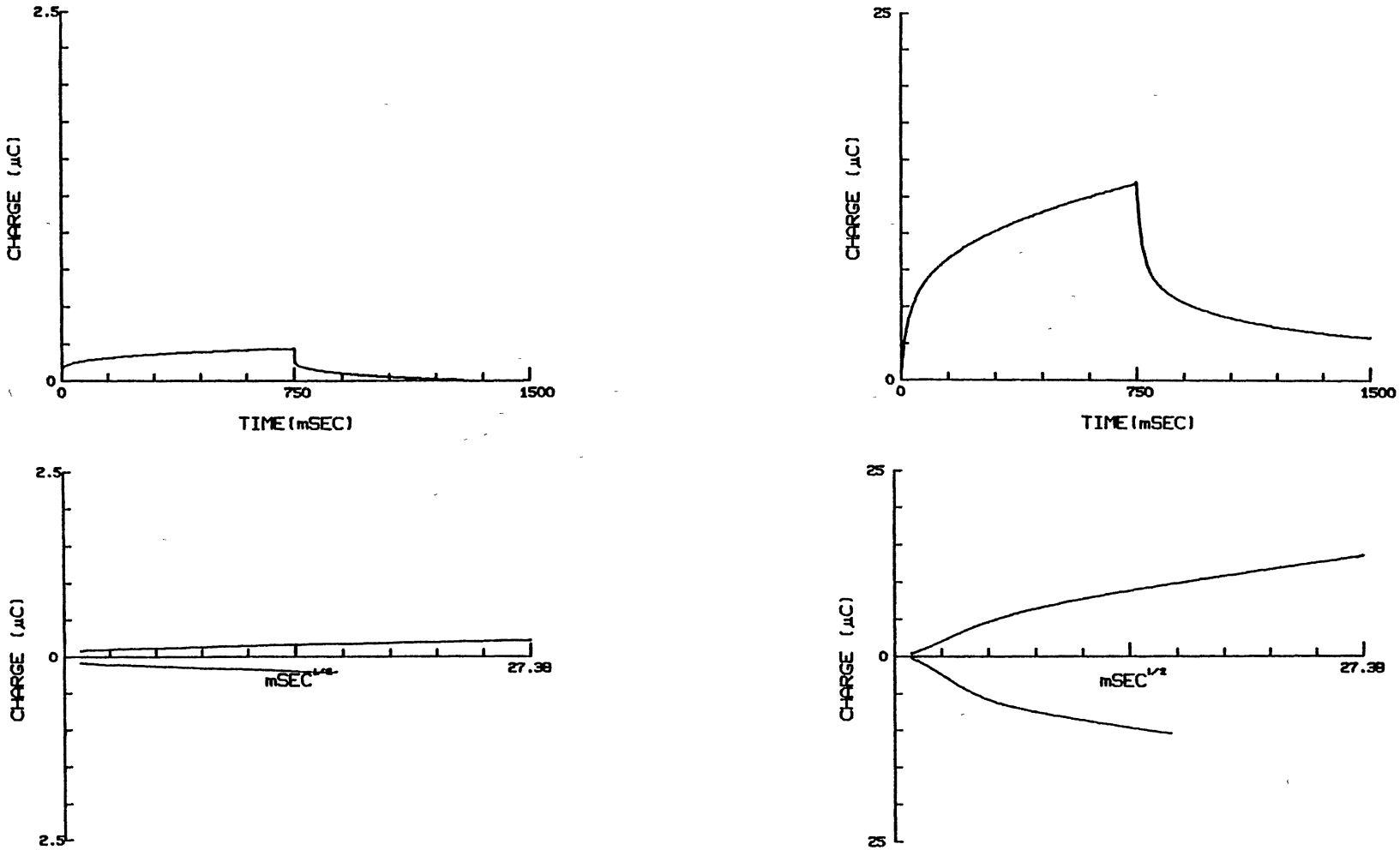


Figure 21. Chronocoulometric plots (top) with their respective Anson plot (bottom); A: before surfactant treatment; B: after surfactant treatment; 2% w/w $Fe(Bath)_3 \cdot 2ClO_4$, 1.0 M $NaClO_4$ supporting electrolyte, E_i = 900 mV, E_f = 1000 mV, pulse width 750 msec

$$Q = \frac{2nFACD^{1/2} t^{1/2}}{\pi^{1/2}} + Q_{dl} + nFA\Gamma \qquad (3)$$

Q = charge, coulombs
n = number of electrons exchanged, equiv/mol
F = Faraday's constant, 9.65×10^4 C/mol
A = electrode area, cm^2
D = diffusion coefficient, cm^2/sec
C = concentration, mol/cm^3
t = time, sec
Q_{dl} = double layer capacitance, coulombs
Γ = surface excess of reactant due to adsorption, mol/cm^2

To separate the components, a plot of Q versus $t^{1/2}$ can be made which is commonly referred to as an Anson plot. The slope of the line is $2nFACD^{1/2}$ while the intercept is $Q_{dl} + nFA\Gamma$. By subtracting the intercept of the reverse step from the intercept of the forward step Q_{dl} can be eliminated if it is assumed that it is the same for both steps. This leaves a value of $nFA(\Gamma_{red} - \Gamma_{ox})$ which can be used to indicate whether an excess of the oxidized or reduced form adsorbs at the electrode surface.

The initial and final potentials for the chronocoulometry experiments were chosen from a cyclic voltammogram of the perchlorate complex MCPE. $E_i = E_{pa} + 100$ mV and $E_f = E_i + 100$ mV to insure that the experiment would be conducted in the anodic region. The final values were $E_i = 900$ mV and $E_f = 1000$ mV. A pulse width of 750 msec was used because it gave better correlation coefficients for the Anson plots.

Table I & II compares data obtained from a blank CPE, a

perchlorate complex MCPE, and a salicylate complex MCPE before and after treatment with a surfactant. Comparison was also made with an electrode surface that had been resmoothed after surfactant treament. Measurements were made such that the "tooth paste" effect had already reached its maximum so that the swelling of the paste would not be a factor. The forward step (fwd.) and the reverse step (rev.) are evaluated to compare the differences between the oxidized form and the reduced form.

