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Electrochemical Investigation of Electronically Conductive Polymer

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Reginald M. Penner, Leon S. Van Dyke and Charles R. Martin

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Department of Chemistry
Texas A&M University
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A small amplitude current-pulse method which is uniquely suited for solving the myriad problems associated with electrochemical analyses of electronically conductive polymers has been developed. This method was used to obtain D_{app} values for the electronically conductive polymer, polypyrrole. The results of these experiments are described here. In addition, a procedure for controlling the morphologies of electronically conductive polymers has been developed. This procedure involves the electrochemical growth of the conductive polymer at an electrode surface which has benn masked with a microporous polymer membrane. The pores in this membrane act as templates for the nascent electronically conductive polymer. Because the template membrane contains linear cylindrical pores, cylindrical conductive polymer fibrils are obtained. We will show in this manuscript that microfibrillar polypyroole films prepared via this approach can support higher rates of charge-transport than conventional polypyrrole.

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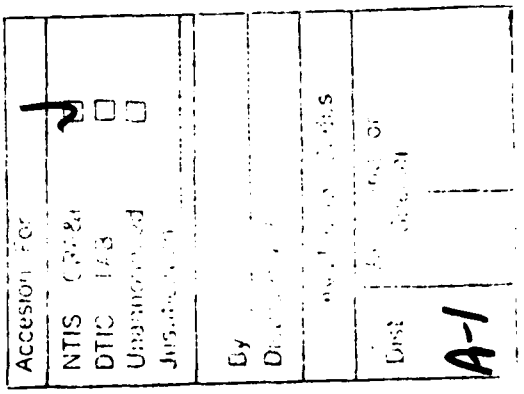


ELECTROCHEMICAL INVESTIGATION OF ELECTRONICALLY CONDUCTIVE POLYMERS

Charles R. Martin, Reginald M. Penner, and Leon S. Van Dyke

Department of Chemistry
Texas A&M University
College Station, TX 77843-3255

INTRODUCTION

Electronically conductive polymers are a fascinating new class of materials with unique electronic, electrochemical, and optical properties (1). One of the most interesting aspects of these polymers is that they can be reversibly "switched" between electronically insulating and electronically conductive states. Numerous researchers in a variety of different fields of science are currently investigating this insulator/conductor transition (1). In addition to being an interesting scientific phenomenon, this switching process plays an integral role in nearly all of the proposed chemical applications of electronically conductive polymers (2-13).

Assuming that the polymer is insulating in the reduced form and conductive in the oxidized form, the insulator-to-conductor switching reaction could be expressed as:

$$\text{-(Py)}_z\text{-} + nX^- \text{ -----> } \text{-(Py)}_{z-n}(Py^+X^-)_n\text{-} + ne^- \qquad [1]$$

where -Py- and $-Py^+-$ symbolize reduced and oxidized monomer units, respectively, and X^- is a charge compensating anion; X^- is initially present in a contacting solution phase but, upon oxidation of the polymer, is incorporated into the polymer phase. Equation 1 shows that, the switching reaction involves a charge-transport process, in which oxidized monomer sites and charge compensating counterions move through the polymer film.

While the case is far from closed, the bulk of the currently available evidence suggests that the rate of this charge-transport process is controlled by ionic diffusion in the polymer phase (14-18). Because diffusional mass-transport plays a role in many electrochemical experiments, it should be possible to assess the rate of the conductor/insulator switching reaction using an electrochemical method. For example, large amplitude electrochemical methods have been used to assess the rates of charge-transport in redox polymer films on electrode surfaces (19-24). These experiments yield an apparent diffusion coefficient, D_{app}, which is a quantitative measure of the charge-transport rate (19-24).

Because large amplitude electrochemical methods have proven useful for evaluations of charge-transport rates in redox polymers (19-24), analogous

experiments have recently been conducted on polypyrrole and other electronically conductive polymers (25-29). While this may appear to be a logical extension of the redox polymer work, we have shown that it is difficult, if not impossible, to obtain meaningful D_{app}, data for conducting polymers using large amplitude methods (30).

We have recently developed a small amplitude current-pulse method which is uniquely suited for solving the myriad problems associated with electrochemical analyses of electronically conductive polymers (30, 31). This method was used to obtain D_{app} values for the electronically conductive polymer, polypyrrole (30). The results of these experiments are described in this manuscript.

In addition, we have recently described a procedure for controlling the morphologies of electronically conductive polymers (32). This procedure involves the electrochemical growth of the conductive polymer at an electrode surface which has been masked with a microporous polymer membrane. The pores in this membrane act as templates for the nascent electronically conductive polymer. Because the template membrane contains linear cylindrical pores, cylindrical conductive polymer fibrils are obtained (32). We will show in this manuscript that microfibrillar polypyrrole films prepared via this approach can support higher rates of charge-transport than conventional polypyrrole.

