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DEVELOPMENT OF ELECTRO SUPERCAPACITORS

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EXECUTIVE SUMMARY

Nonfluorinated proton conducting superionic molecular tunnel electrolytes (PSMTE) exhibiting high proton conductivity ($\sim 10^{-2}$ Scm^{-1}) have been synthesized. The highly hygroscopic nature of these polymers yielding deliquescent films has precluded their use in supercapacitors. Fluorinated analogs of these PSMTE's were synthesized to provide higher conductivity and greater hydrophobicity. Fluorinated PSMTE's exhibit higher conductivity than Nafion (1.3×10^{-2} vs. 2.1×10^{-4} Scm^{-1}) under identical conditions of relative humidity and temperature. Fluorinated PSMTE's show good film forming properties suitable for fabrication of supercapacitors. However, these materials have not yet been utilized in supercapacitors.

Polymer films of aniline and its various derivatives having electron donating ($-OCH_3$) and electron withdrawing groups ($-SO_3H$, $-NO_2$) were formed electrochemically using platinum and nickel substrates. These films were characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The electron withdrawing groups ($-SO_3H$, $-NO_2$) increased the voltage at which the redox reaction occurs for aniline. The electron donating groups ($-OCH_3$) moved the redox potential in the negative direction. The monomers were also deposited on Nafion coated Pt. These films gave multiple oxidation-reductions peaks and better discharge characteristics as compared to films on bare Pt. They also exhibited electrochromic bahavior.

To demonstrate "proof of concept," different combinations of the polymers and Pt black were used as electrodes with a thin (0.001") Nafion membrane to form a capacitor/battery. The capacity and the energy density were determined for the cells. The cells were able to pulse charge-discharge for times as low as 0.1 ms.

Significant material and electrochemical problems remain to be solved to yield a "working" supercapacitor. These include testing of the new superionic molecular tunnel electrolytes, increasing capacity by many orders of magnitude, and the prevention of rather fast self discharge rate.

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INTRODUCTION

Electrosupercapacitors are being developed to deliver electrical energy under near pulse conditions, with charge and discharge times as short as a few milliseconds being required for some applications (e.g., for rail guns and space-based weapons). In this respect, electrosupercapacitors resemble dielectric capacitors. However, the energy requirements of the devices that electrosupercapacitors are designed to drive demand that they possess large energy densities, and that they can be charged and discharged over many cycles (hundreds or thousands). In this regard, electrosupercapacitors resemble secondary batteries. Indeed, an electrosupercapacitor is probably best described as an "ultrahigh-(charge and discharge) rate secondary battery."

The problems inherent in developing electrosupercapacitors are illustrated schematically in Figure 1, in which the energy density is plotted against power density for the two classes of electrical energy storage systems (capacitors and batteries). Thus, classical secondary batteries (e.g., NiCd, lead-acid, silver-zinc) are characterized by high energy densities, but they exhibit comparatively low power densities. The charge and discharge processes occur via electrochemical reactions that are characterized by finite rates, which may depend on mass transfer phenomena in porous electrodes. On the other hand, dielectric capacitors (e.g., mica capacitors) exhibit high power densities, but have unsuitably low energy densities for the applications of interest.

Basically, two options exist for developing electrosupercapacitors, with the objective of locating the performance characteristics of the device in the cross-hatched region shown in Figure 1, namely, 1) increase the power densities of batteries or 2) increase the energy densities of capacitors. This objective must be achieved despite fundamental electrochemical limitations in current battery and capacitor technology. Therefore, the necessary improvements for both options identified here require the introduction of radically new concepts.

We had proposed to develop monolithic electrosupercapacitors based on proton conducting superionic molecular tunnel electrolytes (PSMTE) and on organic or inorganic polymer redox (positive and negative) electrodes and hydrogen discharge pseudo-capacitive negative electrodes. Monolithic structures will permit the use of very thin solid polymer
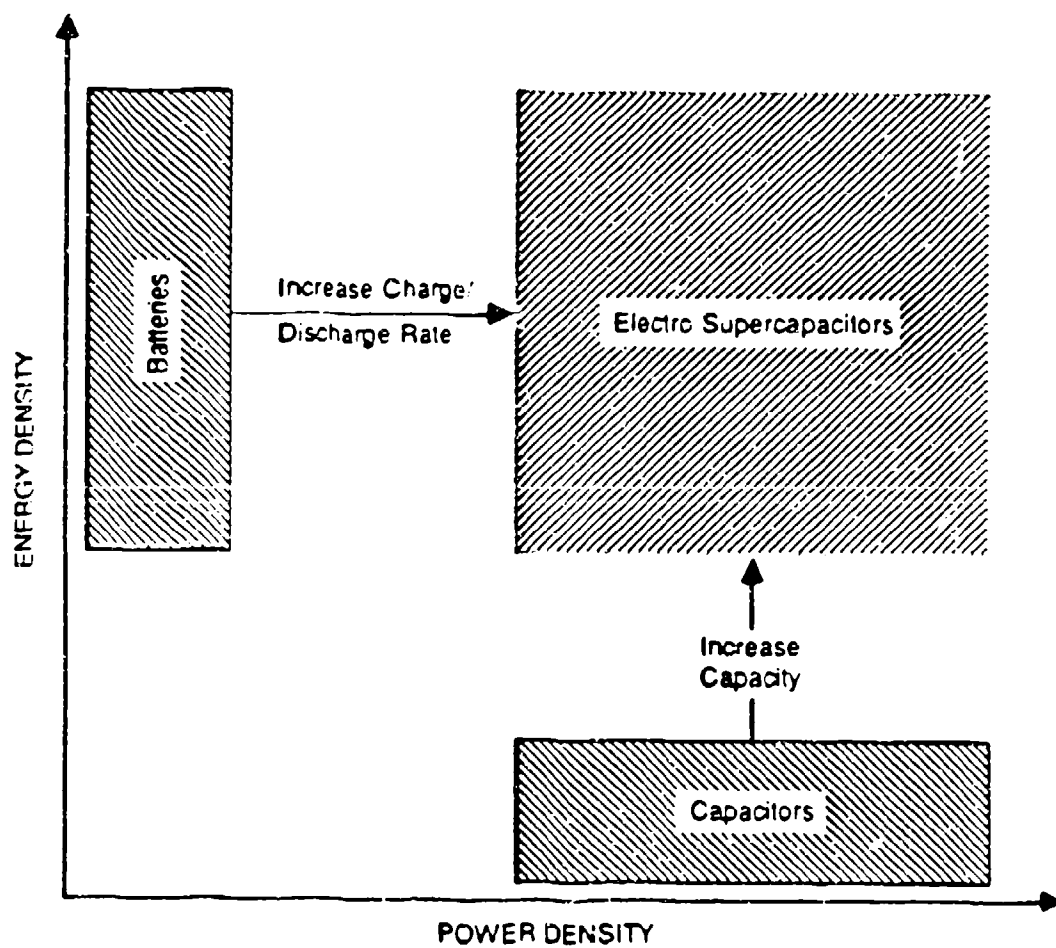
Figure 1. Schematic classification of electrical energy storage systems

electrolytes, containing exceptionally high densities of sulfonic acid channels. Furthermore, *in situ* polymerization will allow high utilization of the charge storage capacities of porous Pt or C(Pt) black negative electrodes because of interpenetration of the electrode and electrolyte phases. The ultimate objective of this work was to deliver five bipolar multicell electrosupercapacitors, based on either a "pancake" or "Swiss roll" configuration, to the LABCOM program manager for further evaluation.
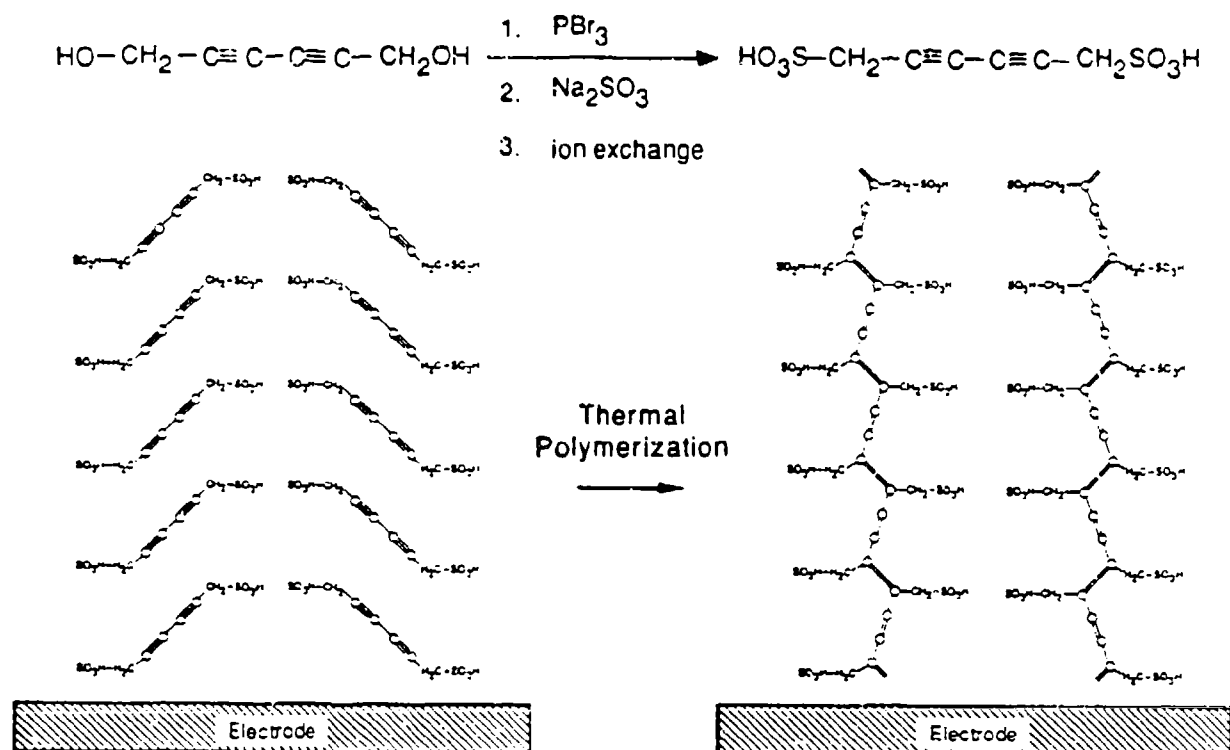
PROGRESS

We proposed to explore the following innovative approaches to increase the energy and power densities of electrosupercapacitors:

- Synthesis of proton-conducting superionic molecular tunnel electrolytes (PSMTE).

- Synthesis of high-energy density inorganic and organic polymer redox electrodes, in which charge transfer is mediated by proton transport.

- Fabrication and demonstration of monolithic thin-film bipolar supercapacitor stacks based on the technology outlined here.

In our opinion, practical electro supercapacitors must combine the high energy density characteristics of pseudo capacitors such as Pt/H, or three-dimensional polymeric electrode films (e.g., polyaniline), and the high proton conductivities of carefully designed solid polymer electrolytes.

The best polymeric ionic conductor available at this time is Nafion. This material is a perfluorinated sulfonic acid polymer that can be fabricated into moderately thin films for use as an electrolyte. However, a large part of Nafion is insulating, with only a small concentration of sulfonic acid groups (equivalent weight 1100) providing fast ion transport through channels. Our goal is to develop novel monomers and polymers that will provide a large surface density (no/cm2) of proton conducting sulfonic acid channels compared to Nafion. The following diacetylene monomer (Scheme 1) has been synthesized, and thin films prepared by epitaxial growth, followed by topochemical thermal or photo polymerization in the solid state.

Note that the equivalent weight of our diacetylene polymer is only 120, compared to 1100 for Nafion, and thus represents an order of magnitude increase in concentration of SO_3H groups in the electrolyte.
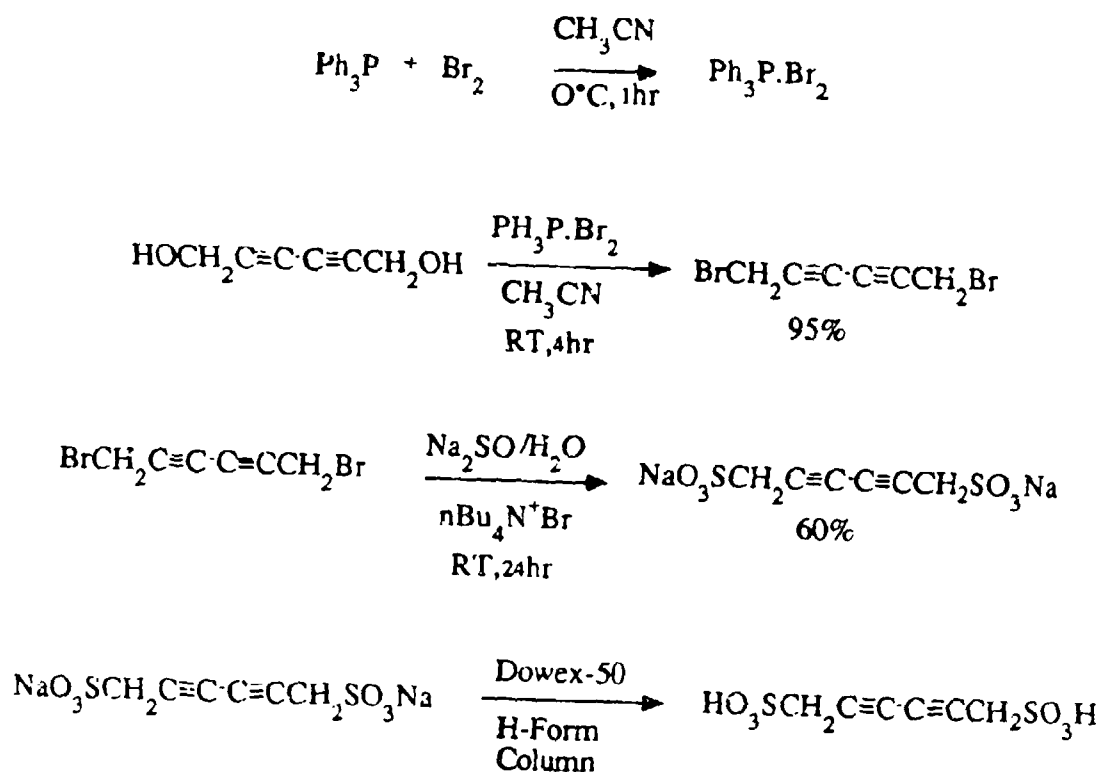
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$$HO-CH_2-C\equiv C-C\equiv C-CH_2OH \xrightarrow[\substack{2.\ Na_2SO_3 \\ 3.\ \text{ion exchange}}]{1.\ PBr_3} HO_3S-CH_2-C\equiv C-C\equiv C-CH_2SO_3H$$

Thermal Polymerization

Scheme 1. SMTE Polymerization

An important aspect of this technology for *in situ* polymerization of SMTEs is that excellent interpenetration of the porous electrodes and the polymer electrolyte should be achieved. This is because the liquid monomer will readily penetrate the porous electrode structures and in a polymerization will therefore form structures in which the proton conducting polymer is in contact with the entire surface area

The reaction of diol with PBr3 failed to yield the desired dibromide in satisfactory purity and yield. Therefore, the following successful synthetic sequence was used (Scheme 2).

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$$Ph_3P + Br_2 \xrightarrow[\text{O°C, 1hr}]{CH_3CN} Ph_3P.Br_2$$

$$HOCH_2C{\equiv}C{\cdot}C{\equiv}CCH_2OH \xrightarrow[\substack{CH_3CN \\ RT,4hr}]{PH_3P.Br_2} BrCH_2C{\equiv}C{\cdot}C{\equiv}CCH_2Br \quad 95\%$$

$$BrCH_2C{\equiv}C{\cdot}C{\equiv}CCH_2Br \xrightarrow[\substack{nBu_4N^+Br \\ RT,24hr}]{Na_2SO/H_2O} NaO_3SCH_2C{\equiv}C{\cdot}C{\equiv}CCH_2SO_3Na \quad 60\%$$

$$NaO_3SCH_2C{\equiv}C{\cdot}C{\cdot}C{\equiv}CCH_2SO_3Na \xrightarrow[\substack{H\text{-Form} \\ Column}]{Dowex\text{-}50} HO_3SCH_2C{\equiv}C{\cdot}C{\equiv}CCH_2SO_3H$$

Scheme 2. Synthesis of Diacetylene Disulfonic Acid

POLYMERIZATION OF DIACETYLENE DISULFONIC ACID

The sulfonic acid is highly crystalline in nature. Therefore, it does not form good films by itself. However, a proton transfer polymeric complex was obtained by dissolving the disulfonic acid in ethylenediamine. This solution provides excellent films on quartz plates that had been cleaned with 10 percent aq. NaOH, deionized water and trichloroethylene, followed by silyation with hexamethyldisilazane. The films were prepared under an argon atmosphere or in a desiccator.

The films were polymerized by exposure to a high-pressure mercury lamp for 4 minutes. The yellowish white film turn deep blue within 60-90 seconds (depending upon film thickness) and then gray-black on further polymerization. The polymerized film is insoluble in common organic solvents, but dissolves in strong acids. Ethylenediamine was removed by heating the film at 160°C under vacuum.

