To the Graduate Council:

I am submitting herewith a dissertation written by Robert Daniel Shelton entitled "Examination of the Response of Polymer-7,7',8,8'-Tetracyano-quinodimethane Polymer Modified Electrodes to Silver (I) Ions." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

James Q. Chambers, Major Professor

We have read this dissertation
and recommend its acceptance:

Accepted for the Council:

Vice Provost
and Dean of the Graduate School

EXAMINATION OF THE RESPONSE

OF POLYMER-7,7',8,8'-TETRACYANOQUINODIMETHANE

POLYMER MODIFIED ELECTRODES

TO SILVER (I) IONS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Robert Daniel Shelton

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ABSTRACT

The field of polymer modification of electrode surfaces has been intensely researched in the past few years, with much effort being directed towards the detection and quantitation of trace ions in aqueous solutions. The purpose of this thesis has been to study the effect of the incorporation of silver(I) ion into a polymeric-7,7',8,8'-tetracyanoquinodimethane (TCNQ) matrix, using either polyester-TCNQ or a polyurethane-TCNQ. Silver was chosen as a test marker because of its simple one-electron electrochemistry, and because of recent interest in silver-TCNQ optically-active complexes.

Cyclic voltammetry was used to collect data measuring the amount of incorporation of silver(I) ion into the polymer matrix, while spectroscopic methods were used to ascertain the position and oxidation state of the silver within the film. Silver(I) ion was incorporated into the polymer films, following the timed reduction of the film in aqueous electrolytes, by treatment with silver nitrate solutions varying in concentration from 1.0E-1M to 1.0E-8M. Results show that silver(I) ion can be incorporated into polymer-TCNQ films from low ionic strength, quiescent aqueous solutions, conditions which mimic many environmental systems. Silver(I) ion can be detected at concentrations as low as 1.0E-8M after twenty

minutes, a detection limit roughly three orders of magnitude better than standard ion selective electrodes. Data also suggest that the procedure outlined could be applied to the detection of mercury(II) ion, and possibly other ions as well. Spectroscopic information suggests that the silver exists in the film as dispersed silver metal, probably in the form of stable metal clusters.

Finally, this thesis presents some preliminary data on the effect of a magnetic field upon the electrochemical properties of the polymer-TCNQ films. The data indicate that the magnetic field can affect the polymer structure of the film, producing changes in the polymer electrochemistry dependent on the rigidity of the polymer backbone.

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INTRODUCTION AND BACKGROUND MATERIAL

The purpose of this thesis is to present information supporting the possibility of using a polymer-7,7',8,8'-tetracyanoquinodimethane (TCNQ) modified electrode to detect low concentrations of silver (I) ion in low ionic strength, quiescent solutions. A large number of methods have been developed for the detection of trace metal ions, including silver, and these methods tend to fall into two general categories: flame spectroscopy and voltammetry.

Spectroscopy of metal ions can be broken into three main areas: 1) absorbance of incident radiation to produce a decrease in the transmitted signal, 2) emission of radiation from a thermally excited state, and 3) fluorescence following the absorbance of radiation. In atomic absorption (AA) spectroscopy, the basic configuration of the system consists of a burner for the atomization of the sample, with a hollow cathode lamp (HCL) of the ion being detected directed through the flame and collected in a monochromator. The amount of metal ion in the aspirated sample is gauged from the decrease in beam strength via a calibration chart, and can routinely detect silver ion at 0.001 part per million (ppm)

concentrations (1). One inherent disadvantage of this system is that it requires a high degree of discrimination by the detection system in order to detect very small changes in signal.

In atomic emission (AE) spectroscopy, the sample is usually aspirated through an inductively coupled plasma (ICP) system to produce thermal excitation of the sample. Detection of the radiation of de-excitation of the sample can be complicated by ionization interferences, where a high percentage of the analyte atoms are ionized and do not thermally de-excite, and by spectral interferences within the ICP source. These interferences can reduce the sensitivity of the system, limiting the detection to approximately 0.004 ppm concentrations (2).

In atomic fluorescence (AF) spectroscopy, the overall system of the input beam, flame, and monochromator detector are the same, except that a laser is used as the input beam, and the monochromator is placed to the side of the flame to detect fluorescent radiation in the direction perpendicular to the input beam direction. This type of system is more sensitive to silver ion than AA, with a detection limit at 0.0001 ppm concentrations (2), due to the fact that one measures the difference between the background and a detected signal. However, the high cost of the instrumentation of the system limits its application.

All three of the spectroscopic methods outlined above have a number of disadvantages, inherent to the basic parameters of atomic spectroscopy, which make the system less useful for on-site detections. The major disadvantage of atomic spectroscopy is due to the fact that most atomic spectroscopy systems are not man-portable. This means that the sample to be tested must be brought to the instrument. Thus, sample contamination or change becomes a major problem, especially in the case of very low concentrations of ions. Sampling problems can be divided into three main categories. First, the sample container may serve to contaminate the sample, dependent upon conditions used to clean the container and the chemical composition of the container itself. Second, the sample may be adsorbed onto the surface of the container, leaving the matrix with little or none of the species of interest in the sample. Finally, the time required for the sample to be introduced into the instrument could allow the sample to outgas, change pH, etc., producing situations where the original sample and the sample injected are not the same.

Obviously, then, it would be much better to sample the system at the site and carry out the analysis there, or immobilize the sample in a stable matrix for transport. With the recent miniaturization of electronic components leading to compact electrochemical analysis systems,

voltammetric methods centered around the concepts of anodic stripping voltammetry (ASV) and ion-selective electrodes (ISEs) have come into favor for direct sampling of systems.

Anodic stripping voltammetry is based on the concept of using a hanging mercury drop electrode (HMDE) as a large surface area electrode for the reduction and amalgamation of metal ions from solution (3). This amalgam is then oxidized, and the electrochemical position and maximum current of the peaks can be related to a species and its concentration in solution. Sensitivities of 1.0E-9 M can be achieved with this method. However, there are complications introduced by the effect of matrices in the sample on the accumulation of metal ions on the HMDE, by low ionic strengths of solutions inhibiting the completeness of deposition on the HMDE, and by the inherent toxicity of the mercury used in the system.

Ion-selective electrodes (ISEs), on the other hand, are not usually inherently toxic. The main principle upon which ISEs are based is the fact that the observed potential of the electrode changes as the activity of the ion of interest changes in solution, based on the equation (4):

$$E = E'_{const} \pm \frac{RT}{nx(F)} \log [A_x + \Sigma k_{xy} A_y^{nx/ny}] \quad [1]$$

where: A_x = activity of the ion of interest

A_y = activity of interfering ion(s)

nx = charge of the ion of interest

ny = charge of interfering ion(s)

k_{xy} = selectivity constant

There are a number of ways in which ISEs can be constructed. ISEs can be based on doped glasses, inorganic salt crystals, hydrophobic membrane/ion-exchange systems, or a secondary membrane incorporating a standard ISE. For the detection of silver ion, ISEs are usually composed of specialty glass, or solid state silver sulfide pellet membranes. Although these ISEs may have a linear range of five orders of magnitude, and usually don't contaminate the sample, the limit of detection is approximately 1.0E-5 M, and usually is best characterized in high ionic strength solutions.

Thus, for certain types of analyses, including environmental systems, which incorporate parameters of low ionic strength of the matrix, low concentration (1.0E-7 M or less) of the ion of interest, and relative inaccessibility of the sample to a bulky analysis system, a polymer modified electrode system which can assimilate

the ion of interest into a matrix, effectively increasing its relative concentration, could be extremely valuable. Research in this area has already been done by Lane and Hubbard (5), using a platinum electrode modified with an olefin-attached salicylate ligand to complex Fe(III), and by Cheek and Nelson (6), using an amidized carbon paste surface to coordinate silver (I), which was then exposed to chloride ion and electrochemically reduced.

Since it has been shown that 7,7',8,8'-tetracyanoquinodimethane (TCNQ) will form charge-transfer complexes with specific aqueous metal ions (7), and since several TCNQ polymers were at hand (8,9), the feasibility of the use of TCNQ-polymers to detect low concentrations of a metal ion, specifically silver ion, in aqueous solution has been investigated.

Additionally, this thesis attempts to explore the effect of the imposition of a magnetic field to modify, temporarily or permanently, the electrochemistry of polyester-TCNQ and a polyurethane-TCNQ polymer.

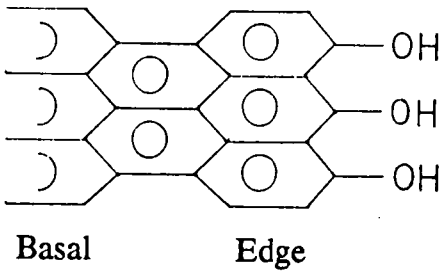
A) CHEMICAL/POLYMER MODIFICATION OF ELECTRODES

1) Electrode Modification Via Adsorption

In order to understand the advantages of the polymer modified electrodes used in this study, it will be necessary to partially review the steps which have brought the field of electrode modification to its present state. A comprehensive review of the material, however, is beyond the scope of this thesis. Up until a few decades ago, electrode modification, or fouling, was considered to be a unavoidable problem with some electrochemical experiments. However, after several years of extensive research on adsorbed materials, Fred Anson published a classification system for adsorbates in the early 1970's (10), correlating prior empirical observations which had made little sense into an overall framework. Anson recognized five classes of adsorbed materials, with several subclasses for clarification. While Anson was in the process of classifying systems, other researchers were at work utilizing chemisorption to produce chemically modified electrodes (CMEs) modified with redox centers. One of the first systems to be studied involved olefins adsorbed on platinum incorporating both redox active and

electroinactive substrates (5,11). One of the most important observations from this series of experiments was that the electrochemical reactivity of attached groups of certain systems was strongly dependent on the orientation of the adsorbate relative to the electrode surface.

These initial observations were to generate the excitement which led to several discoveries. Since the adsorption of olefin groups on platinum represents a special system, research was applied to finding a more generalized system, and centered on the use of pyrolytic carbon or glassy carbon electrodes (12). It was found that the interaction of the pi-electrons on the basal planes of electrochemically modified and virgin carbon



electrodes with molecules containing extended pi systems could be exploited to produce relatively well-defined monolayer systems. Brown et al. (13) proved further that it would be possible to modify adsorbed groups on an electrode through alteration of the electrolyte solution, a two-stage modification of the carbon electrode which enlarges the number of possible final states of the system.

In more recent years, the majority of work using surface groups irreversibly adsorbed on carbon electrodes has been directed towards the development of electro-catalytic systems, especially for the reduction of molecular oxygen to water, an important system for the development of fuel cells. Collman and Anson have made significant progress in this area utilizing face-to-face dimeric porphyrins with two cobalt centers (14). This system exhibits very high catalytic activity for the reduction of oxygen to water without significant production of hydrogen peroxide, an important factor in any real application of fuel cells for extended life power systems.

An alternate system which has received increased attention in recent years is the modification of electrode surfaces using Langmuir-Blodgett films (15,16). These films are composed of monolayers of amphiphilic materials, where layers can be of differing structures with spatial regions of electroactive and/or insulating groups (17). Langmuir-Blodgett layering techniques have been used to assemble polypyridine osmium and ruthenium complexes attached to the surfaces of tin oxide electrodes (18), and have recently been used for the incorporation of amphiphilic TCNQ salts (19).

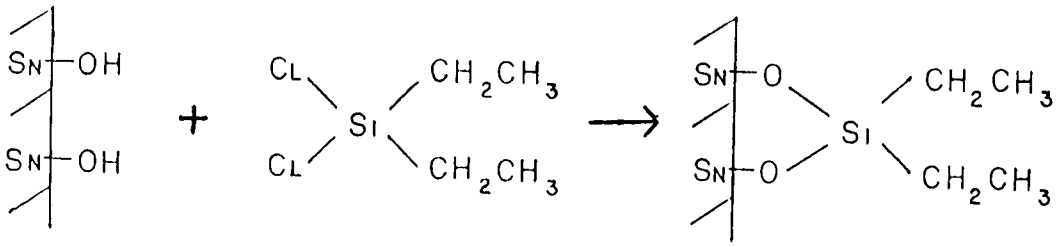
Although a great deal of research has been done involving adsorbed layers, there are two problems which

limit the use of these systems. Primary among these problems is the recognition that, in the presence of sufficient energy, the equilibrium adsorption process can be reversed. Such a reversal would, of course, lead to the destructive desorption of the layer, and the cessation of essentially all electrochemical or electrocatalytic activity. It is obvious that, for certain applications, a more robust film would be needed than can be produced by adsorption techniques. Second, the coverage of the electrode provided by adsorption is usually limited to the monolayer range. One of the biggest problems with monolayers is the low signal output due to the limited amount of electroactive material on the electrode. These two problems, inherent to adsorption on a surface, have limited the application of adsorbed films.

2) Electrode Modification Via Chemical Bonding

An obvious answer to the problem of the adsorption/ desorption of materials on an electrode is to bond the material of interest directly to the surface of the electrode. Most of the initial research in this area was produced by Murray et al. using organosilane groups (20,21,22). These workers successfully derivatized surface hydroxy groups on oxidized tin, platinum,

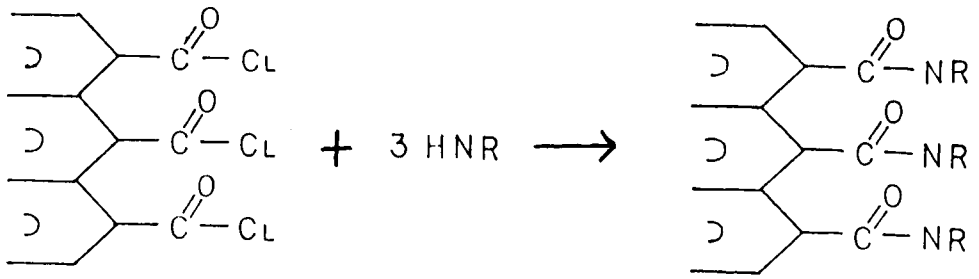
to produce species attached covalently via siloxane bonds.



One of the most versatile of these organosilanes was found to be ß-trichlorosilyl(2-ethyl)pyridine, which was useful for coupling a wide variety of redox units to oxidized electrodes. An alternate approach is to use a silane incorporating a coordinating group to modify the electrode surface which is then exposed to a solution of a metal complex containing a weakly-held ligand (23). Murray has published an extensive review on the subject, which contains detailed listings of redox centers immobilized via silane chemistry (24). Yet another approach is to use other groups to bind to the metal oxide electrodes, which can then be modified. Useful groups include basic chromium complexes (25), chlorinated silicas (26), cyanuric chlorides (27,28), and surface esters (29,30).

Due to earlier research involving adsorption, carbon electrodes were also examined for use as functionality bases. It was found that the adsorptive interaction of carbon edge planes with extended pi systems resulted in well-characterized, stable modified surfaces (31). The first step for the attachment of groups of interest was

the functionalization of the carbon surface to produce useful oxygenated attachment points, such as carboxylic acids, phenols, and ketones (32,33). The electrode could then be treated with thionyl chloride to produce acid chloride groups on the surface, followed by further



treatment with amino-substituted species to produce amide-linked covalent bonds (34). This approach can be extended to metalloporphyrins of iron, copper, and zinc (35-37), and for ferrocenes (38) and ruthenium complexes (39), although in the latter two cases, the coverage of the electrode is extremely low.

An alternate approach involves the reaction of cyanuric chloride with surface hydroxy groups. Using this method, a variety of groups have been attached to electrode surfaces, among them viologens (40), ferrocene derivatives (41), quinones (42), and glucose oxidase (43). Yet another approach is to use carbon paste instead of glassy carbon or pyrolytic carbon electrodes (44-46). The active ingredient is mixed in with the carbon paste, and is cast directly in the electrode. The resultant surface is very easy to regenerate, but since the material of

is very easy to regenerate, but since the material of interest is not immobilized in the matrix, dissolution of the reactant can become a problem.

3) Polymer Modification of Electrodes

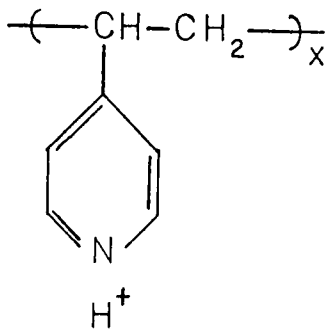
Although chemical modification of electrodes offers a wide variety of possibilities, the field of polymer modification of electrodes is perhaps even more alluring. There are a number of advantages of polymer modified electrodes (PMEs) over chemically modified electrodes, including the possibilities of many monolayers, catalytic stability, and deliberate structuring of surfaces.

Polymer modified electrodes can be divided into two main groups: the ion-exchange PME, where the redox active unit is incorporated into the polymer as a counterion; and the redox PME, where the redox active unit is part of the backbone of the polymer. Both groups can be classified further by the nature of the redox group, whether fully organic or containing inorganic components.

a) Ion Exchange Polymers

The first experiments using cationic ion-exchange PMEs were carried out in 1980 by Oyama and Anson (47). Using a procedure they called electrostatic binding, redox

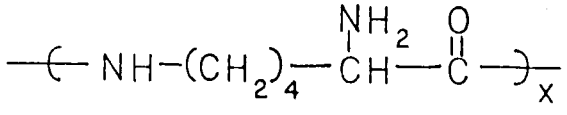
active counterions were incorporated into a polyionic film cast on an electrode. Their early work utilized poly(4-vinyl pyridine) (PVP) in a protonated form, PVPH+, which was "doped" with ions such as $Fe(CN)_6^{3-/4-}$ and $Ir(Cl)_6^{2-/3-}$,



at coverages of approximately 1.0E-7 mol/cm^2. Once the electrodes were modified, they produced well-defined electrochemical responses in electrolyte solutions. However, these responses were not stable, due to leaching of the ions from the polymer. This problem could be remedied by adding a small amount of the counterion of interest to the electrolyte solution. A second system which was used was quaternized PVP, PVPR+, into which was incorporated $Ir(Cl)_6^{2-/3-}$, $Mo(CN)_8^{3-/4-}$, $Fe(CN)_6^{3-/4-}$, and $Ru(CN)_6^{3-/4-}$ (48-51).

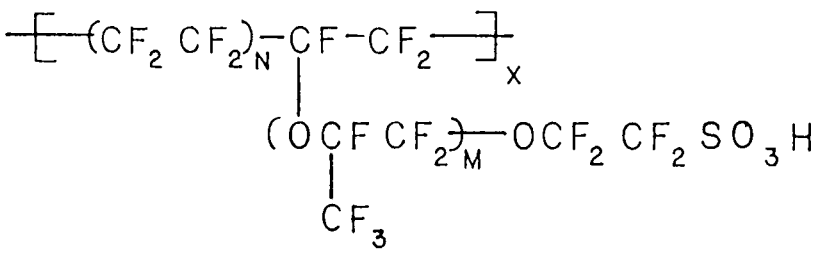
One problem recognized for both systems was the low values of the counterion diffusion coefficients in the polymer film. These low values are caused by a combination of cross-linking effects and poor swelling of the film by the electrolyte. Since several fields of

interest for PMEs, especially electrocatalysis, require high rates of charge transfer, interest was focused on the development of polymers with large, porous structures. One of the major developments in this field was the discovery of the properties of poly-l-lysine, which



exhibits a high degree of swelling in aqueous systems, and allows for both electrostatic binding and rapid charge transfer (52,53). Another system recently developed has been the use of block copolymers of styrene and p-(diethylaminomethyl) styrene, doped with $Fe(CN)_6^{3-/4-}$, which exhibit high loadings of the redox component, coupled with rapid charge transport and well-defined electrochemistry. Experiments using random copolymers indicate that the polymer structure plays a critical part in the utility of the polymer system (54).

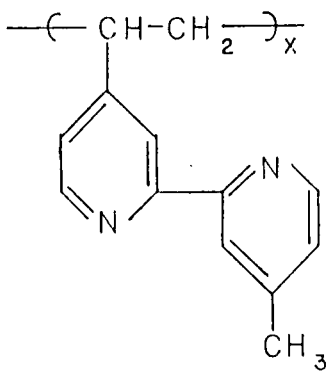
Cation exchange polymers have also been used to modify electrodes. The anionic polymeric material which has been the object of most research is the perfluoro-sulfonate material, Nafion (55). Nafion is a cation



exchanger due to the presence of the sulfonate side chain, but exhibits none of the standard properties of other sulfonate resins. On the contrary, Nafion exhibits a very hydrophobic nature, has a low ion-exchange site density, and has essentially no cross-linking. A variety of redox cations have been incorporated into Nafion films, including $Ru(bpy)_3^{2+}$ (56), methyl viologen (57), and $Co(bpy)_3^{2+}$ (58). Nafion systems have been used in studies for the electrocatalysis of oxygen reduction (59,60) and for electron transport properties (61). Another anionic polymer which has been studied is polystyrene sulfonate, doped with $[Co(bpy)_3]^{3+}$, $[Ru(bpy)_3]^{2+}$ (62), and similar species (63). A similar polymer system is p-chloro-sulfonated polystyrene, which was used to incorporate polypyridine complexes of osmium and ruthenium (64,65), and has recently been used for the electrocatalytic oxidation of water and chloride ion.

b) Redox Polymers/Conducting Polymers

The field of redox polymers can be divided into four groups: 1) transition-metal-complex polymers generated in situ, 2) preformed transition-metal-complex polymers, 3) organic polymers generated in situ, and 4) preformed organic polymers. The first of these categories is well-represented by the vinylpyridine (v-py) and vinyl-



bipyridine (v-bpy) complexes of ruthenium, osmium, and iron, as reported by Abruña et al., which undergo electroreductive polymerization to produce electrochemically active films (66). A variation of this technique, using different monomers to produce copolymers, can create polymer electrodes incorporating multiple redox states, allowing a wide range of possible electrochemical behavior.

A likely mechanism for the formation of these polymers, which has been the object of a great deal of research, involves radical coupling through the ligand

(67), and leads to ligand-bridged extended structures (68). The resulting polymers are relatively stable, exhibit well-defined electrochemical responses, and are fairly uniform in surface coverage (69). This allows these films to be used in electrocatalyst (70,71) and photoactive (72) systems, as redox conductors (73) and bilayer electrodes (74), and as systems which mimic electronic devices (75).

In recent years, a number of transition metal systems using organic components other than vinylpyridine and vinylbipyridine have been developed. Complexes derived from pyridineacetylene (76), vinylterpyridine coupled with iron and ruthenium (77), $[Ru(bpy)_2(v\text{-}py)_2]^{2+}$ [bpy= bipyridine] (78), aminophenanthroline (79), pyrrole-substituted pyridine and bipyridine (80-82), cobalt(II) tetraazaannulenes (83), and acylnickel derivatives (84) have been produced, and display properties which could lead to novel electrochemical devices.

The second method by which transition metal complexes may be placed upon an electrode surface is, of course, pre-formation and subsequent deposition of polymer on the electrode. For example, Oyama and Anson have used graphite electrodes coated with polyacetonitrile or polyvinylpyridine films to incorporate Ru(EDTA) and $Ru(NH_3)_5$ complexes (85). A fundamental observation for these systems was that the electrochemical behavior was a

function of the oxidation state of the ruthenium present in the solution where incorporation took place. Oyama and Anson were also able to prepare electrodes which could incorporate two different redox centers, further extending the utility of the system (86).

Other research in this area of electrode modification has produced copolymers of pyrrolidone and iron porphyrin groups, which exhibit good swelling characteristics despite the insolubility of the polymer in water (87). Films based on $[Ru(terpy)(bpy)]^{2+}$ [terpy= terpyridine] in PVP have been studied in detail, and there are indications of significant interactions between the chromophores on the polymer chains at high loadings (88). Another method for film production is the electrochemical generation of an open coordination site on a metal complex, which then binds with a pyridine site in the PVP film.

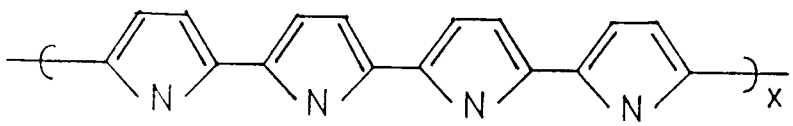
An unusual method which has produced systems which are applicable to bilayer electrodes (89) and various photoactive polymers (90,91) involves the reaction between p-chlorosulfonated polystyrene and hydroxy, carboxylate, and amino groups incorporated on redox centers to yield sulfonester, sulfonanhydride, and sulfonamide linkages. Of these, the sulfonamide linkage is the strongest, leading to the emphasis on polypyridine complexes of ruthenium and osmium, nickeltetraazides, aminoferrocenes, and other compounds.

There are many redox polymers in which the redox unit in the chain is organic and is not composed of transition metal complexes. The field of organic PMEs generated in situ can be divided into two subgroups, one composed of redox polymers and the other composed of 'organic' metals. In general, organic PMEs generated in situ are produced via a monomer which is exposed to appropriate stimuli to initiate polymer formation. For redox polymers, the stimuli are usually of a chemical nature, while for organic metals, the stimulus is usually electrical in nature.

One of the most well-characterized systems for the formation of redox polymers in situ is the group of hydrolytically unstable silanes developed by Wrighton et al. (92,93). These modified electrodes are formed by hydrolysis of unstable silyl groups attached to specified redox molecules (94,95). This strategy, which produces a stable, siloxone-linked polymer, has been used to produce a variety of polymer systems, with most emphasis on systems incorporating ferrocene (96) and viologen (97) groups, although systems with tetraalkylbenzenediamine derivatives (98) have recently received attention. The polymers modified with viologen have been attached to p-type silicon electrodes to produce systems where the photoassisted evolution of hydrogen gas can occur at photovoltages of approximately 0.5 V (97,99). Viologen

polymers have also been used in the catalytic reduction of bicarbonate to formate (100,101), in the mediated reduction of cytochrome C (102), and have been found to exhibit a very well-defined electrochromic response (103). Other polymers of this type have been produced as naphthoquinone derivatives, which exhibit the ability to photochemically and electrochemically reduce oxygen gas to hydrogen peroxide when cast on p-WSe_2 and platinum electrodes (104). In a similar manner, an immobilized benzenediamine derivative has been used in the mediation of ferro/ferri-cytochrome C (105).

Polypyrrole, synthesized electrochemically by Diaz et al. (106), is one of the first organic synthetic metals



which was recognized as having useful, and unique, electrochemical properties. Burgmayer and Murray have used coatings of polypyrrole to produce membranes which can act as ion-selective gates (107). Closely following this development, Albery et al. produced polymeric films of thionine on tin oxide and platinum electrodes, which were used to test the photogalvanic properties of a variety of redox couples (108). Anodically electro-

polymerized hydroxyphenazine on glassy carbon has the ability to mediate a number of redox processes, such as the reduction of molecular oxygen and ferric ion (109). Anodically electropolymerized vinyltriphenylamine has been used in the electrocatalyzed oxidation of carboxylate anions (110), while graphite electrodes have been modified with sulfonated phenothiazines and used for the catalytic oxidation of NADH (111).

The use of substituted pyrroles to form electropolymerized films has recently been the subject of intense research. Deronzier et al. (112) have used a pyrrole-substituted viologen derivative to produce electrodes incorporating a polymeric viologen film. These modified electrodes display electrochemistry substantially different from normal polypyrrole electrochemistry, with two well-defined reductions occurring within the film. Viologen has also been incorporated into vinyl systems to produce active films by Murray and Willman (113), and Elliott and Martin (114). These electrodes illustrate the reason for the intense interest in this area, i.e. that an electrode can be custom modified for the system in use, taking into account a wide variety of factors before the deposition of the polymer film.

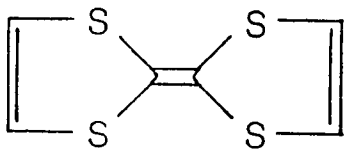
The final group of redox polymers is that composed of a preformed organic redox unit which is cast on an electrode to form the electroactive film. The obvious

advantage of this type of film preparation is that the polymer can be synthesized, purified, and characterized by other methods before the electrochemistry is studied, thus eliminating some aberrations due to impurities in the polymer. The most commonly employed polymers are those incorporating quinones (115,116), viologens (117), and aromatic nitro groups (118,119), because of their synthetic variability and well-behaved electrochemistry. One of the first examples of this type of PME was produced by Miller et al., using quinones (120) and dopamine (121) to produce polymers which were coated on platinum or carbon electrodes.

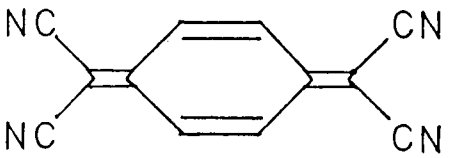
Another family of polymers, studied by Miller and Degrand, was derived from the condensation of poly(ethylenimine) and 2-anthraquinonecarbonylchloride (122). This polymer was cast on carbon and mercury electrodes and a wide variety of responses were observed, which were dependent on solvent properties, surface coverage, degree of cross-linking, and, most importantly, polymer chain motions. In addition, Miller has studied films which could be used for the electrocatalytic reduction of aromatic halides (123), and the oxidation of NADH using a bound dopamine moiety (121).