TABLE I

CHRONOCOULOMETRIC RESPONSE
COMPARISON OF SLOPES

	Blank CPE		ClO_4^-		Salicylate$^-$	
	fwd.	rev.	fwd.	rev.	fwd.	rev.
untreated	0.011	0.009	0.019	0.016	0.011	0.002
treated	0.011	0.009	0.076	0.072	0.481	0.202
resmoothed	0.013	0.010	0.037	0.036	0.440	0.249

TABLE II

CHRONOCOULOMETRIC RESPONSE
COMPARISON OF INTERCEPTS

	Blank CPE		ClO_4^-		Salicylate$^-$	
	fwd.	rev.	fwd.	rev.	fwd.	rev.
untreated	0.150	0.154	0.157	0.171	0.064	0.127
treated	0.151	0.144	0.637	0.662	3.779	4.240
resmoothed	0.150	0.169	0.310	0.320	2.732	3.295

After the surfactant treatment, the blank CPE shows no change in either slope or intercept and no apparent increase in area. This is a reasonable result due to the fact that there are no active sites. Before surfactant treatment the modified electrodes show slopes of comparable values indicating similar electrode/solution interfaces. The perchlorate complex MCPE shows a significant increase in slope and intercept as compared to the blank. This is caused by the removal of the oil film at the electrode surface, thus exposing the complex to the solution interface. The fact that the slope and intercept increase by the same proportions suggests that the concentration term in the slope and the term in the intercept are one in the same. Considering the time scale on which the experiment takes place the complex would appear to be immobilized which is equivalent to being adsorbed on the surface.

The salicylate complex MCPE showed a much more significant increase in both slope and intercept compared to the perchlorate complex after the surfactant treatment. Comparing the respective increases reveals some inconsistency in that they do not increase by the same proportions. This may be explained by the fact that the salicylate form of the paste shows a more dramatic "toothpaste" effect than the perchlorate form. The salicylate form may also be disintegrating and thus continually renewing its surface.

When one evaluates the slopes of the forward step with the reverse step for the perchlorate form they are very comparable; this is not so for the salicylate form. The forward step was consistently higher than the reverse step which would be expected for a quasi-reversible electron exchange. At the given step potentials the complex is more easily oxidized than reduced. This is reflected in the intercepts as the reverse step being significantly higher than the forward. The perchlorate form is operating under a common ion from the electrolyte solution and thus gives a predictable behavior. The salicylate form would be operating under mixed counterion conditions of salicylate and perchlorate. This could have a significant effect on the double layer capacitance, Q_{dl}.

Conclusions

The above experiments indicate that the optimum amount of modifier is in the range from 2-5%. More than 5% does not seem to increase the response significantly and would not be making efficient use of the modifier. Using less than 2% would require stricter control since this is on the steeply rising portion of the electrode response curve (Fig. 16). Small changes in the amount of modifier would result in larger changes in electrode response. A percentage between 2-5% is on the plateau portion of the curve and thus the preparation would not have to be as strict.

While the leaching of the complexes could not be observed spectrophotometrically, it was observed electrochemically. The linearity of the i_{pc} versus $v^{1/2}$ plot gives added confirmation to the diffusion process that is occurring.

Although the salicylate complex gave consistently higher responses and the rate of leaching is approximately 3 times less than the perchlorate complex, the perchlorate complex was chosen as the preferred modifier because it forms a more physically stable paste. This is based on the overall smoothness of its curve (Fig. 17) and minor appearance of the "tooth paste" effect. The salicylate complex on the other hand produces a more erratic curve and suffers from a more pronounced "tooth paste" effect. It is noted that even though the cathodic peak current decreases

about 37% for the perchlorate complex after 8 hours of use, the peak current is still of significant magnitude.

The complex appears to be chemically stable under low pH conditions which is essential for its practical application. In fact a slight increase in sensitivity may be realized at extremely low pH's.

Chronocoulometry studies show how the surfactant treatment removes the oil film at the electrode surface and thus exposes the modifier to the electrolyte solution. Given the time scale under which the experiments are done, the complex behaves as if it is immobilized at the surface. The perchlorate form follows a more consistent pattern when comparing the slopes and intercepts. On the other hand the salicylate form shows some discrepencies which are due to the fact that mixed counterions are involved.

From these studies, it appears that the perchlorate complex would be the most suitable modifier for the MCPE in terms of physical and chemical stability. The next chapter deals with the practical application of this electrode in a continuous flow system.

CHAPTER IV

APPLICATION OF THE MODIFIED CARBON PASTE ELECTRODE IN A CONTINUOUS-FLOW SYSTEM

Besides furthering the knowledge of carbon paste electrodes modified by admixing, one of the most important goals is the practical application of this modified carbon paste electrode (MCPE). This chapter describes the rationale for using amperometric detection in a continuous flow system and the operating performance of the MCPE in this configuration. The gas used for rating the performance was $NO_2(g)$, an atmospheric target pollutant.

Experimental

Reagents

All chemicals were of reagent grade unless otherwise noted. Gaseous NO_2 was made by exposing HNO_3 (Fisher Scientific Company, Fairlawn, NJ) in a sealed glass container to sunlight. The gas was standardized for calibration purposes using a method outlined by M. J. Taras (71). The container contained a rubber septum to allow withdrawing of gas by a syringe as needed. All other chemicals have been previously described.

The carrier solution was composed of 0.10 M $NaClO_4$ acidified to pH 4.00 with 60% perchloric acid (Allied Chemical, Morristown, NJ). The carrier flow rate was measured to be 2.3 mL/min.

Apparatus

For amperometric detection an LC-4B potentiostat/amplifer (Bioanalytical Systems) was used as was a thin layer cell (Bioanalytical Systems) and a Ag/AgCl, 3 M KCl reference electrode (Bioanalytical Systems). The auxilliary electrode consisted of a small metallic (stainless steel) tube attached to the reference cell holder; this tube also served as the waste exit for the samples.

The injection valve was a Rheodyne type 50 four-way Teflon rotary valve. The tubing used for carrier and sample transport was of Teflon (1.07 mm i.d., Cole-Palmer, Chicago, IL). The sample loop was 2.5 cm long which translates into a sample size of 22.5 ul. Figure 22 illustrates the system used.