Under ambient conditions, the conductivity of this polymer was 2.17×10^{-2} Scm^{-1}, as measured by ac impedance spectroscopy using stainless steel electrodes. However, this
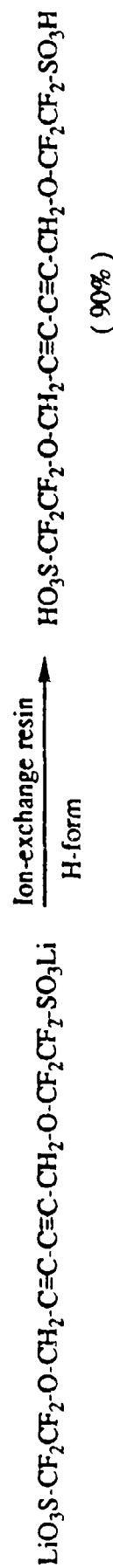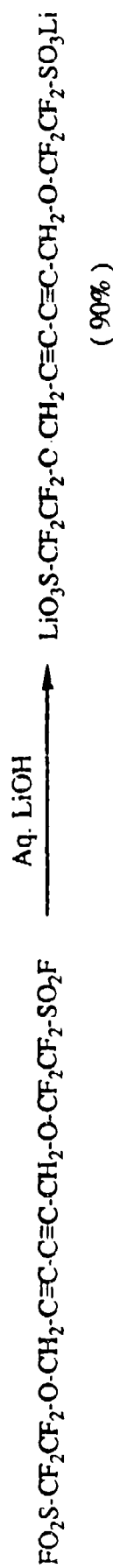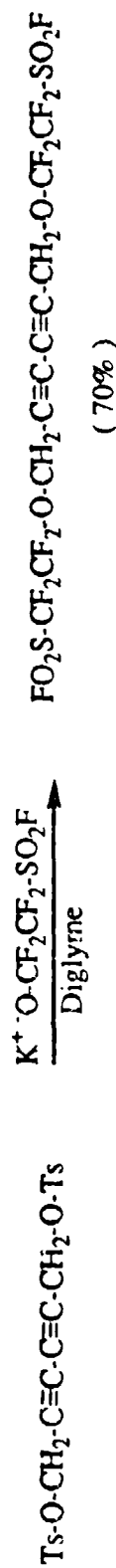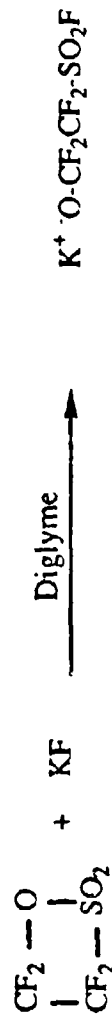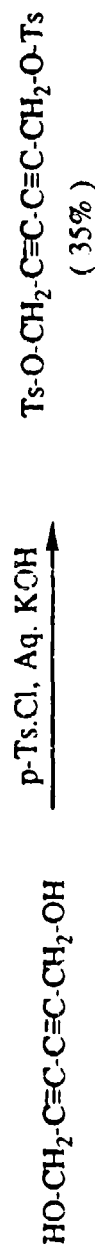
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film was highly deliquescent and was not suitable for use in a supercapacitor because of its free flowing properties. When the polymer was dried thoroughly, the conductivity decreased to 1.83×10^{-5} Scm^{-1}.

In view of these observations, we decided to prepare a fluorinated polymer electrolyte. We expected the fluorinated analog (even though it had higher equivalent weight) to exhibit higher conductivity, greater hydrophobicity and superior film-forming properties. The fluorinated polymer was synthesized from the diacetylene diol as shown herein (Scheme 3). The diol was tosylated using p-toluenesulfonyl chloride. The ditosylate was treated with perfluoroethylenesultone and potassium fluoride to yield the corresponding bisperfluorosulfonyl fluoride, which was converted to the lithium sulfonate derivative by treatment with aqueous lithium hydroxide. The lithium salt was converted to the free acid by ion exchange on a column for H^{+}-form ion exchange resin. The resulting free acid was freeze dried to yield a film, followed by thermal polymerization at 80°C for 20 hours. The resulting polymer was washed with methanol to remove the monomer followed by drying under vacuum (10 mm) at 60°C for 24 hours. The product was characterized by IR, NMR. When the polymer film was exposed to 70 percent relative humidity for 24 hours at room temperature, its conductivity was 1.3×10^{-2} Scm^{-1}. (A film of Nafion -H^{+}, exposed under identical conditions had a conductivity of 2.1×10^{-4} Scm^{-1}). The perfluorinated polymer not only shows higher conductivity than Nafion under identical conditions, but also maintains its film forming properties. We propose to use these electrolytes in supercapacitors in the future.

SYNTHESIS OF REDOX ORGANIC POLYMER ELECTRODES

Extensive work over the past decade has identified a number of organic polymer redox electrodes that are suitable for battery applications and which involve proton transport for charge compensation. Of these, aniline and copolymers of aniline with other aromatic entities are particularly attractive, partly because they offer high energy densities but also because they can be easily and reproducibly fabricated into thin, continuous films.

Apart from the work referred to here, very little has been reported on the electrochemical properties of polyaniline. Oxidation of polyaniline in its reduced form involves proton transport for charge compensation in a manner that is analogous to that of the inorganic electrodes like IrO$_2$/IrOOH. Other attractive features of the polyaniline system include:

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$HC \equiv C\text{-}CH_2\text{-}OH$ $\xrightarrow{O_2,\ CuCl,\ NH_4Cl}$ $HO\text{-}CH_2\text{-}C \equiv C\text{-}C \equiv C\text{-}CH_2\text{-}OH$ (85%)

$HO\text{-}CH_2\text{-}C \equiv C\text{-}C \equiv C\text{-}CH_2\text{-}OH$ $\xrightarrow{p\text{-}Ts.Cl,\ Aq.\ KOH}$ $Ts\text{-}O\text{-}CH_2\text{-}C \equiv C\text{-}C \equiv C\text{-}CH_2\text{-}O\text{-}Ts$ (35%)

$$\begin{matrix} CF_2 \!\!-\!\! O \\ | \qquad | \\ CF_2 \!\!-\!\! SO_2 \end{matrix} + KF \xrightarrow{Diglyme} K^+ \ {}^-O\text{-}CF_2CF_2\text{-}SO_2F$$

$Ts\text{-}O\text{-}CH_2\text{-}C \equiv C\text{-}C \equiv C\text{-}CH_2\text{-}O\text{-}Ts$ $\xrightarrow[Diglyme]{K^+ \ {}^-O\text{-}CF_2CF_2\text{-}SO_2F}$ $FO_2S\text{-}CF_2CF_2\text{-}O\text{-}CH_2\text{-}C \equiv C\text{-}C \equiv C\text{-}CH_2\text{-}O\text{-}CF_2CF_2\text{-}SO_2F$ (70%)

$FO_2S\text{-}CF_2CF_2\text{-}O\text{-}CH_2\text{-}C \equiv C\text{-}C \equiv C\text{-}CH_2\text{-}O\text{-}CF_2CF_2\text{-}SO_2F$ $\xrightarrow{Aq.\ LiOH}$ $LiO_3S\text{-}CF_2CF_2\text{-}C\ CH_2\text{-}C \equiv C\text{-}C \equiv C\text{-}CH_2\text{-}O\text{-}CF_2CF_2\text{-}SO_3Li$ (90%)

$LiO_3S\text{-}CF_2CF_2\text{-}O\text{-}CH_2\text{-}C \equiv C\text{-}C \equiv C\text{-}CH_2\text{-}O\text{-}CF_2CF_2\text{-}SO_3Li$ $\xrightarrow[H\text{-form}]{Ion\text{-}exchange\ resin}$ $HO_3S\text{-}CF_2CF_2\text{-}O\text{-}CH_2\text{-}C \equiv C\text{-}C \equiv C\text{-}CH_2\text{-}O\text{-}CF_2CF_2\text{-}SO_3H$ (90%)

Scheme 3. Synthesis of Fluorinated Diacetylene Disulfonic Acid.

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- Excellent cyclicability, provided that the potential does not exceed ~0.8 V (SCE), at which degradation occurs.

- The redox reaction appears to be nearly revisible, implying fast kinetics for proton insertion/removal.

In order for polyaniline to be viable as a positive electrode for electro-supercapacitors, it is necessary to increase the voltage at which the redox reaction occurs by about 0.6 V. This will require substituting strong electron withdrawing groups (e.g., SO_3H, $-NO_2$) on the aromatic ring, particularly in the 2,6 positions.

Conversely, it should be possible to move the redox potential in the negative direction to form a viable polyaniline negative electrode for an electrosupercapacitor by introducing strong electron donating groups onto the aromatic ring (e.g., dialkylamino, methoxy, and thioethers). Of particular interest is the possibility of fabricating a high energy density, all-polymer electrosupercapacitor (battery) in which charge transport occurs via the movement of protons through a superionic molecular tunnel polymer electrolyte.

Substitution of a single nitro group in the ortho position shifts $E_{1/2}$ for aniline in acetonitrile from 0.54 V (vs Ag/Ag$^+$, 1 N) to 1.07 V on the same scale. A second nitro group in the para position on aniline causes a further increase to 1.48 V. Likewise, substitution of a methoxy group on the ortho position reduces the potential to 0.34 V and substitution of a second methoxy group should have a similar effect ($E_{1/2}$ probably of the order of 0.14 V). Thus the cell (-)poly(2,6-dimethoxyaniline) ISMTElpoly(2,6-dinitro-aniline)(+) might be expected to display a potential of >1.3 V, which would be more than adequate for an electrosupercapacitor, provided that the kinetics of charge and discharge are rapid (proton transport controlled).

The following polymer films were grown on platinum electrodes:

(1) Aniline

(2) O-Anisidine

(3) 2,5 Dimethoxy Aniline

(4) 3,5 Dimethoxy Aniline

(5) Aniline-2-Sulfonic Acid

(6) 2-Nitro-Aniline

The polymer films were formed on platinum and nickel by anodic oxidation of their respective electrolytes. The monomers (1)-(5) were dissolved in 0.1M H_2SO_4. 2-Nitro-Aniline was dissolved in acetonitrile containing lithium perchlorate.

The electrooxidation was performed in a one compartment cell using Pt or nickel as the working electrode. Ag/AgCl was used as the reference electrode. Platinum and nickel were polished on Grit 180 silicon carbide paper before use. Table 1 gives the potentials the working electrode had to be polarized for the film formation. To enhance the film adhesion on the substrate, the potential was cycled to about 200 mV above the polarization potential at a sweep rate of 50mV/sec. It normally took 5-6 hours to form a film of appreciable thickness. The film formation reaction is usually accompanied by the formation of a colored product.

Table 1

POTENTIAL FOR FILM FORMATION ON Pt ELECTRODE

Monomer	Potential V (Ag/AgCl)
Aniline	0.8
O-Anisidine	0.6
2,5 Dimethoxyaniline	0.6
3,5 Dimethoxyaniline	1.1
Aniline-2-Sulfonicacid	0.9
2-Nitroaniline	1.4

Electrochemical impedance data for the polymer films were taken in 0.1M H_2SO_4 using a Pt counter electrode and a Ag/AgCl reference electrode. These data were recorded automatically on either a Solartron 1250 or 1255 Frequency Response Analyzer. Both instruments were interfaced (via a IEEE 488 interface bus) to Apple II Plus microcomputer, which stored data on floppy disks. Data were normally recorded over a range of frequencies from 0.1 Hz to 5000 Hz.

For all impedance measurements, the Solartron sine wave output was superimposed on an applied DC bias from a two channel PAR model 173 potentiostat. Solartron potential

and current input leads were taken directly from the cell and not from the potentiostat electrometer and current output jacks. This configuration allowed accurate impedance measurements to be obtained irrespective of the frequency response of the potentiostat.

The impedance data for the films were recorded over a range of applied dc bias potentials. The film was polarized for half an hour (till constant current was reached) at each of the dc bias potentials. The impedance spectra were then recorded. The potential was increased, usually by 100 mV, and another impedance spectrum was recorded. This procedure was normally repeated up to about 800 mV.

Cells (Figure 2) were fabricated using different combinations of the polymers and platinum black. The polymers were deposited on nickel and Pt substrate. The 2-nitroaniline and aniline-2 sulfonic acid were used in the reduced form. Thin (0.001") proton conducting Nafion membranes were used. These membranes were fabricated in our lab. The cells were charged-discharged galvonostatically using blocking electrodes (Figure 3).

In pulse charge-discharge experiments, a programmed pulse wave from a PAR 175 programmer was imposed on a PAR 173 potentiostat. The voltage and the current were periodically recorded using a Nicolet oscilloscope and an X-Y recorder.

CYCLIC VOLTAMMETRY

The cyclic voltammograms were usually recorded between -0.2V (Ag/AgCl) and 1.2V (Ag/AgCl) using PAR 362 potentiostat in 0.1M H_2SO_4. The polymer coated electrodes were thoroughly rinsed in distilled water before the experiment. They were made the working electrode and polished Pt foil was the counter electrode.

Figures 4-7 show the CV's of the aniline , 2,5 dimethoxyaniline (monomer with electron donating group), and aniline-2-sulfonic acid and 2-nitroaniline (monomers with electron withdrawing groups). As seen in Figures 4 and 5 the electron donating group (-OCH_3) moves the redox potential in the negative direction and the electron withdrawing groups (-NO_2 and -SO_3H) move the redox potential in the positive direction, as compared with aniline redox potential. Figure 6 shows the comparison of the CV's for a 2-nitro aniline film and bare Pt. Distinct oxidation and reduction peaks are observed for 2-nitroaniline film. Due to the low thickness of the 2-nitro aniline film, some characteristics

polymers deposited on Ni

Lexon casing

Lexon casing

rubber gasket

Nation membrane (0.001")
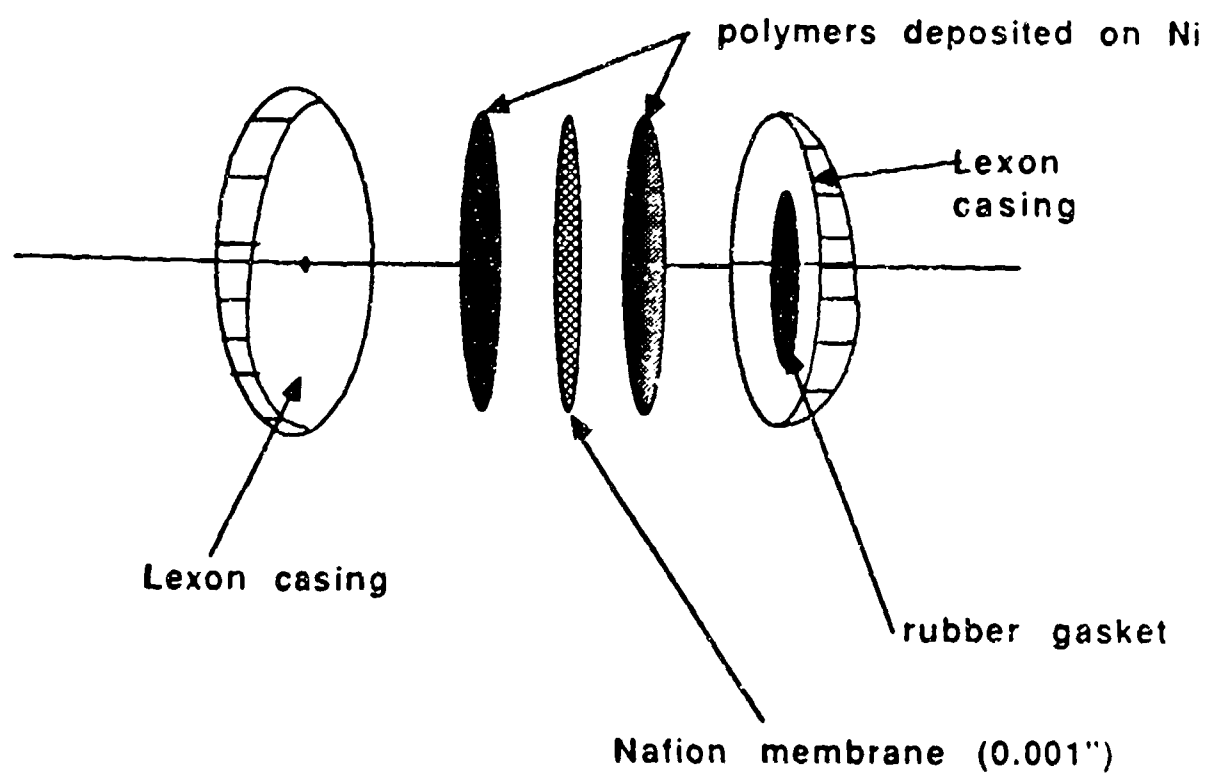
Figure 2: A single capacitor/battery.