Kaufman et al. have studied polymers which incorporate tetrathiafulvalene (TTF) (124), ferrocene (125) and pyrazoline (126) substituents on a poly(vinyl

benzylchloride) backbone. These materials are especially attractive in light of possible structural special effects, due to similarities to tetrathiafulvalene/ 7,7',8,8'-tetracyanoquinodimethane (TTF/TCNQ). The



TTF



TCNQ

polymers were deposited by spin-coating on platinum from tetrahydrofuran (THF) solutions, and electrochemistry was carried out in acetonitrile solutions. It was found that the electrochemical behavior was dependent on the type of electrolyte, and that the polymer morphology changed significantly upon electrochemical oxidation. These films have been studied in relation to charge transport properties, and it is theorized that charge propagation occurs via an electron self-exchange reaction between reduced and oxidized neighboring groups in the film (127). Chambers et al. have performed extensive research on TCNQ-containing polymers, which will be discussed below (128-138).

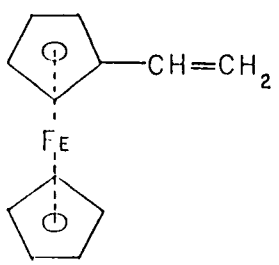
Other unusual systems which have been produced include Funt and Hoang's copolymers of styrene and poly(vinyl p-benzoquinone) (139), Degrand and Laviron's copolymers of poly(ethylenimine) and p-phenylazobenzoyl

chloride (140), and Abruña and Bard's polyxylyl-viologen system incorporating platinum on p-Si electrodes (141), which upon illumination in aqueous or nonaqueous electrolytes evolves hydrogen gas.

4) Other Methods of Modifying Surfaces

There are several other methods of electrode modification, besides the three main methods discussed above, which have been found useful for selected systems. One method utilizes precipitated films of polynuclear transition metal cyanides of general formula $M_k^A[M^B(CN)_6]_l$ (142). Iron(III) hexacyanoferrate(II), also known as Prussian Blue, is a highly insoluble polymeric material which can be reduced to yield Berlin green, or oxidized to yield Everitt's salt. The electrochemistry of films of this type has been extensively studied by Itaya et al., who have also studied ferric osmocyanide (osmium purple) and ferric ruthenocyanide (ruthenium purple) (143).

A second method uses an argon ion plasma to clean and activate a carbon surface, then to polymerize reagents such as vinyl ferrocene (144,145) or vinylpyridine (146)



onto the activated surface. Although this plasma polymerization process yields robust films, it is difficult to control the thickness of the film, and the plasma discharge usually causes some damage to the film.

Several other specialized methods for electrode modification have been developed in the past few years. Bocarsly et al. found that, when nickel was dissolved in the presence of ferricyanide ions, films of nickel hexacyanoferrate were formed that adhered well to the surface of the electrode (147,148). Miller and Majda have produced porous alumina films which are coated with polymers incorporating redox centers (149), and have examined systems of self-assembling monolayers containing viologen (150). In addition, several types of zeolites structures have been examined for suitability as media for the incorporation of polymers containing redox systems (151,152).

5) Basic Electrochemistry

In order to understand the remainder of this dissertation, a brief discussion of the basic processes of electrochemistry in CMEs and PMEs is needed. Cyclic voltammetry is the process most used to study these systems, and consists of applying a triangular waveform potential between a CME and a reference electrode immersed

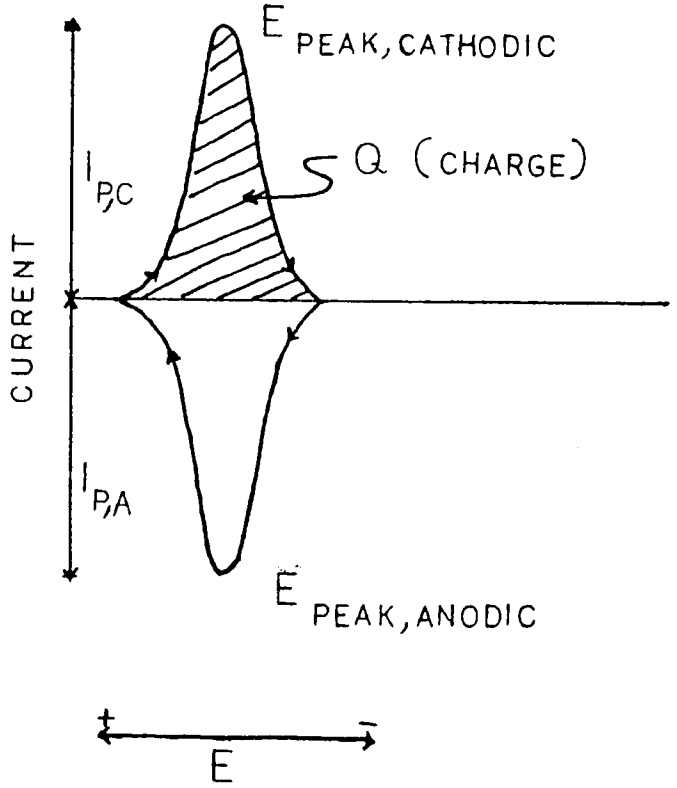
in an unstirred solution of supporting electrolyte. A voltammogram is a plot of the resulting measured current versus the applied potential. For a chemically and electrochemically reversible redox couple on a CME, the voltammetry is characteristic of a surface reaction which is not influenced by diffusion of redox species or electrons through the surface layer (See Figure 1). The difference in peak voltages, ΔE_p, should be zero as long as the sweep rate, v, does not exceed the rate of charge transport in the system. If the surface concentration of the redox species and the activity are equal, then the current-potential behavior of the film is given by the equation:

$$i = \frac{n^2 F^2 \Gamma v}{R T} \frac{X}{[1 + X]^2} \qquad [2]$$

where: $X = \exp[(nF/RT)(E-E^0)]$.

Γ = total amount of reactant initially present at electrode surface (mole).

v = sweep rate (V/sec).



Γ (surface coverage) = Q/nFA

Thin Layer Control:

peak current $\propto$ sweep rate

Figure 1. Representation of the cyclic voltammetry associated with a chemically modified electrode.

The peak current is:

$$i_p = \frac{n^2 F^2 \Gamma v}{4 R T} \qquad [3]$$

and thus the peak current will be linearly dependent on the sweep rate, v. The surface coverage, Γ, can be calculated by integrating the area under the voltammogram wave to obtain the charge Q, in coulombs, and using the equation:

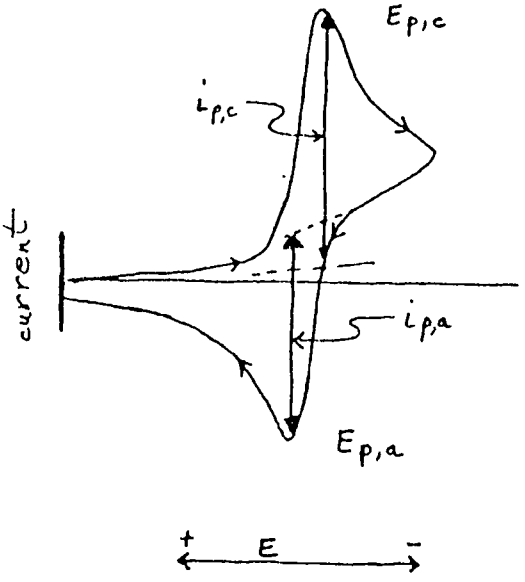
$$\Gamma = \frac{Q}{n F A} \qquad [4]$$

where: F = Faraday's constant = 96,485 coulombs

A = area of the electrode (cm^2)

Finally, for non-interacting neighboring redox species, the full width at half maximum height of the voltammogram for a surface wave should be 90.6 mV/n at 25 °C, where smaller values reflect stabilizing, and larger values repulsive interactions.

For real PMEs, the voltammetry is considerably more complicated, and is usually viewed as a compromise between pure surface control, as described for the CME above, and pure diffusional control (See Figure 2). In a diffusion controlled process, electroactive species, which are in the bulk of the electrolyte solution, must move to the electrode surface to be electrolyzed, which requires a



Polymer modified electrodes vary between two cases:

Thin Layer Control- peak current $\propto$ sweep rate

Diffusion Control- peak current $\propto$ (sweep rate)$^{1/2}$

Figure 2. Representation of the cyclic voltammetry associated with a polymer modified electrode.

discrete amount of time. For a reversible redox process, at 25 °C, under conditions of semi-infinite linear diffusion, the following criteria apply:

1) the ratio of the anodic peak current to the cathodic peak current is unity.

2) the separation between the peak potentials of the cathodic and anodic peaks is equal to 58/n mV.

3) the peak current is given by the Randles/Sevcik equation:

$$Ip=2.69x10^5\ n^{3/2}\ A\ D^{1/2}\ C_b\ v^{1/2} \qquad [5]$$

where: n = number of electrons transferred.

A = area of the electrode (cm^2)

D = diffusion coefficient (cm^2/sec)

C_b= bulk concentration (moles/cm^3)

v = sweep rate (V/sec)

Thus, Ip is proportional to $v^{1/2}$.

The exact behavior of a PME is complicated by a variety of factors, including electron transfer and electron transport rates, polymer chain movement, counterion flow, and solvent effects. Thus, the electrochemical behavior of a PME is usually dependent upon the charge transport diffusion coefficient, D_{ct}. The critical parameter is $D_{ct}\ \tau/\delta^2$, where τ is the time scale

of the experiment, dictated by the sweep rate, and δ is the polymer film thickness. When $D_{ct}\ \tau/\delta^2 << 1$, i.e. a thick film, then the response is that of a diffusion controlled process, and when $D_{ct}\ \tau/\delta^2 >> 1$, the response is that of a thin layer in Nernstian equilibrium with the substrate electrode.

6) Advantages and Disadvantages of PMEs over CMEs

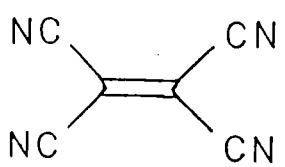
There are several distinct advantages of PMEs over CMEs in voltammetric applications. First, the synthesis and preparation of a PME is subject to a large number of possible modifications, which allows for optimization of the nature of the redox group, the spacing of the redox centers, and the supporting polymer matrix. The pathway leading to a CME may not be accessible to sufficient modification to make it optimal for the purpose in mind. Second, the polymer film can be considered to be composed of a large number of monolayers, which produce a larger signal than a corresponding CME with monolayer coverage of electroactive groups. This increase in signal produces greater sensitivity in analytical applications.

The disadvantages of PMEs arise, to a large part, from problems inherent in the polymeric nature of the film. One main problem is due to the polymer chain movement and change in morphology experienced as a PME is

driven between oxidized and reduced states. This effect is coupled with the changes in morphology caused by solvent effects of the electrolyte, and by the incorporation of counterion into the polymer. All of these effects combine to change the localized nature of the film from moment to moment, and thus change the apparent electrochemistry of the film. This everchanging process makes interpretation of polymer film electrochemical behavior extremely difficult.

B) EXAMINATION OF SPECIFIC POLYMER SYSTEMS

In order to understand the data which are presented in the remainder of this thesis, it will be necessary to review in some detail the specifics of the polymer-TCNQ systems which were used in the experiments. The electron acceptor, 7,7',8,8'-tetracyanoquinodimethane (TCNQ) is one of a handful of stable, monomeric quinodimethanes which have been produced. Substitution by the four cyano groups into the quinodimethane structure produces several unique properties which are similar to those properties exhibited by tetracyanoethylene (TCE).



TCE

TCNQ was synthesized initially (153) via a condensation reaction of malononitrile with 1,4-cyclohexanedione in aqueous solution, followed by reaction with pyridine and bromine to produce a rust-colored solid with a melting point of 293.5-296 °C. Infrared spectroscopy showed two prominent bands, one related to the cyanide stretch at 2220 cm^{-1} and the other related to the carbon double bond stretch at 1540 cm^{-1}.

TCNQ is characterized as a strong Lewis acid, because of its high affinity for electrons. This high electron affinity is due to a structural property of TCNQ (7). The presence of the four cyano groups produces a strong electron withdrawing force from the central portion of the molecule, heightening the need for electrons in the delocalized pi-ring structure.

TCNQ has the ability to form three types of electrically conductive compounds. First, TCNQ can form crystalline pi-complexes, usually with electron rich structures like tetrathiafulvalene (TTF). The resulting complexes are much less soluble in acetonitrile than the components, which aid their formation, and may possess unusual electrochemical properties (154,155). Second, TCNQ can form simple salt-like derivatives of the general formula $M^{n+}(TCNQ^{-})_n$, where M^{n+} is a metallic or organic cation. This form of TCNQ can be produced by the reaction of neutral TCNQ with zero-valent metal in acetonitrile, or

by the reaction of metal cations in aqueous solution with the highly reactive lithium-TCNQ simple salt. Finally, TCNQ can form complex salt-like derivatives of the general formula $M^{n+}(TCNQ^{\cdot})_n$-$TCNQ^{\circ}$, where a simple salt is bonded to a neutral TCNQ molecule. Such compounds are characterized by their relatively low electrical resistivity.

In the present study, we are most interested in the second form of TCNQ derivatives, the simple salts, as they are formed at the TCNQ sites incorporated into a polyester or polyurethane backbone.

a) Polyester-TCNQ

Polyester-TCNQ (PE-TCNQ) was first synthesized by Day et al. (128) by the reaction of the TCNQ diol, 2,5-bis(2'-hydroxyethoxy)-7,7',8,8'-tetracyanoquinodimethane, with a stoichiometric amount of adipyl chloride in N,N'-dimethylacetamide at room temperature. The material was isolated as a red-purple solid and found via gel permeation chromatography to have a molecular weight of 5K-10K, corresponding to an oligomeric polymer of structure as shown in Figure 3. Solution cyclic voltammetry of this low- molecular-weight polymer in acetonitrile exhibited two sets of peaks, corresponding to the production of the TCNQ anion and the TCNQ dianion, as shown in Equation 6. Visible absorption (132) and

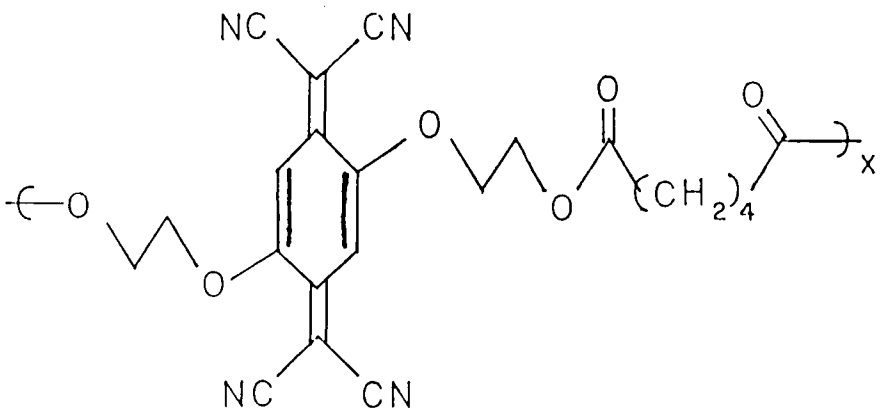


Figure 3. Structure of the Polyester-TCNQ repeat unit.

electron spin resonance spectra (129) have been reported.

$$(TCNQ)_x \underset{0.06\ V\ vs\ SCE}{\rightleftharpoons} (TCNQ^{-})_x \underset{-0.390V\ vs\ SCE}{\rightleftharpoons} (TCNQ^{-2})_x \qquad [6]$$

A great deal of research has been aimed at understanding the mechanism for the electroactive behavior of PE-TCNQ films. For a redox site incorporated into the backbone of the polymer, the model for electron hopping charge transport shown in Figure 4 could apply. For this system, rapid charge transport would be favored by a high density of redox sites in the matrix, and by the proper alignment of these sites which would minimize the energy barriers due to the distance between redox sites. Inzelt et al. (131) have found that the charge transport rate through the film can be highly influenced by the coupling of the proton transfer and electron transfer reactions, which results in the decrease of the effective diffusion coefficient for charge transport by up to a factor of 100. The coupling effect can also limit the electroactivity of the film to a fraction of the available redox sites.

Proper alignment of the redox sites in the polymer will be highly dependent upon the segmental motions of the polymer chain, which in turn will be dependent upon the amount of swelling of the polymer film in the electrolyte

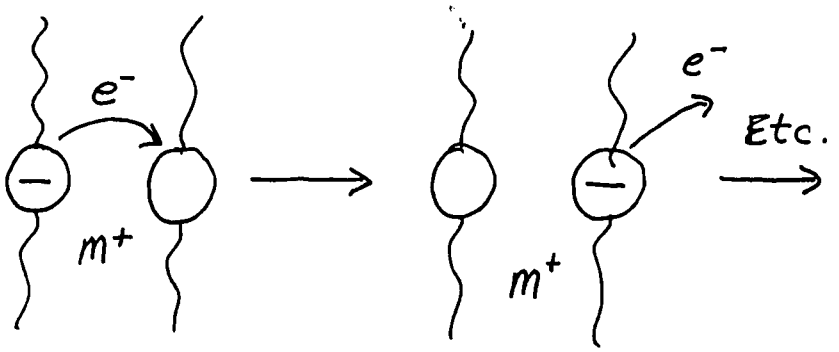


Figure 4. Model for electron hopping charge transport between stationary units.

solution. Inzelt et al. (134,138) have found that, as the concentration of the electrolyte increases, the polymer adopts a more closely packed structure, which decreases the counterion flow in the film, and results in decreased film electroactivity. The net effect of these changes in electrolyte concentration is the switching of the polymer film between surface- and diffusion-controlled behavior, a possibly useful circumstance.

b) Polyurethane-TCNQ

Polyurethane-TCNQ (PU-TCNQ) was synthesized by C. Francis (137) via the condensation reaction of the TCNQ diol with the diisocyanate monomer of choice in N,N'-dimethylacetamide (DMA) using dibutyltin dilaurate (T-12) as a catalyst at low temperatures. The resulting product was a shiny, black substance which displayed the TCNQ electrochemistry. The three polyurethane systems which were used were formed of methylenebis(4-phenylisocyanate), MDI, 1,4-toluene diisocyanate, TDI, or 1,6-hexamethylene diisocyanate, HMDI, to produce the polymeric structures illustrated in Figure 5. Of the three PU-TCNQ redox polymers, PU-MDI has the most rigid structure, while PU-HMDI has the most flexible structure.

In this study, the PU-MDI polymer was used since its rigidity makes a good contrast in properties to the PE-

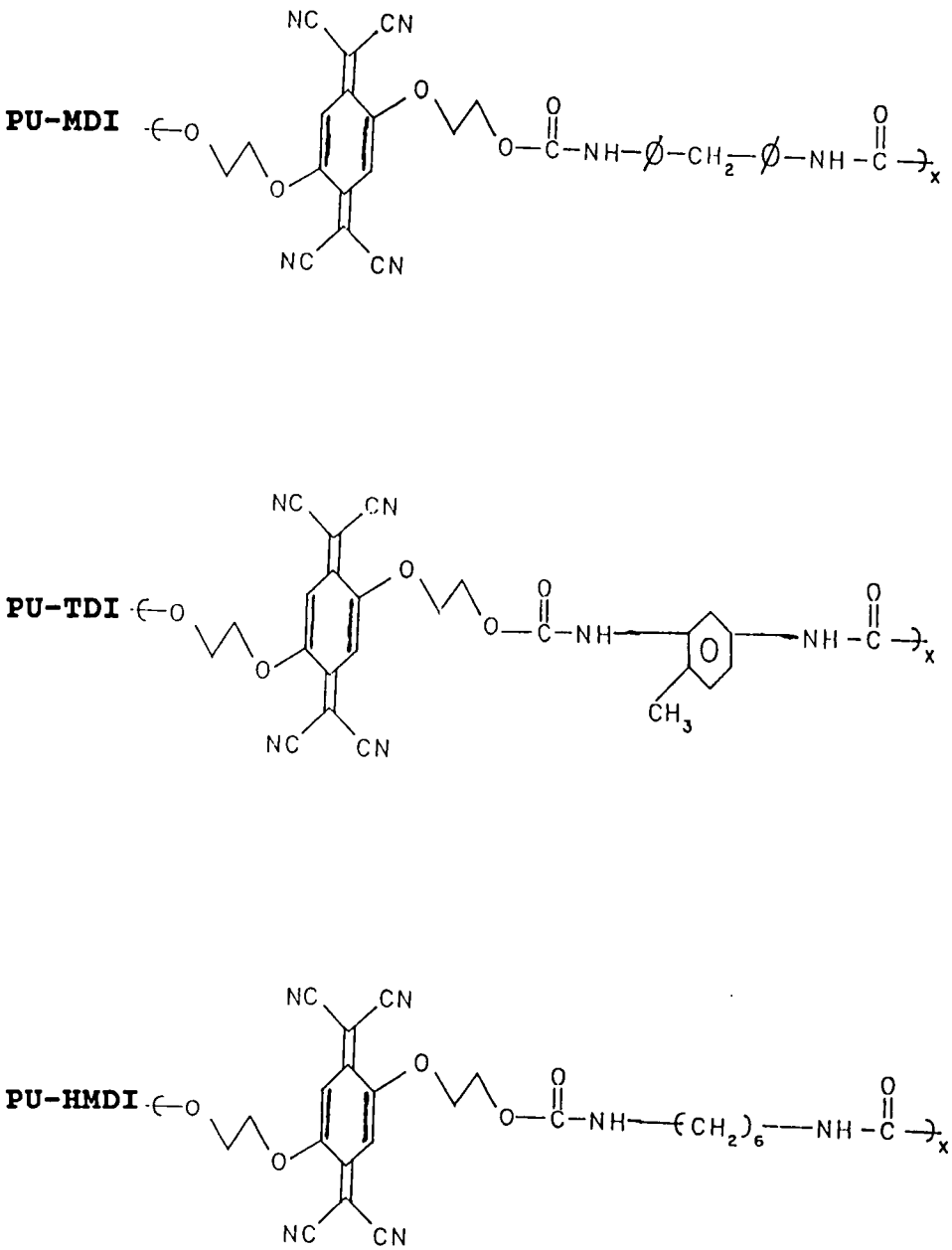


Figure 5. Structures of the three Polyurethane-TCNQ repeat units.

TCNQ polymer. Films were cast following the procedure outlined by Francis, in which a measured amount of the polymer was dissolved in DMA/acetone solution, and drop coated on the electrode, which was then baked at 110 °C for 2-3 minutes to remove solvent. Cyclic voltammetry of the PU-MDI film in aqueous LiCl electrolyte shows one set of peaks between the electrochemical limits of +0.4 V vs SCE and -0.5 V vs SCE, corresponding to the one-electron redox process of $TCNQ^{0/-}$. Francis found that the rate of charge transport in PU-MDI was slower than in the PE films for aqueous solutions. In acetonitrile, the diffusion coefficient of PU-MDI was found to be only about 10% of the value for PE-TCNQ.

C) BASIS FOR THE SILVER EXPERIMENTS

1) Silver (I/0) Electrochemistry

There are a number of reasons to study the silver (I/0) couple at polyester- and polyurethane-TCNQ modified electrodes. First, the electrochemistry of silver in chloride ion media is that of a simple one electron exchange:

$$AgCl + e^- \text{ ====> } Ag + Cl^- \quad E^\circ = 0.2223 \text{ V vs NHE.} \quad [7]$$

and the voltammetry of this reaction is thus relatively well-defined. A number of researchers have used this well-defined one-electron silver redox process to characterize specific systems (6,156). Most of the processes tested have used an enhanced complexation of the silver(I) ion with some immobilized species, followed by chloride ion precipitation of the insoluble salt, the amount of which was electrochemically determined using a variety of techniques. In the present study, the silver is to be incorporated into the prereduced TCNQ polymer film from quiescent, low ionic strength aqueous solutions of silver(I) nitrate,

$$(TCNQ^-)_x + x\ Ag^+ \text{ -----> } (Ag^+TCNQ^-)_x \qquad [8]$$

followed by electrochemical measurement in lithium chloride solutions using cyclic voltammetry.

These experimental parameters bring to mind a variety of possible uses for the polymer system, such as the detection of silver at remote sites with subsequent quantitation, the detection of silver in a method analogous to anodic stripping at a hanging mercury drop electrode without the mercury contamination problem, or the accumulation and recovery of trace silver from waste solutions.

2) Optical/Thermal Properties of Silver-TCNQ Salts

The second reason for using silver is the well known photo-optic effect of silver salts. It has been recognized for centuries that a number of silver salts, most notably silver(I) chloride and silver(I) bromide are light sensitive (157). This light sensitivity has been intensively studied, and our modern photographic processes are the result of that research (158-162). The basis for modern photography is the formation of a latent image, requiring only a few photons of light, as opposed to a full exposure requirement for the formation of the image. The process for the formation of the latent image can be summarized in the Gurney-Mott model (163). As silver halide is illuminated by photons of energy greater than the bandgap energy for the halide, free electrons form and can combine with interstitial silver ions to form silver atoms. These silver atoms can then form catalytic surfaces for the deposition of other silver atoms, forming clusters which become stable after the deposition of only 3-5 silver atoms. The Gurney-Mott model is illustrated below:

$$h\nu \longrightarrow e^- + h^+ \qquad [9]$$

$$e^- + Ag^+_i \longleftrightarrow Ag^0_1 \qquad [10]$$

$$e^- + Ag^\circ_1 \text{ <---> } Ag^-_1 + Ag^+_i \text{ <---> } Ag_2^\circ \text{ <---> } Ag_n^\circ \qquad [11]$$

where n is the number of silver atoms required for a stable cluster.

Thus, the clusters can be produced by the absorption of between 6 and 30 sufficiently energetic photons, and this latent image can then be developed in a chemical reducer. Hydroquinone, which has been used as an image developer, catalyzes the reduction of the exposed grains to produce silver metal, the 'real' image.

It has been recognized since TCNQ was first synthesized by Hertler and Acker that TCNQ could form a light sensitive, blue-colored salt with silver(I) ion by the reaction of LiTCNQ with silver metal or aqueous silver(I) nitrate solutions (7). Furthermore, in the past few years, researchers have discovered that these silver salts, as well as similar copper-TCNQ salts (165,165), have photo-optic and thermal properties conducive to their use in optically read computer memory devices. In the case of the silver-TCNQ charge transfer complex, the reaction is:

$$(AgTCNQ)_n \underset{\text{heat}}{\overset{\text{light}}{\rightleftharpoons}} Ag_x^\circ + TCNQ_x^\circ + (AgTCNQ)_{n-x} \qquad [12]$$

[blue] [colorless]

The energetic photons causing the bleaching process are those of a helium-neon laser, focused on the silver-TCNQ polycrystalline film, while heating effects can be supplied by a carbon dioxide infrared radiation laser (166). At present, it would appear that the process is essentially completely reversible, allowing high density read and write operations to be performed.

The importance of the photoreactivity of silver-TCNQ salts can be recognized in the probable formation of silver-TCNQ as the complexation step of the silver incorporation into the prereduced TCNQ polymer. If such a salt is produced in the polymer, then in the presence of sufficiently active photons, there should be a photo-enhancement of the deposition process, similar to the catalyzed formation of the latent image in the standard photographic mechanism outlined in the Gurney-Mott model. Also, if the polymeric TCNQ forms a silver-TCNQ polysalt in the polymer matrix, it may be possible to use the polymers in a manner analogous to the proposed usage of polycrystalline silver-TCNQ and copper-TCNQ salts as optical RAM disks (167). These films would have possible advantages over the polycrystalline disks in terms of the stability of the polymer matrix and the amount of photoactive material required to initiate the photo-optic reading and thermal erasure processes.

A corollary to this interest in silver-organic systems can be found in recent research in the enhancement of the Raman spectroscopy scattered signal from rough silver surfaces (168-170). It is probable that a silver modified PME could be used for novel applications for scattering Raman spectroscopy, including the possibility of simultaneous electrochemical/Raman scattering-type studies.

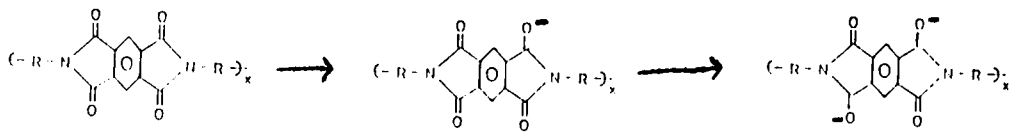
3) Bioelectrochemical Applications

Silver has been used for years as a sensitive stain for the detection of biological molecules, including deoxyribose nucleic acid (DNA) and a variety of individual amino acids (171-184). An analogy to this reactivity of silver with biological components is the increased reactivity of relatively electroinactive biological systems, such as cytochrome C (185) and certain organohalides (186), at silver metal electrodes or on silver metallized films. It has been shown that thyroxine and tyrosine halides can undergo reduction on silver at potentials as great as 1.0 V less negative than on dropping mercury electrodes, and that the reduction occurs in one step on silver, as opposed to stepwise at the dropping mercury electrode. This research points towards

the possible utility of silver metallized or modified PMEs for the detection of biological molecules.