With the valve (V) in the appropriate position (fill), the sample loop is filled with NO_2(g)/air. Excess gas is passed on to waste. This allows for consistency in sample size which may have an effect on electrode response. The valve is then switched to the inject position so that the sample loop comes in-line with the carrier stream. The

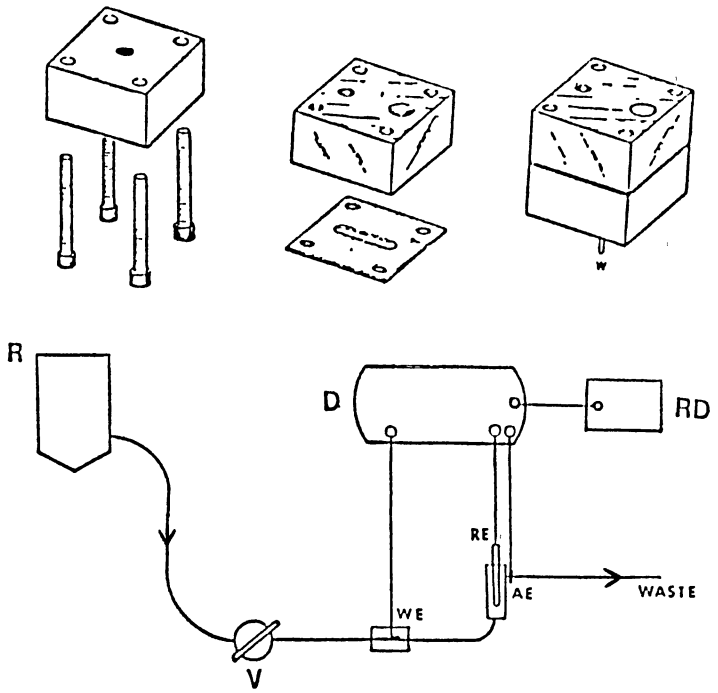


Figure 22. Configuration of Continuous-Flow System

unique feature about the valve is that it allows for the continual flow of the carrier solution through the system regardless of whether the valve is in the fill or inject position. The importance of this will be discussed in a later section.

The electrolyte/carrier stream is fed into the system by means of gravity flow so as to minimize noise caused by turbulence in the flow stream. As it is used here, the sample will travel as a well-defined gas bubble from the point of injection to the working electrode (WE). As the sample passes over the working electrode a response will be measured due to the oxidation or reduction of the analyte or modifier, provided that an appropriate potential is applied. This current response is ideally directly related to analyte concentration. The sample will then pass out to waste.

The WE is held at a constant, preselected value with respect to a reference electrode (RE) by means of the potentiostat. To maintain a constant potential, "communication" with the WE is done via an auxilliary electrode (AE). The amplifier part of the LC-4B converts the current response at the WE to a voltage which can be amplified and fed to a strip chart recorder (RD).

Some of the merits of using this system are that it provides easy, consistent, and rapid sample handling. It can also be automated quite easily. The high sensitivity and selectivity will give it competitive limits of detection

and wide utility. Because of the simplicity of the design, it is rugged, compact, relatively inexpensive, and can be easily tailored to suit the needs of each individual analysis.

Results and Discussion

Description of Electrode Response

Oxidation or reduction processes at the electrode surface will manifest themselves as peaks which are proportional to $NO_2(g)$ concentration as shown in Figure 23.

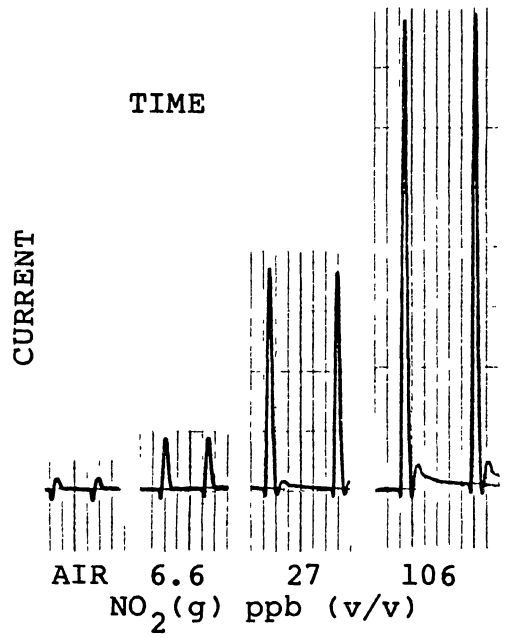


Figure 23. Flow-injection peaks of $NO_2(g)$

There are two prominent features shown by the electrode response. The initial downward peak is due to the momentary change in resistance between the WE and the AE as the gas plug travels between the two electrodes. The carrier stream has the whole cross section of the tubing available for conducting current and will have a certain amount of resistance associated with it. With the introduction of the gas plug the full cross section is not available, only the micro conducting channels of electrolyte that exist in the tubing wall are available for conducting current. It can be seen that these channels are going to have a total resistance that is less than the previous condition.

From ohm's law voltage/resistance = current, the voltage will be constant due to the nature of the electrochemical technique and the resistance will be switched back and forth between two "constant" values. We see that the current will change as the gas plug travels into and out of the system.

The positive peak arises from the re-establishment of the equilibrium that will exist at the electrode surface at a given potential. According to the Nernst equation, at a given potential there will exist a given Fe(II)/Fe(III) ratio. Reaction of the $NO_2(g)$ with the iron centers will change this ratio causing a dynamic condition aimed at re-establishing the original ratio, i.e. a current flow.

Hydrodynamic Voltammogram of $NO_2(g)$

In this study the electrode response to $NO_2(g)$ at various fixed potentials is evaluated to obtain the potential which produces the maximum sensitivity. The potentials chosen were 0.00, 0.30, 0.60, and 0.90 volts versus a Ag/AgCl, 3 M KCl reference electrode. These potentials were chosen because the background current due to the supporting electrolyte was minimal. This becomes a shortcoming at higher potentials where the electrode becomes much more sensitive to changes in flow rate. Switching the injection valve from fill to inject causes a momentary stop in carrier flow which will manifest itself as a small peak on the chart recorder.