conducting
polymer electrode

electrical
connection
(Ni foil)
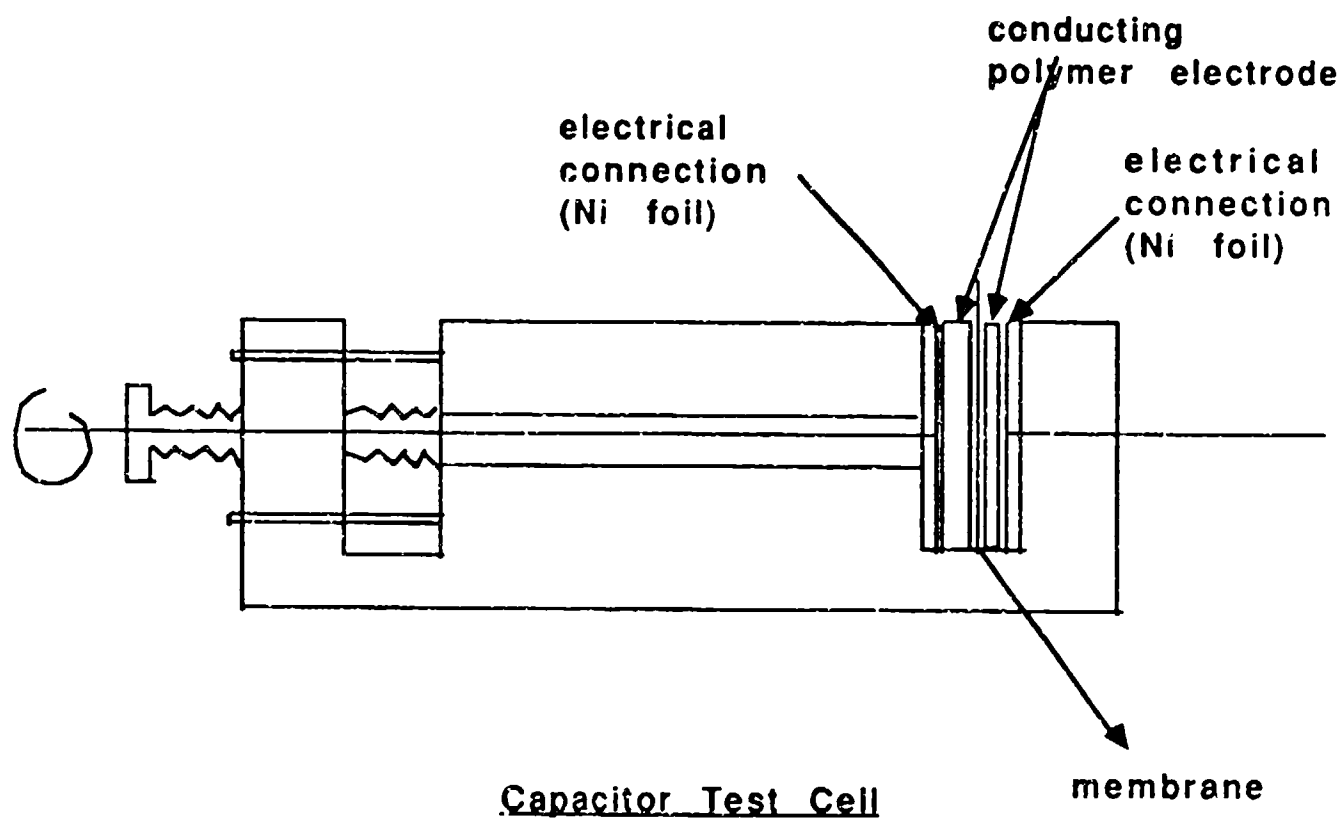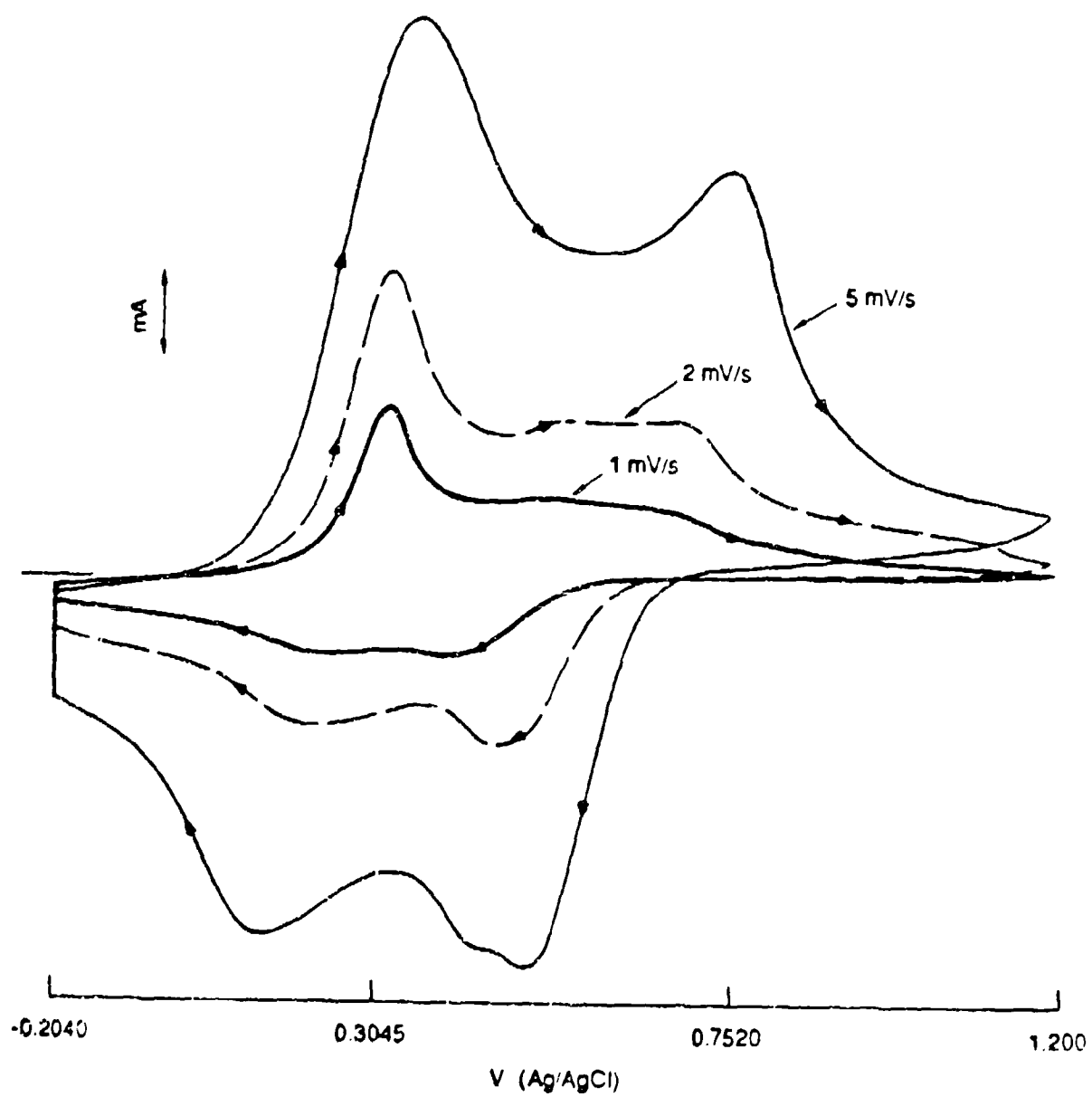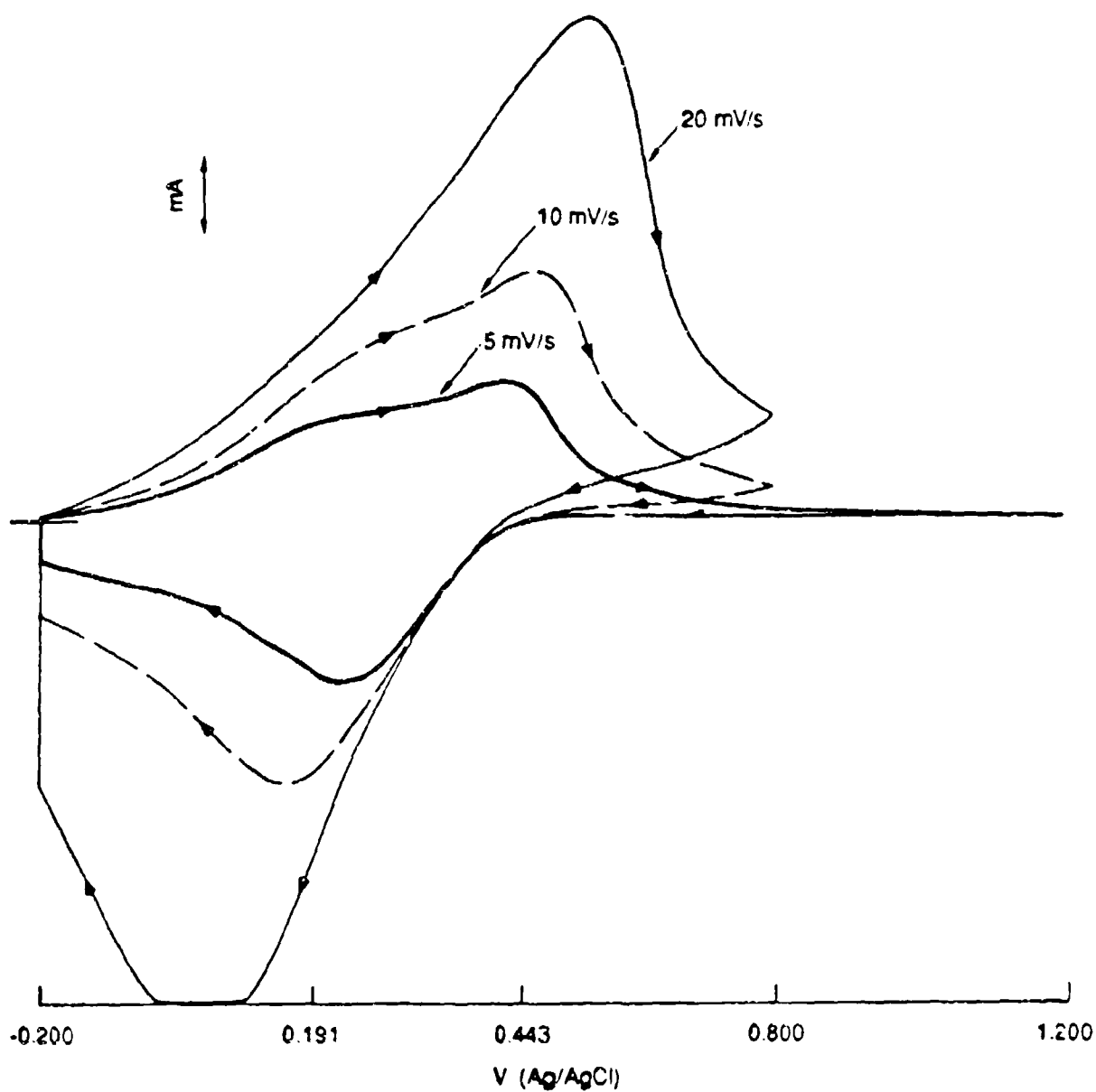
electrical
connection
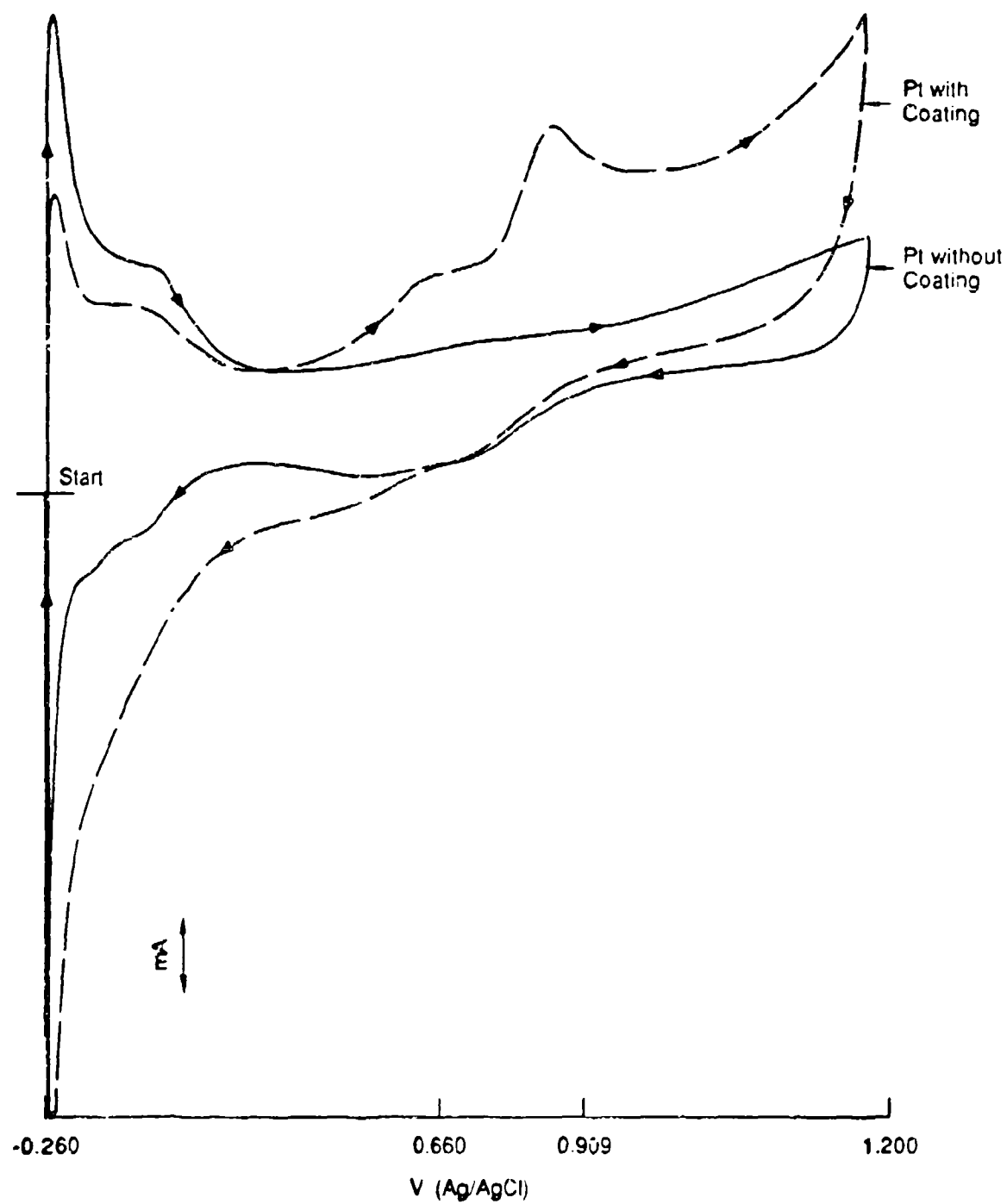(Ni foil)

Capacitor Test Cell

membrane

Figure 3: Blocking electrode test cell.

Figure 4: Cyclic voltammogram of aniline film on Pt in 0.1M H_2SO_4.

Figure 5: Cyclic voltammogram of 2,5 Dimethoxyaniline film on Pt in 0.1M H_2SO_4.

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Figure 6: Cyclic voltammogram of 2-nitroaniline film on Pt and bare Pt in 0.1M H_2SO_4.

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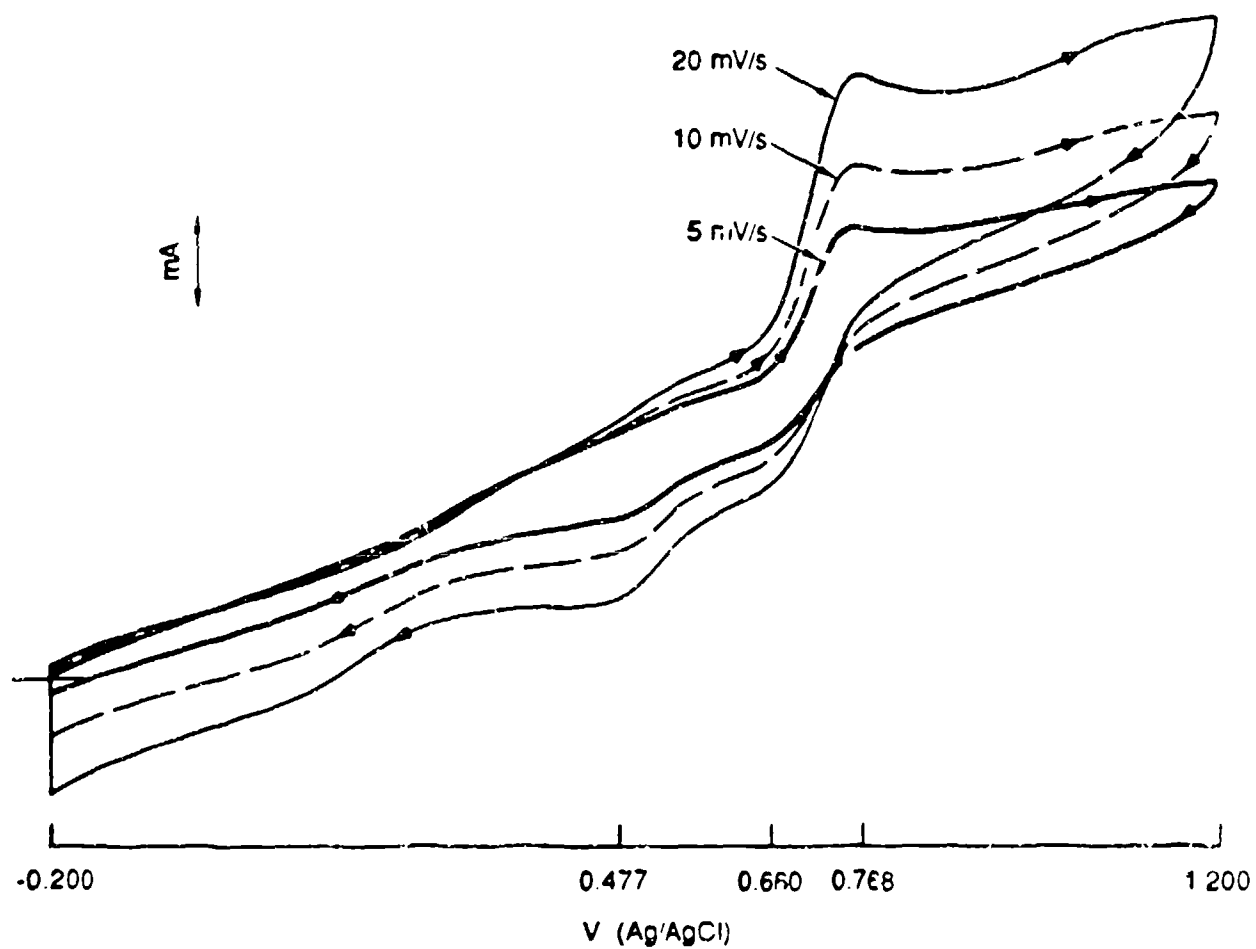
Figure 7: Cyclic voltammogram of aniline-2-sulfonic acid film on Pt in 0.1M H_2SO_4.

of the bare Pt show on the 2-nitroaniline film CV. The films are conducting in both the anodic and cathodic directions.