4) Silver Layers in Polyimides

A primary motivation for the study of silver "doped" TCNQ-polymer films is the recent research of Mazur and Reich (187) on the formation of zero-valent, well-defined metal interlayers, specifically silver, copper, and gold, in polyimide films. Their research was based in turn on earlier reports by Haushalter and Krause (188) that free-standing polyimide films could accept electrons to form stable anion radicals and dianions. These anionic



polymers could then be used to reduce metal cations from solution to give metal films or particles on the surface of the polyimide film. These interlayers are produced by the reduction of the polyimide film in the presence of the silver ion solution. This results in an optically reflective, electrically conductive film, consisting of a dense interlayer and a broad diffuse region. The diffuse region is located in the area of the polymer/cathode

interface, while the interlayer is located in the area of the polymer/solution interface. It was found by Mazur and Reich that the exact position of the interlayer was dependent upon the applied potential and the metal ion concentration, and to some extent upon the ligand of the original metal ion solution. The basis for the process is the steady-state balance of the fluxes of electrons and silver(I) at the plane where the interlayer is formed. The microparticles of silver in both regions appear to be similar, in the face centered cubic lattice configuration for silver, and composed of between one to five stable silver clusters.

A fundamental difference between this polyimide system and the TCNQ-polymer system is in the way in which the radical anions are produced. In the polyimide, the electrolysis guarantees a continuous supply of anions, but for the TCNQ-polymer films, the anions are available only on a limited basis, dictated by the prereduction time of the polymer. However, it is possible that clues to the mechanism of the reduction of silver ion by the TCNQ-polymer could be obtained from the processes recognized in the production of these interlayers in polyimide films.

D) BASIS FOR THE MAGNETIC FIELD EFFECT EXPERIMENTS

The effect of magnetic fields upon the mechanical, chemical, and electrochemical behavior of diverse systems is a discipline which has been subjected to increased scrutiny in the past twenty years (189-197). Although the effect of a magnetic field on ferrocenters has been recognized for centuries, and the effect of the magnetic field on the ionic centers and electrons has been recognized for decades (198), only more recently has research been applied to an actual understanding of the chemical effects on systems, and to the quantitation of the various mechanical (199) and chemical effects which can occur. Such research has developed into a variety of techniques for analyzing and/or modifying polymeric systems (200). It has been found that when a magnetic field is applied to a sample of a polymer substituted with paramagnetic organometallic units, the polymer chains are pulled into line. This alignment of the polymer can cause significant changes in the conductivity, optical, and mechanical properties of the system (201). A variation of this experiment is the use of magnetic fields to produce liquid crystal alignment behavior in short chain DNA and ribose nucleic acid (RNA) strands. It was found that DNA and RNA exhibit cholesteric liquid crystal behavior in a magnetic field, and that the alignment of the field and

the sample can produce well-defined optical differences useful in studying the protein molecules (202).

In terms of chemical effects, the role of a magnetic field has been assumed to be related to the presence of radical species in the reaction mixture. There have been several theoretical treatments of the magnetic field effect on chemical reactions (203-205); most revolve around the effect of the magnetic field on degenerate triplet and singlet states as outlined by McLauchlan (206). An interesting example is the observation by Turro et al. that low magnetic fields have profound effects upon the yields and the effective molecular size of the product for certain photoinduced polymerizations (207), especially those occurring inside micellar systems (208). It was concluded that the magnetic field decreased the effectiveness of the singlet to triplet radical intersystem crossings, increasing the number of radicals which escaped without terminating polymerization.

In relation to electrochemical effects, there have been a number of theories proposed to deal with the different mechanisms which could be occurring in the system. Gak was one of the first to attempt to apply classical magneto-hydrodynamic theory to the movement of ions in strong electrolytes (209,210), and did a great deal of research on the current-potential effects of moderate magnetic fields (211,212). Further progress was

made by Fahidy (213) and Mohanta (214), who proposed mathematical models to explain experimental phenomena which seemed to indicate that enhanced mass transport processes occurred at the electrodes. These mathematical models were extended to a variety of other electrochemical conditions and methods, and proved relatively successful in dealing with new parameters and situations (215). Fahidy later published a review on magnetoelectrolysis (216) which examined a number of possibilities besides mass transport, including changes in electrolyte properties such as viscosity, thermal differences, and kinetic effects, which were shown to be essentially negligible. This review also described the orientation effect of a low-power magnetic field on the electrochemical processes, noting that mass transport increased when the magnetic field was perpendicular to the electrode and decreased when the magnetic field was parallel to the electrode.

Kelly, on the other hand, was interested in the effects of an intense magnetic field on the corrosion of metal surfaces and the breakdown of electrolytes (217). His research seemed to indicate that charge-transfer processes could also be modified by the presence of a moderate magnetic field. He concluded that intense magnetic fields would affect structural defects, enhance localized corrosion, and cause reduction and oxidation of

the electrolyte species, leading to the extreme of causing electrolyte degeneration to occur.

If both mass transport and charge transfer can be affected by the presence of the magnetic field, then it should be possible to reproducibly modify the structure and electrochemical behavior of certain polymeric films. Structural modification could occur due to the changes introduced in the random walk of the polymer molecules in the film, and possibly due to reorientation of the radical centers in the chains of the polymer. This realignment of the chains, whether permanent or dependent on the imposition of the magnetic field, coupled with changes in the overpotential, could profoundly effect the redox chemistry of the polymer.

CHAPTER II

CHEMICALS AND EXPERIMENTAL PROCEDURES

Given that the idea is to produce an electrode which is sensitive to silver ion in low ionic strength and quiescent conditions, it would be helpful to examine the electrochemical behavior of the electrode system during the initial treatment of the film with silver ion and as the silver ion is allowed to accumulate in the polymer film. The presence of interferences should be documented and the amount of error introduced should be estimated. This information can then be correlated into charts for the incorporation of silver into the polymer matrix. Given the possibility of unusual opto-electronic properties of the silver-treated polymer-TCNQ films, the structural placement of the silver in the polymer matrix should be identified. Finally, some thought should be given to the detection of other metal ions using the polymer-TCNQ systems available.

A) Chemicals

Lithium chloride, silver nitrate, lithium nitrate, calcium(II) chloride, copper(II) nitrate, mercury(II) nitrate (Fisher), lithium perchlorate (Ventron), and

lead(II) nitrate (Mallinckrodt) were used as received for the preparation of aqueous electrolyte solutions in doubly-distilled water. Fuming (90% +) nitric acid (Mallinckdrot) was used as received, while concentrated ammonium hydroxide (Allied) was diluted to 6 M for use in the electrode cleaning steps. Vacuum-distilled N,N'-dimethylacetamide, DMA (Mallinckrodt), and spectroscopic grade acetone were stored over 3 Å molecular sieves for three days prior to use to remove traces of water. Argon and nitrogen gases were passed through a molecular sieve packed column to remove traces of water, and were used to remove oxygen from solvents and electrolyte solutions.

Lithium-TCNQ was donated by M. Mansfield (225), while silver-TCNQ was prepared as described by Melby et al. (7)

B) Electrode Construction

For the initial studies of the accumulation of silver into the film, a platinum button electrode of area = 0.1964 cm^2 was used as the substrate for the polymer-TCNQ films. However, for the calibration-type studies of the incorporation of silver into the polymer films, electrodes of smaller effective area were constructed for two reasons. First, the smaller effective area of the substrate allowed for the deposition of thicker films, following the procedure outlined in the next section

(page 57). Second, the construction of a number of these smaller electrodes allowed data to be collected more quickly, and allowed for the standardization of the casting procedure for a specific group of electrodes, i.e. a batch method for the production of the electrodes.

The smaller electrodes, also referred to as gold or gold mini-electrodes, were constructed using gold wire embedded in Teflon. The Teflon unit was machined out of a Teflon rod to a final diameter of approximately 2.5 cm, and a total length of 1.5 cm ± 0.2 cm. One half of the length of the unit was further trimmed to a diameter of 1.2 cm, and turned to a standard screw fitting. The Teflon unit was completed by the boring of a hole, exactly 0.125 cm in diameter, down the axial length of the unit. The bore was filled with a gold wire of diameter = 0.127 cm, which extended by 0.1 cm past the front surface of the Teflon unit, and extended past the screw fitting by approximately 0.5 cm ± 0.2 cm. The electrode was finished by sanding the gold/Teflon front surface with successively finer grades of silicon carbide paper, and polishing with 1.0 μm and 0.3 μm alumina. The electrode assembly was completed by the attachment of the exposed gold wire at the anterior end of the Teflon unit to a copper clip and wire. The wire was then threaded through a glass tube of inner diameter = 1.2 cm, and the glass tube was pushed

onto the screw end of the Teflon unit. A diagram of the completed electrode assembly is shown in Figure 6.

It was found that, after several uses, it was necessary to clean the Teflon electrodes, which was accomplished by disassembly and treatment of the parts with solutions of DMA, nitric acid, and ammonium hydroxide in a manner similar to that detailed above. Upon reassembly, it was discovered that the parts did not fit as snugly as before, which could allow leakage of electrolytes or trapping of species of interest in the electrode with no relation to film action. It was found that the electrode could be reassembled using paraffin, which upon heating to 125 °C for two minutes acted as a sealant, and did not seem to incorporate any of the species of interest.

C) Doping Process for Metal/Polymer Systems

In order to optimize the response of the electrodes and to ensure uniform data collection, the following procedure was used for voltammetric experiments, except as indicated otherwise.

Step 1: Electrodes were cleaned to remove all traces of polymer, silver compounds, and electrolytes. Initially, the surface of the electrode was wiped with a tissue

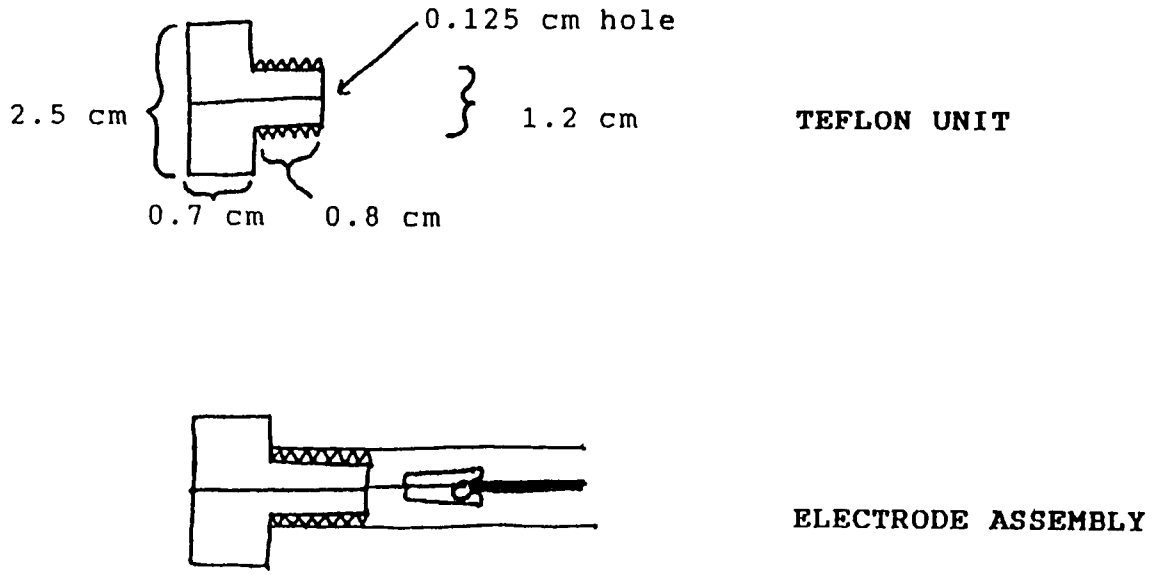


Figure 6. Design diagram for the gold/Teflon electrode.

soaked with vacuum-distilled, dry N,N'-dimethylacetamide (DMA), until no discoloration of the tissue was observed, to remove any adhering polymer. After rinsing with copious amounts of distilled water, the electrode was subjected to two 2-minute immersions in 6 M aqueous ammonium hydroxide to convert any remaining silver(I) chloride to a water-soluble ammonium complex ion. After another rinsing with distilled water, the electrode was immersed in fuming nitric acid to remove any last traces of polymer or silver compound which might adhere to the surface. Electrodes were removed from the acid bath, washed, and visually examined with a hand lens for anomalies, then polished with 1.0 μm and 0.3 μm alumina to a mirror-like surface. Polished electrodes were rinsed with doubly-distilled water, then vacuum dried and stored in a desiccator until use.

Step 2: The polymer casting solvent was prepared by mixing 0.5 ml acetone and 0.5 ml DMA in a 1.0 ml volumetric flask, and degassing with dry argon for one minute. A small amount of polymer, approximately 0.13 mg, was added to the polymer casting solvent, to produce a golden or golden-brown solution. The solution was drop-coated (2-3 drops) onto the electrodes, which were then vacuum desiccated for thirty minutes to remove solvent (128). Further solvent removal was achieved by heat

treatment of the PE-TCNQ films at 125-130 °C for seven minutes or at 110 °C for two to three minutes for the PU-TCNQ films. Films were allowed to cool to room temperature before electrochemistry was performed.

Step 3: The electrodes were placed in 0.5 M aqueous electrolyte solutions which had been degassed with argon for 20 minutes prior to use. The electrolyte is assumed to be 0.5 M aqueous lithium chloride unless specified as otherwise for an experiment. Cyclic voltammograms were obtained to ensure that the electrochemistry of the polymer was within accepted normal limits of behavior for the system, as defined by Inzelt et al. (132), and shown in Figure 7. Surface coverage (Γ) of the electrode by the film was calculated from the average charge of the cathodic and anodic peak, using Equation 4 (See page 29). For the electrodes used in the accumulation studies, coverages varied from 0.4 nmol/cm^2 to 2.0 nmol/cm^2, while for the gold mini-electrodes, the films were thicker, due to the smaller effective surface area of the electrode, and varied from 2.5 nmol/cm^2 to 13.9 nmol/cm^2. These values correspond to film thicknesses of 1.1 nm to 5.5 nm for the accumulation studies, and film thicknesses of 6.9 nm to 38.6 nm for the gold mini-electrodes, as defined by Inzelt et al. (129)

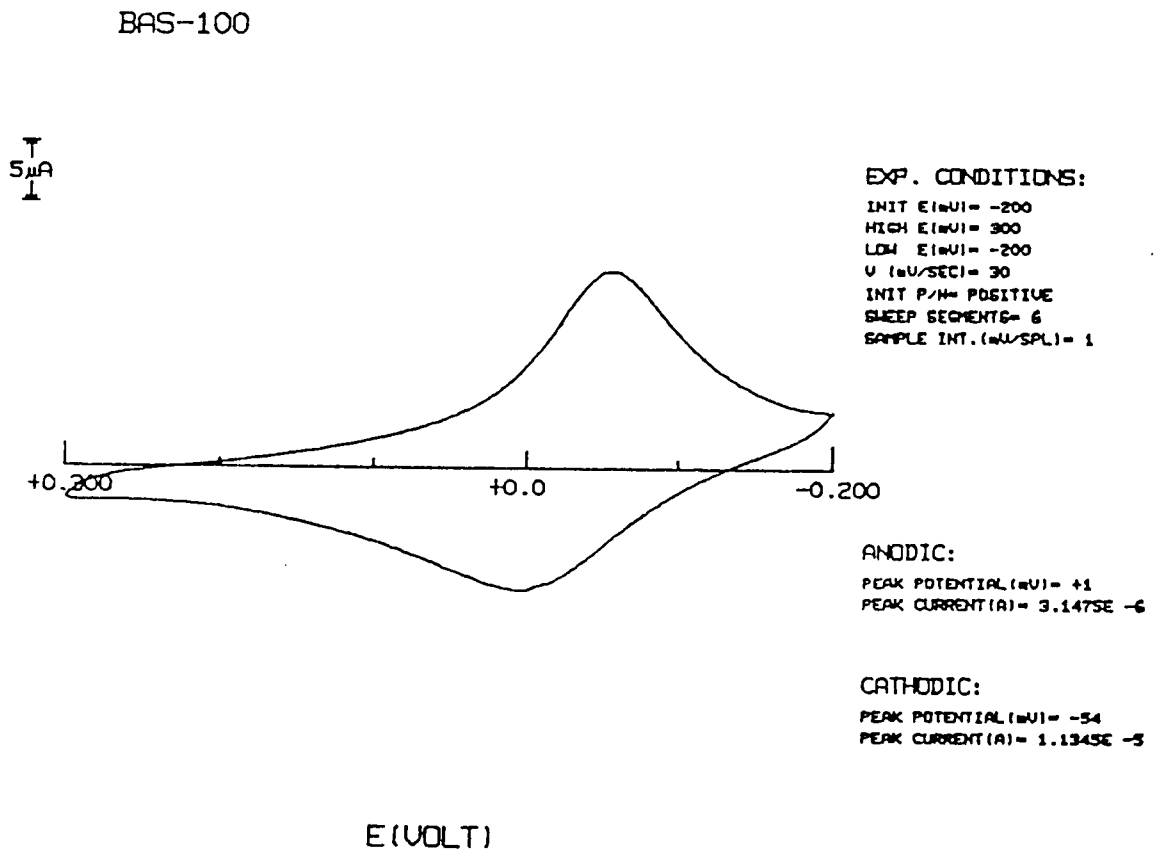


Figure 7. Representative electrochemistry of a PE-TCNQ film cast on a gold electrode and cycled in 0.5 M LiCl.

Step 4: The electrode was reduced in the electrolyte of choice for a predetermined amount of time, hereafter designated by "RN", where N is the amount of time, in minutes. The film was removed from the electrolyte, and rinsed with copious amounts of distilled water, then placed in a quiescent aqueous solution of silver(I) nitrate, or other aqueous metal ion, for a specified amount of time, hereafter designated by "SM", where M is the amount of time, in minutes. At the expiration of the allotted time, the film was removed from the treatment/ doping solution, rinsed with copious amounts of doubly-distilled water, and placed in the electrolyte of choice for the continuation of the experiment. It should be recognized that, due to the lack of convective stirring of the silver(I) solutions, i.e. quiescent conditions, mass transport will be less than ideal, and this effect contributes to the decrease in control and precision of the experiment.

Step 5: Cyclic voltammetry was carried out to determine the electrochemical behavior of the metal complex incorporated into the film. Both the peak currents and the charge, Q, under the anodic and cathodic curves were recorded.

Step 6: For accumulation or 'block' studies, repeat steps 3 through 5 to build up the metal ion concentration in the film. Otherwise, return to step 1.

D) Electrochemistry

A Bio-Analytical Systems BAS-100 Electrochemical Analyzer, connected to a Bausch and Lomb DMP-40 X-Y plotter, was used to obtain cyclic voltammograms and to perform the time-controlled electrolysis of the films. A three-electrode cell arrangement of volume ≈ 30 ml was used, with a platinum mesh counter electrode, and either a saturated calomel reference electrode (S.C.E.) or a silver/silver(I) chloride reference electrode. In those cases where it was desirable to exclude chloride ion from the reaction, the reference electrode was separated from the test solution by a lithium nitrate salt bridge of equivalent concentration to the test electrolyte.

1) Calculation of Charge(Q) Values

In the development of any analytical procedure, it is desirable to eliminate as many sources of variation as possible. In the initial research for the study of the accumulation of silver onto a polymer-TCNQ electrode, the data were collected in the form of the peak current of the

cathodic or anodic wave of the silver modified or the polymer-TCNQ electrode. However, it was noted that the peak shape of the silver-modified electrode would change as the concentration of silver increased in the polymer-TCNQ film, and that not all of the polymer-TCNQ films showed ideal behavior. Therefore, it was decided to use the charge under the anodic peak, as calculated by either a cut-and-weigh method or a triangular estimation method, as a standard measure of the amount of silver incorporated into the polymer film. The amount of charge due to the available TCNQ sites was evaluated by integrating the complete charge under the cathodic peak of the undoped polymer-TCNQ film. (See Figure 8, single-hatched area plus [double-hatched area times two] equals complete charge.)

2) Calculation of Surface Coverage (Γ) Values

Once the charge under a voltammetric peak is obtained, the surface coverage of the film can be calculated using Equation 4 (page 29), where the charge of the peak is divided by the geometrical electrode area, reported in units of nmole/cm^2.

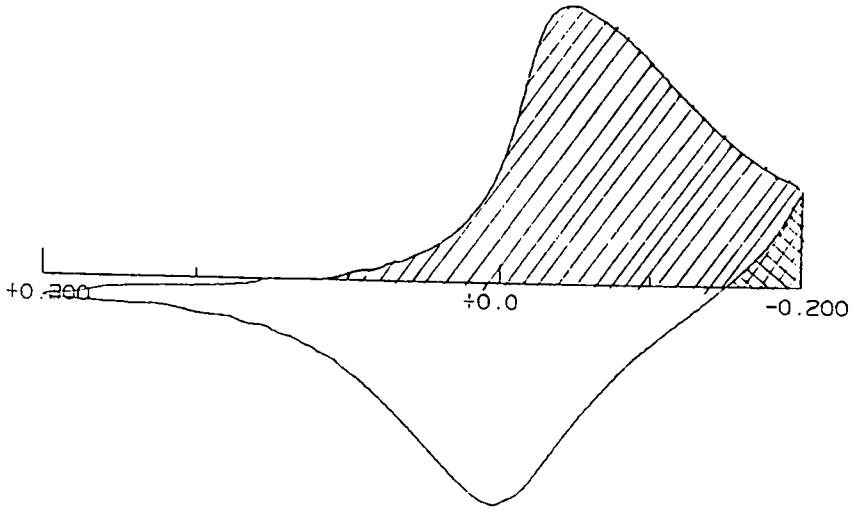


Figure 8. Representative voltammetric curve illustrating the method used to find the total charge of the film.

E) Electron Spectroscopy for Chemical Analysis

ESCA was carried out on polymer samples cast on platinum substrates (1.5 cm x 1.0 cm) by D. Harkins. The substrates were mounted in standard sample holders and scans were carried out in a Model PHI 5100 ESCA spectrometer. Sputtering of the film was accomplished using an argon ion beam.

F) Raman Reflectance Spectroscopy

Raman Reflectance Spectroscopy was carried out on a PE-TCNQ coated platinum electrode placed ex-situ in a clean ESR thin layer cell. Laser radiation at the 488 nm line was provided by a Coherent Innova 100-15 argon ion laser, fitted with a 488 nm narrow bandpass interference filter to remove plasma lines from the beam. Laser power was measured at the sample, and the illuminated area was estimated at 1 mm x 5 mm. Reflected radiation was measured using a SPEX 1877 0.6 m triple spectrograph attached to a Tracor Northern 512 channel Model 6130 gatable intensified diode array detector and Model 6500 computer data station. Able assistance and instruction were provided by Anna Edwards and Dave Trimble.

G) Magnetic Field Experiments

Experiments analyzing the magnetic field were carried out using a three electrode electrochemical cell supported in the 7.5 cm gap of a Varian E-Line EPR Spectrometer water-cooled magnet. Electrochemical data were accumulated via the Bio-Analytical Systems BAS-100 Electrochemical Analyzer.

CHAPTER III

RESULTS AND DISCUSSION

A) POLYESTER-TCNQ/SILVER FILMS

1) Electrochemical Studies

a) Fundamental Electrochemistry

In order to understand the potential of the polymer-TCNQ systems for the analysis of metal ions, and in this case, silver ion, it is necessary to have a basic understanding of the processes occurring in the system. Electrochemistry can provide some of this information, and can also be used to test for some possible interferences which could occur in the calibrations for silver ion.

The cyclic voltammetric behavior of the polyester-TCNQ film in a quiescent, aqueous solution of 0.5 M lithium chloride is shown in Figure 9. This behavior is a result of the one-electron transfer between the neutral TCNQ species and the radical TCNQ anion (128), where the difference in peak potential is due to the less than ideal conditions for electron transfer which exist within the

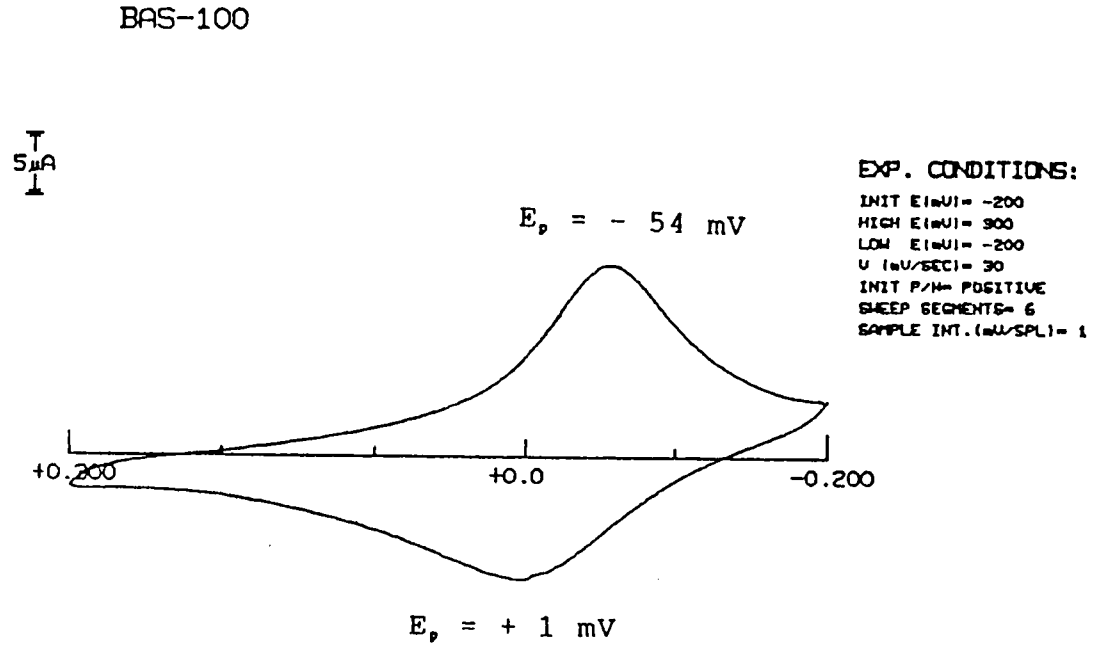


Figure 9. Standard cyclic voltammetric behavior of a PE-TCNQ film cast on a gold electrode and cycled in 0.5 M LiCl using a S.C.E. reference electrode.

film. This electrochemistry can be represented by the reaction:

$$(TCNQ)_x + xe^- \rightleftharpoons (TCNQ^-)_x \qquad [13]$$

It should be noted that significant tailing occurs during the anodic sweep, indicative of a diffusion limited process of velocity lower than the sweep rate. Inzelt et al. (132) have shown that this tailing is related to association and the formation of the mixed valent redox sites that are coupled to the charge transport process. However, for the purpose of this study, the fully reduced form of the $(TCNQ)_x$ polymer film will be written as a radical anion state.

When the reduced film is treated with 1.0E-2 M silver(I) nitrate, R5S1 (Refer to the experimental section, page 62, for a discussion of the RNSM designations) and cycled in 0.5 M lithium chloride, the behavior represented in Figure 10 is obtained. (The "silver-doped" electrodes were assayed in lithium chloride solutions because of the high definition and stability of the anodic silver(0) oxidation wave in this solution.) The dotted lines in Figure 10 represent the baseline behavior of the TCNQ units in the film. The cyclic voltammetric behavior of the film has changed markedly: the peak currents have significantly increased and the

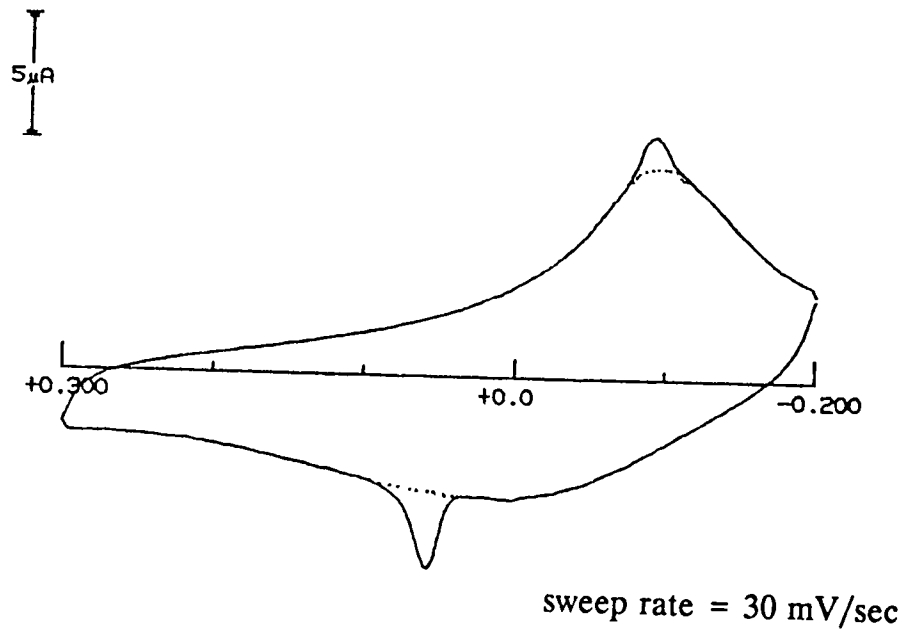


Figure 10. Standard cyclic voltammetric behavior of a PE-TCNQ film cast on a gold electrode after treatment with silver(I) ion and cycling in 0.5 M LiCl using a S.C.E. reference electrode.

peak widths are narrower. In particular, a symmetric anodic peak is observed, indicative of a reversible thin-film surface redox process. In this cyclic voltammogram, the cathodic current is split into two waves. The more positive of these matches the reduction process for the undoped TCNQ polymer films and is assigned to the reduction of the free TCNQ groups. At higher doping levels, this wave is attenuated and the voltammetry is dominated by the second wave. The second cathodic wave is assigned to the reduction of silver chloride which is trapped in the polymer film. (See Equation 7, page 41). Since the reference electrode in this case is a silver/silver chloride reference electrode, the adjusted $E_{1/2}$ value ($E_{1/2} = (E_p^a + E_p^c)/2$) of the silver chloride redox process should be close to zero. Measurements show that the $E_{1/2}$ of the silver treated polyester-TCNQ film, cycled in 0.5 M lithium chloride, is equal to 0.006 V. This measurement provides evidence for the assignment of the redox couple to silver chloride redox chemistry, and not to some other redox species, such as a silver-TCNQ radical anion salt.