THEORY SECTION

Why Large Amplitude Methods Should not be Used to Obtain D_{app}'s for Electronically Conductive Polymers

Our objections to large amplitude methods can be illustrated by considering a chronoamperometric experiment at a conducting polymer film-coated electrode (33). The first problem which must be addressed concerns the area of the electrode. Analysis of chronoamperometric data via the Cottrell equation requires semi-infinite linear diffusion to a planar electrode of known area (34). If the experiment is initiated in the potential region where the polymer film is conductive, one has, in effect, a large area porous metal electrode (15,31). Thus, the following questions arise - is diffusion in this porous electrode linear and what is the electrode area (35)? These questions are complicated by the fact that during the course of the experiment, the film becomes non-conductive; clearly the electrode area changes, but how and when?

One might suggest that the above criticism could be circumvented by initiating the potential step in a potential region where the polymer is reduced. In this case, at time = 0, the substrate conductor defines the electrode area. Therefore, initially, the area is known and diffusion is linear. However, at some time during the course of the experiment, the film becomes conductive and the unresolved questions, noted above, return.

The second problem concerns the capacitive current (i_c). In the potential region where the polymer is an electronic insulator, the film-coated electrode shows capacitive currents which are similar in magnitude to i_c's at the corresponding uncoated electrode. We have shown that these currents are associated with charging the double layer at the electrode/reduced-film interface (30). In contrast, in the potential region where the polymer is conductive, a much larger "capacitive-like" current is observed. This larger i_c has been ascribed to charging the double layer associated with the conductive polymer film itself (15,30,31,36)

The term "capacitive-like" was used above because, although this current has the qualitative appearance of an i_c, it is clear that this

current results from oxidation (or reduction) of the polymer just as the "faradaic" portion of the current (i_f) results from oxidation (or reduction of the polymer (37,38). The following fundamental question arises - becaus both the "faradaic" and "capacitive" currents result from the same chemica process, should the apparent i_c be subtracted from the total current to obtain i_f? Furthermore, because the capacitances of the bare and coated electrodes are very different, background correction would be very problematic (30,31).

In the conventional chronoamperometric experiment, it is often possible to circumvent the i_c problem by waiting for i_c to decay (34). However, because the time course of delivery of the large, capacitive-like current at the conductive polymer-coated electrode is unknown, a correction based on temporal discrimination also seems doubtful. Finally, one might suggest that this i_c problem could be circumvented by conducting a chronocoulometric experiment, in that double layer charging is typically observed as an intercept in the Q vs. $t^{1/2}$ plot (39). Note, however, that this is just another form of temporal discrimination. Again, because the time course of delivery of the capacitive-like charge is unknown, this form of temporal discrimination is also problematic.

The third problem associated with the use of large amplitude methods concerns the drastic changes in the chemical, electronic and morphological properties which occur when the film is converted from one state to the other. The reduced form of polypyrrole is a neutral, insulating, hydrophobic organic polymer. In contrast, the oxidized form is a conductive polyelectrolyte, which contains a high cationic charge density. These are very different materials and it would be surprising if they showed equivalent ion-transport rates. Because the large amplitude method converts the reduced polymer to the oxidized form (or vice-a-versa) this experiment is, in essence, conducted on one material at short times and a very different material at long times.

Finally, an examination of the chronocoulometric data for polypyrrole presented in the literature clearly shows that these data do not conform to simple theory (25). Note, for example, that Diaz et al. show Q vs. $t^{1/2}$ plots with negative intercepts; furthermore, the slopes of these plots increased as the positive limit of the potential step increased. We have obtained identical data in our laboratory (40).

The Advantages of the Small Amplitude Current-Pulse Method

The key features of the method developed here are 1.) The experiment is initiated at a potential where the polymer is in its reduced, nonconductive form (-0.4 V vs. SCE), and 2.) The total potential perturbation during the experiment is so small ($<$20 mV) that the polymer remains in the reduced form throughout the experiment. These features solve all of the above problems.

First, because the polymer is in the reduced form, the electrode area is just the substrate Pt area and, because this Pt electrode is a disk, diffusion must be linear. Second, because the polymer is never converted to a conductor, the large, unknown "capacitive-like" current associated with the conductive form is not observed. The only capacitive current is that associated with charging the double layer at the Pt/film interface and this can be easily measured and corrected (30). Finally, because this is a small amplitude method, the problem of converting one material into a second, very different, material during the course of the experiment is clearly obviated.