Tables 2 and 3 give the oxidation potentials of the peaks A and B for the different polymer films on Pt and Ni respectively. On platinum, most of the films show two distinct regions of electroactivity. On nickel substrate, however, as shown in Table 3, usually one peak (width 10-20 mV) was observed for the different polymers. The nickel substrate tends to shift or eliminate some of the electroactive regions in the polymer films.

The anodic and cathodic peak currents increased linearly with the sweep rate for the different films. This is expected for the redox reaction involving a surface attached species. The films were generally stable in air and did not lose their electroactivity. On continued cycling between -0.2V and 1.2V (Ag/AgCl), the films gave fairly reproducible results.

The redox reaction for the O-anisidine film, is usually accompanied by a color change. The film changes from black when the electrode potential is positive of 0.2V (Ag/AgCl) to green when the potential is negative of about 0.1V (Ag/AgCl). This color change is uniform throughout the film with no evidence of regions with different reactivity. For the other polymers investigated, this color change was not obvious. This may be due to the large film thickness or due to the inherent nature of the film.

POLYMER FILMS ON NAFION-COATED PT

The Nafion coating on the Pt tends to give mechanical strength to the films, as well as improve its charge-discharge characteristics. Pt was coated with a commercially available Nafion solution and dried at 90-100°C in a vacuum oven for 3-4 hours. The films were less than 10 Å thick.

Nafion coated Pt was also used as substrate and the different derivatives of aniline were polymerized using the same procedure as for the films on bare Pt. It normally took less than 1 hr for the film to be formed on Nafion coated Pt.

The cyclic voltammograms of the films on Nafion-coated Pt were determined. The films on Nafion-coated Pt were electroactive. The oxidation and the reduction peaks were observed at roughly the same potentials as for the films on Pt given in Table 2. However, on Nafion coated Pt, multiple oxidation and reduction peaks are observed. These may be due to the nonuniform interaction of the polymer with Nafion in different regions.

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Table 2

POTENTIALS FOR THE ANODIC OXIDATION PEAKS IN 0.1M H_2SO_4 FOR DIFFERENT POLYMERS ON PT:

Monomer	V_a (Ag/AgCl)	V_b (Ag/AgCl)
Aniline	0.305	0.752
O-Anisidine	0.249	0.403
2,5 Dimethoxy Aniline	0.196	0.443
3,5 Dimethoxy Aniline	0.324	--
Aniline-2-Sulfonic Acid	0.534	0.768
2-Nitro-Aniline	0.660	0.909
Pt (no film)	–	–

*not present

Table 3

POTENTIALS FOR THE ANODIC OXIDATION PEAKS IN 0.1M H_2SO_4 FOR DIFFERENT POLYMERS ON NICKEL

Monomer	V_a (Ag/AgCl)	V_b (Ag/AgCl)
Monomers with electron donating groups:		
Aniline	0.938	--
O-Anisidine	0.536	--
2,5 Dimethoxy Aniline	0.618	--
3,5 Dimethoxy Aniline	0.156	--
Monomers with electron withdrawing groups:		
Aniline-2-Sulfonic Acid	0.178	1.05
Ni with no film:		
Ni (no film)	0.163	--

* not present

The films on Nafion-coated Pt also exhibited electrochromic behavior on oxidation and reduction. This behavior is very sensitive and was observed by the naked eye.

Figures 8-10 show the SEM pictures of the different polymers on Nafion-coated Pt and on bare Pt. On bare Pt, the polymer is formed as crystals whereas on Nafion-coated Pt the polymer tends to diffuse in the Nafion giving a composite of low thickness.

The polymer films (area = 0.5 cm^2) were charged and discharged at 0.05 mA in 0.1M H_2SO_4. Figures 11-14 show the potential of the polymer film electrode as a function of time. It appears as if the films on Nafion, tend to give a better discharge characteristics than on bare Pt.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY:

The variation in the magnitude of the impedance $|Z|$,

$$|Z| = (Z_R^2 + Z_X^2)^{1/2}$$

where Z_R and Z_X are the real and imaginary components of the impedances with the applied dc potential at four different frequencies is shown in Figures 15-20. At low applied dc potentials the polymers are in the reduced forms and the impedance shows a systematic increase with potential. At roughly the oxidation potential of the films , the impedance shows a sudden decrease. This potential roughly corresponds to the oxidation potential given in Table 2. The potential shift occurs due to the different thickness of the polymer films taken in the CV and EIS measurements.

For bare platinum, the impedance increases with the dc potential. The magnitude of $|Z|$ for the films is lower than that of bare Pt (Figure 20). This is due to the fact that at a given dc bias potential, the film passes more current through it leading to low impedance compared to bare Pt.

The variation in the magnitude of $|Z|$ with potential is shown in Figures 21-25. The films on Nafion-coated Pt exhibit similar behavior to those on bare Pt. The multiple oxidation-reduction peaks observed in the CV's are not very obvious in the impedance data. This may be due to the different thickness of the films in the two experiments. The magnitude of $|Z|$ of the polymer films on Nafion-coated Pt is greater than that of the films on bare Pt. This nay be due to the low thickness of the films on Nafio-coated Pt.

(b)

(a)
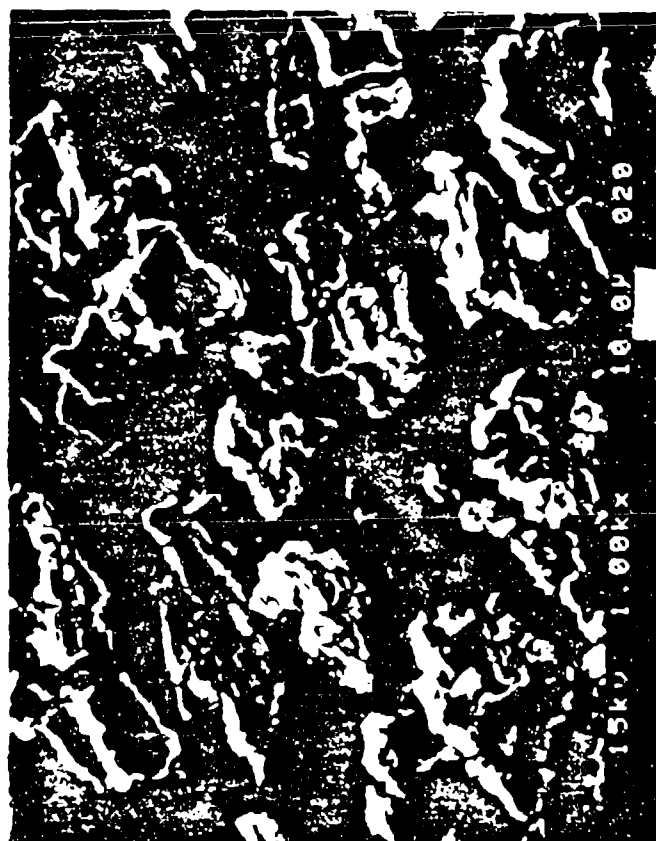
Figure 8: SEM picture of 2-nitroaniline on (a) Pt and (b) nafion coated Pt.

(b)

(a)
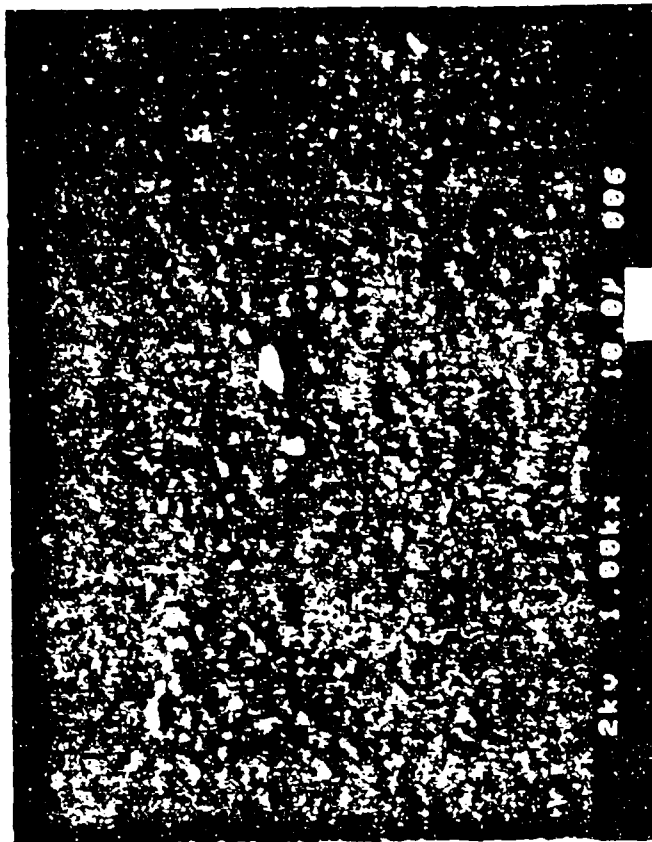
Figure 9:   SEM picture of 2,5 Dimethoxyaniline on (a) Pt and (b) nafion coated Pt

(b)

(a)
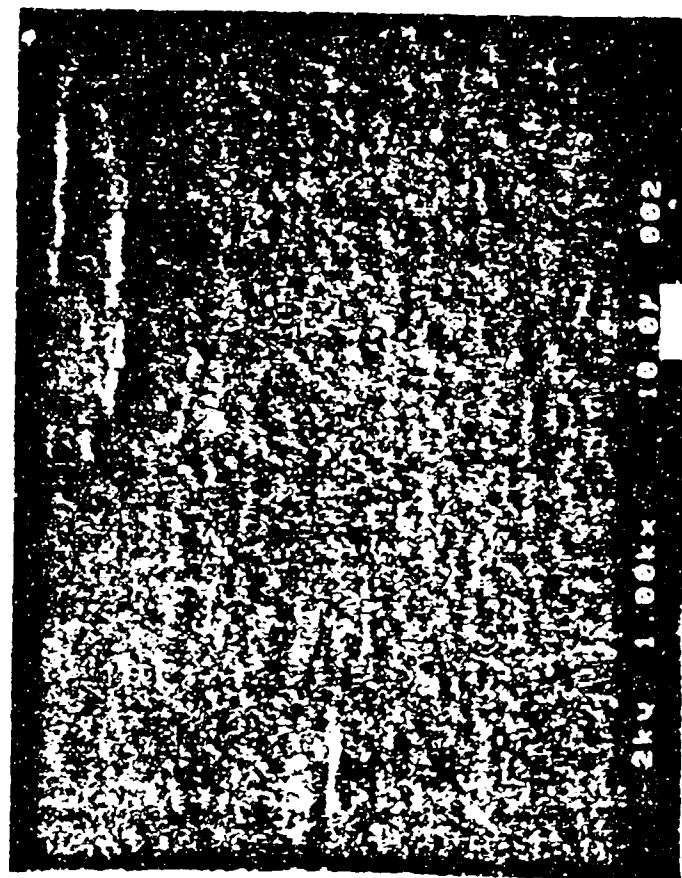
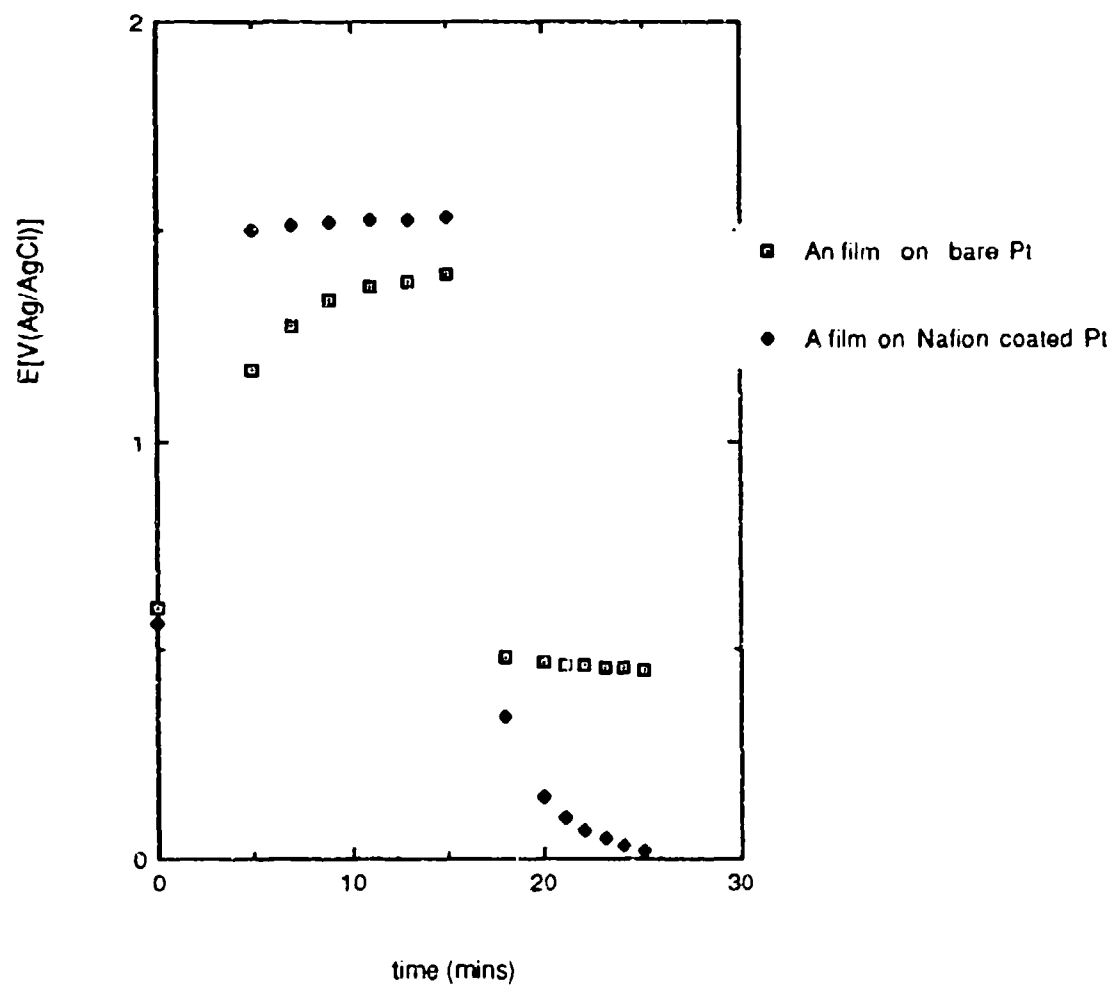Figure 10. SEM picture of O-Anisidine on (a) Pt and (b) nafion coated Pt.

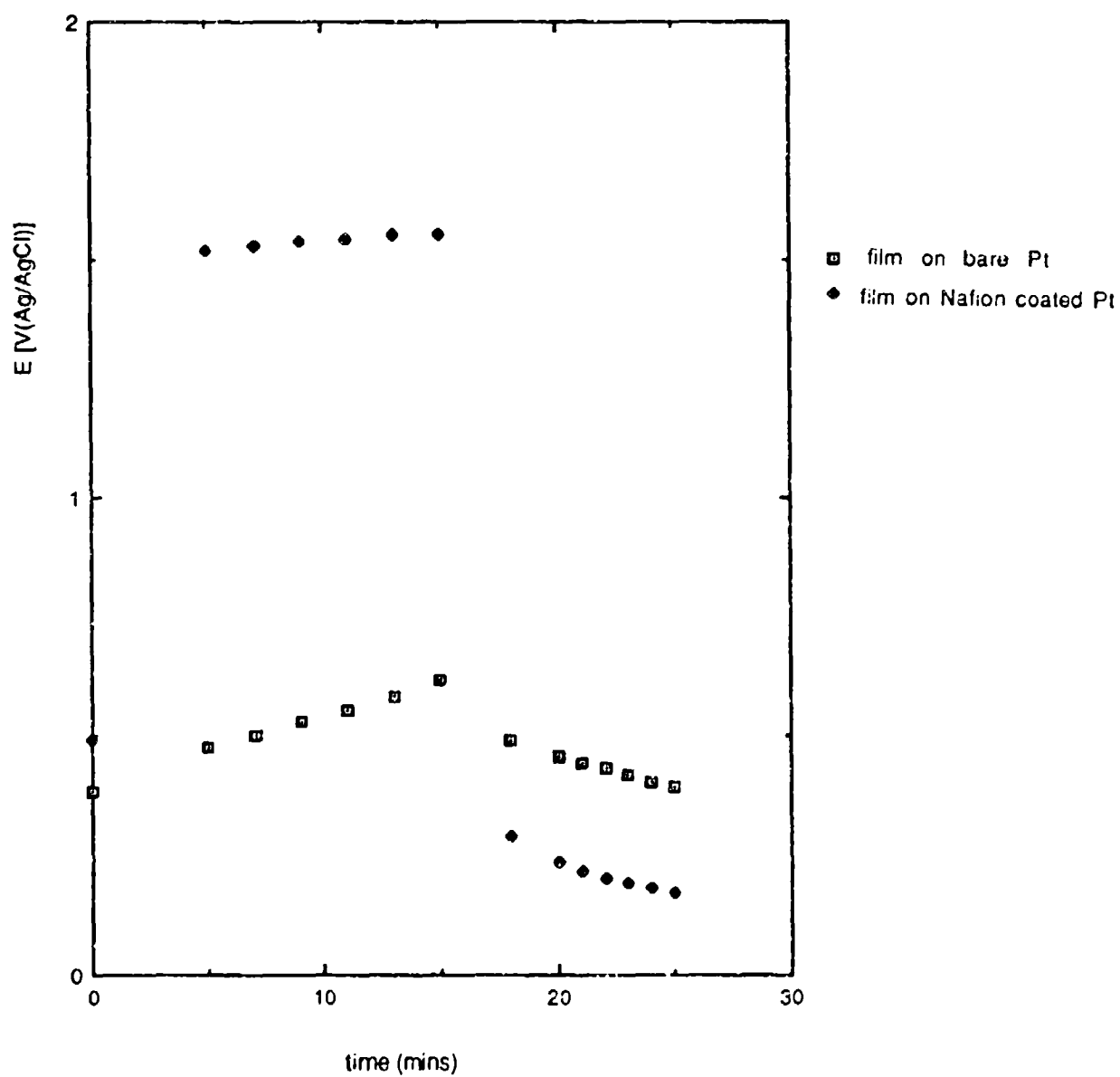Figure 11: Charge-Discharge characteristics of aniline film at 0.05 mA (Area=0.5 cm^2).