Figure 24 represents a typical hydrodynamic voltammogram of $NO_2(g)$ measured in nanoamperes. To further evaluate the reproducibility of injections and to better ascertain the degree of enhanced electrode response, 0.00 and 0.90 volts were chosen as detecting potentials. Table III typifies the results:

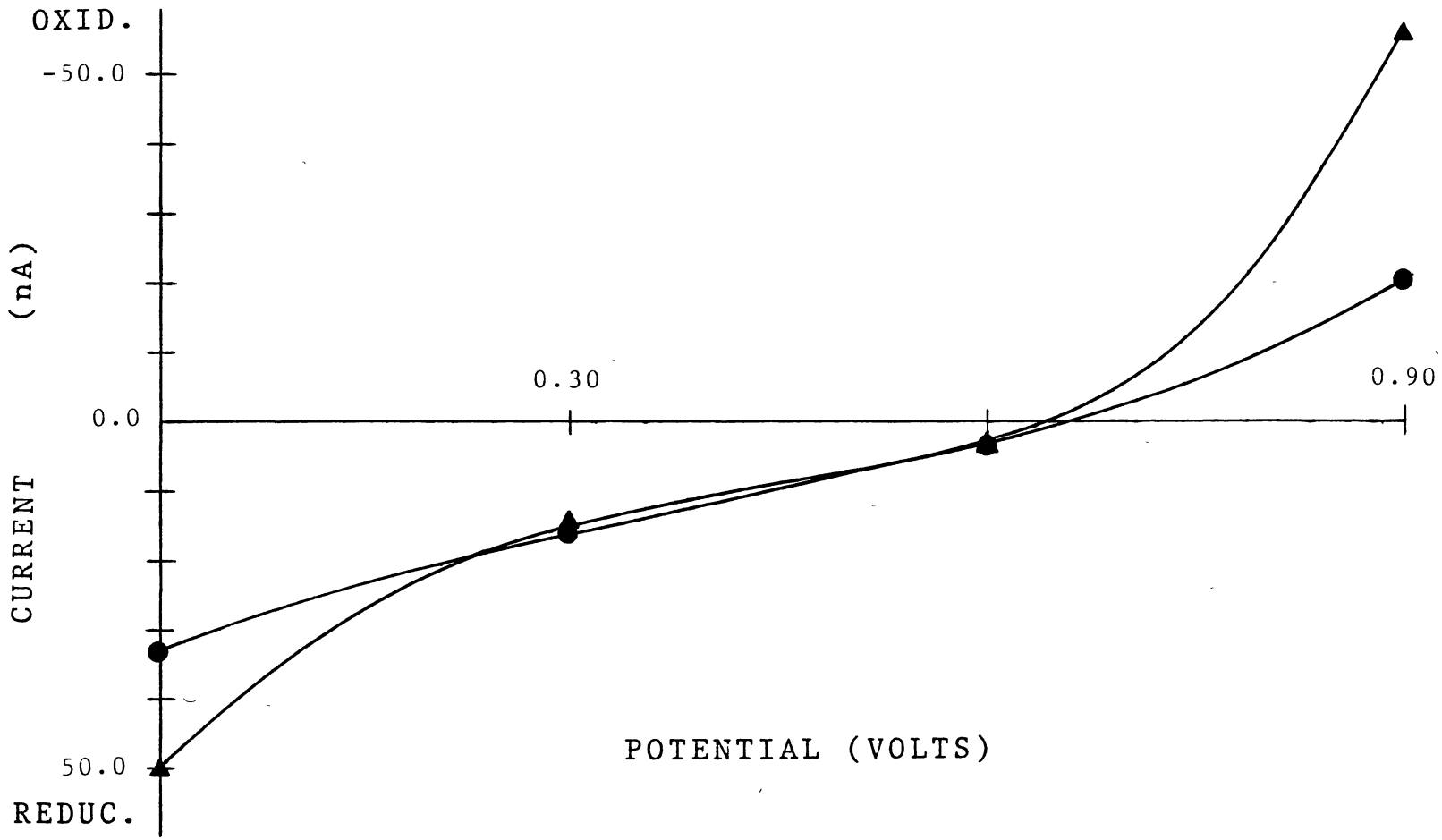


Figure 24. Hydrodynamic voltammogram of $NO_{2(g)}$; carrier 0.10 M $NaClO_4$, pH 4.00; (●) CPE, (▲) 10% $Fe(B)_3$ MCPE.

TABLE III

COMPARISON OF CPE AND MCPE

Trial		CPE	MCPE w/10% modifier
1[a]	i	58.0	73.6
	RSD	2.4%	3.4%
2[a]	i	47.8	78.2
	RSD	4.6%	2.6%
1[b]	i	22.9	50.5
	RSD	7.1%	7.5%
2[b]	i	25.3	53.4
	RSD	13.3%	3.6%

[a]Potential fixed at 0.00 volts.
[b]Potential fixed at 0.90 volts.

It is evident that there is enhancement of sensitivity especially at the higher potential, but the RSD is appreciably higher. This was observed even for the blank injections of air. It is known that application of a high potential will modify the surface of the electrode (16). This modification process could increase the sensitivity of the electrode and account for the dramatic increase in the RSD.

It is also vital that the gas sample passes cleanly into and out of the thin layer cell at a consistent rate without any residual gas bubbles becoming entrapped in the

cell. Inconsistent flow rates cause differing contact times of the sample with the electrode surface. As expected, increasing the contact time causes an increased response. If the entrapment of bubbles occurs the baseline becomes somewhat noisy and the appearance of extraneous peaks may occur.

The following equations show the more probable mechanisms that explain the enhanced electrode response due to addition of the modifier:

At 0.00 V, reduction currents:

$$N(IV) + Fe(II) \longrightarrow N(III) + Fe(III)$$
$$Fe(III) + e^- \longrightarrow Fe(II) \qquad (1)$$

At 0.90 V, oxidation currents:

$$N(IV) + Fe(III) \longrightarrow N(V) + Fe(II)$$
$$Fe(II) \longrightarrow Fe(III) + e^- \qquad (2)$$

Also competing at the graphite surface reduction currents:

$$N(IV) + e^- \longrightarrow N(III) \qquad (3)$$

or oxidation currents:

$$N(IV) \longrightarrow N(V) + e^- \qquad (4)$$

The mechanisms proposed are of the chemical-electrochemical (CE) type where the iron centers first react chemically with $NO_2(g)$ and then return to their original oxidation state electrochemically. In this way, an iron center participates in a catalytic cycle allowing for more

efficient electron transfer.

Further experiments show that the response is due to the reaction of the electrode surface with the $NO_2(g)$ in the gas phase and not other products that may be formed by the dissolving of $NO_2(g)$ into the aqueous phase i.e. HNO_3 and NO. This is shown by the placement of a piece of porous Teflon tubing between the injection valve and the WE. The Teflon tubing allows for the degassing of the sample before reaching the WE. When this configuration was used no signal was observed upon injecting a gas sample. This contrasts with the injection of $SO_2(g)$ which gives an appreciable response even after degassing.