Fundamental Assumptions

This method requires three fundamental assumptions; the first might be termed the "effective medium theory assumption." Because polypyrrole is microporous (15), it is a biphasic system; (i.e., it is composed of solvent-swollen polymer and solvent-filled pores). We assume, however, that as an ion diffuses through the polymer film, it makes so many transitions between these two microphases that its motion can be described by an apparent diffusion coefficient, D_{app}. This D_{app} is the diffusion coefficient for the "effective medium" obtained by intimately mixing the two component phases. Recent work by Chien et al. clearly shows that this effective medium theory approach is valid for polypyrrole (41).

As noted above, the polymer film is an electronic insulator throughout the course of this current-pulse experiment. The question then becomes - if the polymer is not electronically conductive, how is charge transported across the film? We believe that by forcing the polymer to remain nonconductive, we convert the electronically conductive polymer into a redox polymer (42,43). In analogy to the redox polymer situation, we assume that charge (i.e, oxidized monomer equivalents) is transported via electron self-exchange with reduced polymer sites (22-24,42,43). Thus, the theories developed for diffusional electron hopping in redox polymers apply here (19,42).

Finally, we assume that the rate of this diffusional charge-transport in polypyrrole is controlled by counterion motion rather than by the actual self-exchange event. This assumption has been experimentally demonstrated for other redox polymers (44) and, as noted above, is supported by the available data on polypyrrole (14-18,45). Note, however, that even if this assumption proves to be incorrect, the D_{app} values obtained here are still valid quantitative measures of the charge-transport rate.

Background to the Current-Pulse Method

Consider a Pt working electrode which is coated with a thin, electronically conductive polymer film and immersed (along with suitable reference and counter electrodes) into a supporting electrolyte solution. At time (t) = 0 a galvanostat is used to inject a small amplitude anodic current pulse of duration τ and amplitude i_p into this electrochemical cell. At the termination of this current pulse, the working electrode is returned to open circuit and its potential, E_{oc}, is monitored as a function of time.

The anodic current pulse drives the reaction shown in Equation 1, thus increasing the concentration of Py^+ sites at the Pt/film interface. (Note, however, that the magnitude of the pulse is so small that at no time is any portion of the film converted to an electronic conductor.) The Nernst equation says that this increase in $[Py^+]$ will cause a corresponding increase in E_{oc}. After termination of the current pulse, these Py^+ sites will diffuse (i.e. self-exchange) into the bulk of the film. E_{oc} will, therefore, decrease with time; this transient will persist until the concentration of Py^+ is uniform throughout the film. Because the rate of equilibration is controlled by diffusional transport of the Py^+ sites, D_{app} can be obtained from the E_{oc} vs. t transient.

A current-pulse method was employed by Worrell et al. to obtain diffusion coefficients in intercalation compounds (46-49). These authors were able to make a number of simplifying assumptions, including 1) That semi-infinite diffusion obtained, 2.) That the diffusion layer obtained

That a negligible quantity of charge was introduced during the current-pulse (46-49). If these conditions are met, the open circuit potential after termination of the current-pulse varies linearly with the square root of time; D_{app} can be obtained from the slope (46-49).

A Rigorous Theoretical Analysis

Because it is difficult to satisfy the above simplifying assumptions, we were not able to apply the method of Worrell et al. to polypyrrole films (30). A more rigorous theoretical analysis is needed if a current-pulse method is to be applied to electronically conductive polymers. Equations applicable to a finite diffusion situation, starting from a diffusion layer of finite thickness, can be obtained from the heat transfer literature (50). These equations form the basis of this new theoretical analysis.

The details of this theoretical analysis are presented in reference (30); only the salient features will be reviewed here. Because this analysis is mathematically more complex, a simple relationship between Eoc and time does not exist. D_{app} values are obtained by matching experimental and simulated Eoc vs. t transients; D_{app} is the only adjustable parameter (30).

The heart of this new theoretical analysis is the generation of simulated $C_{diff,x=0}$ vs. t transients, where $C_{diff,x=0}$ is the concentration of diffusing specie (i.e. $[Py^+]$) at the Pt/film interface (30,50,53). Two discrete calculations are involved. First, the initial concentration-distance profile for the diffusing species (given the symbol $C_{diff(x',\tau)}$) must be calculated; $C_{diff(x',\tau)}$ is the diffusion layer profile extant after termination of the current pulse, at $t=\tau$ (52,30). This initial distribution is then plugged into the expression for the $C_{diff,x=0}$ vs. t transient for the finite diffusion case; this equation is used to calculate the simulated transients.