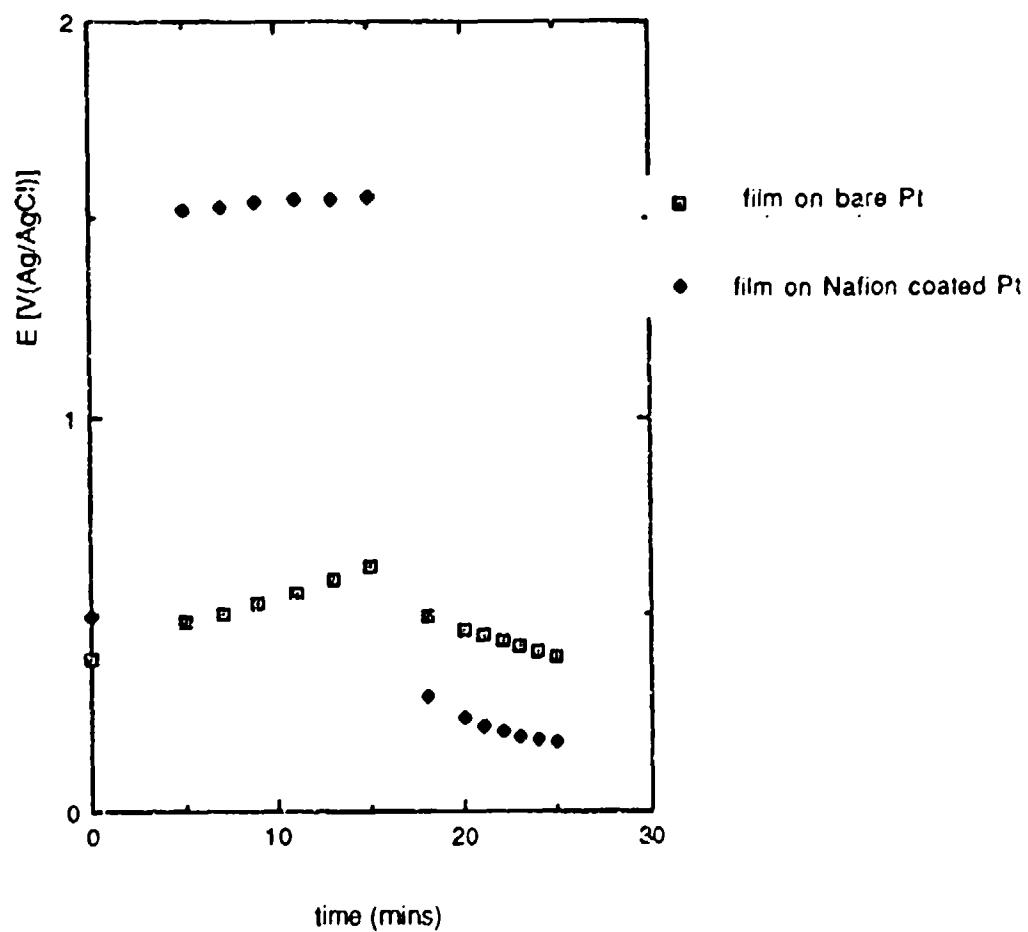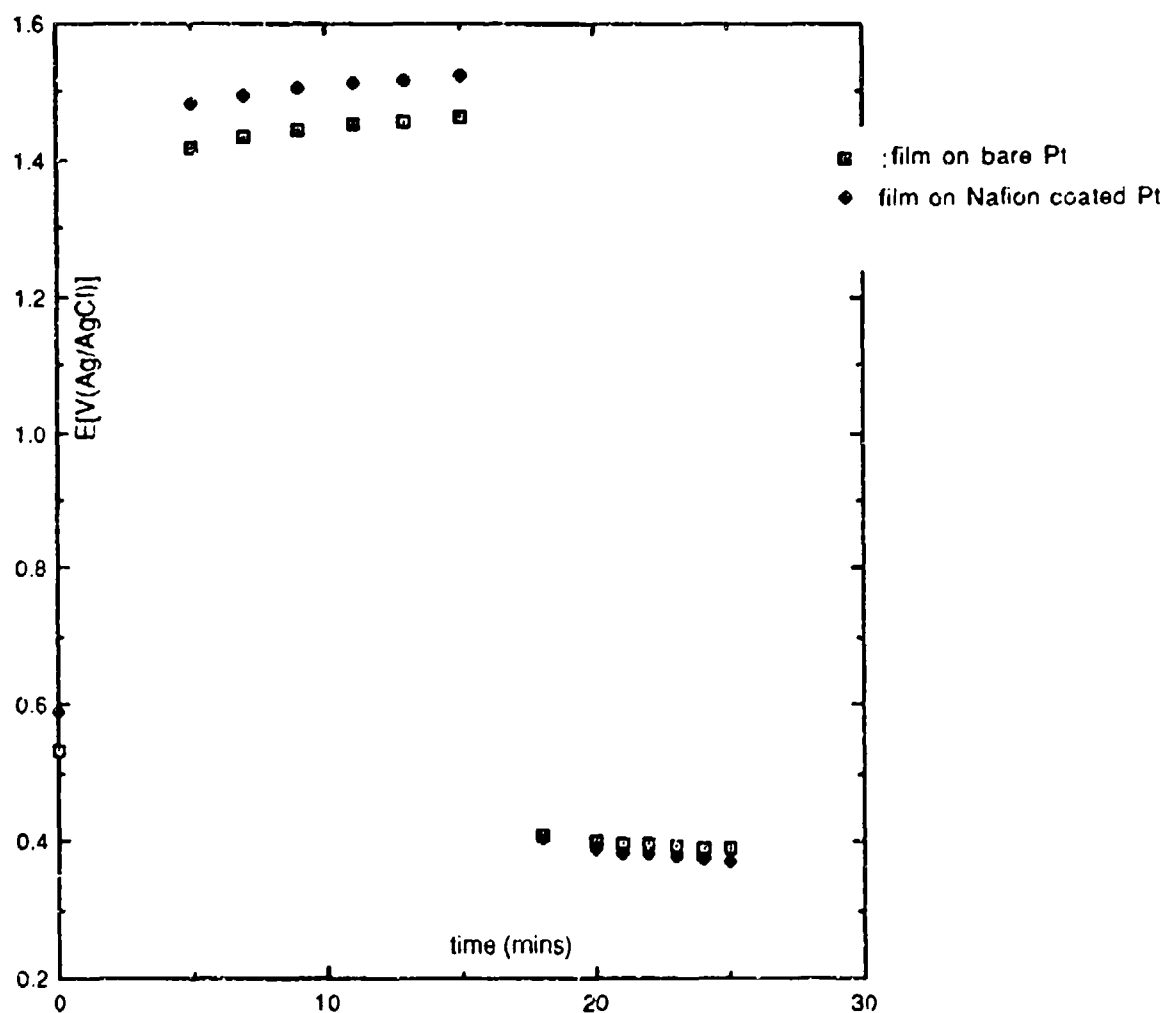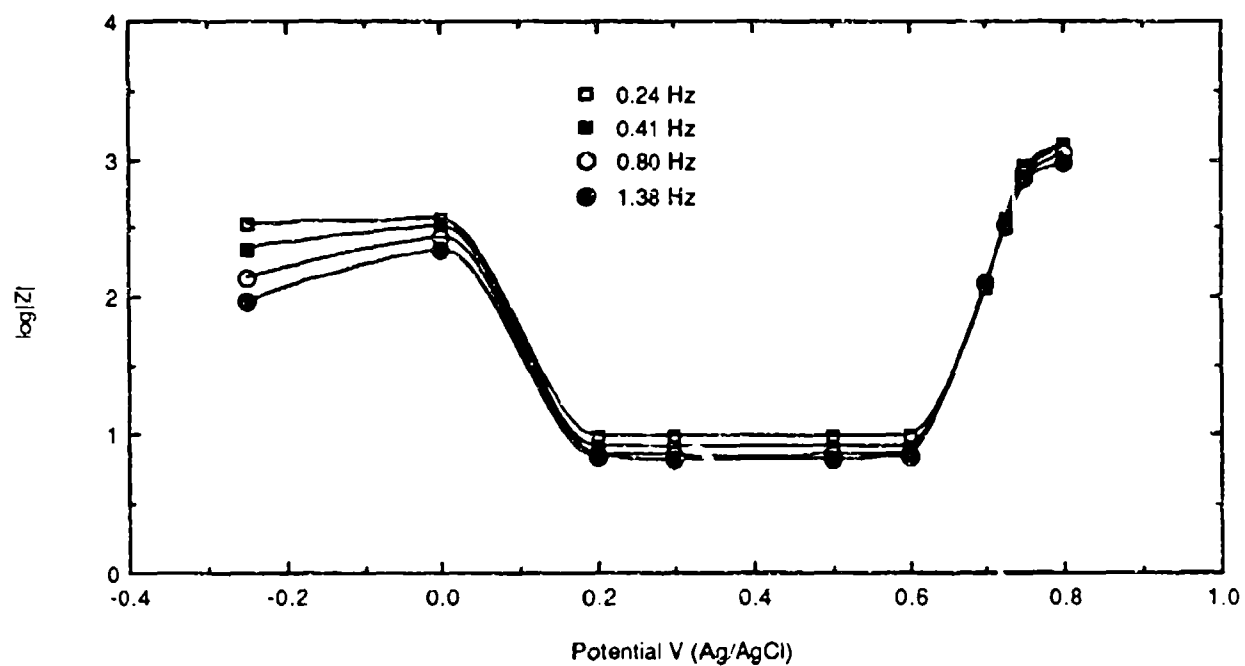Figure 12: Charge-Discharge characteristics of O-Anisidine film at 0.05 mA (Area=0.5 cm^2).

Figure 13: Charge-Discharge characteristics of 2,5 Dimethoxyaniline film at 0.05 mA (Area=0.5 cm^2).

Figure 14: Charge-Discharge characteristics of 3,5 Dimethoxyaniline film at 0.05 mA (Area≈0.5 cm²).