In order to confirm this assumption, voltammograms of silver-TCNQ on silver metal in 0.5 M lithium nitrate and lithium-TCNQ in lithium chloride were obtained. A cyclic voltammogram (CV) of lithium-TCNQ in lithium chloride at a platinum working electrode is shown in Figure 11. The

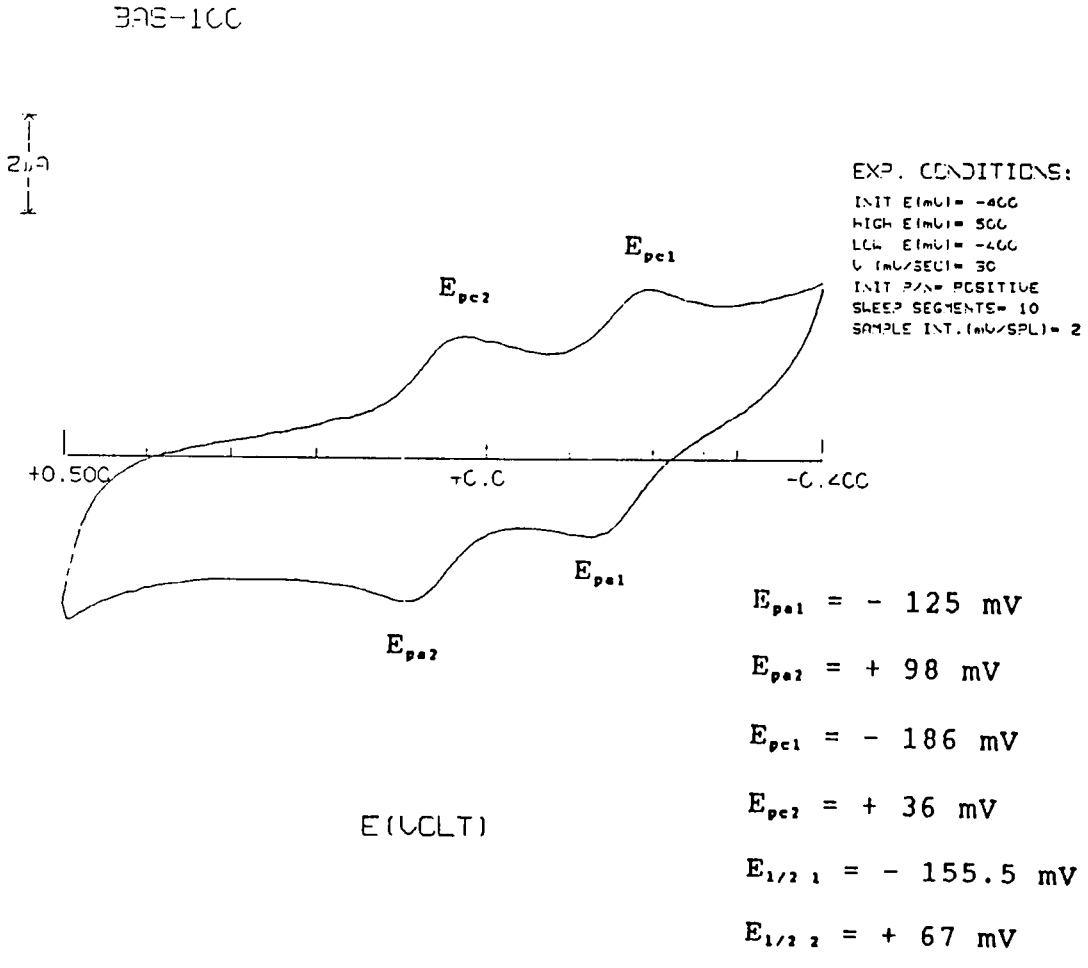


Figure 11. Voltammetric behavior of a dilute solution of lithium-TCNQ in 0.5 M lithium nitrate using a platinum substrate and a S.C.E. reference electrode.

voltammetry is representative of the one-electron transfers which occur to form the $TCNQ^{\cdot}$ radical anion and the $TCNQ^{2-}$ dianion. The half-wave potentials of the two waves provide the evidence that the electrochemistry observed for the silver treated polyester-TCNQ film was probably not due to the presence of lithium-TCNQ radical anion salt. The behavior of the silver-TCNQ salt was examined in the same electrochemical potential range as for the polyester-TCNQ film, using 0.5 M lithium nitrate as the electrolyte. The resulting voltammetry, which is shown in Figure 12, is indicative of a one-electron transfer process, $E_{1/2}$= -0.004 V, which is close to the half-wave potential value of the silver treated polyester-TCNQ film. However, the differences in wave shape and electrochemical potential in the CV of the silver-TCNQ salt in lithium nitrate and the CV of the silver treated polyester-TCNQ film suggest that silver-TCNQ sites are not present in the silver/polyester-TCNQ film which is cycled in 0.5 M lithium chloride solution.

It is also necessary to consider the effect of occluded chloride ion on the uptake and electrochemistry of the silver ion into the film. This was achieved by examining the behavior of the film when electrochemical cycling was performed in an electrolyte such as lithium nitrate which produces a water soluble silver compound. In a typical experiment, a polyester-TCNQ film was cycled

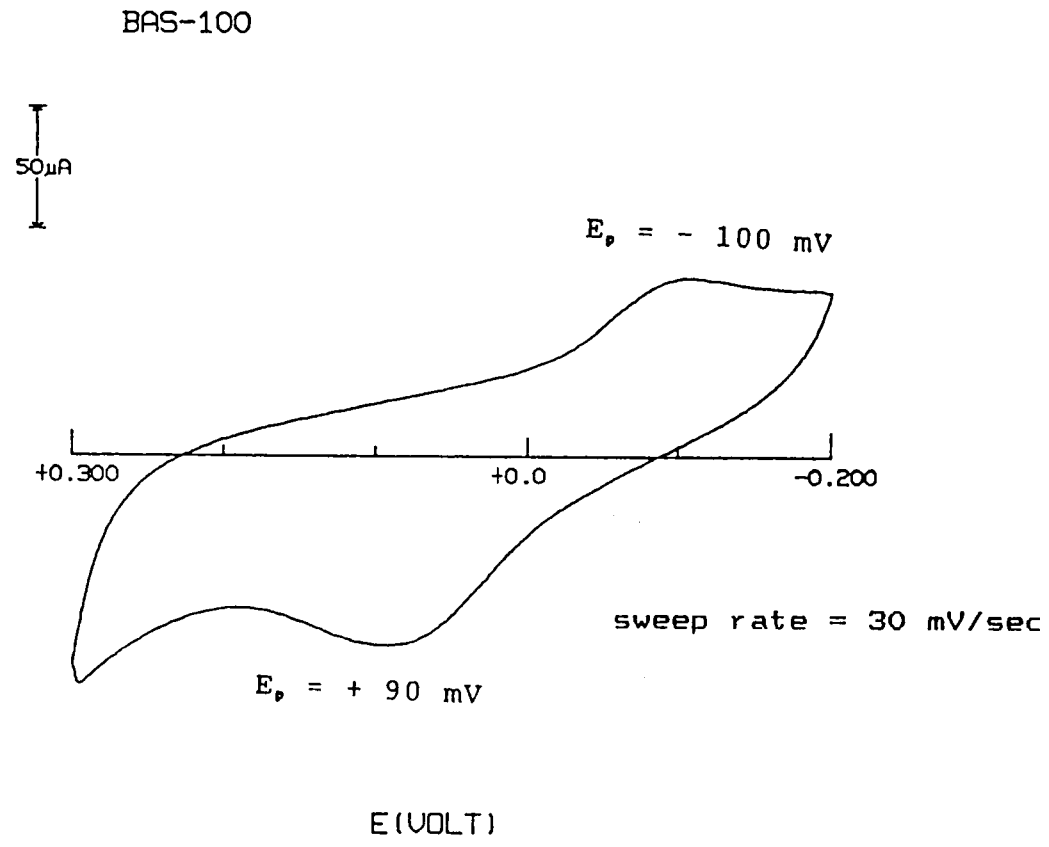


Figure 12. Voltammetric behavior of a silver-TCNQ coated silver electrode cycled in 0.5 M lithium nitrate using a S.C.E. reference electrode.

in 0.5 M lithium nitrate to give the expected behavior, then treated with 1.0E-2 M silver nitrate, and cycled in 0.5 M lithium nitrate. The resulting voltammetry, values for which are given in Table 1, shows that silver ion was incorporated into the film in an amount comparable to the amount incorporated when the film was cycled in lithium chloride solution. The voltammetry also shows that the silver ion seems to partition out of the film with electrochemical cycling, probably in the form of water-soluble silver nitrate, at such a rate that the electrochemical signal due to silver decreases by approximately 80% between the second and third cycles. (The voltammetric data in Table 1 represent that of the first cycle after the standard break-in wave for the polymer-TCNQ film.)

The experiments outlined above suggest the possibility of using nitrate ion solutions to regenerate polyester-TCNQ films by stripping out the silver ions. A polyester-TCNQ film was cast, then treated with silver, and cycled in successive solutions of lithium nitrate. Voltammetry of the films in 0.5 M lithium chloride (See Table 2) shows that the charge due to silver had dropped by approximately 60%-80% after each successive treatment, clearly indicating substantial removal of silver from the film, and supporting the hypothesis that nitrate solutions could be used to regenerate the original behavior of the

Table 1

Silver Deposition in Two Electrolytes

Electrolyte	Q_a/Q_t
0.5 M Lithium Chloride	0.16
0.5 M Lithium Nitrate	0.14

Notes: Silver concentration = 1.0E-2 M

Treatment Parameter: R5S1

Table 2

Removal of Silver in Successive Lithium Nitrate Solutions

Solution #	Cycle #	Anodic Charge, Q_a (μC)	% Decrease
1	2	22.19	68%
1	10	7.13	
2	2	13.17	80%
2	10	2.66	

Notes: Silver Concentration = 0.1 M

Treatment Parameter: R5S5

Electrolyte Concentration = 0.5 M

For the PE-TCNQ films, cycle #1 was due to break-in behavior and was therefore disregarded.

polyester-TCNQ film. The role of the oxidation state of the TCNQ-polymer in the uptake of silver ion into the film was also of interest. A polyester-TCNQ film was cast and cycled in 0.5 M lithium chloride to expected behavior, then oxidized for two minutes at +0.3 V vs SCE, and treated with 20 ml of 0.1 M silver nitrate for five minutes. Electrochemical cycling in 0.5 M lithium chloride revealed that there was no detectable silver in the film ($\leq$ 1.0E-13 mole/cm^2 estimated for silver (I) from the electronics of the BAS-100). This suggests that the reduced state of the polymer is the driving force behind the incorporation of silver into the polymer, and further indicates that the occluded lithium chloride electrolyte plays only a minor role in the uptake of silver into the polymer. Experiments have shown that a polyester-TCNQ film containing residual reduced TCNQ sites does incorporate a small amount of silver into the film, as shown by the data in Table 3, where the silver incorporated is probably due to the reaction of adsorbed chloride with silver(I) on the surface of the polymer. However, this accounts for only 6.3% of the silver uptake which would normally be associated with reduced films of polyester-TCNQ that were treated in this manner.

There is one other obvious mechanism for the uptake of silver: adsorption or photoreduction of silver directly on any exposed platinum surface. Experiments

Table 3

Comparison of Reduced and Neutral PE-TCNQ Films for the Incorporation of Silver

Treatment Parameter	Silver Concentration	Anodic Charge (μC)	Charge Ratio
R5S5	0.1 M	10.74	0.410
R0S5	0.1 M	0.65	0.026

Note: R0S5/R5S5 = 0.026/0.410 = 6.3%

were performed which showed, as per the data in Table 4, that bare platinum surfaces, when held at -0.2 V in 0.5 M lithium nitrate solution and then treated with silver nitrate solution via the procedure outlined for the polyester-TCNQ films, exhibited silver chloride electrochemical behavior when cycled in 0.5 M lithium chloride. The mechanism for this process is not clearly understood, but the magnitude of the silver uptake is less than 5% of the amount which one would associate with a treated polyester-TCNQ film.

Further information about the nature of the film redox process was obtained from the dependence of the peak currents upon the sweep rate. From the earlier discussion of basic electrochemistry, the dependence of the peak current upon the sweep rate will be determined by the extent to which either surface limited or diffusion processes control the electrochemistry of the film. For comparison, the dependence of the peak current on the sweep rate for a silver film deposited on platinum was examined first. The silver film was deposited via electrochemical reduction at -0.2 V vs SCE for two minutes, from a solution of 1.0E-2 M silver(I) nitrate, to produce a rough, gray film of silver. This electrode was cycled in 0.5 M lithium chloride at various sweep rates, and the data plotted in Figure 13 as log (anodic peak current) versus log (sweep rate). The slope of the line

Table 4

Comparison Between Bare Platinum and Reduced PE-TCNQ for the Incorporation of Silver

Treatment Parameter	Electrode Material	Silver Concentration	Anodic Charge (μC)
R5S5	PE-TCNQ	0.1 M	10.74
R5S5	Platinum	0.1 M	0.51

Note: Platinum/Pe-TCNQ = 0.51/10.74 = 4.7%

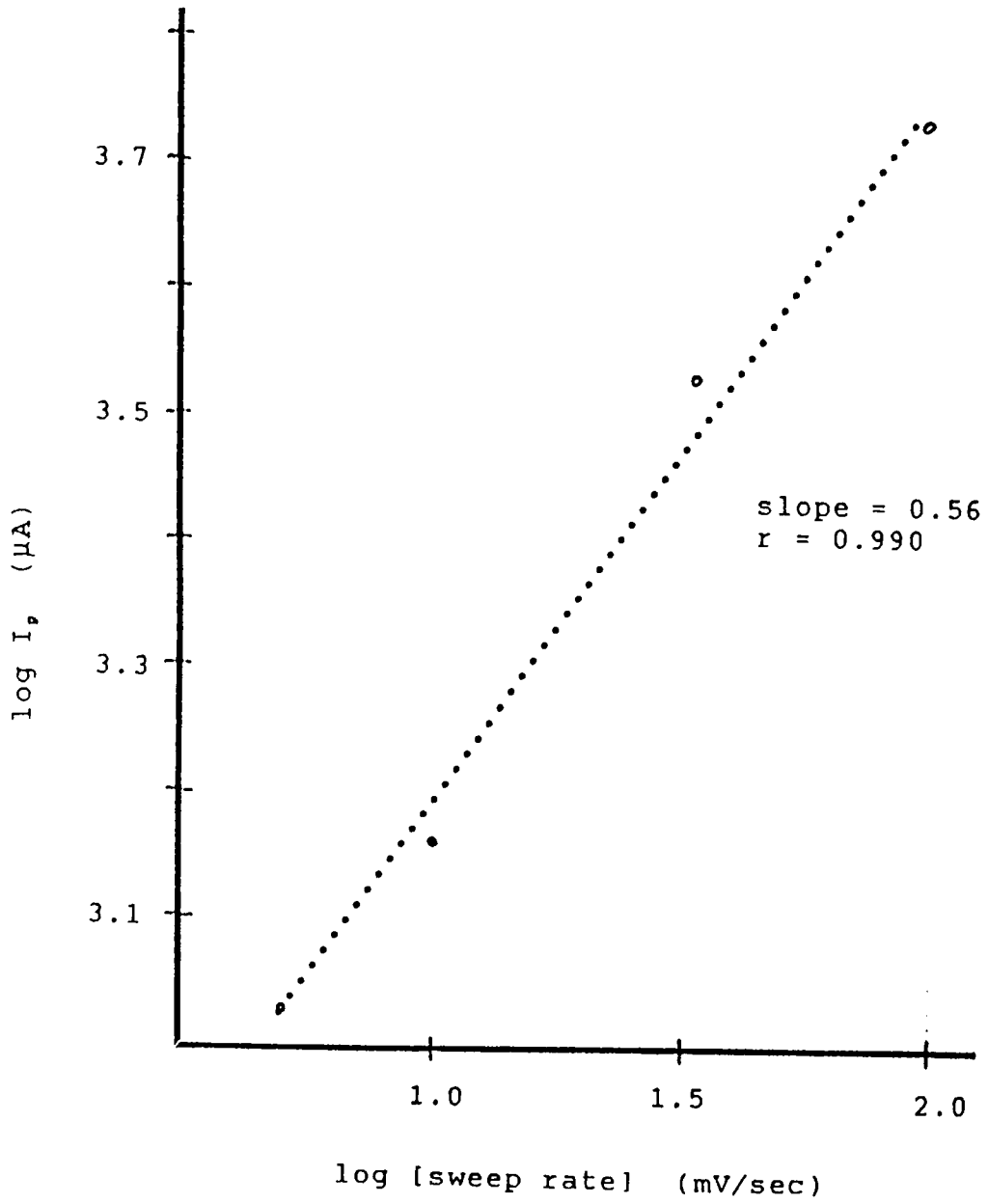


Figure 13. Graphical representation of the dependence of a silver-on-platinum-substrate electrode on diffusion controlled behavior.

was found to be 0.56, which is indicative of a diffusion controlled process, most probably the diffusion of chloride ion from the bulk solution to the surface of the film.

The dependence of the peak current on the sweep rate for an untreated polyester-TCNQ film has been measured by previous researchers (129), and it has been shown that PE-TCNQ exhibits behavior indicating that the process is intermediate between surface and diffusion control, i.e. the slope of the plot of log(anodic peak current) versus log(sweep rate) would be approximately 0.7 for the film thicknesses used in these experiments.

Finally, the dependence of the peak current on the sweep rate for polyester-TCNQ films treated with various concentrations of silver reveals some information about the effect of the silver on the electron transport properties of the film. First, a polyester-TCNQ film was treated via a method to produce a relatively low concentration of silver in the film (Q_a = 10.5 $\mu C/cm^2$) and anodic peak current versus sweep rate data were acquired and analyzed as a log-log plot in Figure 14. The slope of the line, 0.88, indicates that a film with a low concentration of silver behaves like a thin surface layer characterized by rapid and reversible charge transport rates under these conditions. This behavior could be due to the formation of discrete connections between silver

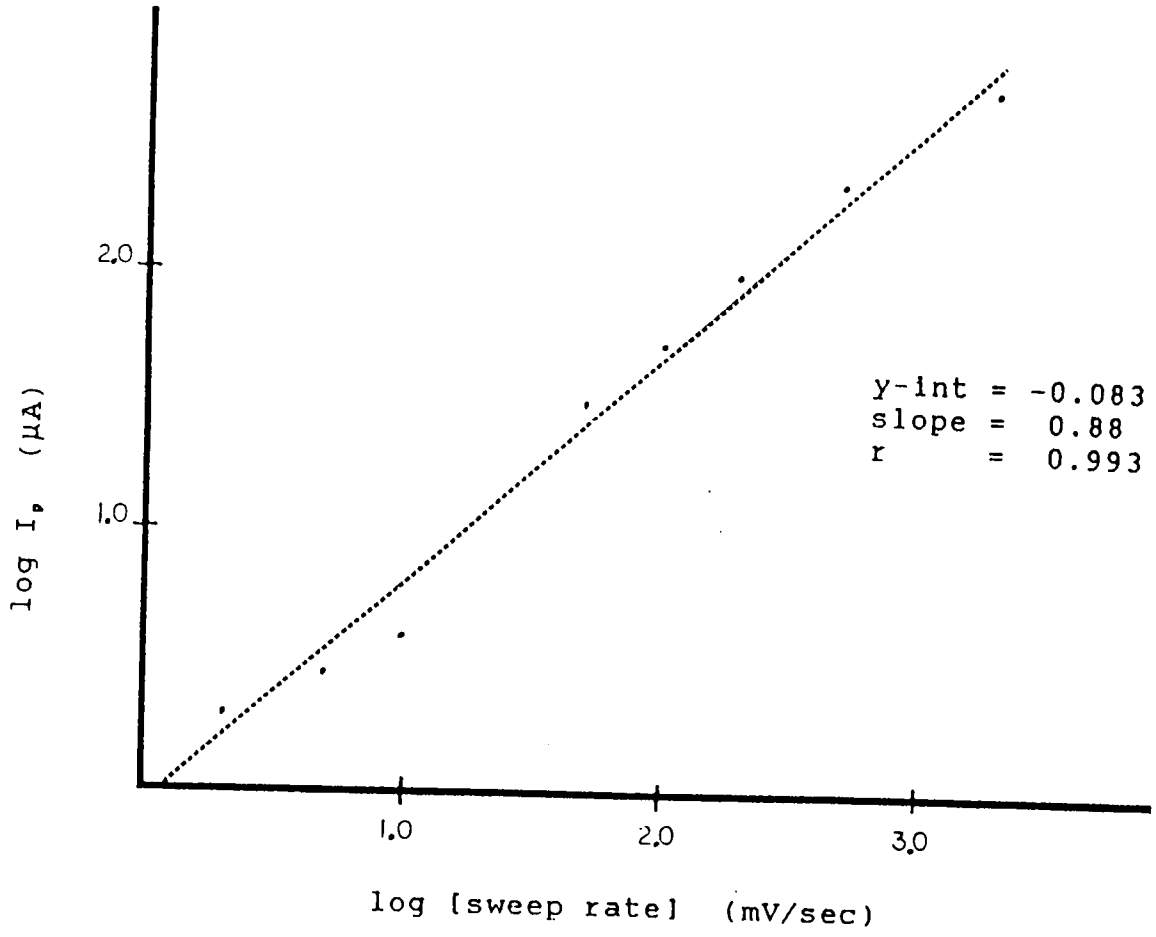


Figure 14. Plot of log (peak current) versus log (sweep rate) for a PE-TCNQ film incorporating a low surface coverage of silver(I) ion.

clusters through the polymer matrix, producing an effective increase in the rate of charge transport without interfering with the diffusion transport of counterions. However, when the surface coverage of silver is increased, as in the second film, (Q_a = 217.9 $\mu C/cm^2$) and the same type of plot is produced, as in Figure 15, a slope of 0.77 is obtained. This indicates that the film is behaving in a manner which has elements of both surface control and diffusion control. This behavior is probably due to the formation of larger clusters of silver in the film which expedite charge transfer, but inhibit counterion diffusion, producing a net increase in the effective polymer thickness.

b) Accumulation Experiments

In order to demonstrate the feasibility of using the polymer-TCNQ films in the detection of metal ions, specifically silver, a number of successive deposition experiments were carried out. Since these experiments used the same polymer film for successive treatments, the silver had a tendency to accumulate, first within the film and then on the surface of the electrode support. In this thesis, these experiments are called **accumulation** or **block** experiments. These experiments naturally resulted in the incorporation of more silver in the film than can be

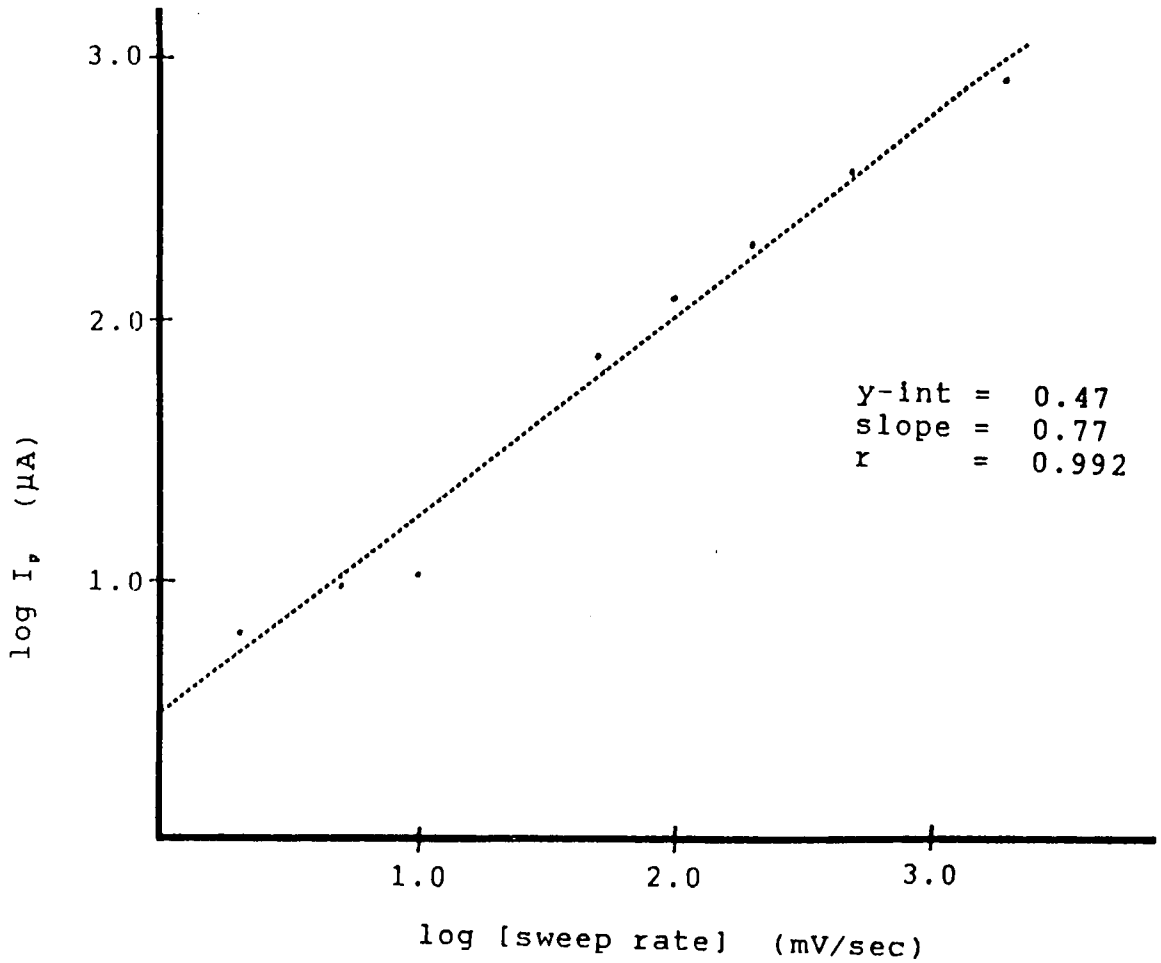


Figure 15. Plot of log (peak current) versus log (sweep rate) for a PE-TCNQ film incorporating a high surface coverage of silver(I) ion.

explained by the number of TCNQ units present within the film. In fact, ratios of silver to TCNQ were found to reach as high as 10 to 1. However, these accumulation studies lead to the following observations: 1) the polymer-TCNQ films can be used to incorporate metal ions in a fashion which can be easily measured and correlated versus the concentration of metal ion to which the film was exposed, and 2) the polymer-TCNQ films can be used to detect metal ions, specifically silver, at very low concentrations, approximately 1.0E-8 M, in quiescent, low ionic strength solutions.