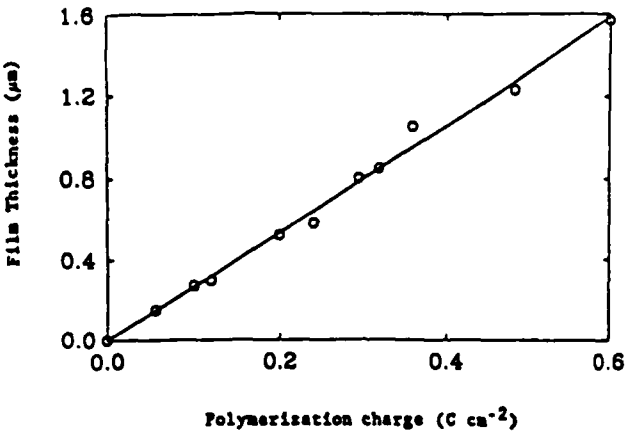
As noted above, D_{app} values were obtained by matching experimental and simulated E_{oc} vs. t transients (30). Note, however, that the theoretical analysis gives $C_{diff,x=0}$ vs. time transients; thus, some means of translating from $C_{diff,x=0}$ to E_{oc} is needed. A coulometric titration procedure was used to accomplish this translation (see Experimental Section).

EXPERIMENTAL SECTION

Materials and Equipment

Tetraethylammonium tetrafluoroborate (99%, Aldrich) was recrystallized from methanol and dried in vacuo at 100° C for ca. 24 hrs. prior to use. Pyrrole (99%, Aldrich) was distilled under N_2 immediately prior to use. Acetonitrile (UV grade, Burdick & Jackson) was used as received. Pt foil (0.254 mm thick, Alfa) and Kel-F rod (dia = 1.27 cm, Afton Plastics) were used to construct the Pt disk working electrodes.

All Electrochemical measurements were accomplished using an EG&G PAR Model 173 potentiostat/galvanostat in conjunction with a PAR 175 Programmer. Transients were recorded with a Nicolet 2090 digital oscilloscope. Cyclic voltammograms were recorded on a Houston Instruments Model 2000 X-Y recorder. Simulated data were calculated using a Compaq Portable II computer.



1. Plot of film thickness vs. charged consumed during polymerization for polypyrrole films.

Electrodes and Electrochemical Cells

Working electrodes were prepared as follows: Pt disks (dia = 3.3 mm) were heat-sealed onto the surface of Kel-F cylinders by melting the Kel-F around the disk with a heat gun and then physically pressing the Pt into the heat-softened surface. Electrical contact was made to the back of the Pt disk with silver epoxy (Epo-Tek 410E, Epoxy Technology). The electrodes were then polished as described previously (21).

Conventional one-compartment glass cells were employed for all electrochemical measurements. A large area, Pt gauze counter electrode (25 x 25 mm, AESAR) and a conventional saturated calomel reference electrode (SCE) were used. Potentials are reported vs. SCE. All solutions were prepared using acetonitrile as the solvent and were purged with purified N_2 prior to use.

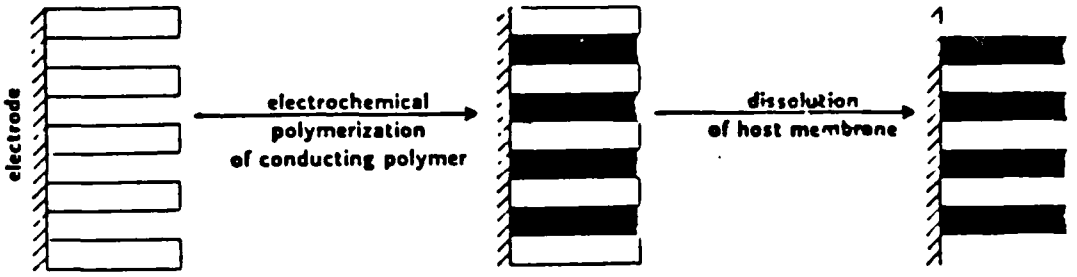
Polypyrrole Film Deposition

Polymerization solutions were 0.5 M in pyrrole and 0.2 M in Et_4NBF_4. Pyrrole was polymerized (and deposited) galvanostatically; a current density of 1.0 mA cm^{-2} was employed. Reproducible steady state potentials of 0.84 V $\pm$ 0.01 V were observed during film deposition at this current density. After deposition, the polypyrrole film-coated electrode was transferred to monomer-free, 0.2 M Et_4NBF_4. All subsequent electrochemical measurements were performed in this electrolyte.