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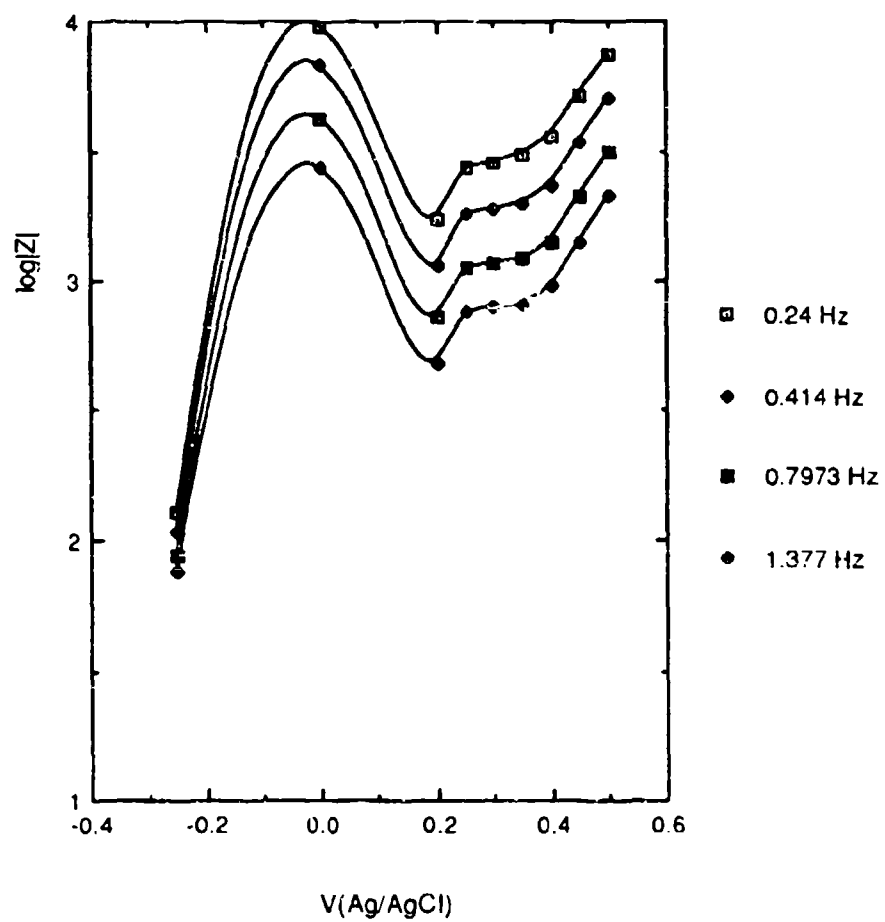Figure 15: Dependence of Z on dc bias potential for aniline film on Pt.
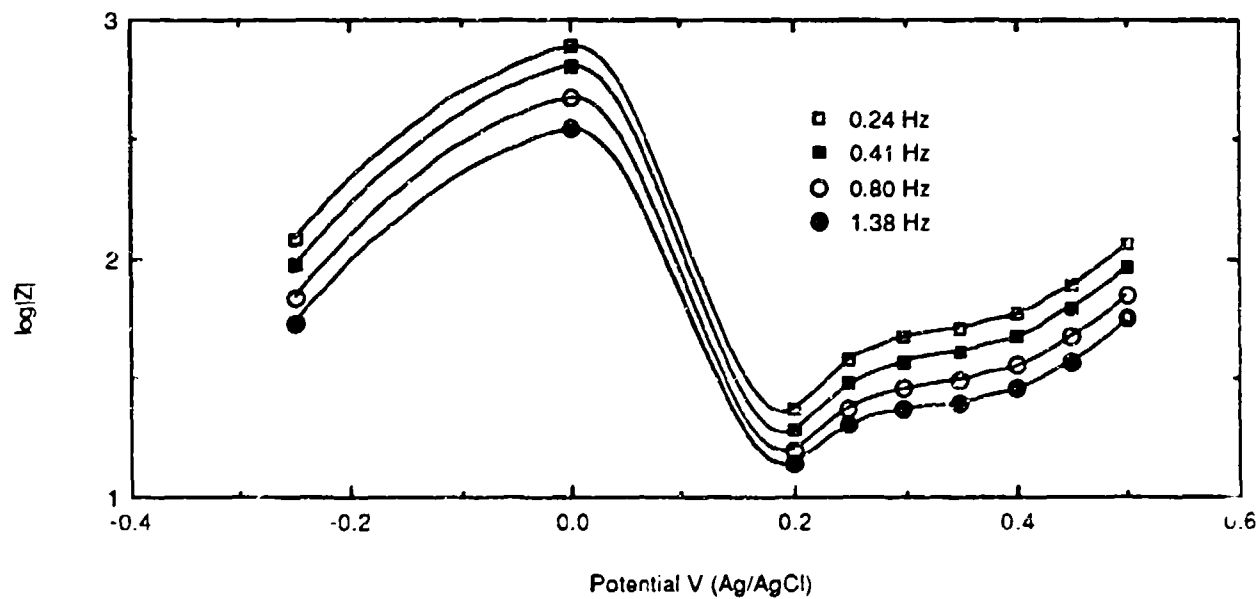
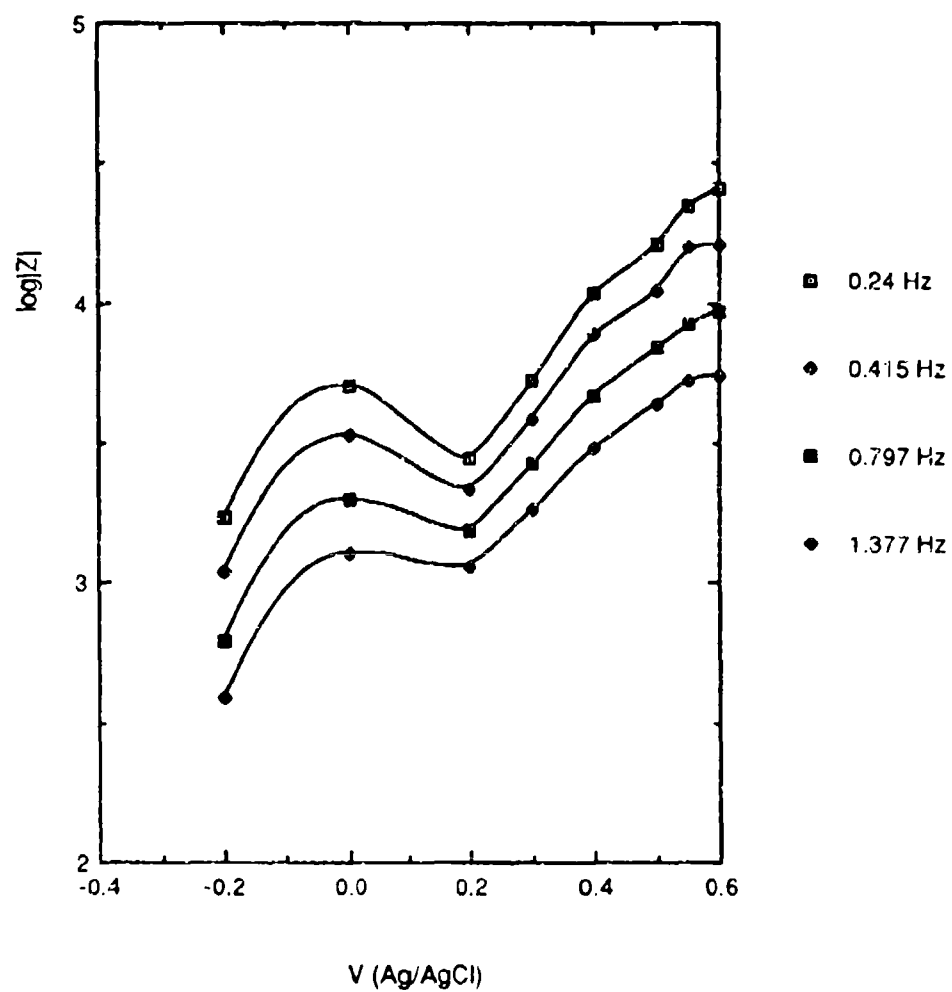Figure 16:   Dependence of Z on dc bias potential for O-Anisidine film on Pt.
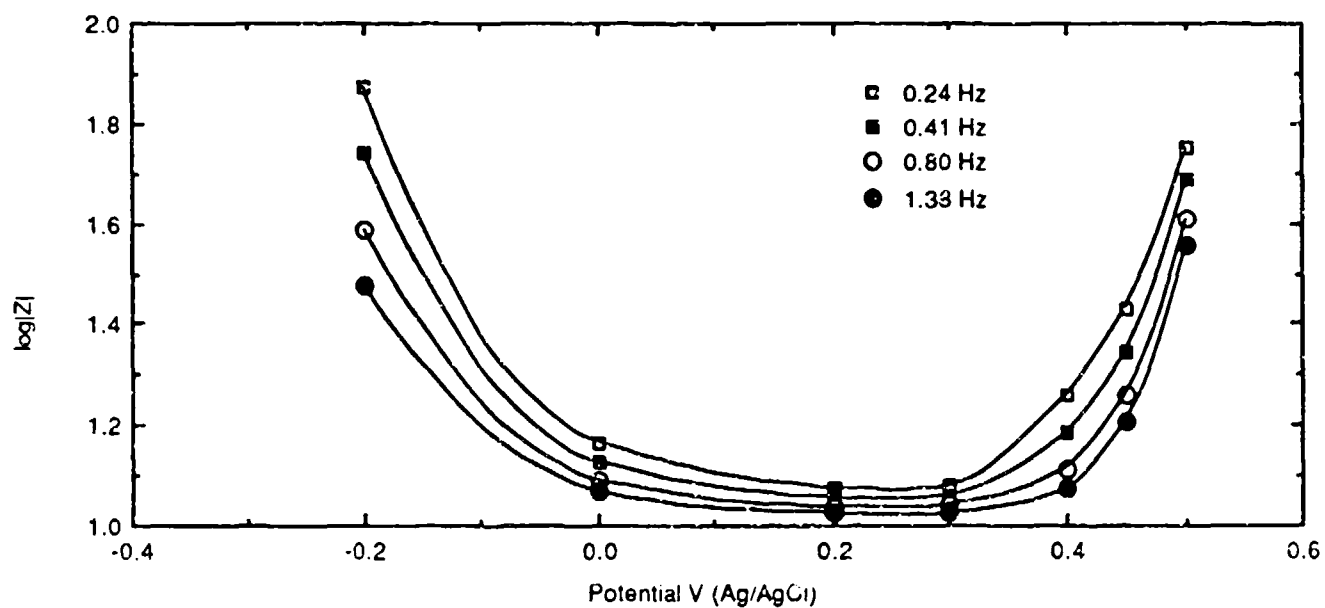
Figure 17: Dependence of Z on dc bias potential for 2,5 Dimethoxyaniline film on Pt.
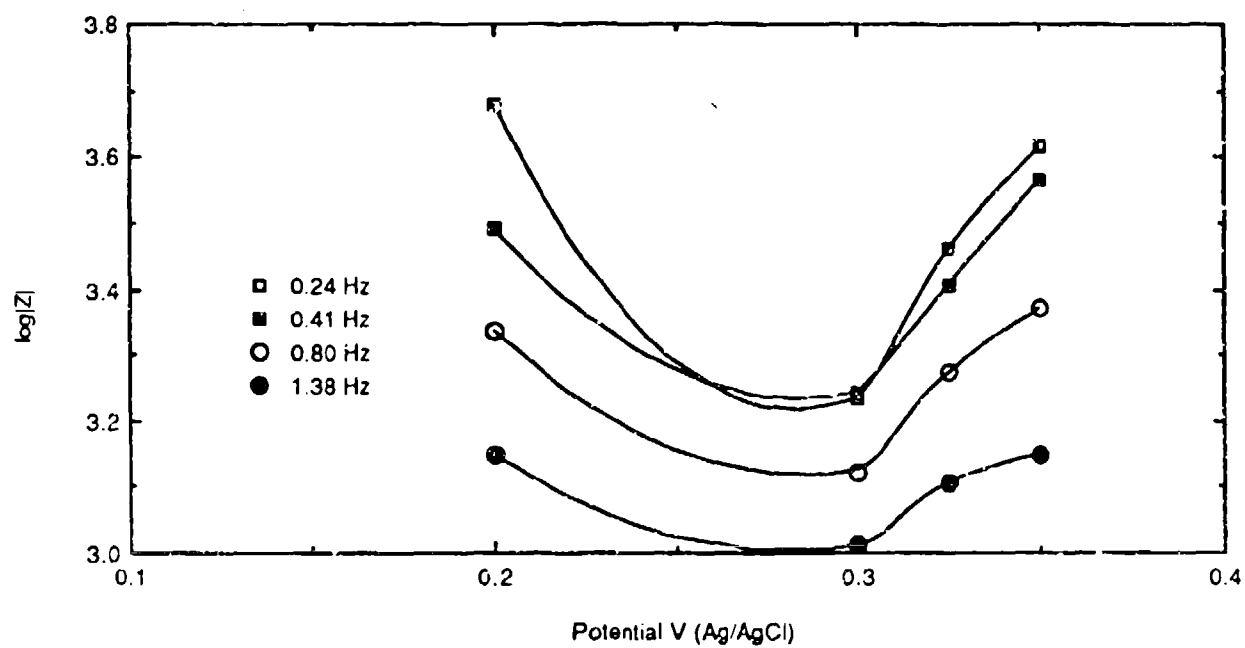
Figure 18: Dependence of Z on dc bias potential for 3,5 Dimethoxyaniline film on Pt.

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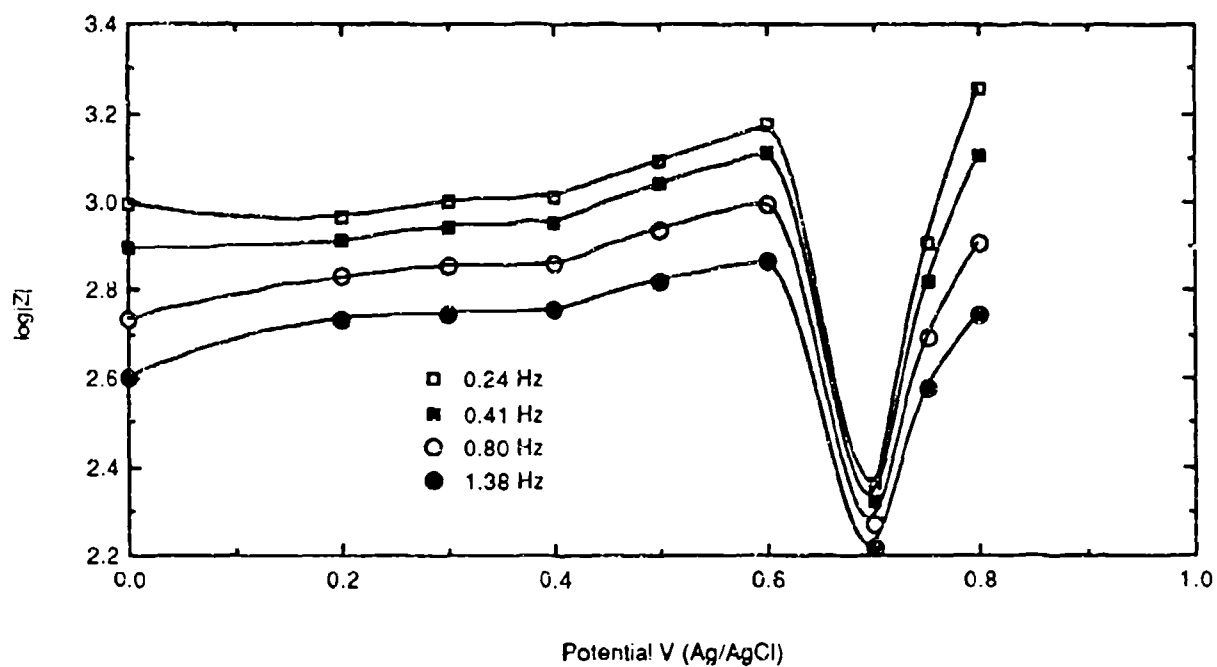
Figure 19: Dependence of Z on dc bias potential for aniline-2-sulfonic film on Pt.
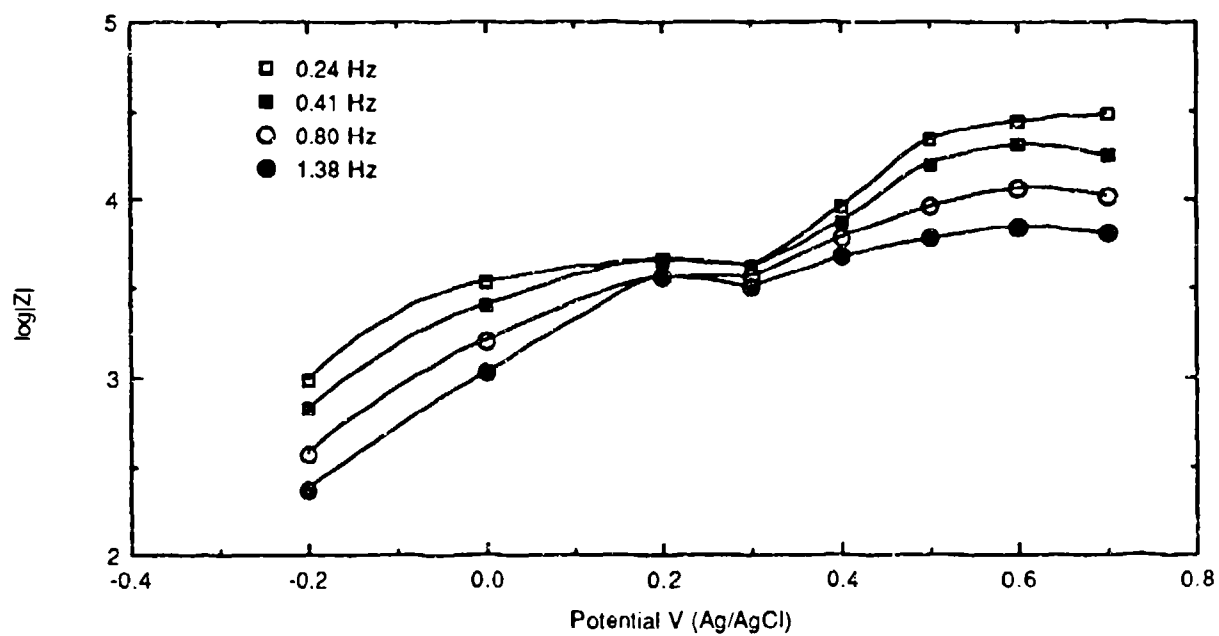
Figure 20:   Dependence of Z on dc bias potential for bare Pt.
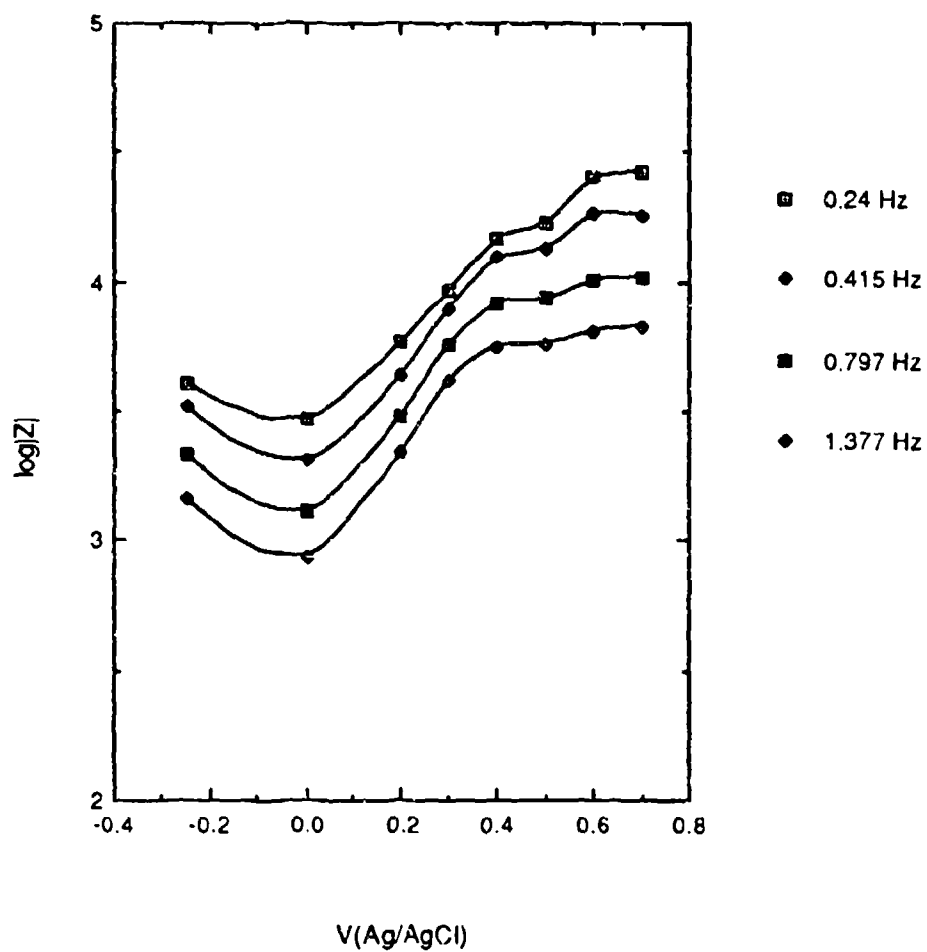
Figure 21: Dependence of Z on dc bias potential for nafion coated Pt.
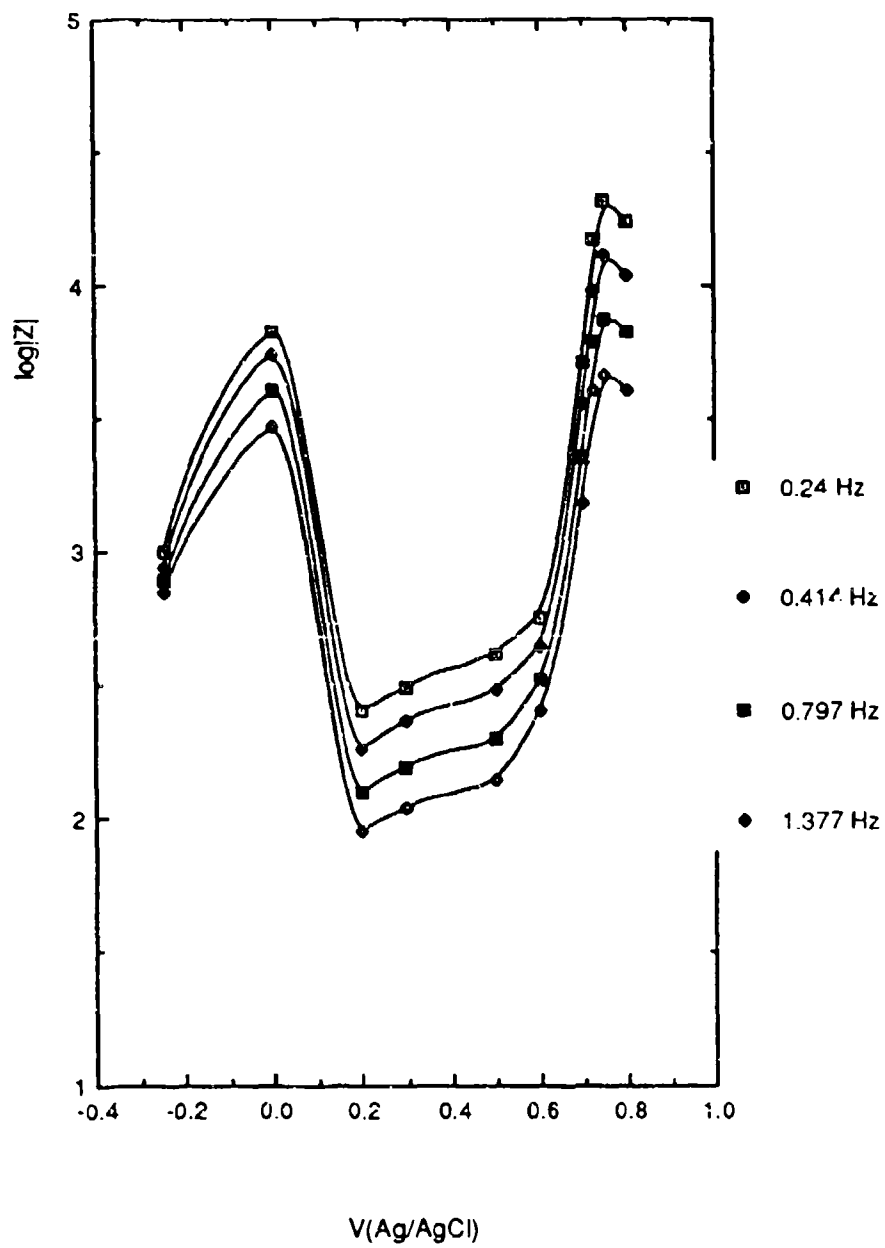
Figure 22: Dependence of Z on dc bias potential for aniline film on nafion coated Pt.