In the first series of experiments, it was decided to examine the effect of increasing but equivalent reduction (R) and treatment (S) times on the incorporation of silver into the polymer. The results shown in Figure 16 were obtained for silver nitrate concentrations of 1.0E-1 M and 1.0E-2 M, and R,S times of one minute to eight minutes. From the graph, two conclusions are immediately evident. First, the values of Q/Q_t, where Q is the anodic charge of the doped polymer and Q_t is the total charge of the original polymer, are well separated for the two concentrations of silver used in the treatments. There are no overlapping data values at short time periods, and the differences increase at longer treatment times. Moreover, the pattern of data points for the two silver concentrations is essentially the same, showing an initial

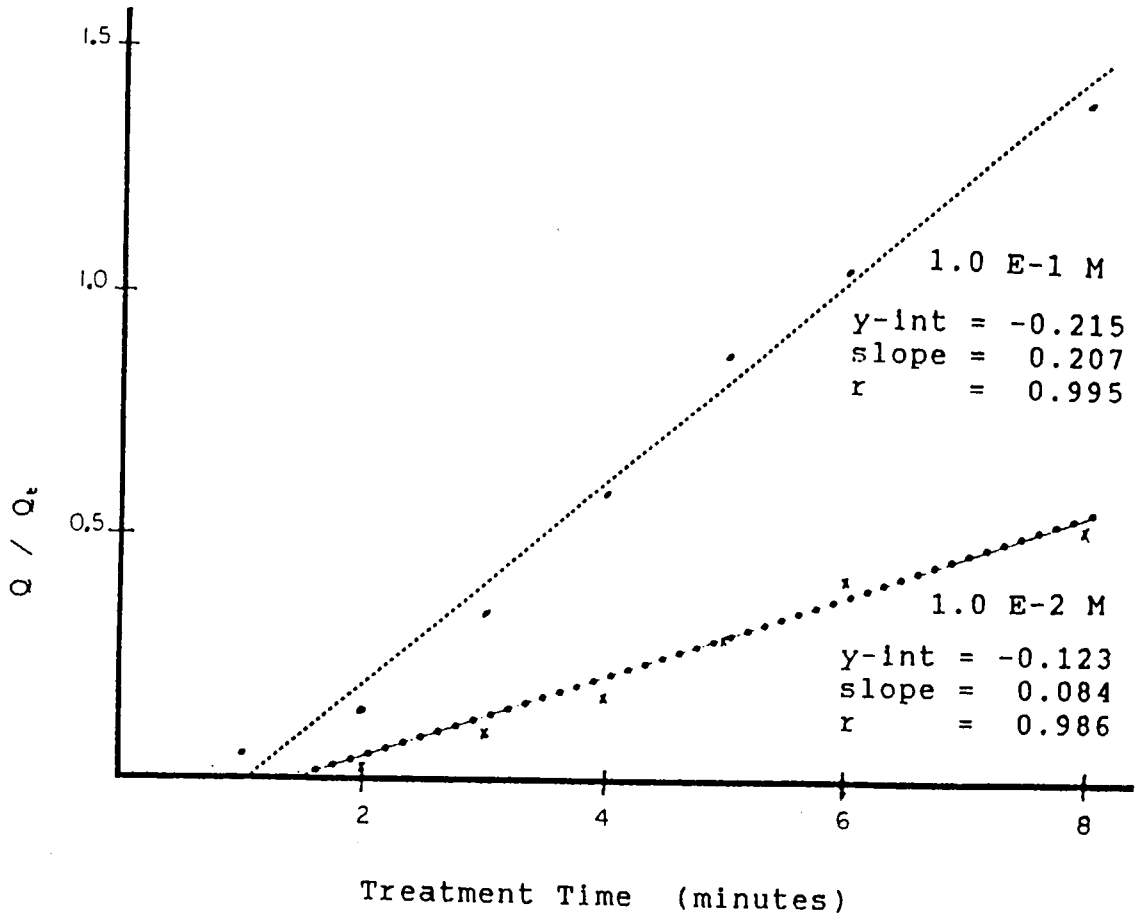


Figure 16. Plot of the charge ratio versus the treatment time for the accumulation of silver in PE-TCNQ films from solutions of 1.0E-1 M and 1.0E-2 M silver(I) ion.

gentle rise. Second, both groups of data points exhibit linear regions. For the 1.0E-1 M silver ion, the linear region of slope = 0.216 and y-intercept = -0.268, with a data point correlation factor of 0.996, exists from a RS time of 2 minutes to a RS time of 8 minutes. For the 1.0E-2 M silver ion, a linear region of slope = 0.101 and y-intercept = -0.199, with a data point correlation of 0.991, exists from a RS time of 2 minutes to a RS time of 6 minutes. The overall conclusion which can therefore be reached using the data in this plot is that the initial evidence for the utilization of polymer-TCNQ films for the detection of silver appears very favorable.

In the second series of experiments, the relationship of response to increasing concentrations of silver ion was examined. A polyester-TCNQ film was treated with 20 ml of quiescent silver nitrate solutions of increasing concentration in ten minute time intervals; the data are plotted in Figure 17. The sensitivity of the film is obvious, even in these initial stages: silver ion in quiescent, low ionic strength solutions can be detected at concentrations as low as 1.0E-7 M, even though the conditions for mass transport are not optimal. Also, the response is relatively linear from 1.0E-7 M to 1.0E-1 M silver ion concentration, with a slope of 0.506 and a data point correlation of 0.992.

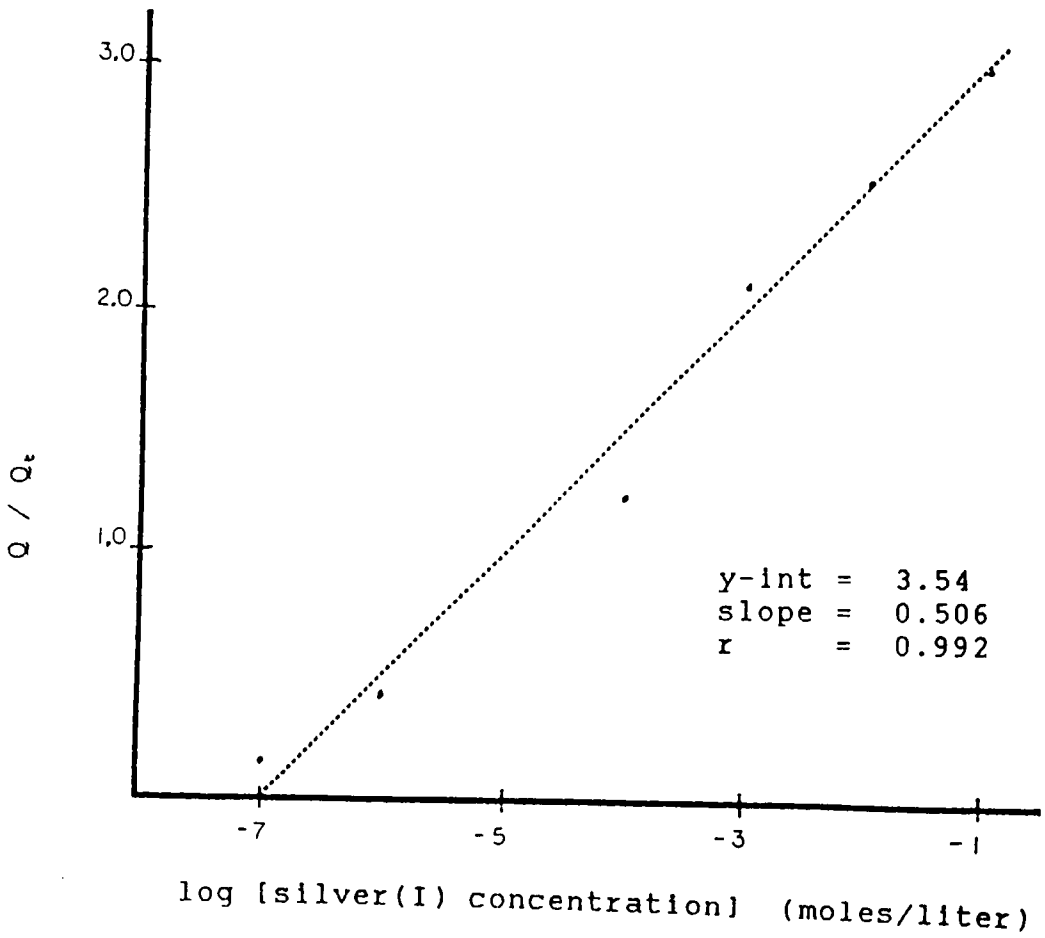


Figure 17. Plot of the charge ratio versus the log (silver(I) ion concentration) for the accumulation of silver into a PE-TCNQ film from solutions of 1.0E-7 M to 1.0E-1 M silver nitrate.

Given the preceding experiments, silver accumulation experiments were carried out for a range of silver concentrations from 1.0 M to 1.0E-8 M silver(I) nitrate, with treatment times of up to 60 minutes for the very low silver ion concentrations. The data are reproduced in Figures 18 and 19. Overall the data show a good spread between the various groups, and indicate that the films should be useful in the detection of silver ions at very low concentrations in low ionic strength, quiescent aqueous solutions. The slopes and correlation coefficients of the data sets for Figures 18 and 19 are shown in Table 5.

Even though the data from the series of experiments above are indicative that an analytical method could be produced using these PE-TCNQ films, it should be obvious that the accumulation experiment technique is not useful in the design of an analytical procedure. This is due to the dependence of the film behavior on prior incorporation of varying amounts of silver into the film. Changes in the polymer morphology due to the extensive swelling of the polymer could further complicate the electrochemistry. Even if these factors could be compensated for in a manner similar to a standard addition procedure, the film would still be limited in its ability to detect very low concentrations of silver ion, due to the difficulty of differentiating between very small signal changes.

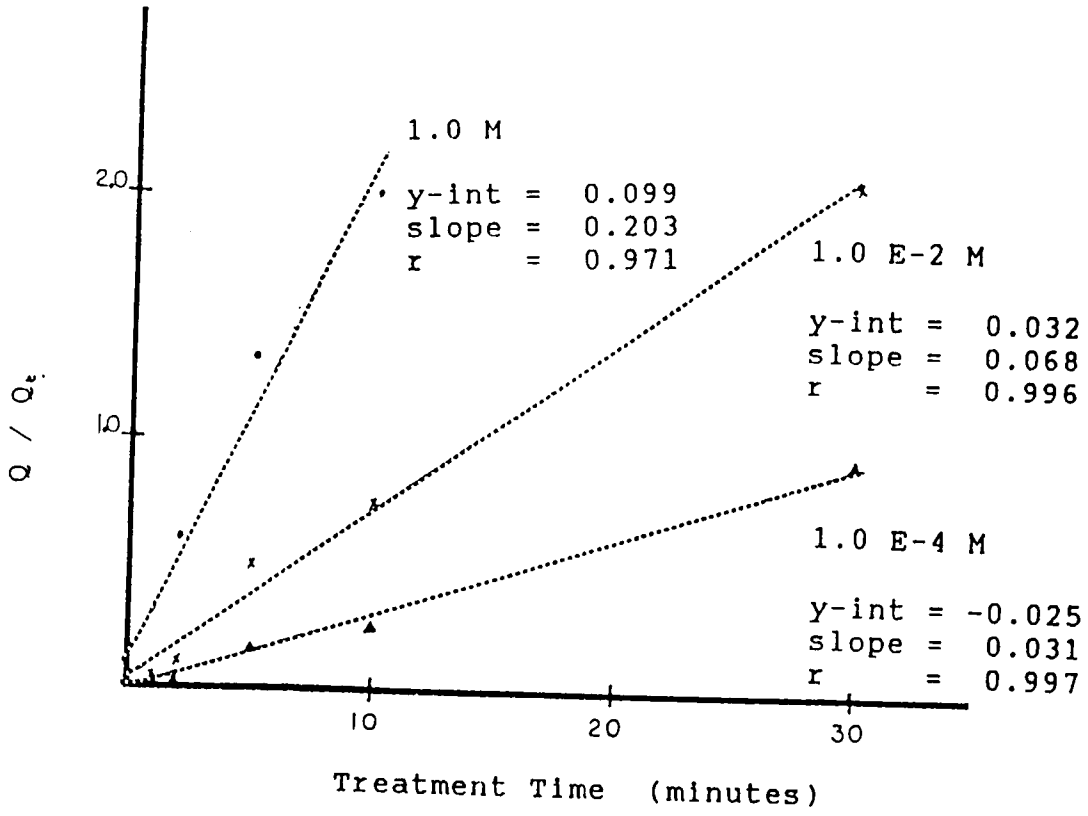


Figure 18. Plot of the charge ratio versus the treatment time for the accumulation of silver from 1.0 M, 1.0E-2 M, and 1.0E-4 M silver(I) nitrate solutions into PE-TCNQ films.

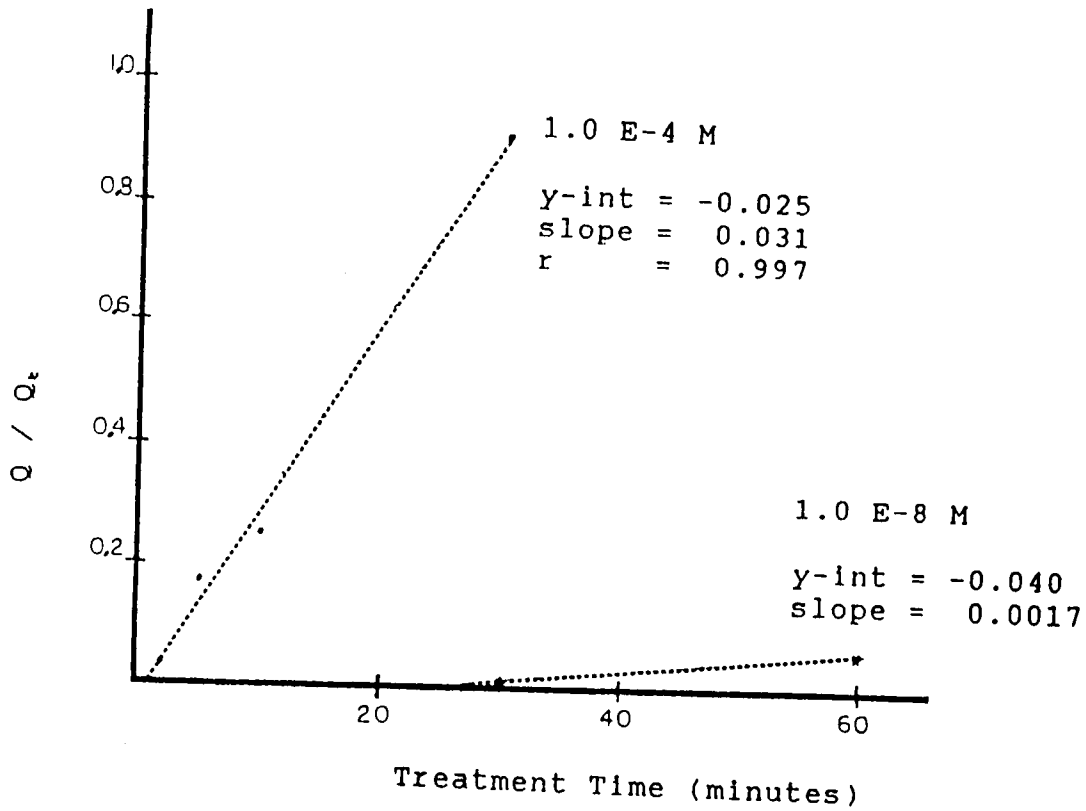


Figure 19. Plot of the charge ratio versus the treatment time for the accumulation of silver from 1.0E-4 M and 1.0E-8 M silver(I) nitrate solutions into PE-TCNQ films.

Table 5

Summary of Slopes and Correlation Coefficients

for Figures 18 and 19

Silver Concentration	Slope	Correlation Coefficient
1.0 M	0.203	0.971
1.0E-2 M	0.068	0.996
1.0E-4 M	0.031	0.997
1.0E-8 M	0.0017	---

Note: The correlation coefficient is not given for the 1.0E-8 M silver ion concentration because there are only two data points.

c) Calibration Series

The calibration experiments differed from the accumulation studies in that each data point was generated by a separate film, deposited and treated as outlined in the experimental section. A standardization series was carried out in standard laboratory lighting conditions, under fluorescent lights, with the reduction time set at five minutes using a variety of silver ion concentrations. The resulting data for silver concentrations of 1.0E-2 M, 1.0E-4 M, 1.0E-6 M, and 1.0E-8 M are shown in Figure 20. The y-axis of the plot is the ratio of the anodic charge of the second CV sweep of the silver-treated film to the total charge of the untreated film, as described in the experimental section, page 63, and the x-axis is the treatment time. The mean value of the data for between two and twelve points given a set of conditions is plotted as the point, and the range of error computed using the t-test for a 90% confidence interval. Mean values of equivalent concentration for each range are connected by dotted lines, while the solid line represents the linear regression "best" line. (Mean values and confidence intervals are listed in Table 6) The errors in the data points could arise from a variety of sources, but are most probably due to minor variations in the polymer casting

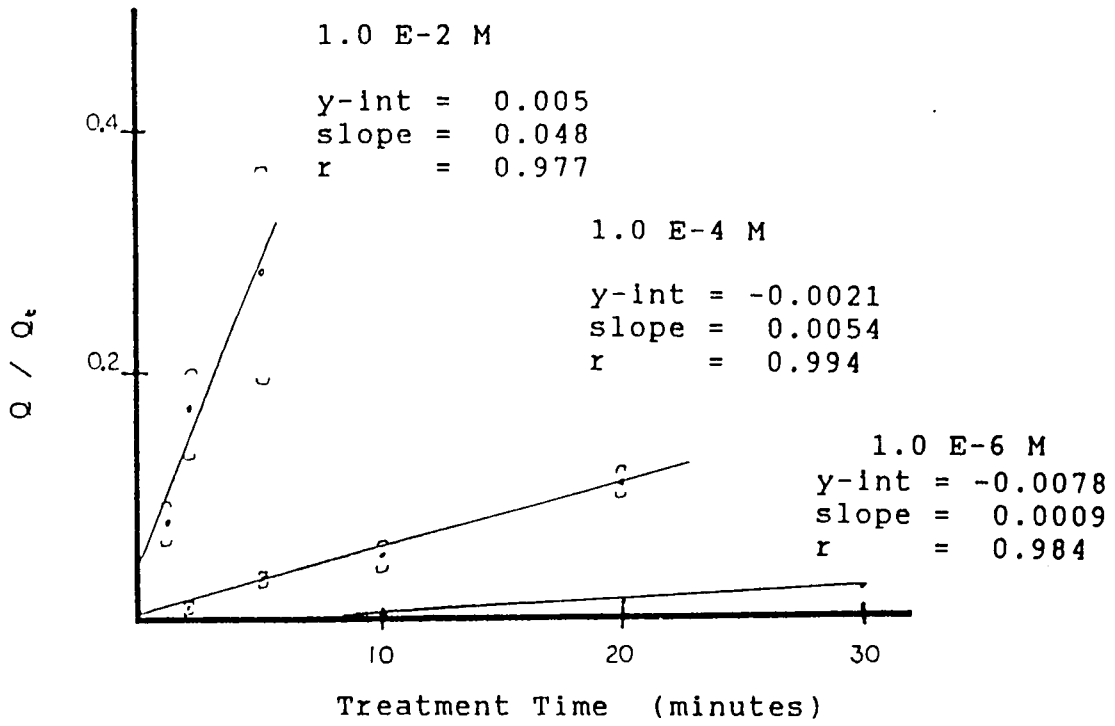


Figure 20. Standardization plot for the incorporation of silver(I) ion from 1.0E-2 M, 1.0E-4 M, and 1.0E-6 M silver(I) nitrate solutions into PE-TCNQ films.

Table 6

Mean Values and Confidence Intervals

for the Data in Figure 20

Silver Concentration	Treatment Time	Number of Values	Mean Value	90% Confidence Interval
1.0E-2 M	1 minute	9	0.078	± 0.018
	2	7	0.170	± 0.030
	5	6	0.280	± 0.090
1.0E-4 M	1	6	0.0033	± 0.0006
	2	5	0.0086	± 0.002
	5	6	0.031	± 0.005
	10	6	0.052	± 0.012
	20	5	0.107	± 0.014

Note: Mean values and confidence intervals are not given in the case of 1.0E-6 M silver(I) due to a lack of multiple data points.

solutions and in the extent of crosslinking produced by the baking process.

The data plotted in Figure 20 illustrate two ideas clearly. First, the separation between the different concentrations of silver ion is very distinct, and indicates that the polyester-TCNQ films can be used for the detection of silver. Second, the polyester-TCNQ films appear to be extremely sensitive to the silver ion at very low concentrations, even when the sampling conditions are not optimal. In 20 ml of quiescent, low ionic strength aqueous 1.0E-8 M silver(I) nitrate solution, a detectable silver signal is produced after 30 minutes of treatment, and a signal is produced for 1.0E-6 M silver(I) nitrate after only ten minutes of treatment. Finally, it should be noted that this procedure limits the amount of silver incorporated into the film to values less than or equal to the number of TCNQ sites in the original polymer film.

These data can also be plotted in a standard calibration curve format, i.e. signal versus the log (silver concentration), producing Figure 21. As for Figure 20, the calibration plot illustrates that the PE-TCNQ modified electrode can be used as a sensitive detector for silver (I) ion, even under the non-ideal mass transport conditions used in this experiment. The lack of linear regions in Figure 21 is probably due to the change in diffusional character of the PE-TCNQ film as the

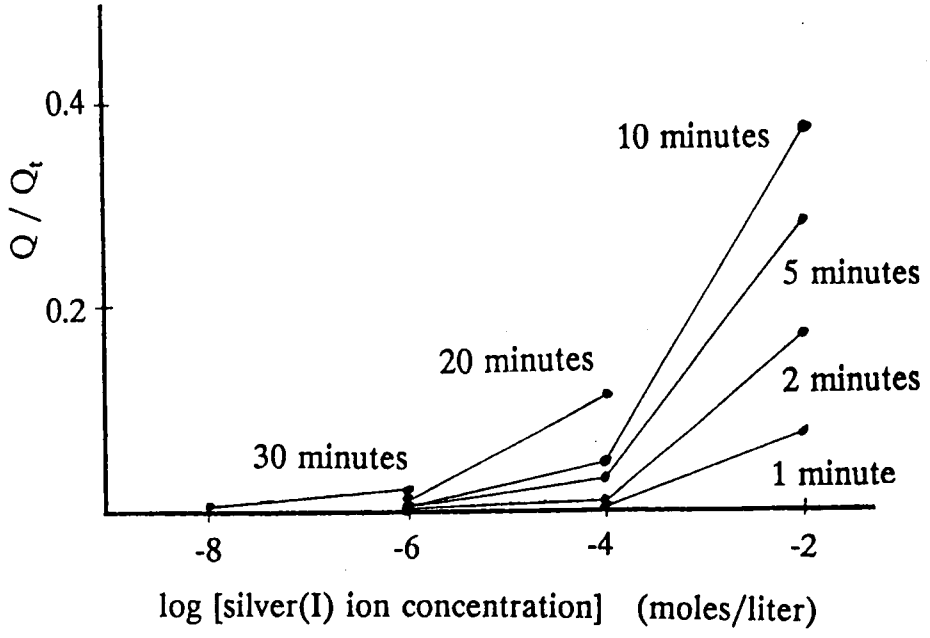


Figure 21. Calibration plot for the incorporation of silver(I) ion from 1.0E-2 M, 1.0E-4 M, and 1.0E-6 M silver(I) nitrate solutions into PE-TCNQ films.

concentration of silver in the film is increased (See page 86). However, this non-linear response can still be applied in the formation of a useable calibration plot.

d) Photoeffects

Since it has been established that silver-TCNQ is a light sensitive compound, and due to the fact that silver chloride is also light-sensitive, the effect of the lighting conditions on the incorporation of silver into the polymer-TCNQ film may be significant. Therefore, one series of films was produced where the films were treated with 1.0E-4 M silver nitrate solutions for varying times in essentially total darkness, i.e. in a photographic darkroom. A second series of films was produced using the same silver ion concentrations and times, but under ultraviolet illumination. The results of these two series are shown in Figure 22, along with a comparison plot for identical conditions under standard lighting. A decrease in lighting does seem to affect the sensitivity of the film at longer treatment times, as predicted earlier, but the effect does not seem to be more than a 5% change in sensitivity, indicating that changes in visible light intensity are not as important as originally suspected at this silver concentration. However, when the lighting is changed to ultraviolet radiation, the sensitivity of the

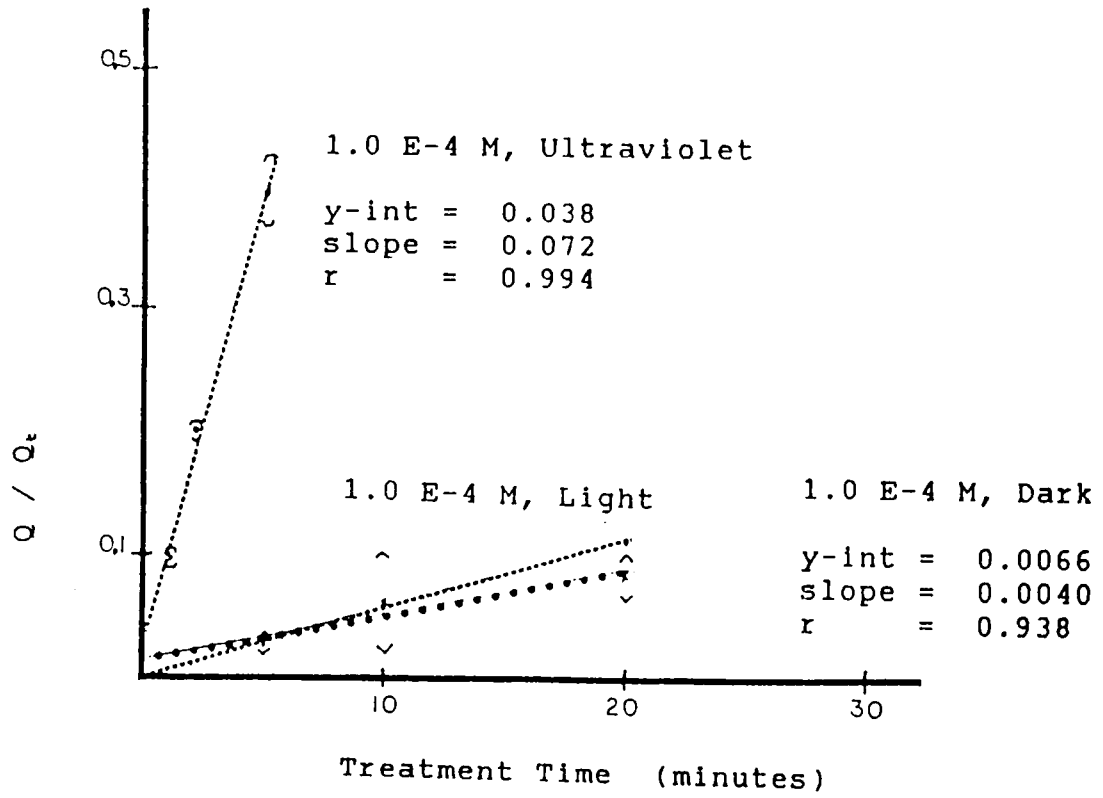


Figure 22. Comparison of the amount of incorporation of silver into a PE-TCNQ film based on lighting conditions from a low concentration (1.0E-4 M) silver (I) nitrate solution.

film increases dramatically. This effect is predictable from the earlier discussion of the photographic process, which depends on the introduction of enough highly energetic photons to produce the latent image.

In order to explore the effect of light on the incorporation of silver into the film, the experiment for light/dark behavior was repeated using a higher concentration of silver (I) ion. The results are shown in Figure 23, and indicate that a light-driven reaction does occur at high concentrations of silver, resulting in a significant difference in signal.