A Tencor Alpha Step profilometer was used to construct a calibration curve of film thickness vs. charge consumed during the polymerization process. As shown in Figure 1, film thickness is linearly related to polymerization charge. While Diaz et al. noted a similar relationship, the slope of their line (4.16 μm-cm^2 C^{-1}) was substantially greater than the slope in Figure 2 (2.64 μm-cm^2 C^{-1}), even though these films were synthesized under identical conditions (54). Film thicknesses for these studies were calculated from the known polymerization charge and the slope of the least squares fit (solid line) to the data in Figure 1.

Determination of the Relationship Between E_{oc} and $[Py^+]$

As noted in the Theory Section, this relationship allows the simulated $C_{Py^+,x=0}$ vs. t transients to be translated into E_{oc} vs. t transients. Because the current pulse experiment used to evaluate D_{app} causes the electrode potential to change from -0.4 V to at very most -0.35



2. Schematic representation of procedure used to synthesize fibrillar/microporous electronically conducting polymer films.

V, the relationship between E_{oc} and $[Py^+]$ needs to be defined only over this narrow potential region. While the Nernst equation should, in principle, define this relationship, these films are non-Nernstian (see Figure 6). Therefore, the relationship between E_{oc} and $[Py^+]$ was determined empirically using a coulometric titration procedure (58-60). This procedure is described in detail in reference (30).

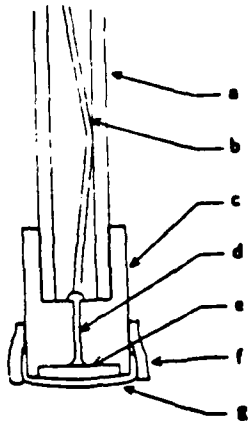
Determination of D_{app}

Experimental E_{oc} vs. Time Transients. Freshly synthesized polypyrrole film was quantitatively reduced at -0.8 V vs. SCE. The reduced film was then potentiostated at an initial potential of -0.4 V. The working electrode was switched to open circuit and a 50 msec anodic current pulse of the desired amplitude (100 to 400 $\mu A\ cm^{-2}$) was applied. The ensuing E_{oc} vs. t transient was recorded using the Nicolet oscilloscope. These experimental transients were then corrected by accounting for the quantity of charge used to charge the double layer (30).

Simulated E_{oc} vs. Time Transients. Programs for generating simulated $C_{Py^+,x=0}$ vs. t transients were written in PASCAL (Turbo Pascal, Borland) and executed on the Compaq Portable II computer. These curves were converted to simulated E_{oc} vs. t transients. Simulated and (corrected) experimental E_{oc} vs. t transients were plotted using LOTUS 1-2-3 (Lotus Development Corporation) graphics. D_{app} values were obtained by manually matching the experimental and simulated curves.

Controlling the Morphology of Electronically Conductive Polymers. Convex Kel-F-insulated Pt disk electrodes ($A = 0.5\ cm^2$) were constructed as described previously (32). The convex electrode surface promoted adhesion between the microporous membrane and the electrode surface (32). These electrodes were pretreated as described previously (32). Nuclepore polycarbonate microporous filtration membranes were used as the template material (32). Membranes with pore diameters of 0.02, 1.0 and 3.0 μm were used.

The procedure for preparing fibrillar/microporous polypyrrole membranes is illustrated schematically in Figure 2. The membrane-coated convex Pt disk working electrode (Figure 3) is immersed into a solution containing the monomer (pyrrole), which is electropolymerized as described above. Ideally (see below) polypyrrole is only synthesized in the pores of the host membrane; a Nuclepore/polypyrrole conductive composite membrane is obtained (Figure 2). Polymerization was terminated before the conductive polymer fibrils reached the Nuclepore/solution interface.



3. Schematic representation of microporous membrane-coated electrode used to synthesize fibrillar/microporous electronically conductive polymer films. a. 7mm glass tube. b. Cu wire. c. Kel-F body. d. Ag/epoxy contact. e. Convex Pt disk electrode. f. Rubber collar. g. Nuclepore microporous filtration membrane.