Effect of Surfactant Treatment

During this study it was thought that the surfactant treatment would enhance the electrode response and indeed this was the case. Figure 25 illustrates typical responses of $NO_2(g)$ at the electrode surface before and after surfactant treatment.

The best enhancement was observed in the lower potential region (-0.20 to 0.40 volts) were the response was seen to increase by a factor of 2 to 3 times. At the higher potentials, 1.00 and 1.20 volts, it was observed that the untreated electrode gave the higher response.

This behavior can be explained by referring to the mechanisms outlined in equations 1-4. At the lower

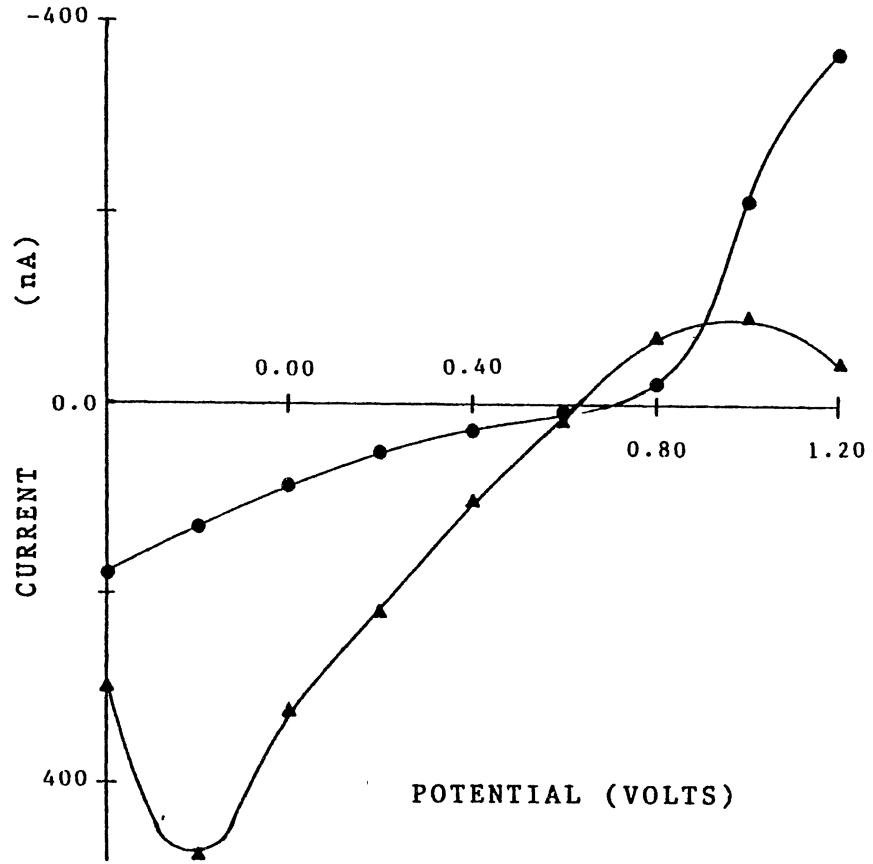


Figure 25. Hydrodynamic voltammogram of $NO_{2(g)}$; carrier 0.10 M $NaClO_4$, pH 4.00; (●) untreated MCPE, (▲) surfactant treated MCPE.

potentials electron transfer predominantly occurs through the CE mechanism (eqn. 2). Treatment with surfactant exposes more complex for mediation and thus enhances signal response. At the higher potentials, electron transfer predominantly occurs through an electrochemical mechanism that relies on graphite surface area (eqn. 4). The CPE treated with surfactant having more graphitic surface area as compared to the MCPE will give the higher signal response.

Table IV shows the further evaluation of the surfactant treatment at 0.20 V which seems to take the best advantage of both modifier and surfactant treatment.

TABLE IV

COMPARISON OF ELECTRODE RESPONSE TOWARDS NO_2(g) BEFORE AND AFTER SURFACTANT TREATMENT

Trial	i_c (nA) before	i_c (nA) after	ratio after/before
1	22.4	42.0	1.9
	7.1% RSD	8.4% RSD	
2	23.2	45.9	2.0
	3.4% RSD	6.5% RSD	

Table V shows that the surfactant treatment gives a considerable enhancement at the given potential. A major drawback found was that the RSD increased about two-fold

from around 4% to about 8%. By removing the oil film from the surface of the electrode it becomes less mechanically stable. Under flowing conditions micro particles of graphite and/or complex are probably being removed from the surface thus exposing new surfaces. This results in a continual change in the number of reactive sites on the electrode surface. This could account for the increase in the RSD.

Another potential drawback is the swelling of the paste that was observed in Chapter III. The depth of the channel of the thin layer cell is around 0.050 mm. A slight swelling of the paste might cause partial blockage of the channel such that the gas sample does not completely pass over the electrode surface. This results in a decrease in the magnitude of the signal as not all of the electrode surface has been exposed to the gas. This problem was not observed even after 4 hours of use. The electrode surface was resmoothed to observe the effect it would have on electrode response. What was observed was a dramatic loss in sensitivity. This is understandable if one considers that resmoothing will partially recoat the electrode surface with an oil film.

Calibration Curve for $NO_2(g)$

As seen from the hydrodynamic voltammograms of $NO_2(g)$ a potential of 0.20 volts would provide maximum sensitivity

and minimal background signal from the blank. As such this potential was chosen to compare the effect of different modifications on the sensitivity and dynamic range of the electrode. Figure 26 shows a typical $NO_2(g)$ calibration curve for an untreated and treated electrode. The RSD's of the two lower concentrations were somewhat higher, just under 4%, while the higher concentrations were relatively lower, around 1%. The LOD (blank + 3σ) was calculated as 1.2 ppb (v/v) $NO_2(g)$ and the linear range seems to be limited from 1-30 ppb (v/v) $NO_2(g)$. The dynamic range for all practical purposes extends up to 100 ppb (v/v) $NO_2(g)$. Beyond this the electrode appears to become saturated. The surfactant treated electrode response is characterized by much higher RSD's around 18% at the lower concentrations and 7.5% at the higher concentration. The LOD is increased to 13.2 ppb (v/v) $NO_2(g)$. The reasons for the higher RSD's have been discussed previously. There appears to be an increase in linear range extending up to 300 ppb (v/v) $NO_2(g)$ but the sensitivity is much lower at the lower concentrations of $NO_2(g)$ as compared to the untreated electrode. The removal of the oil film eliminates the saturation effect such that now the $NO_2(g)$ is free to react directly with the active centers.