2) Examination of Physical Structure

In an attempt to learn more about the nature of silver incorporation into the polyester-TCNQ film, two optical techniques were utilized to study the physical structure of the film, e.g. electron spectroscopy (ESCA) and Raman spectroscopy (SERS).

a) Electron Spectroscopy for Chemical Analysis

Electron Spectroscopy for Chemical Analysis (ESCA) has been used to characterize both the surface and the interior structure of polymeric systems. ESCA is a fairly sensitive technique, which qualitatively identifies

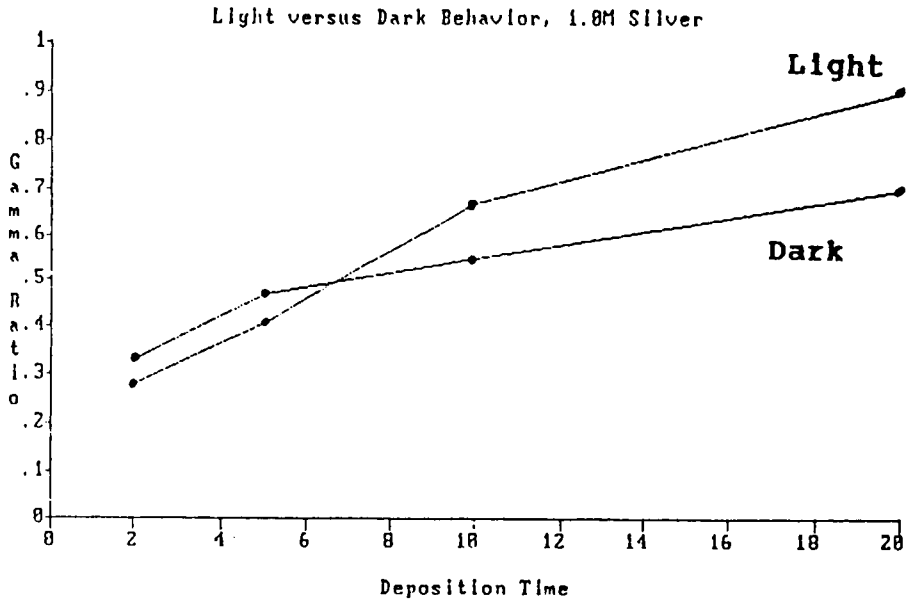


Figure 23. Comparison of the amount of incorporation of silver at a high silver (I) nitrate concentration.

elements in the sample and gives semiquantitative elemental surface concentrations, through the detection and quantitation of both the main electron energy bands and the auxiliary bands known as Auger lines. Often chemical oxidation states can be inferred from the positions of the lines relative to a standard. Unfortunately, in the case of the silver treated polyester-TCNQ films, the Auger lines were not of sufficient intensity to be used for the determination of the chemical oxidation state of the silver in the film. Therefore, data concerning the oxidation states of the silver in the film was extrapolated from peak shifts of the silver(0) doublet lines, which occur at 374.0 eV for the $3d_{3/2}$ electron and at 368.0 eV for the $3d_{5/2}$ electron (218).

Initial experiments used ESCA as a simple probe for the presence and location of silver within the film. Two films were treated identically with silver (R1S5, 0.1 M Ag^{+}), and, after voltammetry to verify the incorporation of silver, the first film was further reduced at -0.2 V vs SCE for one minute, then subjected to ESCA analysis, as shown in Figure 24. After the surface scan, the film was sputtered with an argon ion beam to excavate the film, and scanned again. The data accumulated (see Table 7) seem to indicate that the silver is distributed throughout the film. There does not appear to be a high density silver

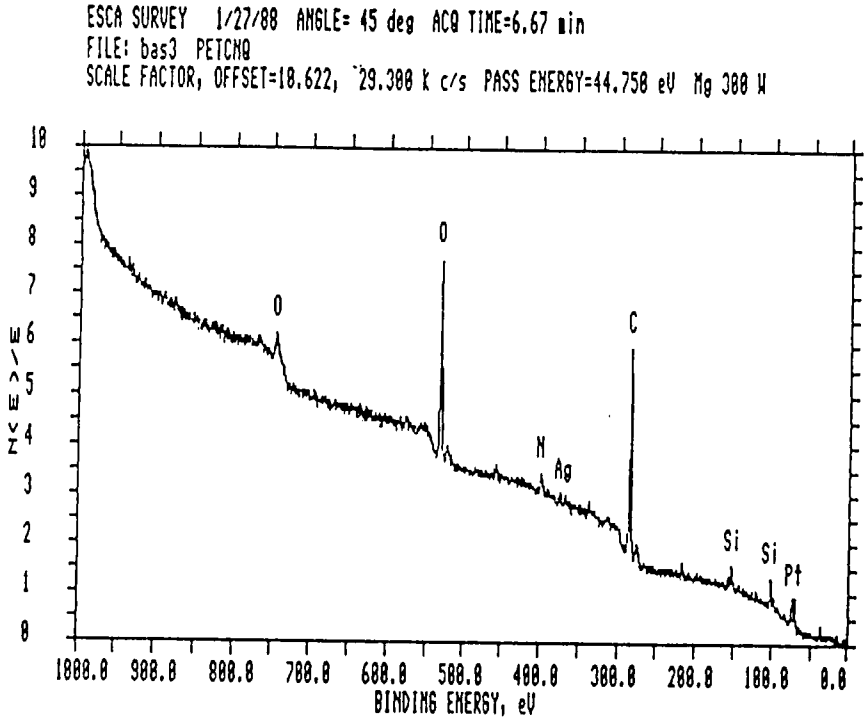


Figure 24. ESCA surface scan of a reduced PE-TCNQ film which was previously treated with silver(I) ion.

Table 7

ESCA Sputtering of Silver-Treated Substrates

	Substrate 1		Substrate 2		Substrate 3	
Time (a)	Pt %	Ag %	Pt %	Ag %	Pt %	Ag %
0	0.93	0.37	1.85	0.30	0.53	0.38
1	4.33	0.67	6.69	0.67	5.62	1.73
3	6.40	0.74	9.73	0.78	8.37	1.90
6	7.87	0.73	11.98	0.75	10.46	2.14

Notes: Percentages are listed in terms of the total signal for all sampled regions.

a) Total sputtering time, in minutes

b) Substrate 1 is the PE-TCNQ film reduced for 1 minute at -0.2 V vs SCE.

c) Substrate 2 is the PE-TCNQ film oxidized for 10 minutes at +0.3 V vs SCE.

d) Substrate 3 is the platinum flag electrode.

interlayer, as has been observed in polyimide films treated with silver, but only a broad diffuse region. The second film treated with silver was held for ten minutes at +0.3 V vs SCE to oxidize the film, which was then surface scanned and sputtered in a manner similar to the first film. The information for the second film, also listed in Table 7, indicates that the position and distribution of silver in the oxidized film is similar to that in the reduced film, i.e. a diffuse region rather than a dense layer on the surface of the polymer or at the polymer/substrate interface. In both films, the magnitude of the carbon and platinum percentages indicate that the argon beam has burrowed into the surface of the polymer, but has probably not reached the platinum substrate, although the presence of any platinum peak may be indicative of pinholes in the film (226). In considering the data produced by sputtering a film, there are two problems, inherent with the process, which must be kept in mind. First, the X-ray beam used to scan the surface of the crater also excites atoms below the surface of the crater. Most of these extra excited ions are absorbed by the surrounding material, but a few escape to the detector. Therefore, the signal detected is not completely spatially resolved. Second, if the scanning X-ray beam is not tightly focused, there is the possibility of scanning the walls of the crater, adding further

erroneous signal and decreasing the apparent spatial resolution of the process.

In order to test the ESCA response of a silver film on a platinum electrode, silver was plated onto a platinum flag electrode via electrolysis of 20 ml of 1.0E-2 M silver(I) nitrate solution at -0.2 V vs SCE for two minutes. The resulting film, which converted to a gray coating upon exposure to the atmosphere, was scanned and sputtered with an argon ion beam in the spectrometer; the results are listed in Table 7 (page 106). The data show clearly the presence of the silver on the platinum surface, and the distribution is indicative of a dense layer of silver on the platinum surface, as evidenced by the very high silver signal. This behavior is significantly different from the silver treated polyester-TCNQ films, where the magnitude of the silver signal leveled off as the platinum substrate was approached.

It is possible to produce data concerning the oxidation state of the silver in the treated polyester-TCNQ films by comparison of the position of one of the bands for the silver doublet in a variety of conditions. The resulting data have been assembled in Table 8. Compensation for electrostatic charging of the sample was accomplished by measuring the position of the carbon 1s electron line in the spectrum and comparing it to the value in the X-ray spectroscopy manual for the instrument

Table 8

ESCA Peak Positions for the Silver $3D_{5/2}$ Electron

in Various Chemical Environments

Time (a)	Film 1 (b)	Film 2 (c)	Film 3 (d)	Film 4 (e)
0	368.1	368.1	367.8	367.7
1	367.9	368.0	368.5	368.5
3	368.0	368.1	368.5	368.8
6	367.9	368.0	---	---

All values given in electron volts (eV)

Notes: Silver metal peak at 368.9 eV.

Silver chloride peak at 368.3 eV.

Silver-TCNQ peak at 368.4 eV.

a) Total sputtering time, in minutes.

b) Film 1 is silver-treated PE-TCNQ which has been oxidized for 1 minute at +0.3 V vs SCE.

c) Film 2 is silver-treated PE-TCNQ which has been reduced for 1 minute at -0.2 V vs SCE.

d) Film 3 is silver-treated PE-TCNQ which has been oxidized for 5 minutes at +0.3 V vs SCE.

e) Film 4 is silver-treated PE-TCNQ which has been reduced for 5 minutes at -0.2 V vs SCE.

(218). Similar adjustments for instrumental errors were produced by measuring the position of a gold standard peak and compensating accordingly. From samples of silver chloride and silver-TCNQ generated in the lab, it was found that there was approximately 0.6 eV difference between the silver(I) and silver(0) redox states for the instrument, after compensation as stated above. Examination of the silver-treated polyester-TCNQ films (films 1-3) shows that the silver in the film exists in a silver(I) form, probably as silver chloride. However, the silver can be changed from a cationic state to a neutral state via reduction at -0.2 V versus SCE, as in film 4. This process does not seem to proceed very rapidly, as a five minute reduction of film 4, which would ordinarily be sufficient to reduce approximately 95% of the TCNQ units in an untreated polyester-TCNQ film, only serves to reduce the layers of the film closest to the platinum substrate. However, a time-dependent reduction process could be significant depending upon the resistance characteristics of the treated oxidized and reduced layers of the film.

b) Raman Spectroscopy

It has been recognized for the past ten years that silver electrodes have surfaces where certain chemical reactions of organic materials are favored. Relatively

electroinactive compounds like thyroxine (186) and cytochrome C (185) have been shown to undergo electron-transfer reactions on silver electrodes at lower potentials than normally expected, and often without the presence of mediator compounds. It has also been observed that silver films can produce enhanced signals for Raman scattering radiation of organic materials deposited on the silver (219-222). Because of these findings, it was surmised that a silver treated TCNQ-polymer film might produce a similar enhancement in signal over a silver-free TCNQ-polymer film.

Accordingly, a platinum flag electrode was coated with a film of PE-TCNQ in the manner described in the experimental section, page 57, and cycled in 0.5 M lithium chloride electrolyte. The surface coverage (Γ) was calculated to be 5.85E-9 mol/cm^2 from the voltammetry (Figure 25) and the film thickness was estimated to be approximately 16 nm (129). The film was placed in an ESR cell positioned in the beam of the laser, and the reflected radiation was directed into the monochromator. Scanning the spectrum where the cyanide stretch peak should be apparent using an excitation radiation of 488.0 nm reveals no signal other than background noise. This lack of signal can be expected considering the surface coverage of the electrode in comparison with other Raman spectroscopy experiments utilizing TCNQ (223).

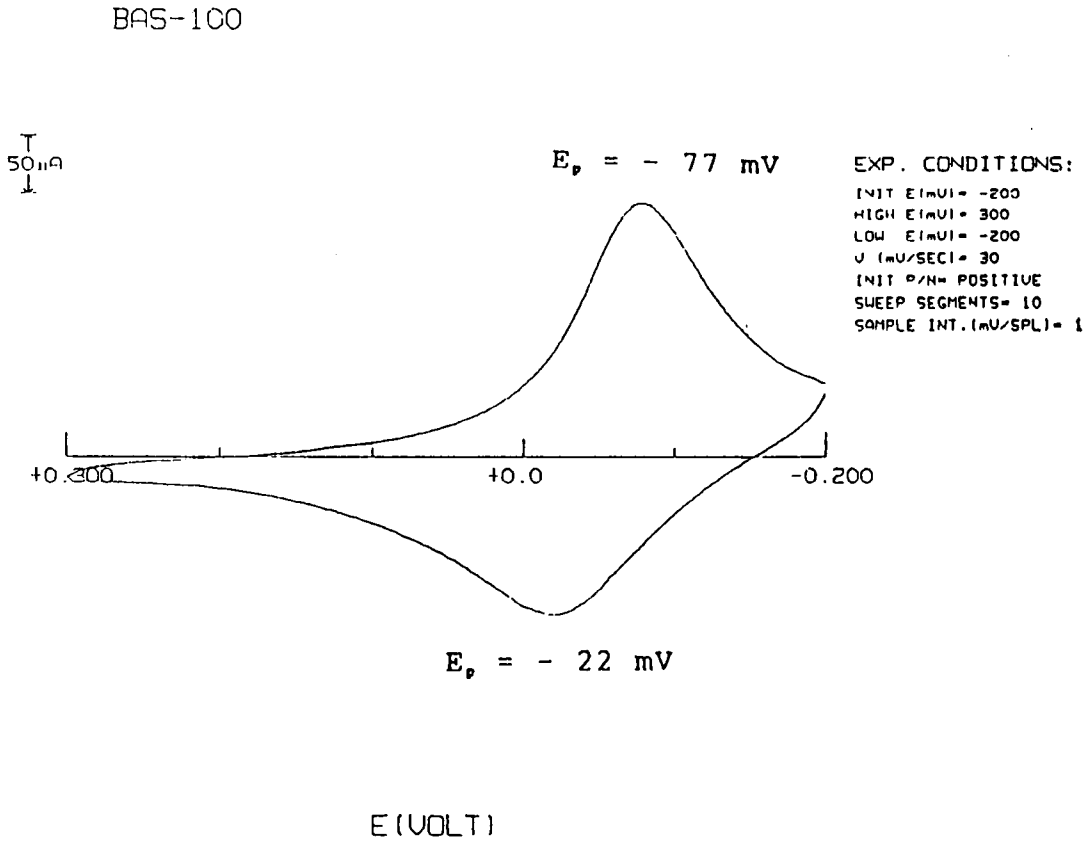


Figure 25. Cyclic voltammetry of a PE-TCNQ film cast on a platinum flag electrode and cycled in 0.5 M LiCl versus a S.C.E. reference electrode, to be used in the Raman reflectance experiment.

Next, the film was treated with silver(I) in the manner described in the experimental section, page 62, (R5S5, 0.1 M silver nitrate). The Raman spectrum of the film, Figure 26, displays a peak at 547.3 nm, corresponding to 2220.3 cm^{-1} and is assigned to the cyanide stretch in neutral TCNQ. Raman values for $TCNQ^0$ at 2223 cm^{-1} and $TCNQ^-$ at 2192 cm^{-1} have been reported in aqueous solution by Van Duyne et al. (223,224) The film was then cycled in 0.5 M lithium chloride to visualize the silver in the film (Figure 27), where the ratio of silver surface coverage to PE-TCNQ film coverage was found to be 0.155, and the film was scanned in the Raman spectrometer to produce Figure 28. Comparison of Figure 26 (page 114) and Figure 28 shows that there is little change in the cyanide stretch signal due to electrochemical cycling, and the position of the peak in Figure 26 at 2220.3 cm^{-1} indicates that the TCNQ units in the film are still in the neutral state.

Unfortunately, due to the lack of signal for the untreated PE-TCNQ film, it is impossible to calculate the enhancement factor for this PE-TCNQ system due to the incorporation of silver. However, one can estimate at least three orders of magnitude increase would have to occur to produce the peak given the intensity of the background signal. This system exhibits properties similar to the incorporation of silver films onto Raman

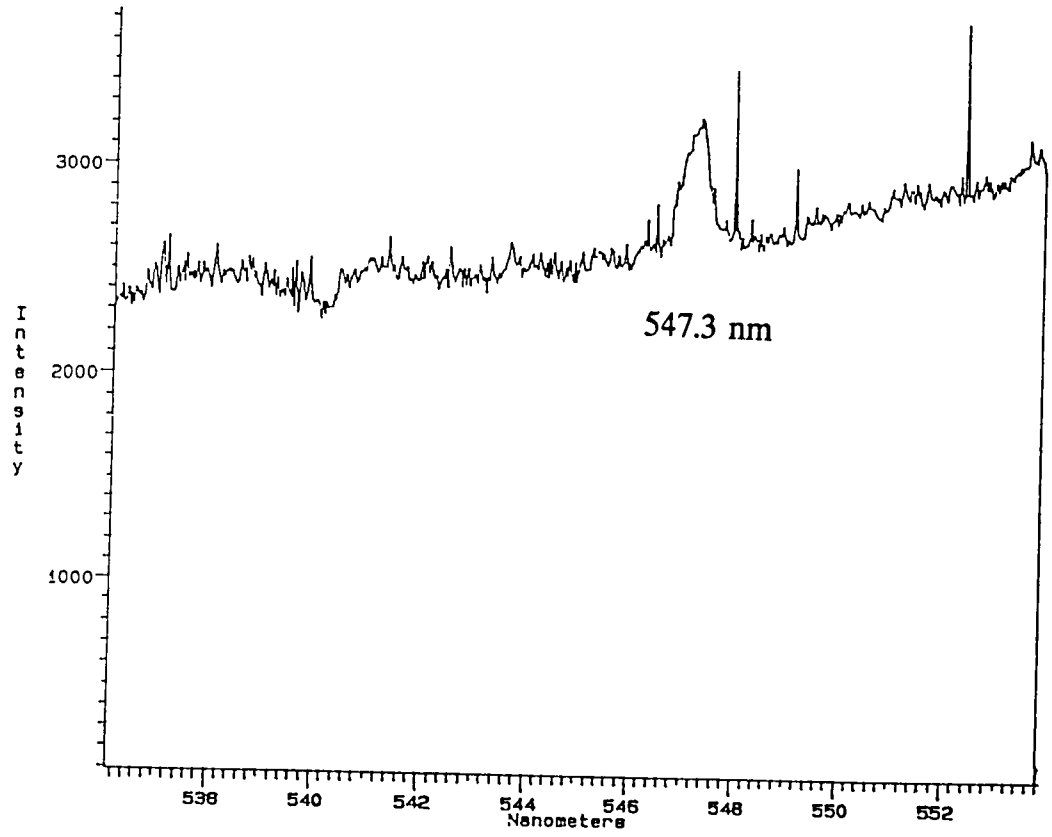


Figure 26. Raman spectrum of the PE-TCNQ film after treatment with silver(I) ion. Laser line = 488 nm.

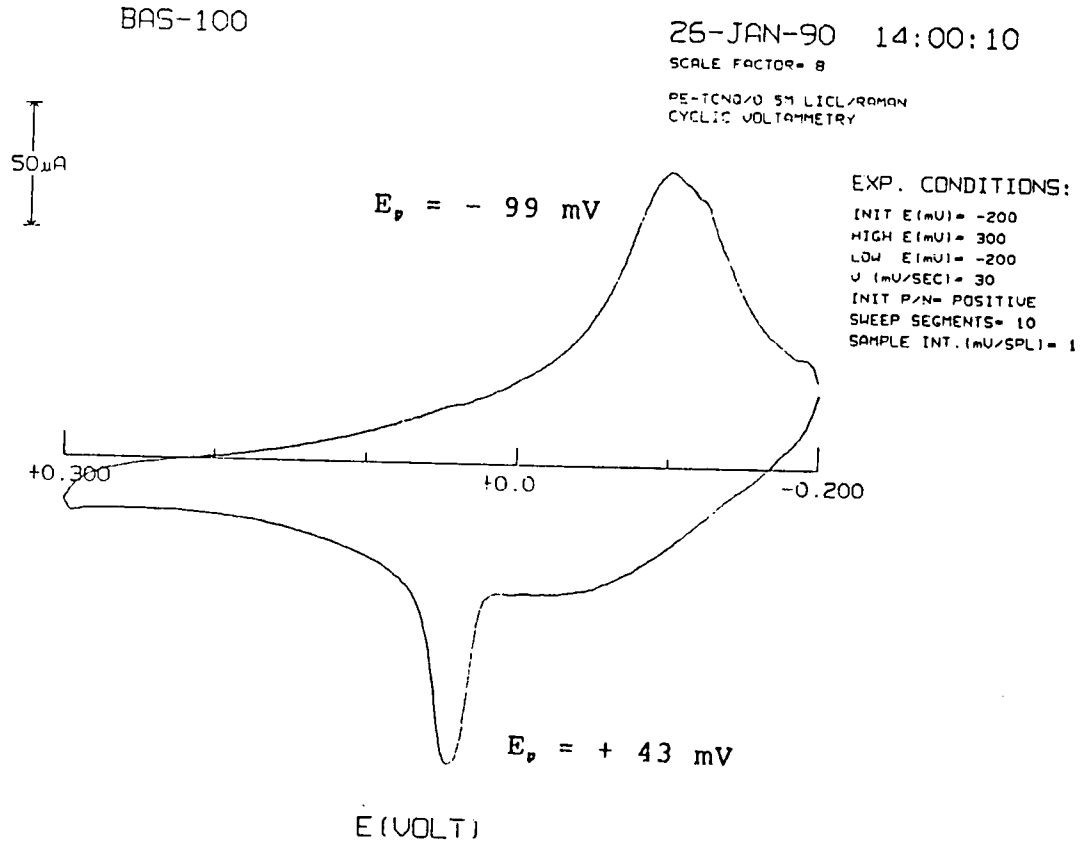


Figure 27. Cyclic voltammetry of the PE-TCNQ film on platinum substrate in 0.5 M LiCl after treatment with silver(I) nitrate.

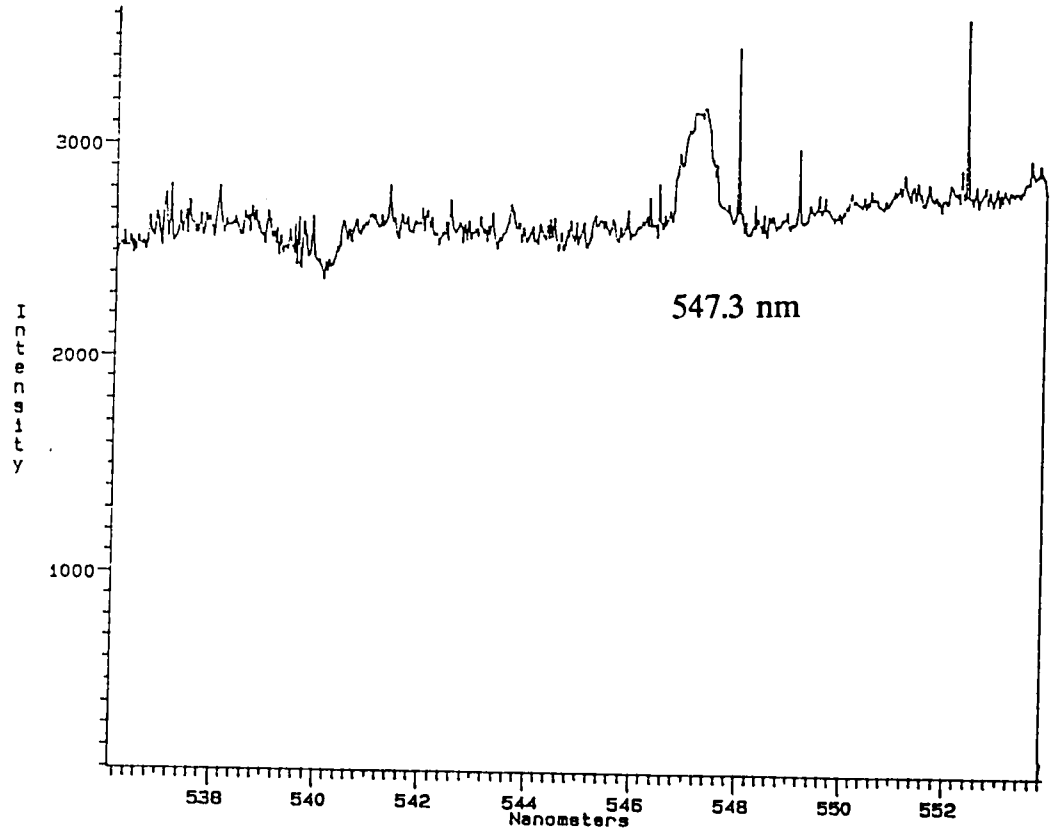


Figure 28. Raman spectrum of the PE-TCNQ film following treatment with silver(I) ion and subsequent cycling in 0.5 M LiCl.

electrodes, i.e. the enhancement of signal from certain organic compounds, and may have similar applications.

3) Possible Mechanism

Equations describing the incorporation of silver into the polyester-TCNQ film are proposed in Figure 29 which correlate all of the previous information. Equation 14 is simply a representation of the process which occurs during the electrochemical cycling and reduction of the film prior to treatment with the silver solution. Equation 15 is the probable reaction taking place during the metal ion treatment phase, as outlined by Hertler et al (7). Equation 16 is the light activated reaction of silver-TCNQ to produce neutral TCNQ and free silver, and equation 17 is the electrochemical reaction of said free silver with occluded chloride ion during the voltammetry required to visualize the silver present. Equation 18 is the summation of the previous four equations, and represents the proposed overall process occurring in the film, which leads to the observed electrochemical behavior. A cartoon representation of equations 14 through 16 is shown in Figure 30.

$$n\ TCNQ^0 + n\ Li^+ + ne^- \longrightarrow n\ Li^+TCNQ^- \qquad [14]$$

$$n\ Li^+TCNQ^- + n\ AgNO_3 \xrightarrow{H_2O}$$

$$n\ Ag^+TCNQ^- + n\ Li^+ + n\ NO_3^- \qquad [15]$$

$$n\ Ag^+TCNQ^- \xrightarrow{h\nu}$$

$$x\ Ag^0 + x\ TCNQ^0 + (n-x)\ Ag^+TCNQ^- \qquad [16]$$

$$x\ Ag^0 + x\ Cl^- \rightleftharpoons x\ AgCl + xe^- \qquad [17]$$

$$(n-x)\ TCNQ^0 + n\ AgNO_3 + (n-x)\ e^- + x\ Cl^-$$

$$\longrightarrow x\ AgCl + (n-x)\ Ag^+TCNQ^- + n\ NO_3^- \qquad [18]$$

Figure 29. Equations for the proposed mechanism which results in the incorporation of silver into the polymer-TCNQ film and the subsequent visualization of the silver.

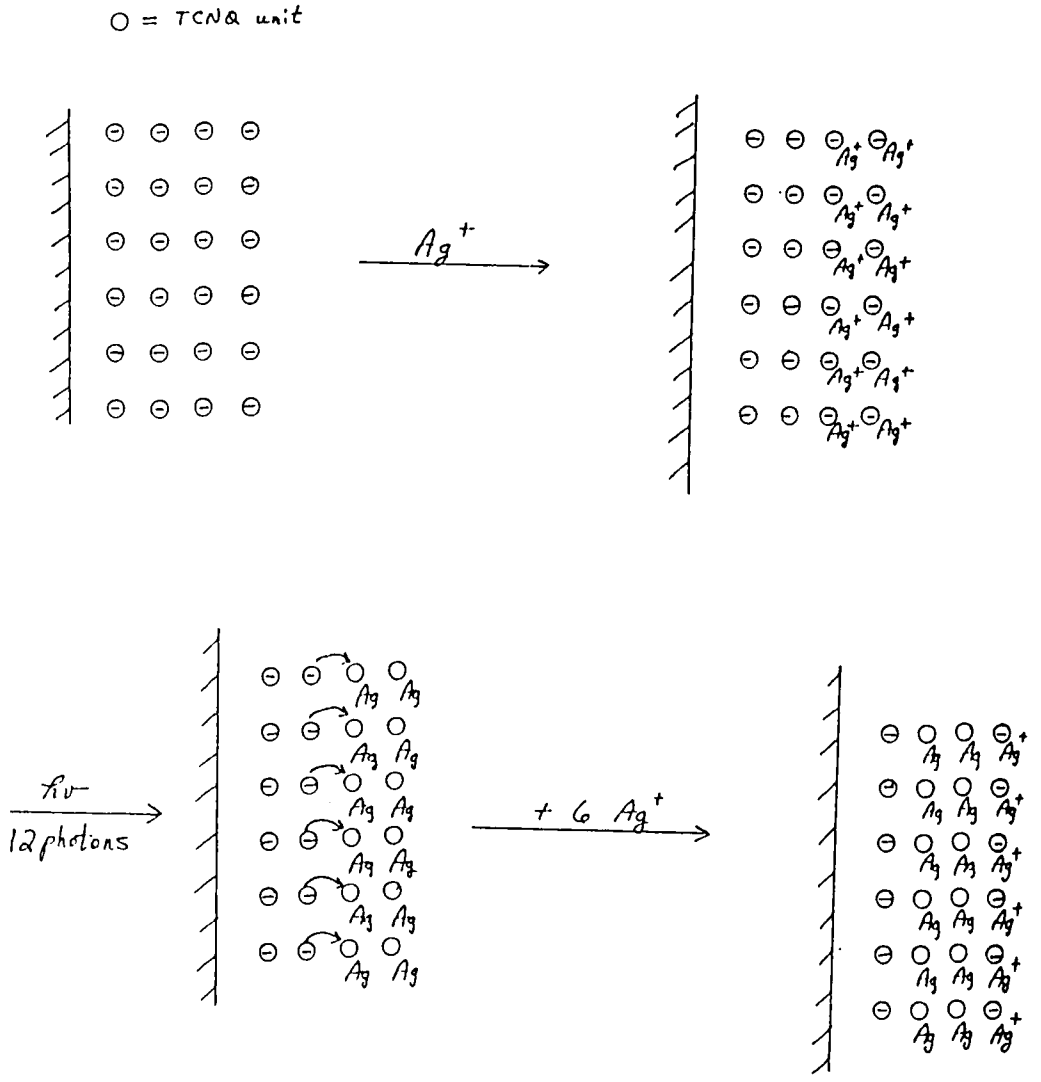


Figure 30. Pictoral representation of Equations 14-16.