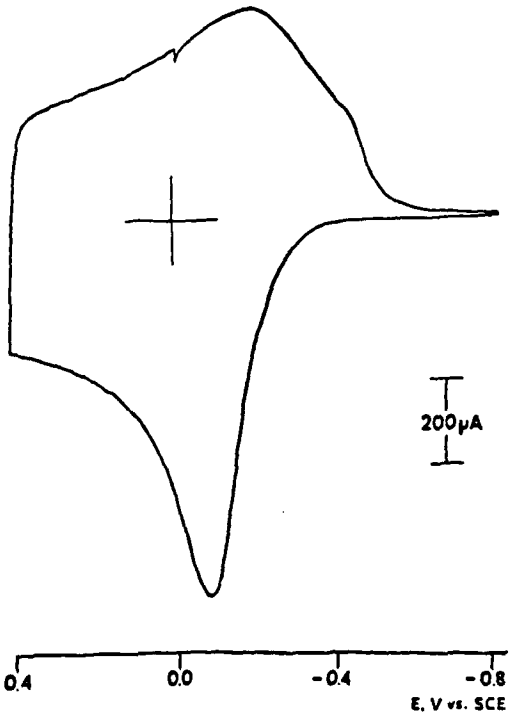
The conductive composite polymer membrane was then immersed in CH_2Cl_2 to dissolve away the Nuclepore (32). Two 60 min. extractions in 100 mL volumes of CH_2Cl_2 were performed. This procedure left an ensemble of conductive polymer fibrils. An electron micrograph (32) of such fibrils is shown in Figure 4.

RESULTS AND DISCUSSION

Cyclic Voltammetry of Polypyrrole

Prior to performing other electrochemical measurements, cyclic voltammetry was routinely used to assess the quality of freshly synthesized films. A typical voltammogram for a 0.27 μm polypyrrole film in 0.2 M Et_4NBF_4, MeCN is shown in Figure 5. Cyclic voltammograms for films up to ca. 1.0 μm in thickness were qualitatively similar.

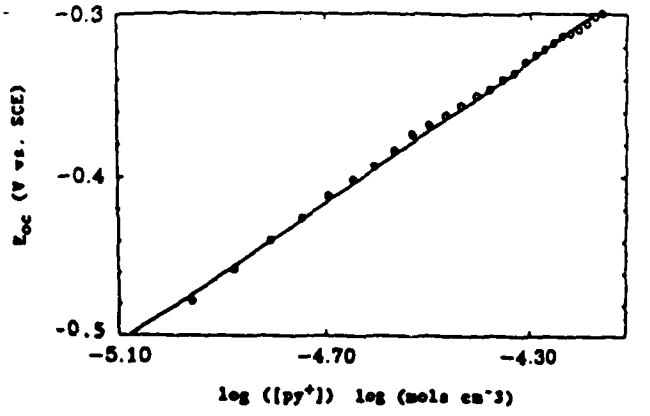
4. Scanning electron micrograph of a typical fibrillar/microporous polypyrrole film prepared using the procedure outlined in Figure 2.



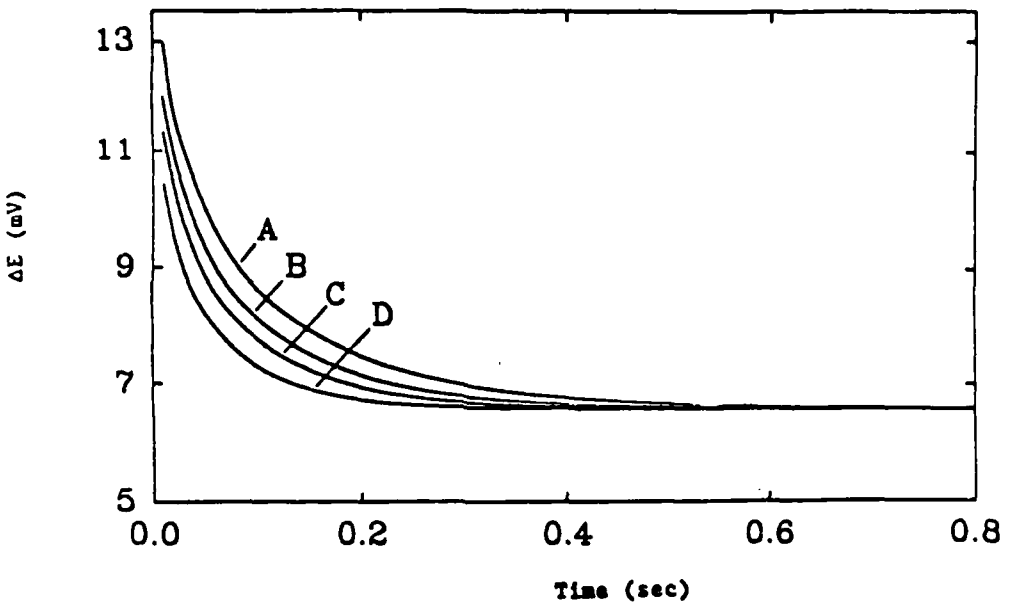
5. Typical cyclic voltammogram for 0.27 μm thick polypyrrole film. Scan rate = 10 mV sec^{-1}. Solution was 0.2 M Et_4NBF_4 in acetonitrile.