Figure 23: Dependence of Z on dc bias potential for O-Anisidine film on nafion coated Pt.

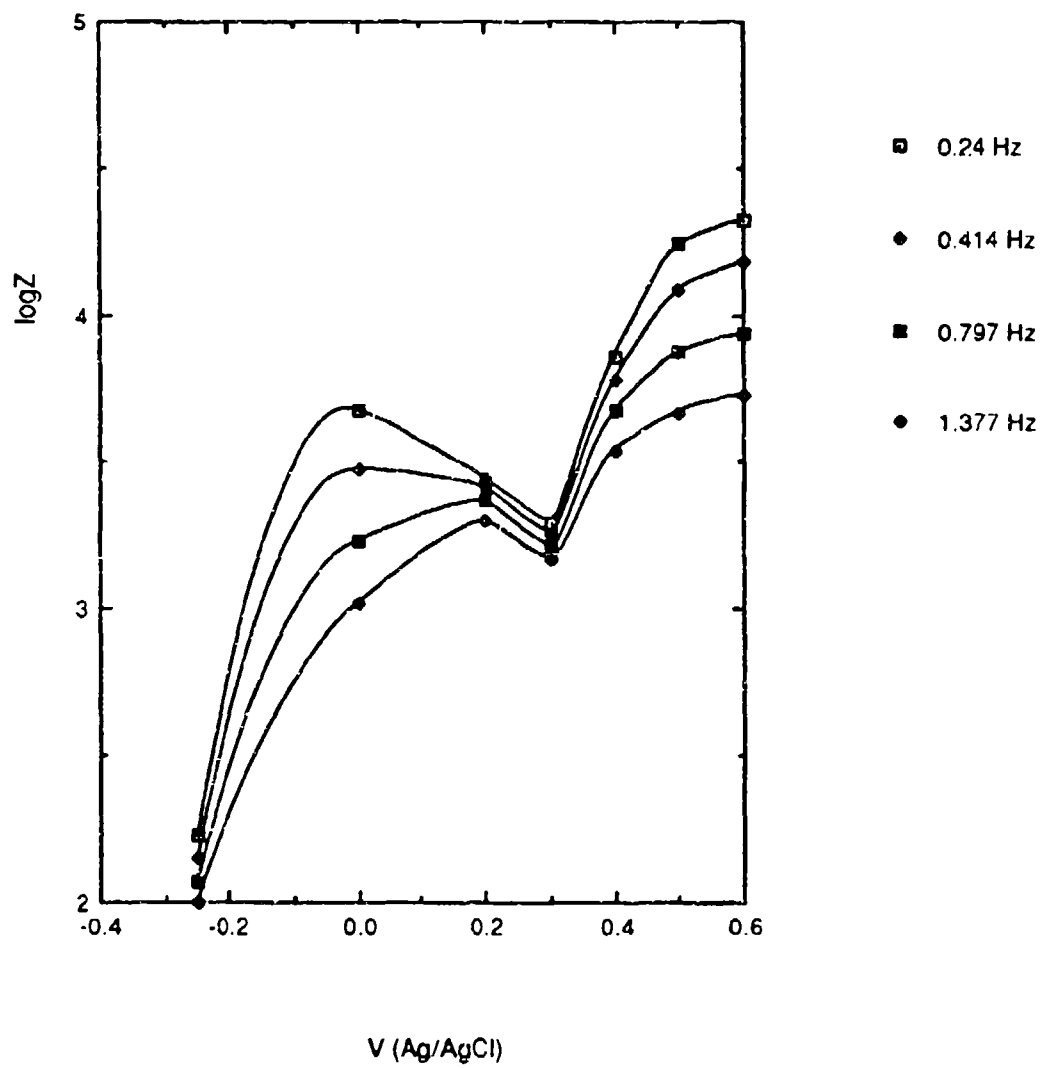Figure 24: Dependence of Z on dc bias potential for 2,5 Dimethoxyaniline film on nafion coated Pt.

Figure 25: Dependence of Z on dc bias potential for 3,5 Dimethoxyaniline film on nafion coated Pt.

CELL CHARGE-DISCHARGE:

As a demonstration of "proof of concept," different combinations of the polymers on Pt were charged-discharged using the cell shown in Figure 3. We emphasize that the charge-discharge conditions were taken at random. No effort has been made to optimize any of the conditions. The 2-nitroaniline and aniline-2 sulfonic acid were used in the reduced forms. Figures 26-30 show the potential with respect to time. The self discharge of the cells was also recorded and is shown in Figures 26-30. In the self discharge experiments the cell was charged at a given current density and the potential recorded during self discharge. The initial drop in the potential may be due to the IR drop. During the short self-discharge times investigated, the voltage was fairly constant, as seen in Figures 26-30. The capacity and energy density of the different cell combinations were calculated. These, along with experimentally measured open circuit voltage, are given in Table 4. The open circuit voltage roughly equals the difference in the oxidation and redox potentials of the two polymers used.

To further demonstrate the "proof of concept," the different cell combinations were pulsed charged-discharged. The charge potential was 0.61 V and the charge time was 0.1 ms. The discharge potential was -0.15V and the discharge time was 0.2 ms. These are not the optimum conditions. This was done for aniline/Nafion/Pt black using a cell shown in Figure 3. On charging, the current increased and on discharge the current decreased. This gives evidence that the concept proposed in this research is feasible. Table 5 gives the maximum charge-discharge currents for the different cell combination. The charge-discharge cycles were continued for almost five hours. There was no appreciable degradation of the polymeric electrodes and shift in the current maximums.

Impedance measurements were also done on this cell using a 2-electrode configuration. Figures 31-33 show the Nyquist and Bode plots. These plots are consistent with an equivalent circuit consisting of two partially resolved R-C combinations.
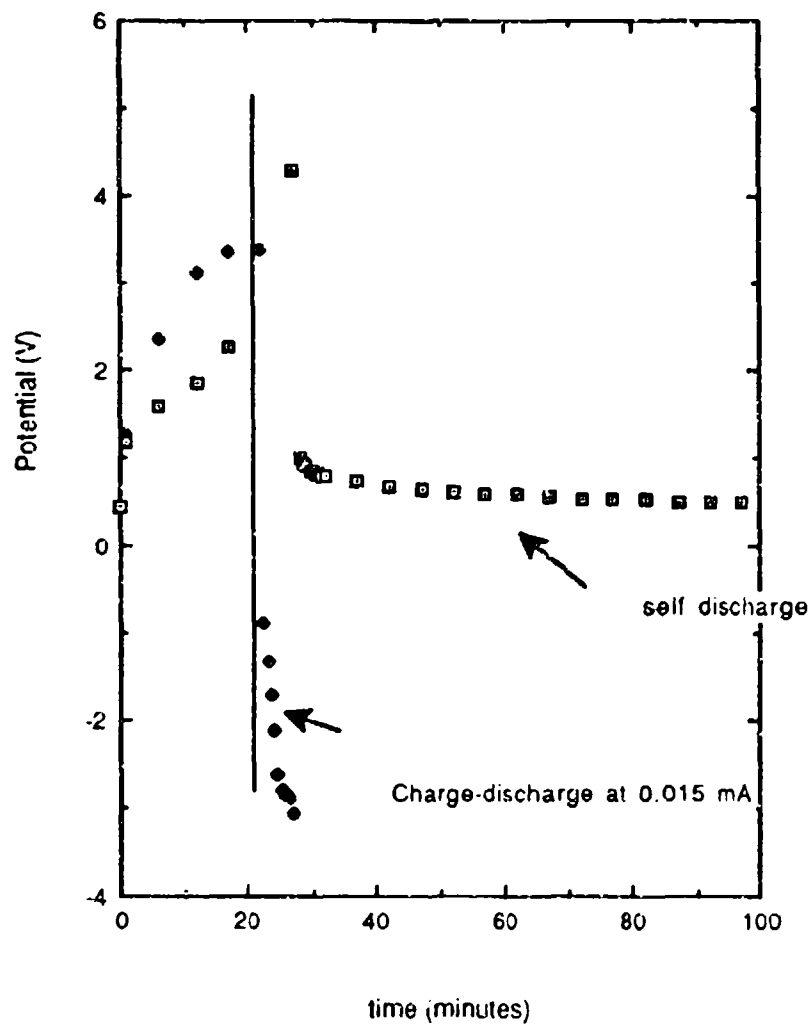
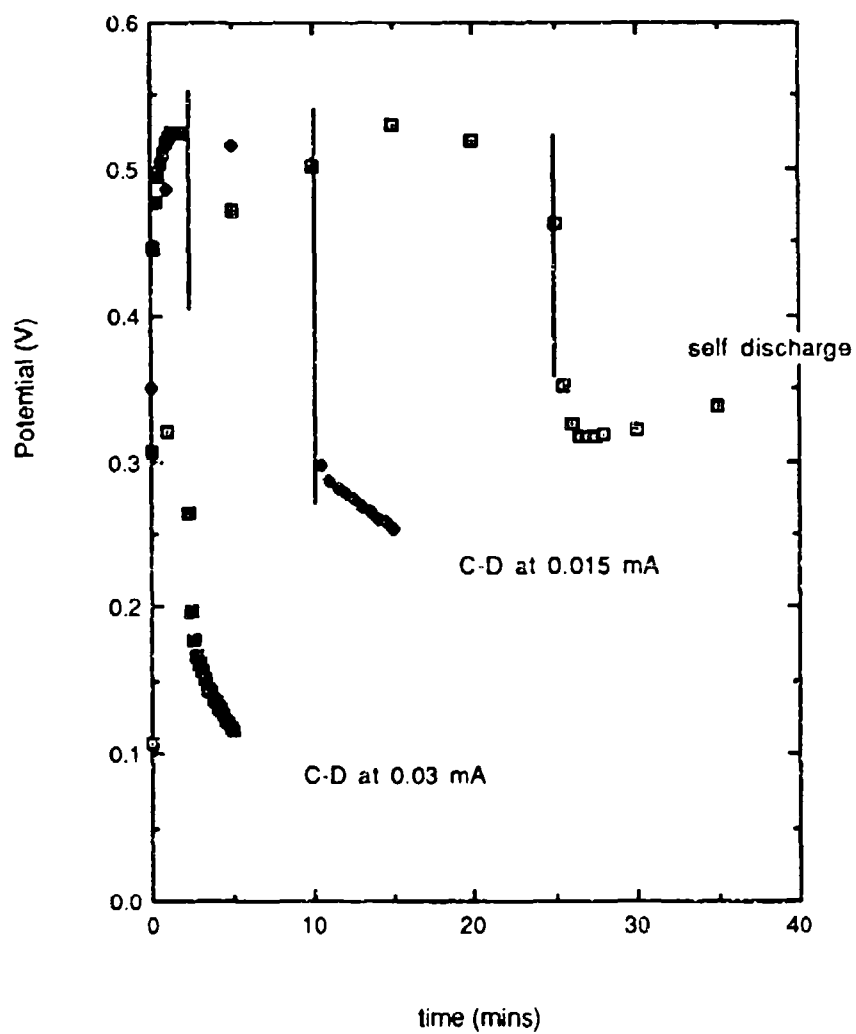Figure 26: Charge-Discharge data for 2,5 Dimethoxyaniline/Nafion/ 2-nitroaniline cell.

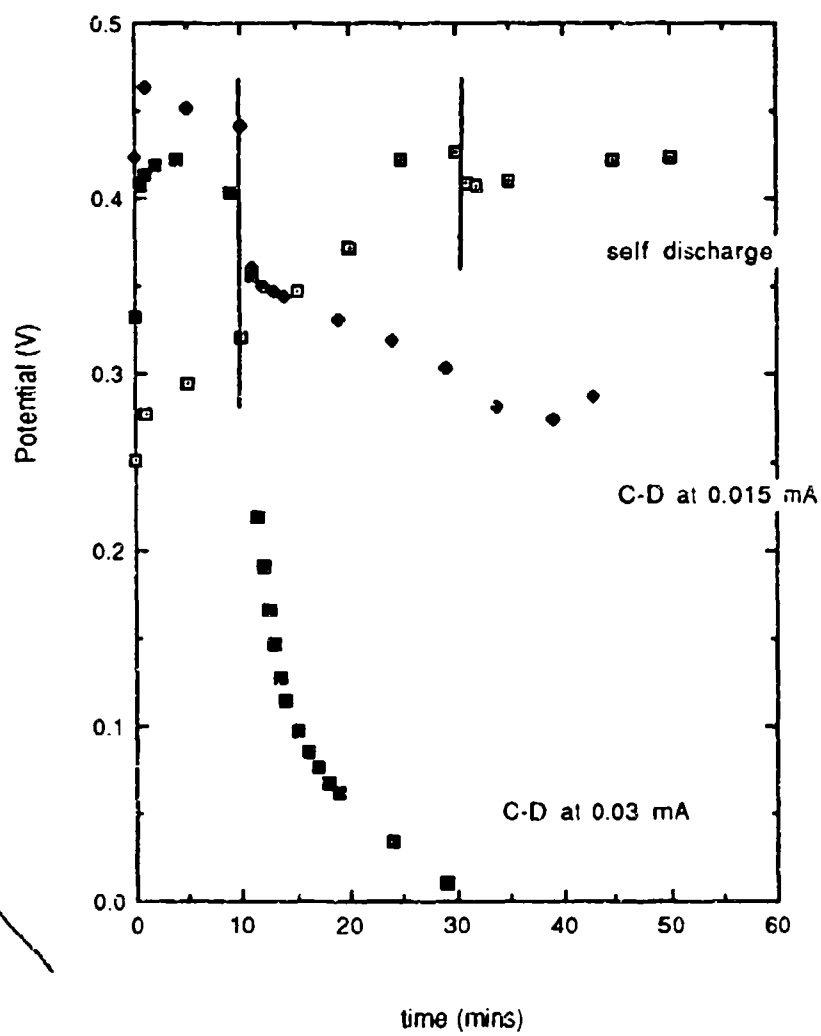Figure 27:   Charge-Discharge data for Aniline/Nafion/ 2-nitroaniline cell.