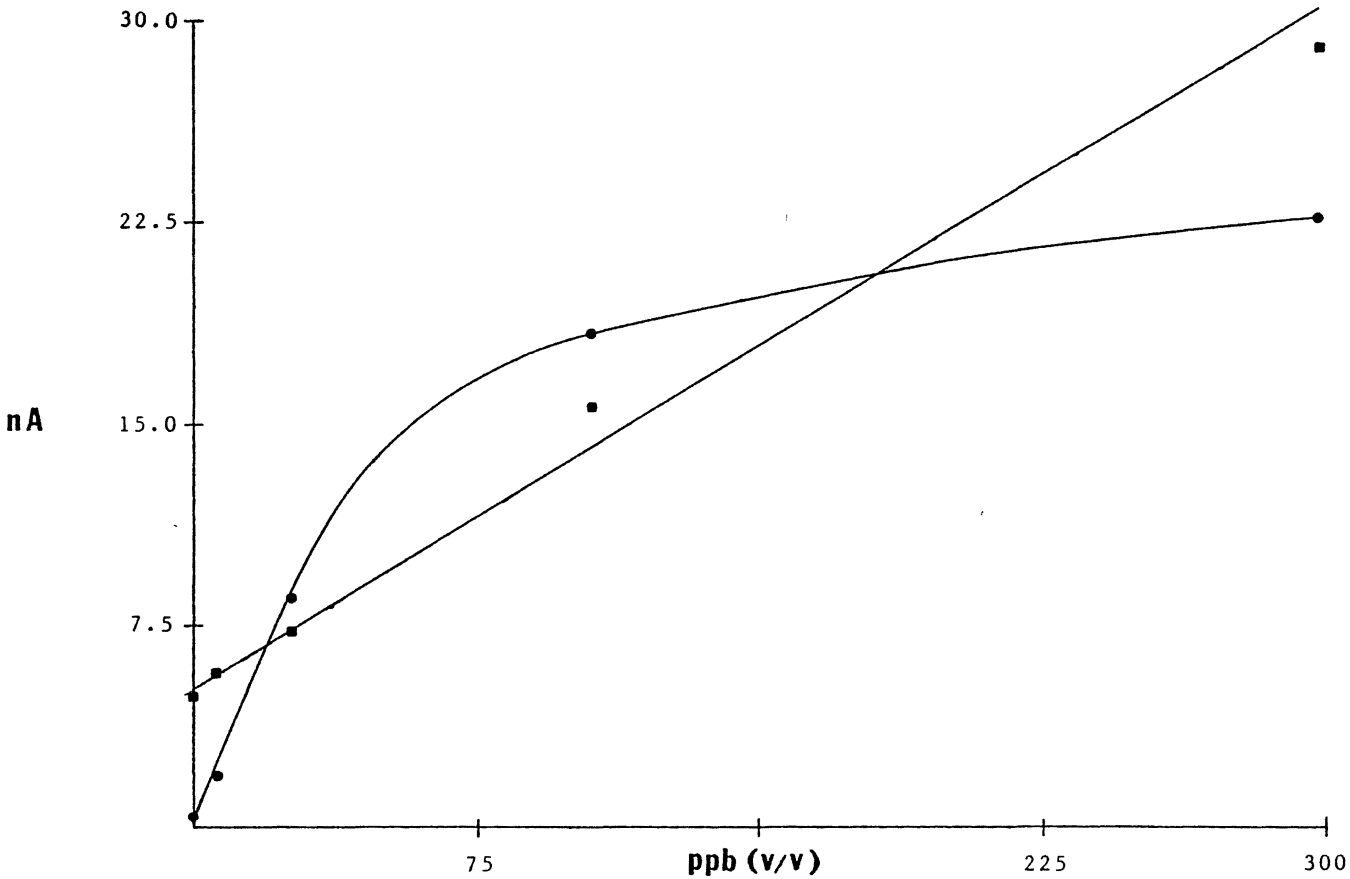


Figure 26. Calibration curve for NO_2(g), ppb (v/v); 10% $Fe(B)_3 \cdot 2ClO_4$ MCPE, (●) untreated, (■) surfactant treated electrode

Conclusions

At higher potentials the electrode showed much less reproducibility between injections. This may be due to a modification process that is occurring at such potentials (16). For this reason, a lower potential was chosen to minimize this effect and, indeed, worked quite satisfactorily. Upon addition of the modifier to the carbon paste a small enhancement in reduction currents is seen due to the catalytic effect of the iron centers. This results in more efficient electron transfer.

The dynamic range of the untreated electrode seems to be somewhat limited. This appears to be caused by the saturation of the thin oil layer that coats the graphite particles with $NO_2(g)$. The diffusion of the $NO_2(g)$ into and out of the oil film then becomes the rate limiting step. The removal of this film by surfactant treatment extends the dynamic range since the diffusion process has been minimized and the $NO_2(g)$ can react directly with the iron centers. In this configuration the electrode surface has lost some of its mechanical stability due to lack of binder. Because of this, the electrochemical surface area is continually changing as micro particles of grapite and complex are being detached from the surface. This would cause an increase in the RSD's since the $NO_2(g)$ will be reacting with a differing electrode surface.

All things considered, the untreated electrode shows

the better response at lower concentrations of $NO_2(g)$ in terms of a lower LOD, higher sensitivity, and better reproducibility. The surfactant-treated electrode, on the other hand, offers a larger linear dynamic range giving it a wider utilization range. Although the RSD's are higher and given the low levels of concentration, the electrode responds very satisfactorily.

CHAPTER V

SUMMARY AND CONCLUSIONS

Of the many methods of modifiying an electrode surface, admixing an insoluble modifier into a carbon paste electrode was chosen mainly because 1) it can be prepared easily, 2) one has more control over the degree of modification, 3) the electrode surface is easily renewed, and 4) there is greater flexibility in the types of modifiers which can potentially be incorporated.