E_{oc} vs. log[Py^+] Calibration Curves

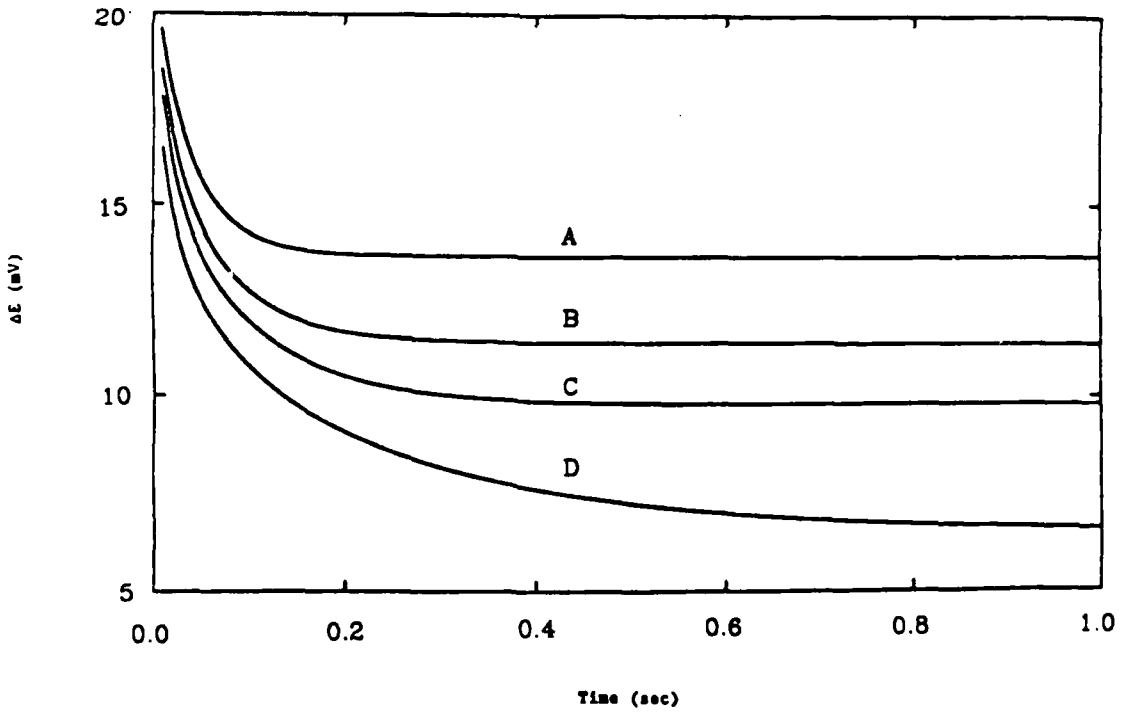
As discussed above, the relationship between E_{oc} and [Py^+] was determined empirically using a coulometric titration experiment (30). Figure 6 shows a typical semi-log (or Nernst) plot of these data. Data were obtained only over the narrow potential window accessed by the current-pulse experiment used to obtain D_{app}. Over this window E_{oc} varies linearly with log[Py^+]; however, the slope is super-nernstian (0.109 V/log[Py^+]). The data in Figure 6 were used to convert calculated $C_{Py^+,x=0}$ values into the corresponding E_{oc} values so that experimental and simulated E_{oc} vs. t transients could be compared.