Figure 28: Charge-Discharge data for Aniline/Nafion/Pt black.
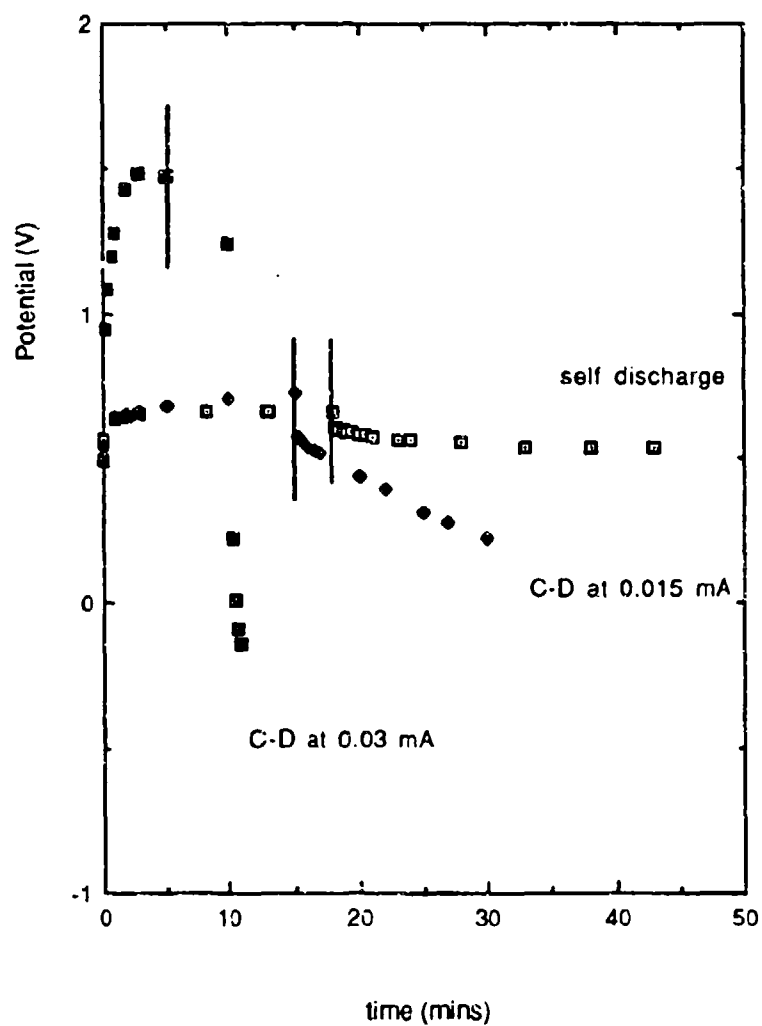
Figure 29: Charge-Discharge data for O-Anisidine/Nafion/ 2-nitroaniline cell.
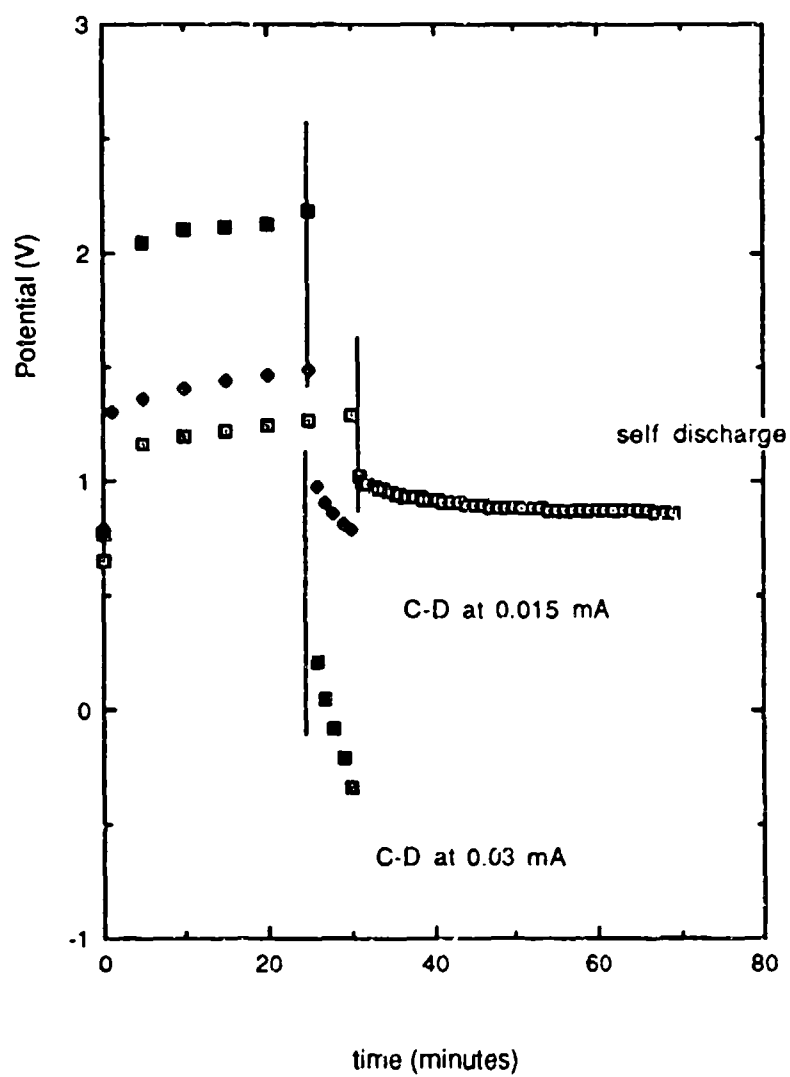
Figure 30: Charge-Discharge data for 2,5 Dimethoxyaniline/Nafion/ Pt black.
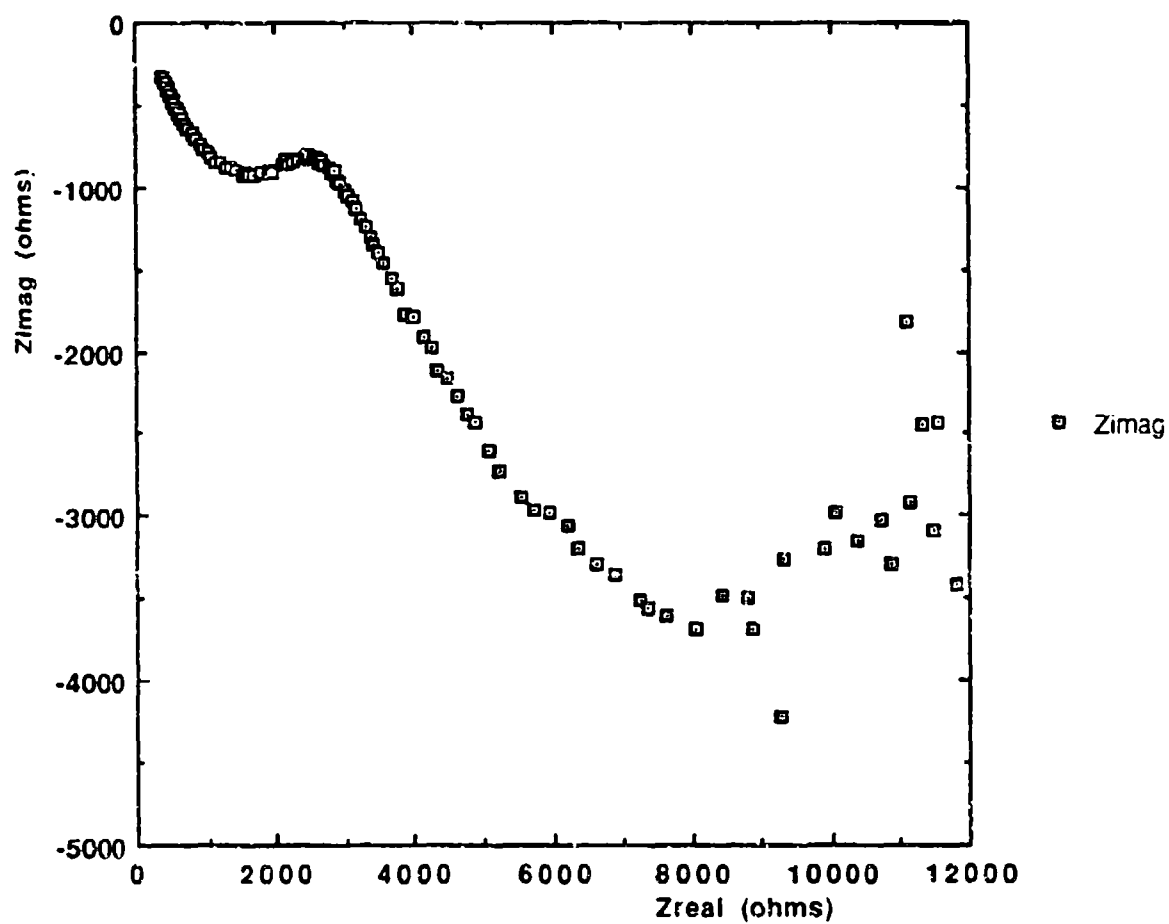
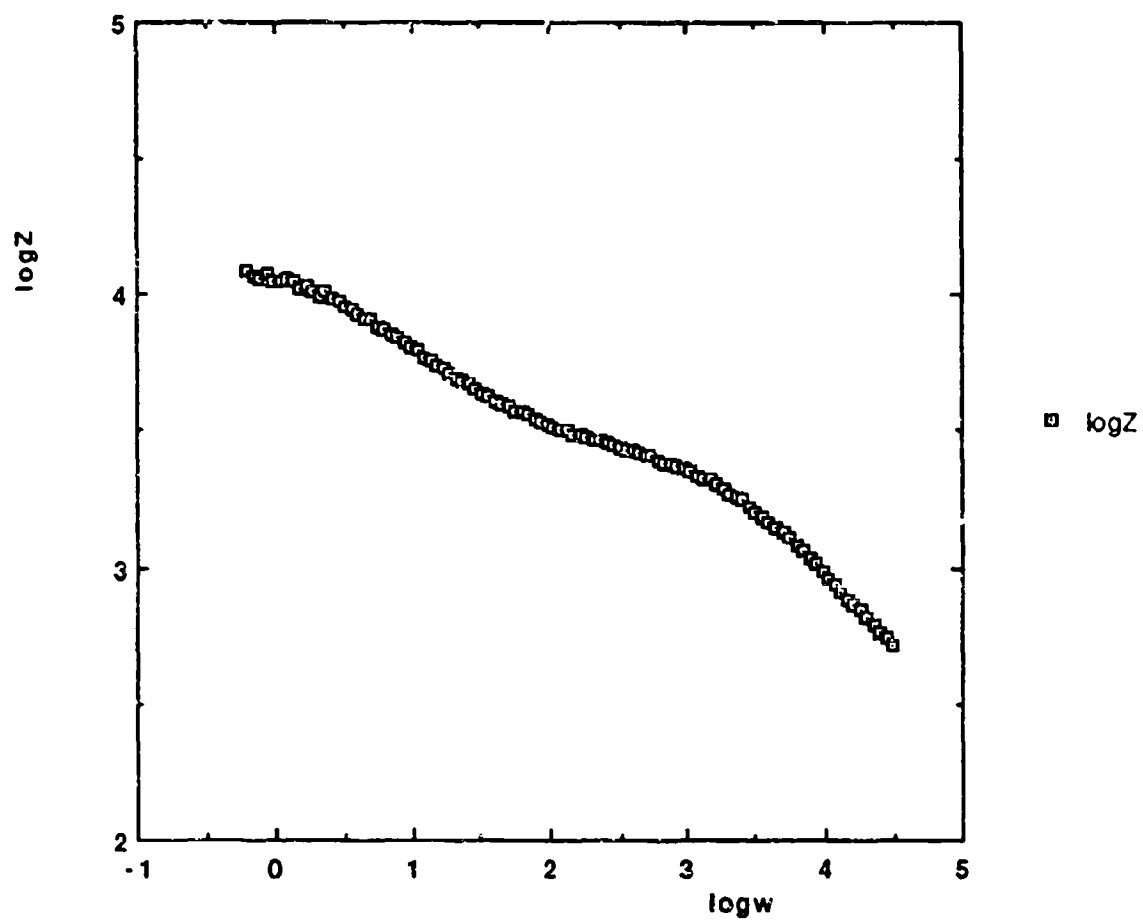Figure 31: Nyquist plot of Aniline(Ni)/Nafion/Pt black(Ni) cell.DC Bias potential = -0.15V

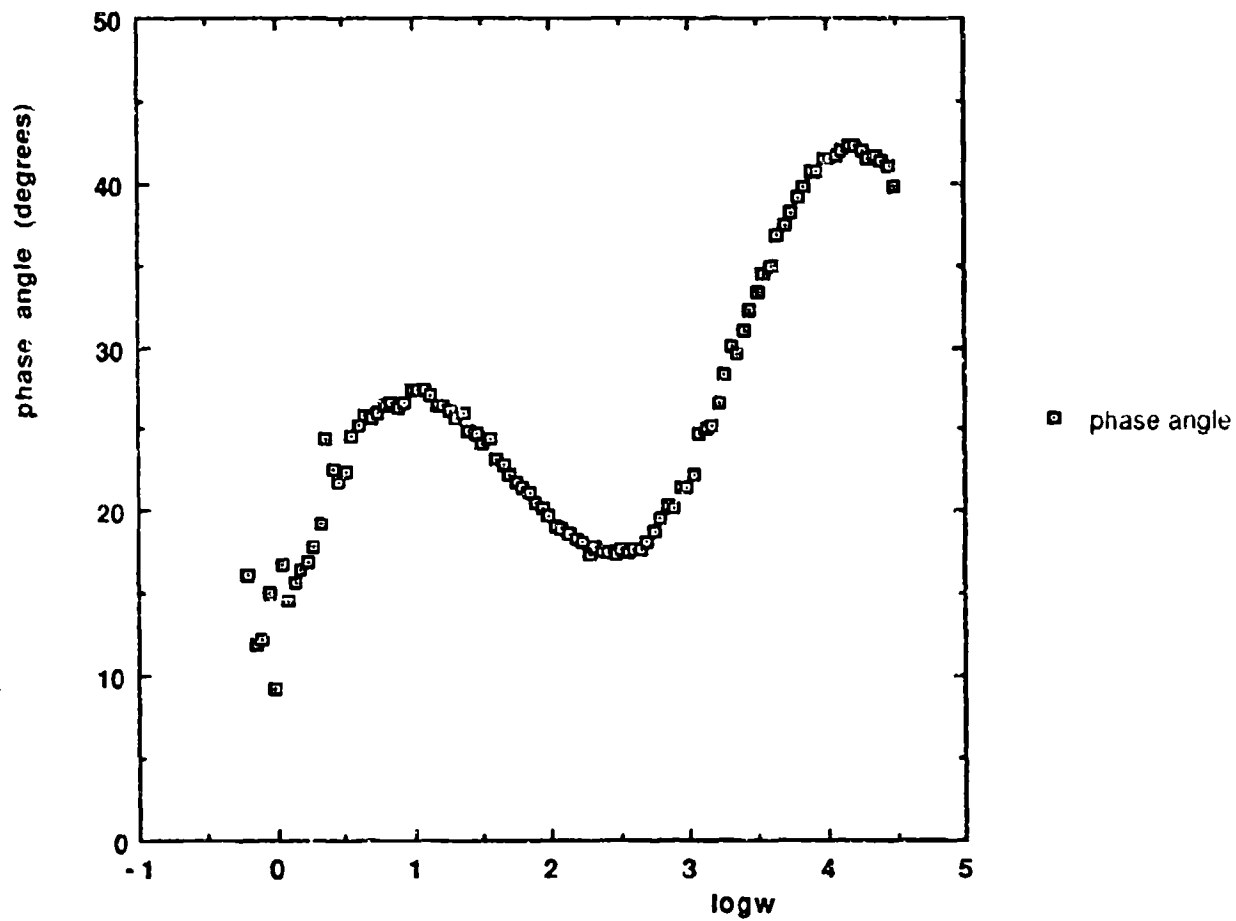Figure 32: Bode plot of Aniline(Ni)/Nafion/Pt black(Ni) cell.DC Bias potential = -0.15V

Figure 3S: Bode plot of Aniline(Ni)/Nafion/Pt black(Ni) cell.DC Bias potential = -0.15V

Table 4

CHARACTERISTICS OF DIFFERENT CELLS:

The cells were charged-discharged at 0.023mA/cm^2. These conditions have not been optimized.

Cell Type	Capacity (mA hr cm^{-2})	Energy Density (Watt-hrs/Kg)	Open Circuit Voltage (V)
2,5 Dimethoxyaniline (Pt) /Nafion/ Pt black (Pt)	0.00198	0.0269	0.60
O-Anisidine (Pt) /Nafion/ 2-Nitroaniline (Pt)	0.0031	0.0065	0.56
Aniline (Pt) /Nafion/ Pt black (Pt)	0.0065	0.0030	0.25
3,5 Dimethoxyaniline (Pt) /Nafion/ 2-Nitroaniline (Pt)		0.0116	0.56
Aniline (Pt) /Nafion/ 2-Nitroaniline (Pt)	0.0016	0.0034	0.10
2,5 Dimethoxyaniline (Pt) /Nafion/ 2- Nitroaniline (Pt)	0.00198	0.051	0.5
O-Anisidine (Ni) /Nafion/ Pt black (Ni)		0.0355	0.247

Table 5

PULSE CHARGE-DISCHARGE CHARACTERISTICS

The cells were charged to 0.61V for 0.1 ms and discharged to -0.15V for 0.2 ms. The charge-discharge cycles were continued for 4-5 hrs.

Cell Type	Charge current (maximum) (mA/cm^2)	Discharge current (maximum) (mA/cm^2)
2,5 Dimethoxyaniline (Pt)		
/Nafion/		
Pt black (Pt)	0.105	0.1438
O-Anisidine (Pt)		
/Nafion/		
2-Nitroaniline (Pt)	0.1275	0.117
3,5 Dimethoxyaniline (Pt)		
/Nafion/		
2-Nitroaniline (Pt)	16.19	16.10
Aniline (Pt)		
/Nafion/		
2-Nitroaniline (Pt)	82.7	51
2,5 Dimethoxyaniline(Pt)		
/Nafion/		
2-Nitroaniline (Pt)	38.095	22.22
O-Anisidine (Ni)		
/Nafion/		
Pt black (Ni)	0.028	0.048

CONCLUSIONS

Proton conducting superionic molecular tunnel electrolytes (PSMTE) have been synthesized which exhibit higher proton conductivity than Nafion. They show good film forming properties suitable for use in electrosupercapacitors.

Different derivatives of aniline with electron donating and electron withdrawing groups were polymerized on platinum and nickel surface. The films were electroactive as shown by cyclic voltammetry and impedance measurements. The polymeric films were also formed on Nafion-coated Pt. The films on Nafion-coated Pt gave better discharge characteristics.

As a demonstration of "proof of concept," different combinations of the polymeric electrodes with 0.001" proton conducting Nafion membranes were shown to pulse charge-discharge for times as low as 0.1 ms. Five of these cells with different electrode combinations have been sent to Dr. Michael Binder under separate cover. Problems of low capacity and unacceptable self discharge rate need to be addressed before a practical supercapacitor can be built.