4) Detection of Other Cations

The PE-TCNQ polymer of Day was also used in an attempt to detect other metal cations. Since silver(I) is considered as a Group I ion, i.e. forming a precipitate with chloride ion, the use of the other two Group I ions, mercury(I) and lead(II), should introduce few chemical interferences into the measurements. Also, due to research interest in the formation of copper-TCNQ salts, the incorporation of copper(II) was attempted. PE-TCNQ films were cast as noted previously, and treated for five minutes with 0.5 M solutions of lead(II) and copper(II) and a saturated solution of mercury(I). The only positive result for the series of experiments is shown in Figure 31 for the treatment with mercury(II), although the voltammetry for the copper test indicates that a polymer with a wider electrochemical range would probably result in a positive test. The voltammetry of the system after treatment with the mercury(II) solution exhibits an anodic peak at +0.113 V vs S.C.E. due to the presence of incorporated mercury. Due to the well-defined wave shape of this peak, and the fact that the test was carried out for approximately 1.0E-3 M mercury(II) ion due to the insolubility of mercury(II) nitrate in doubly-distilled water, it is concluded that a detection system for mercury

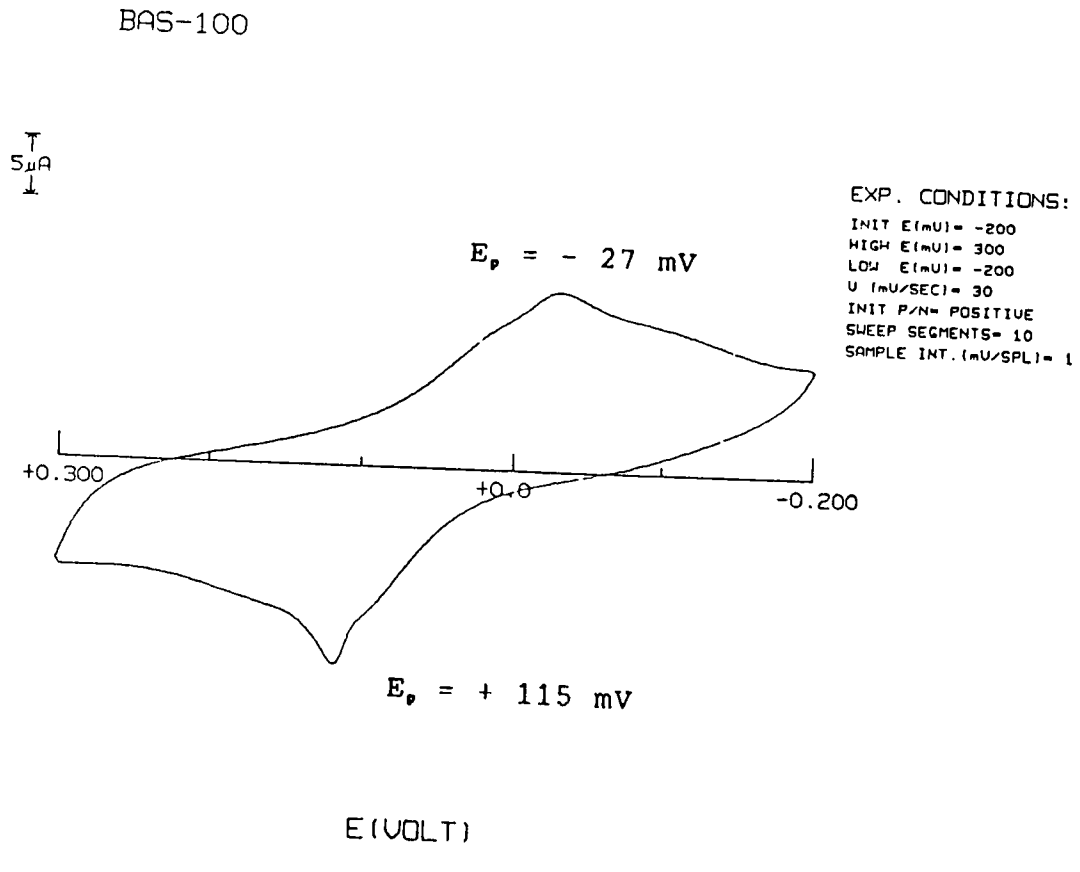


Figure 31. Cyclic voltammetry of the PE-TCNQ film after treatment (R5S5) with a saturated aqueous solution of mercury(II) nitrate. (S.C.E. reference electrode)

(II) ion using a PE-TCNQ polymer modified electrode could be constructed.

B) POLYURETHANE-TCNQ

1) Electrochemistry and Physical Structure of Polyurethane-TCNQ/Silver Films

A study of the behavior of the polyurethane-TCNQ systems was undertaken to investigate the role of the polymer structure on the uptake of silver in these redox films. The polyurethane-TCNQ polymers have a wider electrochemical potential range than the polyester-TCNQ polymer in aqueous solutions, because of the irreversibility of the second electron addition to form the dianion state. One of the limiting factors in using the polyester-TCNQ to test for other metal ions has been the limit on electrochemical stability imposed by the polymer matrix. Thus, the polyurethane-TCNQ polymer, PU-MDI, was used in a series of experiments similar to those performed with PE-TCNQ.

a) Fundamental Electrochemistry

The electrochemistry of the PU-MDI polymer cast on platinum and cycled in 0.5 M LiCl is shown in Figure 32,

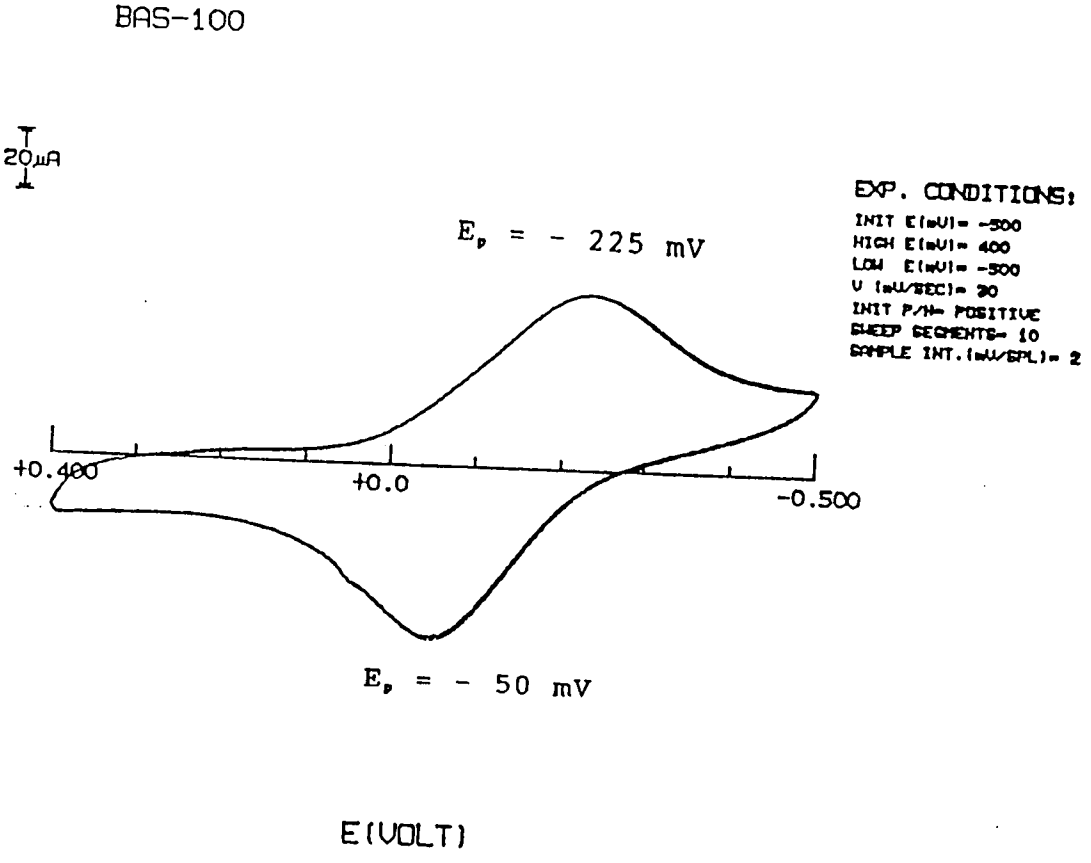


Figure 32. Cyclic voltammetry of a PU-MDI film cast on platinum and cycled in 0.5 M LiCl. (S.C.E. reference electrode)

and is similar to the previous electrochemistry shown for the PE-TCNQ system. The only difference is in the amount of tailing on the peaks, which is presumably related to the rigidity of the polymer that produces slower electron and mass transfer rates than found in the PE-TCNQ films. This limits the electroactivity to about 30% of the TCNQ units in the PU-MDI polymer film under these conditions. When the PU-MDI film is treated with silver(I) ion in a manner similar to the prior PE-TCNQ films, the voltammetric behavior shown in Figure 33 is obtained. As for the PE-TCNQ films, the one-electron transfer between silver chloride and silver(0) is evident.

It is expected that the fundamental electrochemical behavior of the PU-MDI polymer and the PE-TCNQ polymer will be essentially the same. For instance, the PU-MDI polymer can be treated with silver(I) ion, and then the silver can be removed quantitatively by cycling in 0.5 M lithium nitrate in a manner similar to the PE-TCNQ. However, for the PU-MDI, probably due to the more rigid structure, the amount of silver which can be removed from the polymer with each electrolyte solution is much less than in the PE-TCNQ case. Where two solutions of lithium nitrate were sufficient to remove approximately 90% of the silver from a PE-TCNQ film, (See previous Table 2, page 77) the same two solution treatments remove only 56%

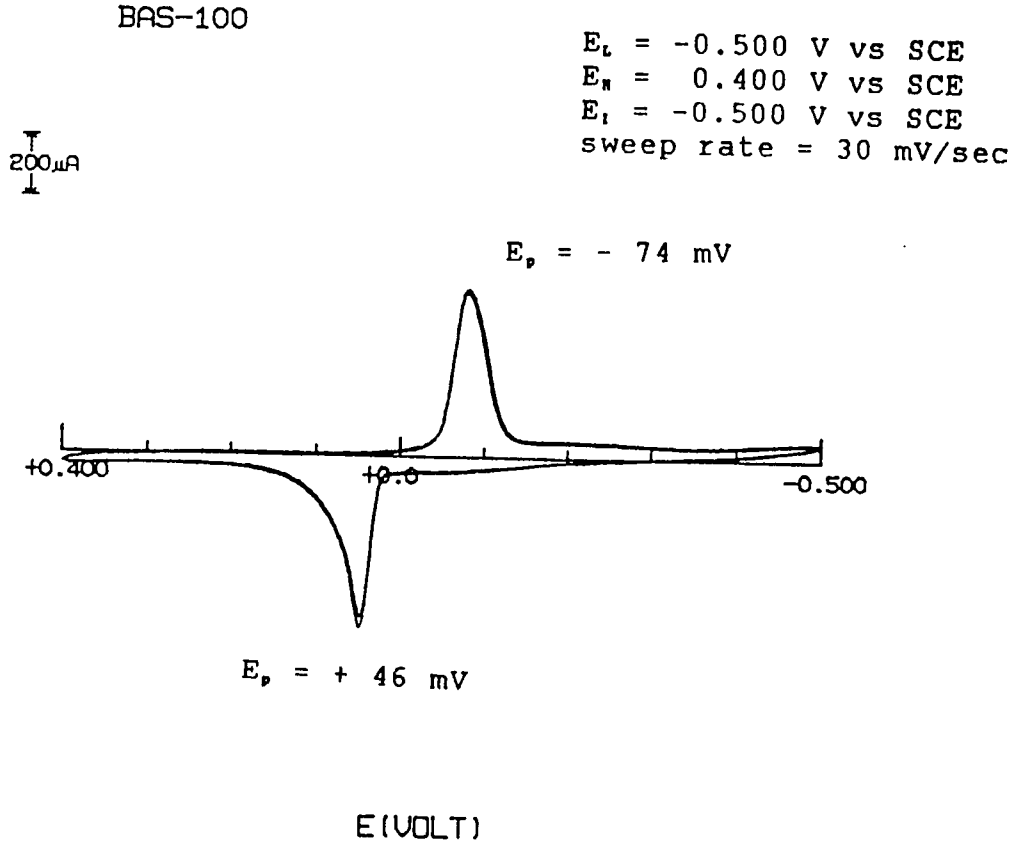


Figure 33. Cyclic voltammetry of a PU-MDI film in 0.5 M LiCl after treatment with 0.5 M silver nitrate (R10S1). (S.C.E. reference electrode)

of the silver from a PU-MDI polymer film, as shown by the data in Table 9.

From the above behavior, one would expect the ratio between surface controlled behavior and diffusion controlled behavior to be somewhat different, and skewed in the direction of diffusion control for the PU-MDI relative to the PE-TCNQ films. The plot of log(anodic peak current) versus log(sweep rate) for a PU-MDI film treated with a low concentration of silver(I) is shown in Figure 34. The slope of the line is calculated to be 0.623, with a correlation coefficient of 0.994, as opposed to the slope of 0.88 for a similarly treated PE-TCNQ film (page 84). This slope is approaching 0.5, the value for a purely diffusion controlled reaction, and is indicative that the PU-MDI polymer film, even with a silver treatment, is diffusion limited.

b) Accumulation Experiments

A series of accumulation studies were prepared using the PU-MDI films in a method similar to the PE-TCNQ block experiments. In the first experiment, the PU-MDI film was cast on platinum and exposed to successively increasing concentrations of silver(I) ion. A plot of the ratio of the anodic silver peak charge to the total charge of the untreated polymer film versus the log(silver(I) ion

Table 9

Removal of Silver (I) from PU-MDI Films

Using Successive Lithium Nitrate Solutions

Solution #	Cycle #	Anodic Charge, (μC)	% Decrease
1	2	75.6	36%
1	10	48.4	
2	2	51.3	35%
2	10	33.3	

Notes: Silver Concentration = 0.5 M

Treatment Parameter: R10S1

Electrolyte Concentration = 0.5 M

Cycle #1 was due to break-in behavior and was therefore disregarded.

Total decrease in signal = 56%

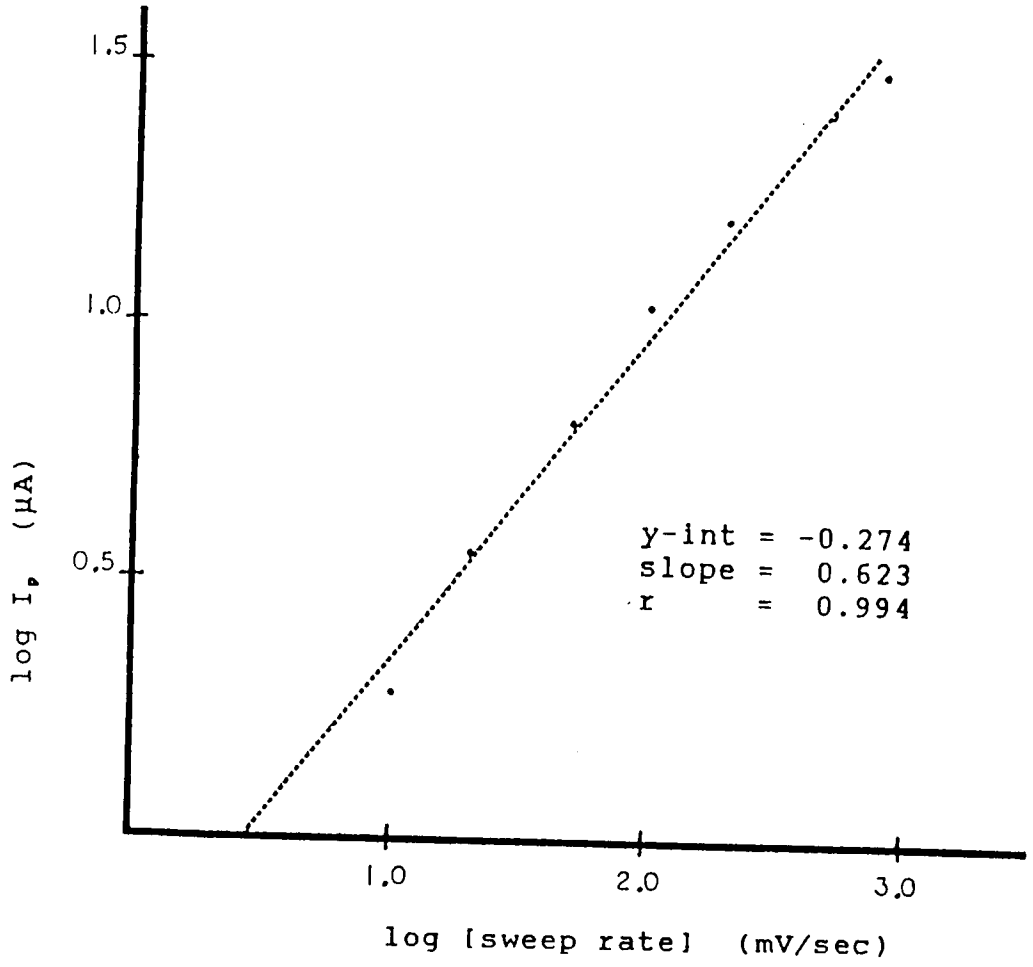


Figure 34. Plot of log (peak current) versus log (sweep rate) for a PU-MDI film doped with a low surface coverage of silver, illustrating a diffusion controlled process.

concentration) of the treatment solution, shown in Figure 35, indicates that it should be possible to use the PU-MDI films for the detection of silver in low concentration solutions. Unfortunately, the plot in Figure 35 does not exhibit the linearity which was found in the case of the polyester-TCNQ films, except over very limited ranges, but this does not contraindicate an analytical application. The remarkable increase in the charge ratio at the higher silver concentrations can probably be ascribed to the limited electroactivity of the polyurethane-TCNQ films, as silver incorporated into the film increases the accessibility of TCNQ units.

The sensitivity of the PU-MDI polymer to lower concentration silver solutions can be demonstrated by the data in Table 10 and Figure 36. The polymer film exhibits a detectable amount of silver after only twenty minutes of treatment in a 1.0E-8 M silver nitrate aqueous solution, as indicated in Table 10. Furthermore, the film remains relatively stable through a sixty minute reduction and treatment with silver, and although the increase in background current does obscure the data somewhat, as shown in Figure 36, the silver behavior in lithium chloride is still very well-defined.

The second series of block experiments for the PU-MDI polymer system used three different blocks of time for treatment of the film in increasing concentrations of

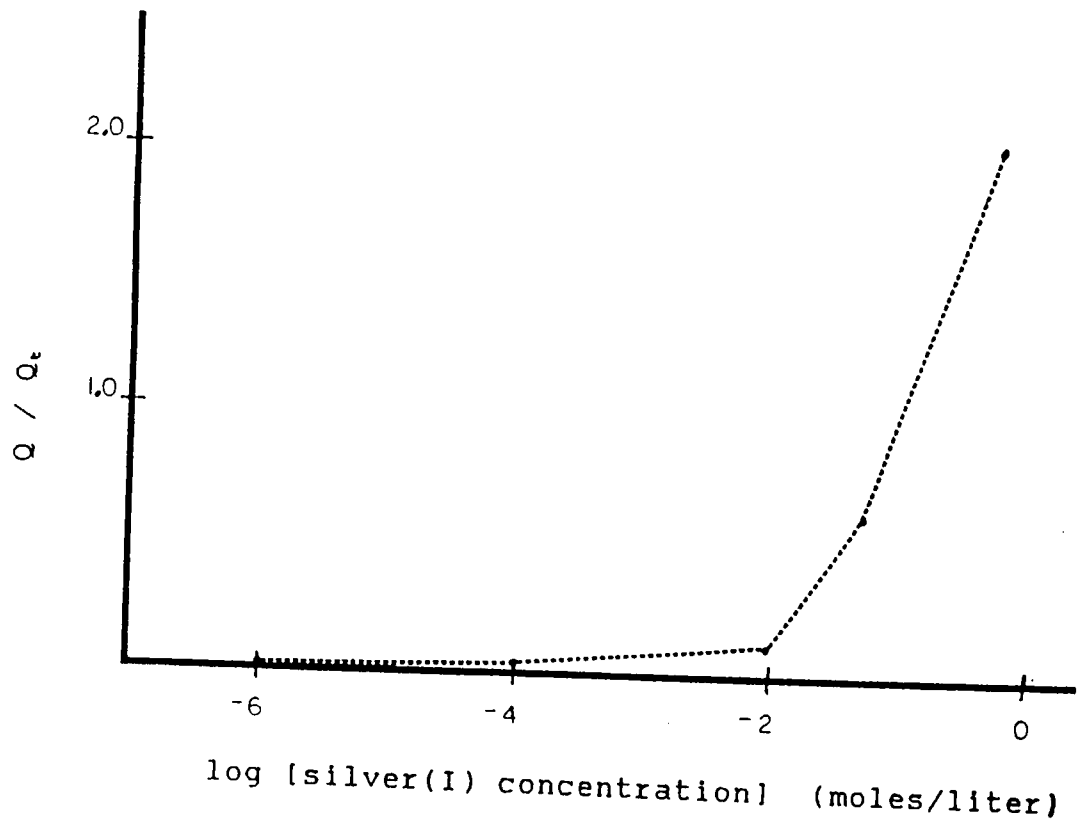


Figure 35. Plot of the charge ratio versus the log (silver(I) concentration) for a PU-MDI film treated with increasing concentrations of silver nitrate.

Table 10

Extended Values for Long Treatment Times

of PU-MDI with 1.0E-8 M Silver (I)

Treatment Time	Q/Q_t
20 minutes	0.021
60 minutes	0.036

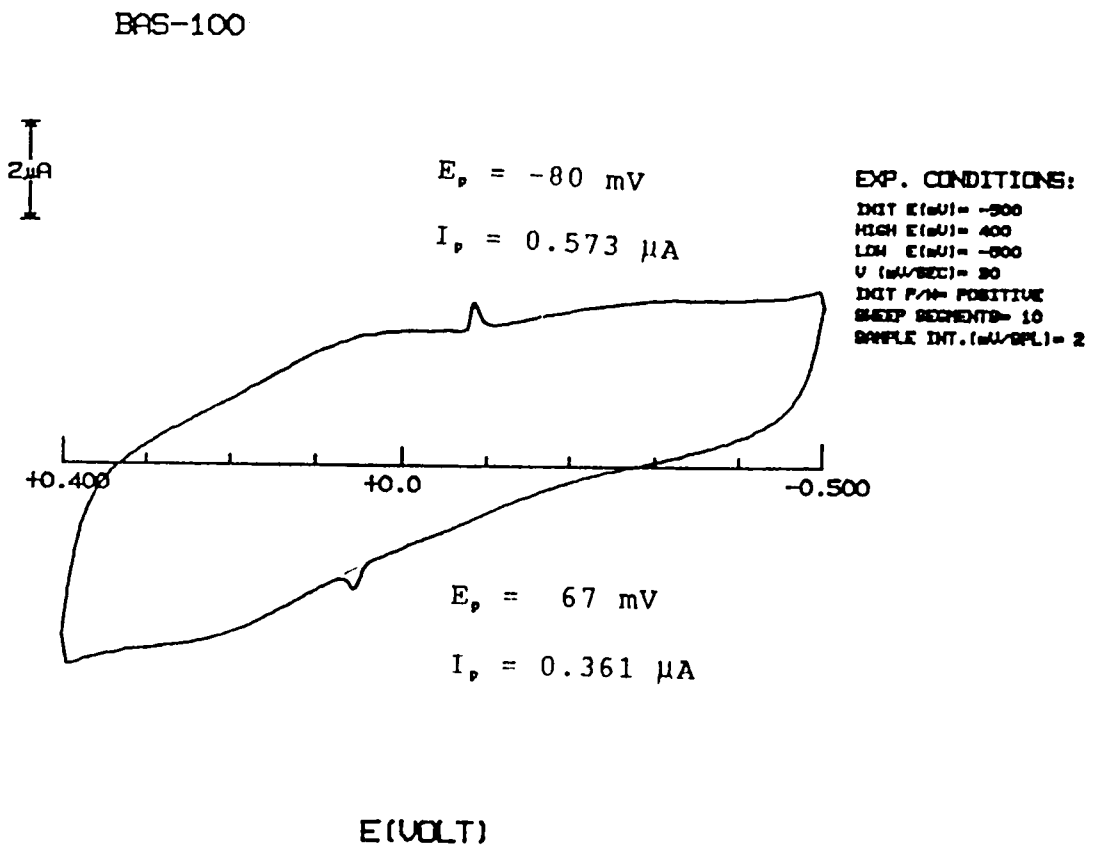


Figure 36. Cyclic voltammetry of a PU-MDI film in 0.5 M LiCl illustrating the peaks associated with the detection of 1.0E-8 M silver nitrate after a treatment time of sixty minutes.

silver(I) ion, and the results are shown in Figure 37. Two points immediately become obvious about this plot, the first of which is that the Q/Q_t values are much higher than for a comparative experiment utilizing PE-TCNQ. This behavior is again probably due to the non-electroactivity of a large percentage of the TCNQ units in the PU-MDI film exposed to aqueous solutions. However, these higher effective ratios also mean that lower concentrations of silver would be more easily characterized using the polyurethane-TCNQ films than the polyester-TCNQ films. Second, the plots for the different blocks of time are well-separated, indicative that a calibration chart similar to that for the polyester-TCNQ films could be produced for the PU-MDI polymer films.

c) Calibration Series

In a manner similar to that used for the PE-TCNQ films, a number of calibrations for the detection of low concentrations of silver ions were carried out using the PU-TCNQ polymer, PU-MDI. The ratio for the amount of charge detected was calculated in the same way as for the PE-TCNQ films, and the resulting data for the calibration are shown in Figures 38 and 39. As mentioned in the previous section, the values for incorporation of silver in the PU-MDI polymer films are much higher than

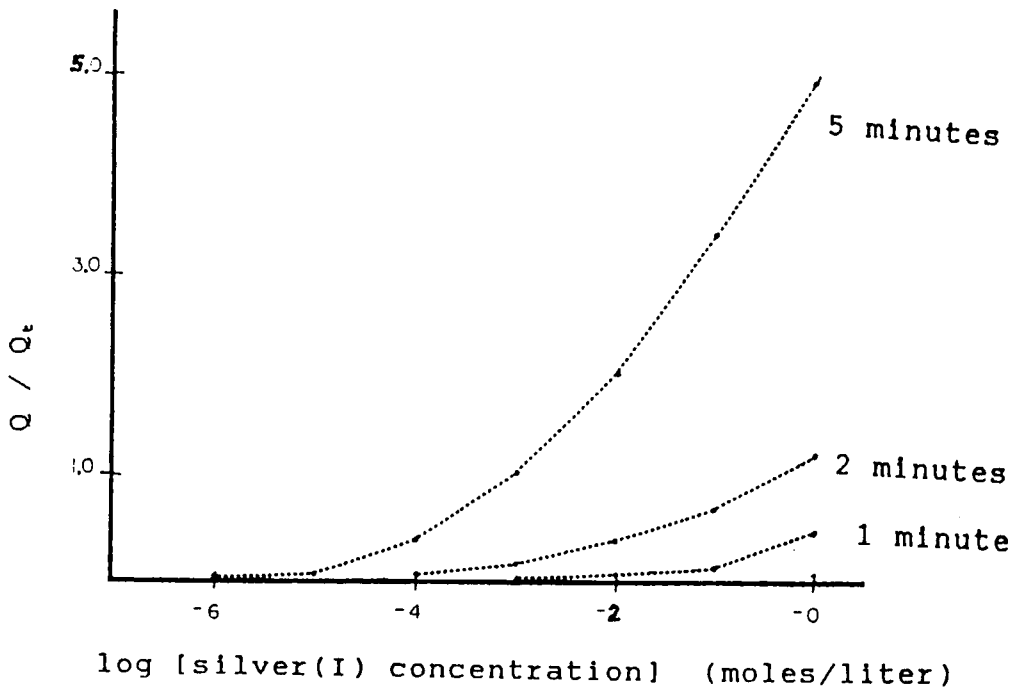


Figure 37. Plot of the charge ratio versus the log (silver(I) concentration) for the accumulation of silver into a PU-MDI film for treatment times of one to five minutes.