Several ligands containing the -N=C-C=N- moiety (as in 1,10-phenanthroline) along with several counteranions were evaluated for their ability to form an insoluble electroactive complex. Tris 4,7-diphenyl-1,10-phenanthroline Fe(II) precipitated with either perchlorate or salicylate was finally chosen as the modifier of choice because of its insolubility. A cyclic voltammogram of the modified electrode yielded one discernable reduction peak around 0.840 volts versus a 3.0 M Ag/AgCl (RE) which can be attributed to the prescence of the incorporated iron complex. The ligand itself can be incorporated into the carbon paste and is shown to be capable of complexing Fe(II). Treatment of the complex modified electrode with a surfactant greatly enhances the electrode response by

removing the thin oil film on the electrode surface. This electrode was futher characterized by cyclic voltammetry and chronocoulometry.

Initial contact of the modified paste with the electrolyte solution caused a slight swelling (more so using surfactant as counteranion) of the paste which could be detected electrochemically. After an initial swelling period (approx. 2 h) the modifier is observed to leach from the paste. Fortunately the electrode retains most of its initial response even after 12 hours of soaking in electrolyte solution.

The electron transfer for the MCPE was found to be quasi-reversible with a peak separation of around 175 mV. A plot of scan rate versus peak current showed that the electron exchange is diffusion controlled. This is another indication of modifier leaching from the paste.

Since ferroin is known to form a dimer when oxidized at low pH's there was concern that the derivative used would also show the same behavior. Cyclic voltammograms of the MCPE at pH's from 1.00 to 5.00 revealed that this was not the case for the given complex. All the voltammograms showed the same basic qualities indicating stability of the MCPE.

Chronocoulometry experiments shows how the surfactant treatment exposes the complex to the electrolyte solution through removal of the oil film that exists at the electrode surface. It is also observed that the complex behaves as if it were immobilized at the electrode surface. Due to paste

swelling the salicylate form shows a higher number of active sites compared to the perchlorate form. This is evident when comparing slopes and interecepts. Since the salicylate form is operating under mixed counterion conditions this may have a significant effect on the value of the double layer capacitance giving rise to extremely high intercept values.

Evaluation of the MCPE in a continuous flow system using $NO_2(g)$ as the analyte of interest reveals that the addition of 10% modifier to the carbon paste enhances the amperometric response by a factor of two. The increased response can be explained by the participation of the iron centers in a catalytic cycle. The LOD for the MCPE was found to be 1.2 ppb (v/v) $NO_2(g)$ with very low RSD's (1-4%) and a dynamic range from 1.2-30 ppb (v/v). Beyond this range the electrode behaves as if it were saturated. After treating the electrode with surfactant the LOD is raised by a factor of 10 but the linear dynamic range extends beyond 300 ppb (v/v) $NO_2(g)$. The major drawback is that the RSD's are higher (7.5-18%). Given the low concentrations of $NO_2(g)$ used this is not too unreasonable.

The use of electrochemical detection is shown to offer very competitive limits of detection using very inexpensive instrumentation. The modification of the electrode with the Fe(II) complex and surfactant treatment is shown to enhance the electrode response.

BIBLIOGRAPHY

1. Murray, R. W.; Ewing, A. G.; Durst, R. A. Anal. Chem. 1987, 59, 379A.

2. Adams, R. N. In "Electrochemistry at Solid Electrodes"; Marcel Dekker: New York, 1969; pp 19-29, 280-283.

3. Sawyer, D. T.; Roberts, J. L. Jr. In "Experimental Electrochemistry for Chemists"; John Wiley & Sons: New York, 1974; pp 60-74.