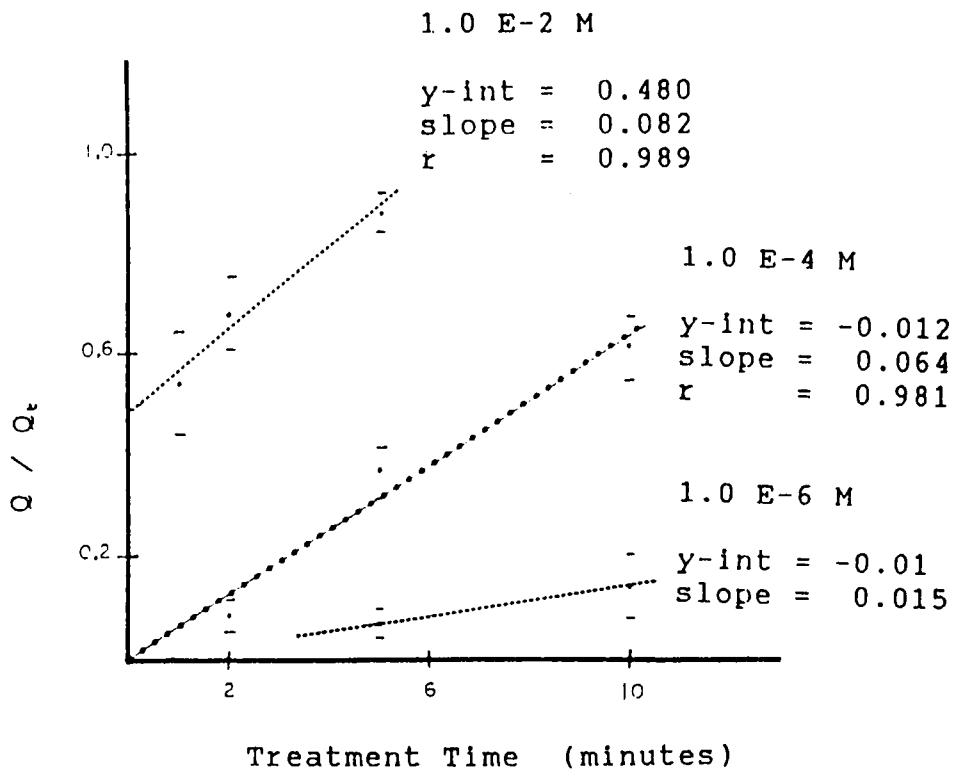


Figure 38. Standardization plot of the charge ratio versus the treatment time for the PU-MDI film using silver(I) concentrations of 1.0E-2 M, 1.0E-4 M, and 1.0E-6 M.

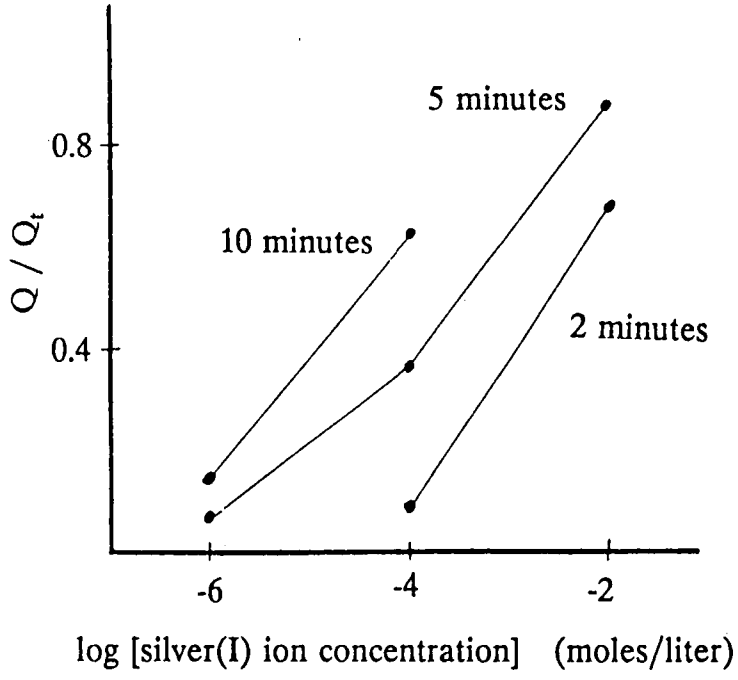


Figure 39. Calibration plot of the charge ratio versus the treatment time for the PU-MDI film using silver (I) concentrations of 1.0E-2 M, 1.0E-4 M, and 1.0E-6 M.

corresponding values for the PE-TCNQ system, and the polyurethane films also exhibit higher background currents. However, the higher ratios also indicate that the PU-MDI films could be very useful in very low concentration situations, and a comparison of the charge values and treatment times for Figure 21 (See page 99) and Figure 38 confirms this assumption. Also, the calibration plot for the PU-MDI film shows much more linear behavior than in the PE-TCNQ case. This is probably due to the fact that the PU-MDI film is diffusion-limited even at low incorporations of silver (I) ion, unlike the PE-TCNQ films, which show elements of thin layer control at low incorporations of silver (I) ion.

d) Electron Spectroscopy for Chemical Analysis

Electron Spectroscopy for Chemical Analysis (ESCA) was applied to the PU-MDI films treated with silver(I) ion in order to determine the relative positions of the silver in the reduced and oxidized films. In accord with the procedure outlined above, two PU-MDI films were cast on platinum and treated with 1.0 M silver(I) nitrate (R5S5). The first film was reduced for five minutes at -0.2 V versus SCE in 0.5 M LiCl, then placed in the ESCA chamber, and a number of surface and interior scans were obtained. The data, which are shown in Table 11, are similar to

Table 11

ESCA Depth Profile of PU-MDI Films

Treated with Silver(I) Ion

Time (minutes)	% silver, film 1	% silver, film 2
0	0.13	0.48
1	0.26	0.31
3	0.35	0.13
6	0.38	0.06

Notes: % silver is the percentage of total counts due to silver.

Film 1 is the reduced film.

Film 2 is the oxidized film.

those obtained on the reduced PE-TCNQ films studied above. The second film was oxidized at +0.3 V versus SCE for five minutes and scanned, and the data are also shown in Table 11. In this case, the distribution of the silver is not the same as in the similarly treated PE-TCNQ film. In the PU-MDI film, it seems that there is a high concentration of silver on the surface of the film which decreases as the film is penetrated. This indicates that the diffusion of the silver(I) ion into the film is much slower for the PU-TCNQ films than for the PE-TCNQ films.

C) MAGNETIC FIELD EFFECT ON POLYMER ELECTROCHEMISTRY

The final section of this thesis attempts to examine an unusual aspect of chemistry which has recently been receiving attention, e.g. the effect of magnetic fields upon chemical and electrochemical reactions. Because of the possibilities for the modification of polymer structures and for changes in electrochemistry as presented in the introductory sections, a combination of the effects which might be present in an electroactive film was thought to be of some interest. Unfortunately, despite repeated attempts at optimizing results, the data presented in this section of the thesis are both incomplete and inconclusive. However, some of the results are of interest and are presented here in the hopes that

they might be of some future reference to other researchers with a greater understanding of the interactions between electric and magnetic fields.

1) Changes in PE-TCNQ Electrochemistry

Systems utilizing redox units like TCNQ offer a unique opportunity to attempt to separate the effect of the magnetic field into components dependent on electrochemistry and components dependant on polymer mechanics. Because the electrochemistry of PE-TCNQ polymer has been more intensively studied than the PU-TCNQ systems, that system was chosen as the first to be studied. A PE-TCNQ film was cast on platinum, then cycled in 0.5 M LiCl to assure Inzelt-type behavior (132) (Figure 40). The film was exposed to a 0.5 T magnetic field, and the electrochemical behavior of the film was observed to decrease rapidly to less than 10% of the original behavior (Figure 41). Upon removal of the film from the magnetic field, it was observed that the change in electrochemical behavior was permanent (Figure 42), indicating a probable change in the polymer structure.

The PE-TCNQ film behaves similarly when cycled in 0.1 M calcium(II) chloride. However, for this experiment, the magnetic field was engaged as electrochemical sweeping occurred, resulting in a view of how the electrochemistry

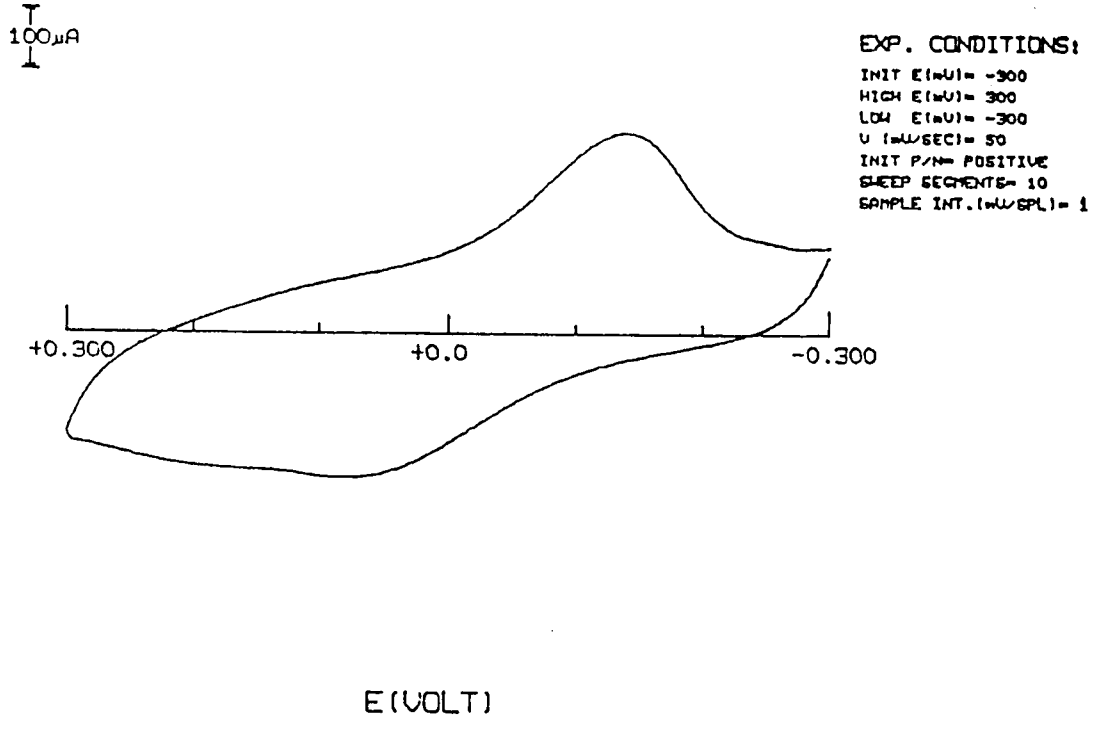


Figure 40. Cyclic voltammetry of PE-TCNQ cast on platinum and cycled in 0.5 M LiCl while in the magnetic field cavity with the magnetic field strength equal to zero.

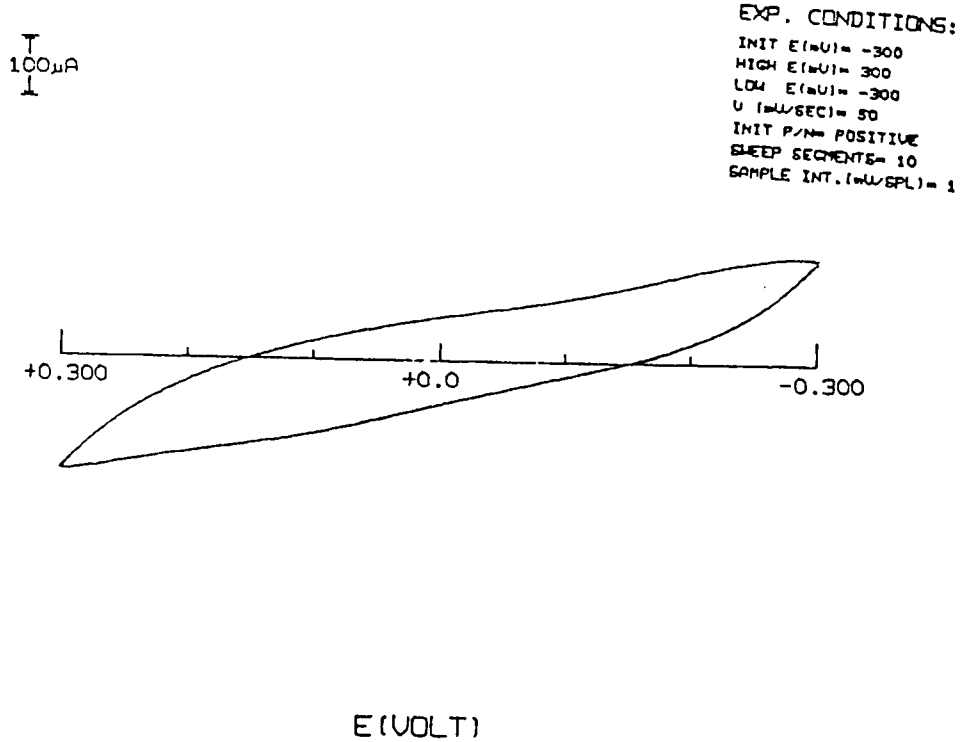


Figure 41. Cyclic voltammetry of a PE-TCNQ film in 0.5 M LiCl at a magnetic field strength of 0.5 T.

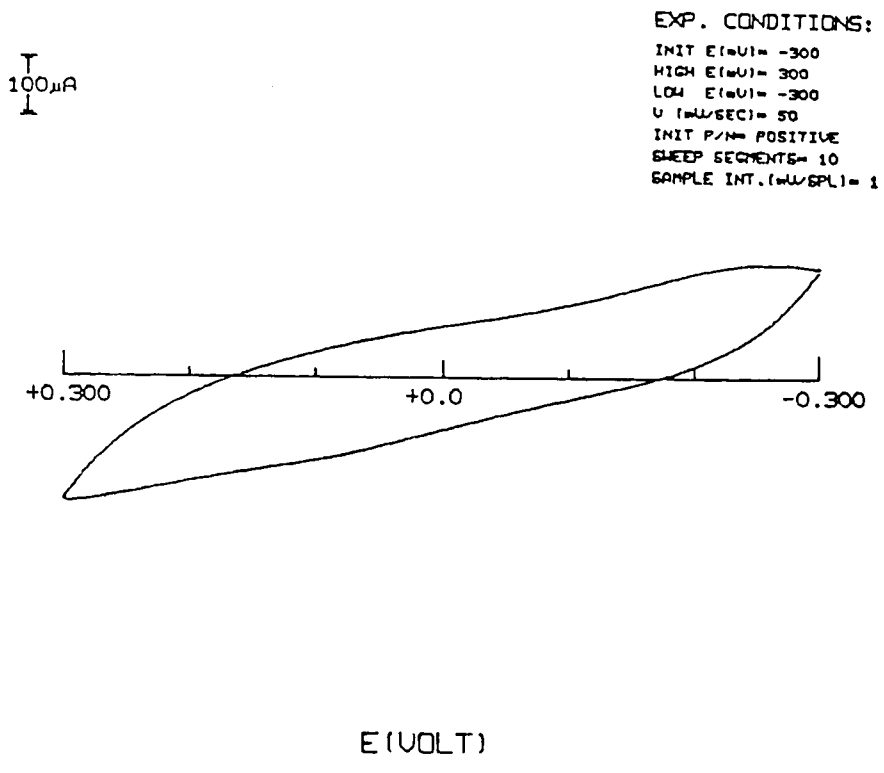


Figure 42. Cyclic voltammetry of a PE-TCNQ film in 0.5 M LiCl at a magnetic field strength of zero after exposure to a magnetic field of 0.5 T.

of the film is changing due to the influence of the magnetic field, and shown in Figure 43. It appears that the film will ultimately decrease in electrochemical activity to exhibit behavior similar to that seen for the LiCl system seen above. However, in this case, the original behavior of the film can be regenerated by heat treatment of the film (Figure 44). This points to a mechanical explanation for the change in electroactivity of the film. It appears that the magnetic field has the effect of changing the orientation of the TCNQ sites such that the probability of electron transfer decreases. Upon heating the film to 120 °C, the initial behavior is restored, in agreement with evidence by Day that the glass transition temperature for the PE-TCNQ system is near 60 °C.

2) Changes in PU-TCNQ Electrochemistry

Given the above behavior for the PE-TCNQ system, it is expected that the application of a magnetic field to a PU-TCNQ system would produce the same result. However, there are three different PU-TCNQ systems to choose from, ranging from the HMDI system which is relatively plastic, to the MDI system which is relatively rigid. Given that the PE-TCNQ system is similar in plasticity to the HMDI system, the MDI system, representing the other end of the

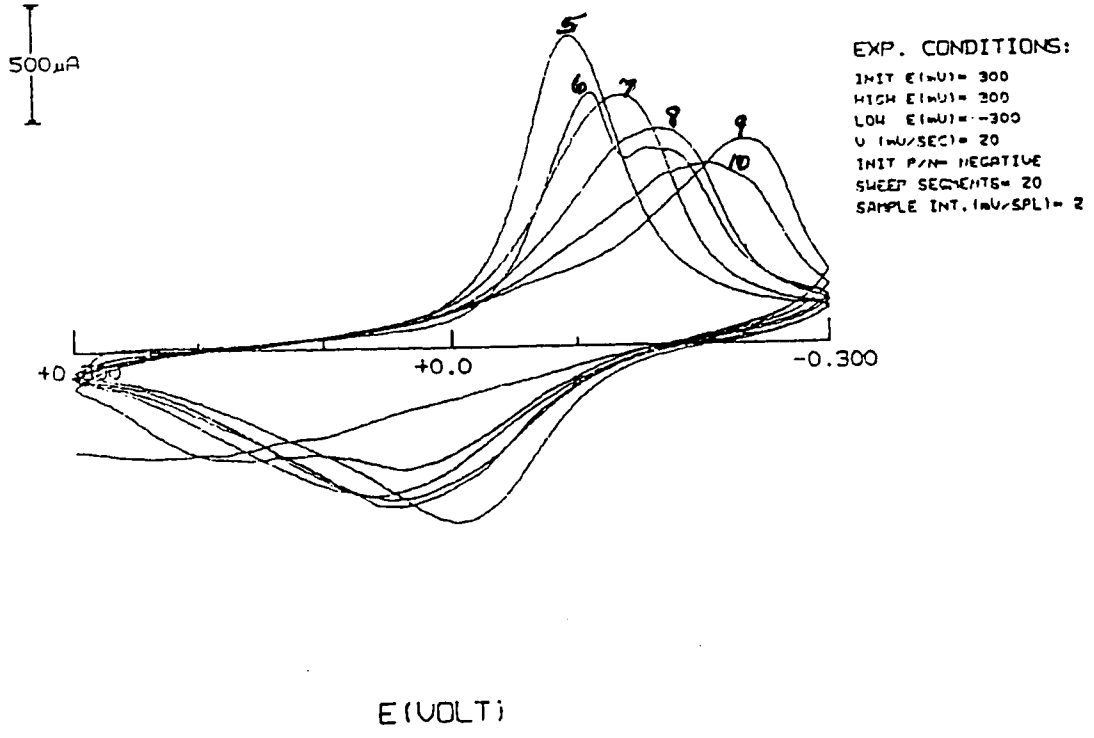


Figure 43. Cyclic voltammetry of a PE-TCNQ film in 0.1 M calcium(II) chloride as the magnetic field strength is increased from 0.0 T to 0.5 T.

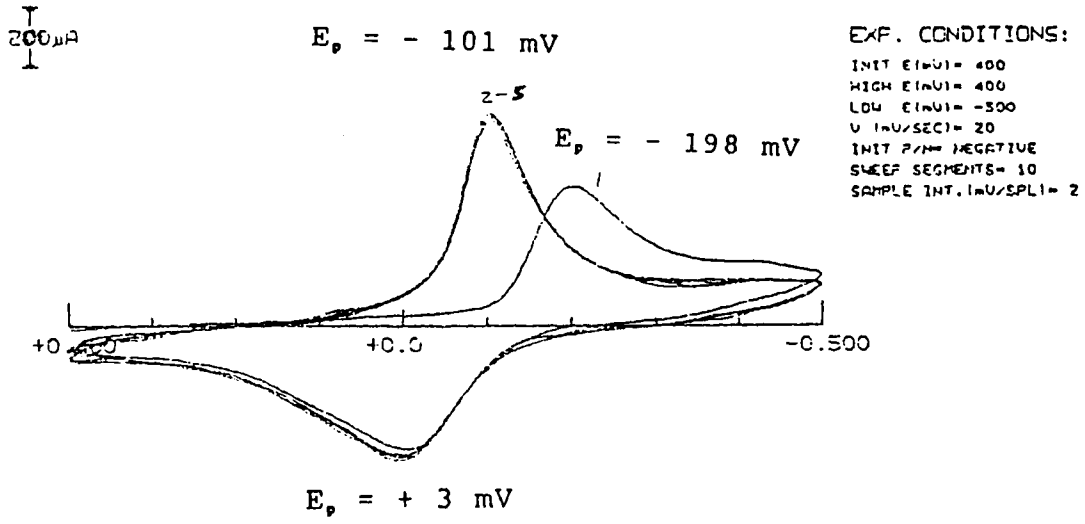


Figure 44. Cyclic voltammetry of a PE-TCNQ film in 0.1 M calcium(II) chloride after exposure to a 0.5 T magnetic field and subsequent heat treatment.

polymer stability spectrum, was chosen. Accordingly, PU-MDI films were cast on platinum and cycled in 0.5 M LiCl to stable behavior, then exposed to a magnetic field. As expected, the electrochemical behavior of the film decreased rapidly, but upon removal of the magnetic field the electrochemistry of the film regenerated rapidly, as shown in Figure 45. This behavior makes it extremely likely that the observed magnetic field dependence of electrochemistry for polymeric-TCNQ systems is due to realignment of the polymer structural chains leading to changes in electron transfer, and is not a mass transport effect. The transient effect of the magnetic field on a PU-MDI polymer film suggests a possible usage as a magnetic field detector or a magnetic field switch.

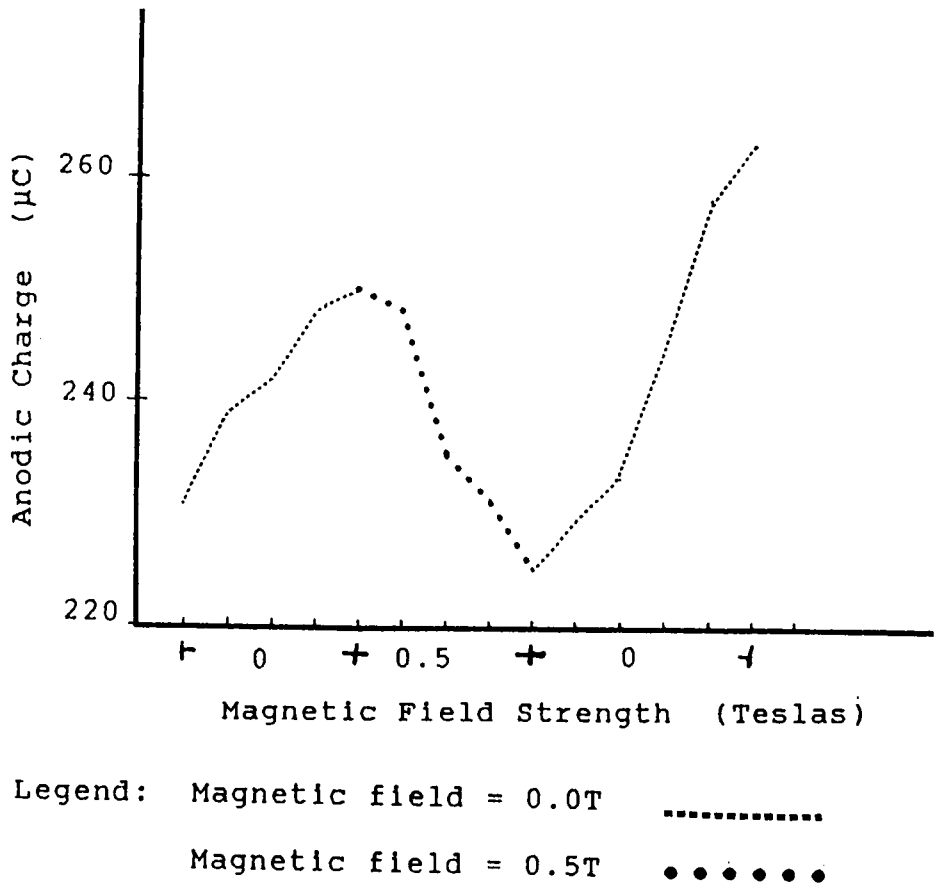


Figure 45. Plot of the anodic charge versus the magnetic field strength for a PU-MDI film in 0.5 M LiCl as the magnetic field is switched from 0.0 T to 0.5 T, illustrating a field dependent response.

CHAPTER IV

CONCLUSIONS AND FUTURE DIRECTIONS

From the data presented in this thesis, we can come to a number of conclusions about the incorporation of silver (I) ion into polymer-TCNQ modified electrodes. First, the polyester-TCNQ and polyurethane-TCNQ films are very sensitive to silver (I) ion in aqueous solutions at silver nitrate concentrations of 1.0E-8 M and higher (See Figure 19, page 93 and Figure 36, page 132). The current response is sharp, with a noticeable lack of heading, indicating either a fast electron-transfer process or a lack of diffusion of the electroactive species to the electrode. Response to the accumulation of silver, in terms of the charge ratio, is linear over wide ranges of treatment time and silver ion concentration for a given set of treatment conditions for the polyester-TCNQ films, and the response characteristics at different concentrations of silver (I) ion are well-separated (See Figure 18, page 92). Charge ratio response is well-characterized despite the lack of optimal silver (I) ion treatment conditions, e.g. the use of low ionic strength solutions and quiescent (diffusion limited) conditions. Further, since interferences in the procedure due to pinholes, photoreduction of silver on platinum, and

occluded chloride ion total approximately ten percent, calibration curves can be prepared for the detection of silver at different concentrations for the two polymers (See Figure 21, page 99 and Figure 39, page 136).

As far as the mechanism of incorporation of silver into the films, the data presented above strongly indicates that the major source of silver incorporation into the film is due to the presence of the TCNQ units in the film, and is not a simple chloride ion precipitation reaction. The data further indicates that the TCNQ units must be in a reduced state for major incorporation of silver (I) ion to occur. Silver which is incorporated into the polyester-TCNQ films is dispersed throughout the film rather than being concentrated in any one region of the film, although optically the film retains some of the reflectance characteristics which have inspired recent interest in using silver films in Raman spectroscopy. The incorporation of silver (I) ion into the film may be an optically sensitive process, although the data reported herein are not conclusive concerning the effect of room light on incorporation at low silver (I) ion concentrations. However, the data concerning the same incorporation under ultraviolet light exhibit an enhancement of at least one order of magnitude for the polyester-TCNQ films (See Figure 22, page 101), and bear further investigation. Finally, the polyester-TCNQ films

appear to be sensitive to mercury (II) ion, although the current response is not as well-defined as in the case with the silver (I) ion.

Although the data concerning the effect of the magnetic field upon the polymer electrochemistry are not well understood, a few generalizations can be made. The imposition of a high-power magnetic field (0.5 T) generally results in a decrease in the amount of current observed for the polymer-TCNQ films. In PE-TCNQ films, the effect is irreversible in that the electrochemical behavior cannot be restored by cycling the electrode potential in the absence of the magnetic field. The response can be restored, however, by re-melting the polymer. On the other hand, in PU-TCNQ (MDI) films, the effect is transient and dependent upon the direct application of the magnetic field (See Figure 45, page 148). These three observations lead to the conclusion that the observed effect is due to a modification in the polymer structure, decreasing the efficiency of electron-hopping within the film.

There are several directions which future research could explore using the polymer-TCNQ films. The sensitivity of the films to other trace metal ions should be documented, and the effect of well-stirred solutions on the response and calibration characteristics should be explored. Furthermore, the surface characteristics and

internal structure of the films needs to be explored, perhaps using scanning electron microscopy, and the possibility of unusual optical properties should not be ignored.

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VITA

Robert Daniel Shelton was born in Lexington, Kentucky, on the twenty sixth day of January, 1961, and lived in the land of Daniel Boone for two years. He and the family then moved to Mineola, Florida for a year, where he proceeded to indulge himself in the best Florida oranges which he could find in the grove next door. Following the birth of his sister, Laura Ellen, on the fourth day of March, 1964, he and the family moved to Huntsville, Alabama, a small southern town which was experiencing firsthand the growth of the space race. For the next fifteen years, he developed a number of interests, including a love for books, an appreciation of the great outdoors, a skill for hunting, and an eye for collecting and cutting rocks and gems.

Upon graduation from S. R. Butler High School in 1979, he proceeded to Centre College for four years. Nestled in the heart of Kentucky, near the ancestral home, Centre College provided just the right mixture of small town friendliness combined with instruction of the highest calibre. After receiving a B.S. degree in chemistry in 1983, he proceeded to the University of Tennessee to work for the summer of 1983 in the research group of Jim Chambers. Since those early days in the lab seven years ago, he has developed a high degree of interest in the

modification of surfaces with polymer films, especially as applied to the areas of environmental analysis and neurochemistry. In his spare time, he has picked up certification as a scuba diver.