4. Gaylor, V. F.; Conrad, J. H.; Landerl, J. H. Anal. Chem. 1957, 29, 224.

5. Adams, R. N. Anal. Chem. 1958, 30, 1576.

6. Marcoux, L. S.; Prater, K. B.; Prater, B. G.; Adams, R. N. Anal. Chem. 1965, 37, 1447.

7. Albahadily, F. N.; Mottola, H. A. Anal. Chem. 1987, 59, 958.

8. Armentrout, D. N.; Mc Lean, J. D.; Long, M. W. Anal. Chem. 1979, 51, 1039.

9. Anderson, J. L.; Chesney, D. J. Anal. Chem. 1980, 52, 2156.

10. Weisshaar, D. E.; Tallman, D. E.; Anderson, J. L. Anal. Chem. 1981, 53, 1809.

11. Anderson, J. E.; Tallman, D. E.; Chesney, D. J.; Anderson J. L. Anal. Chem. 1978, 50, 1051.

12. Klatt, L. N.; Connell, D. R.; Adams, R. E.; Honigberg, I. L.; Price, J. C. Anal Chem. 1975, 47, 2470.

13. Ortiz, Patricia I. Unpublished results.

14. Coughlin, R. W.; Ezra, F. S. Environ. Sci. Tech. 1968, 2, 291.

15. Mattson, J. S.; Mark, H. B. "Activated Carbon"; Marcel Dekker: New York, 1971; Chap. 3, pp. 37-86.

16. Rice, M. E.; Galus, Z.; Adams, R. N. J. Electroanal. Chem. 1983, 143, 89.

17. Cheek, G. T.; Nelson, R. F. Anal. Lett. 1978, 11, 393.

18. Albahadily, F. N. Thesis.

19. Kamin, R. A.; Wilson, G. S. Anal. Chem. 1980, 52, 1198.

20. Ravichandran, K.; Baldwin, R. P. Anal. Chem. 1983, 55, 1586.

21. Kuwana, T.; French, W. G. Anal. Chem. 1964, 36, 241.

22. Schultz, F. A.; Kuwana, T. J. Electroanal. Chem. 1965, 10, 95.

23. Korfhage, K. M.; Ravichandran, K.; Baldwin, R. P. Anal. Chem. 1984, 56, 1514.

24. Santos, L. M.; Baldwin, R. P. Anal. Chem. 1987, 59, 1766.

25. Santos, L. M.; Baldwin, R. P. Anal. Chim. Acta 1988, 206, 85.

26. Baldwin, R. P.; Christensen, J. K.; Kryger L. Anal. Chem. 1986, 58, 1790.

27. Thomsen, K. N.; Kryger, L.; Baldwin, R. P. Anal. Chem. 1988, 60, 151.

28. Takeuchi, E. S.; Murray, R. W. J. Electroanal. Chem. 1985, 188, 49.

29. Hynes, C.; Bonakdar, M.; Mottola, H. A. Electroanalysis 1989, 1, 155.

30. Yao, T.; Musha, S. Anal. Chim. Acta 1979, 110, 203.

31. Shu, F. R.; Wilson, G. S. Anal. Chem. 1976, 48, 1679.

32. Matuszewski, W.; Trojanowicz, M. Analyst 1988, 113, 735.

33. Wang, J.; Greene, B.; Morgan, C. Anal. Chim. Acta 1984, 158, 15.

34. Kalcher, K. Anal. Chim. Acta 1985, 177, 175.

35. Wang, J.; Bonakdar, M. Talanta 1988, 35, 277.

36. Hernandez, P.; Alda, E.; Hernandez, L. Fres. Z. Anal. Chem. 1987, 327, 676.

37. Hernandez, L.; Hernandez, P.; Ferrera, Z. S. Fres. Z. Anal. Chem. 1988, 329, 756.

38. Geno, P. W.; Ravichandran, K.; Baldwin, R. P. J. Electroanal. Chem. 1985, 183, 155.

39. Kutner, W.; Meyer, T. J.; Murray, R. W. J. Electroanal. Chem. 1985, 195, 375.

40. Lane, R. F. Society for Neurosciences 1981, 7, 34.

41. Bonakdar, M.; Vilchez, J. L.; Mottola, H. A. J. Electroanal. Chem. 1989, 266, 47.

42. Connor, M. P.; Wang, J.; Kubiak, W.; Smyth, M. R. Anal. Chim. Acta 1990, 229, 139.

43. Murray, R. W. In "Electroanalytical Chemistry"; Bard, A. J., Ed.; Marcell Dekker:New York, 1984; Vol. 13, pp. 263-288.

44. Panzer, R. E.; Elving, P. J. Electrochim. Acta 1975, 20, 635.

45. Hummers, W. S.; Offeman, R. E. J. Am. Chem. Soc. 1958, 80, 1339.

46. Evans, J. F.; Kuwana, T.; Henne, M. T.; Royer, G. P. J. Electroanal. Chem. 1977, 80, 409.

47. Evans, J. F.; Kuwana, T. Anal. Chem. 1977, 49, 1632.

48. Ravichandran, K.; Baldwin, R. P. Anal. Chem. 1984, 56, 1744.

49. Watkins, B. F.; Behling, J. R.; Kariv, E.; Miller, L. L. J. Am. Chem. Soc. 1975, 97, 3549.

50. Firth, B. E.; Miller, L. L.; Mitani, M.; Rogers, T.; Lennox, J.; Murray, R. W. J. Am. Chem. Soc. 1976, 98, 8271.

51. Koval, C. A.; Anson, F. C. Anal. Chem. 1978, 50, 223.

52. Wieck, H. J.; Heider, G. H., Jr.; Yacynych, A. M. Anal. Chim. Acta 1984, 158, 137.

53. Oyama, N.; Brown, A. P.; Anson, F. C. J. Electroanal. Chem. 1978, 87, 435.

54. Elliot, C. M.; Murray R. W. Anal. Chem. 1976, 48, 1247.

55. Untereker, D. F.; Lennow, J. C.; Wier, L. M.; Moses, P. R.; Murray, R. W. J. Electroanal. Chem. 1977, 81, 309.

56. Lin, A. W. C.; Yeh, P.; Yacynych, A. M.; Kuwana, T. J. Electroanal. Chem. 1977, 84, 411.

57. Yacynych, A. M.; Kuwana, T. Anal. Chem. 1978, 50, 640.

58. Ianniello, R. M.; Yacynych, A. M. Anal. Chem. 1981, 53, 2090.

59. Izutsu, K.; Nakamura, T.; Takizawa, R.; Hanawa, H. Anal. Chim. Acta 1983, 149, 147.

60. Zagal, J. J. Electroanal. Chem. 1980, 109, 389.

61. Zagal, J.; Bindra, P.; Yeager, E. J. Electrochem. Soc. 1980, 127, 1506.

62. Zagal, J.; Fierro, C. Rozas, R. J. Electroanal. Chem. 1981, 119, 403.

63. Bonakdar, M.; Yu, J.; Mottola, H. A. Talanta 1989, 36, 219.

64. Clark, L. C. Jr.; Wolf, R.; Granger, D.; Taylor, Z. J. Appl. Physiol. 1953, 6, 189.

65. Hasselberger, F. X. In "Uses of Enzymes"; Nelson-Hall: Chicago, 1978; Chap. 9, pp. 103-116.

66. Luque de Castro, M. D.; Valcarcel, M.; Albahadily, F. N.; Mottola, H. A. J. Electroanal. Chem. 1987, 219, 139.

67. Nyasulu, F. W. M.; Mottola, H. A. J. Autom. Chem. 1987, 9, 46.

68. Rios, A.; Luque de Castro, M. D.; Valcarcel, M.; Mottola, H. A. Anal. Chem. 1987, 59, 666.

69. Smith, G. F.; Banick, Wm. M. Jr. Talanta 1959, 2, 348.

70. Rice, M. E.; Galus, Z.; Adams, R. N. J. Electroanal. Chem. 1983, 143, 89.

71. Taras, M. J. in "Colorimetric Determination of Nonmetals"; Boltz, D. F., Ed.; Interscience Publisher: New York, 1958; Chap. IV, pp. 132-134.

2

VITA

Christopher J. Hynes

Candidate for the Degree of

Doctor of Philosophy

Thesis: CARBON PASTE ELECTRODE CHEMICALLY MODIFIED WITH TRIS-4,7-DIPHENYL-1,10-PHENANTHROLINE Fe(II)

Major Field: Chemistry

Biographical:

Personal: Born in Lake Worth, Florida, September 27, 1963, the son of Michael K. and Jane M. Hynes. Resident of Frederick, Oklahoma since 1973.

Education: Received Bachelor of Science degree in Chemistry from Cameron University, Lawton, Oklahoma, 1985; Completed the requirements for the Doctor of Philosophy degree at Oklahoma State University, Stillwater, Oklahoma in May 1991.

Professional Experience: Obtained Commercial Pilot license fixed wing and helicopter 1982; Instructor Pilot license helicopter 1983; Graduate Teaching/Research Assistant, Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma, since August 1985.