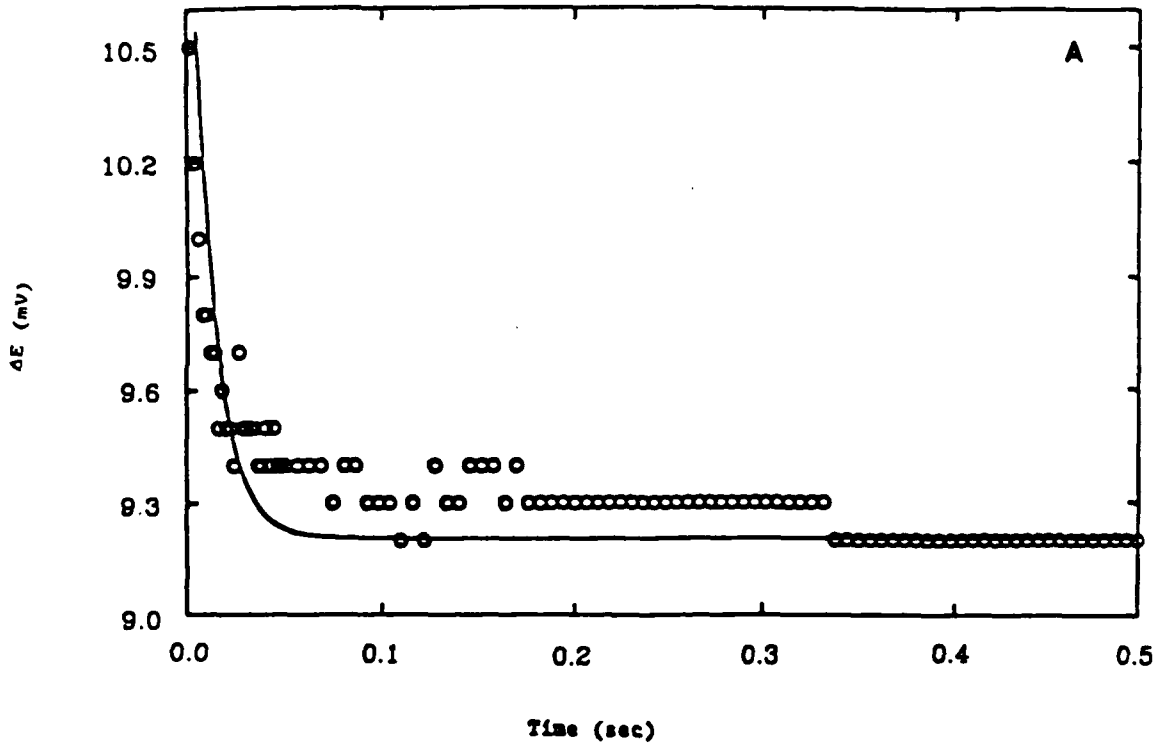
6. Typical Nernst plot for polypyrrole film-coated electrode; obtained from coulometric titration experiment. Film thickness = 0.27 μm. See text.



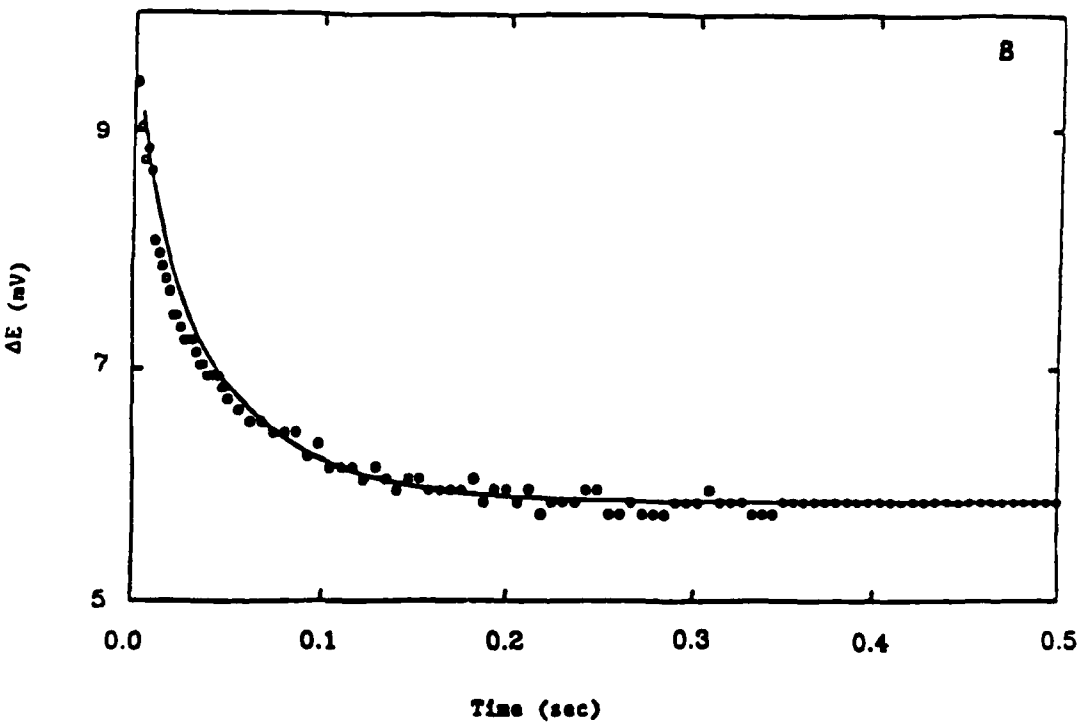
7. Simulated potential-time transients for the current-pulse experiment: Effect of magnitude of D_{app} on the transient. Simulation conditions were as follows: film thickness = 0.5 μm; t = 50 msec; i_p = 100 μA cm^{-2}; initial E = -0.4 V. D_{app}'s were as follows: A. 2×10^{-9} cm^2 sec^{-1}; B. 2.5×10^{-9} cm^2 sec^{-1}; C. 3×10^{-9} cm^2 sec^{-1}; D. 4×10^{-9} cm^2 sec^{-1}.



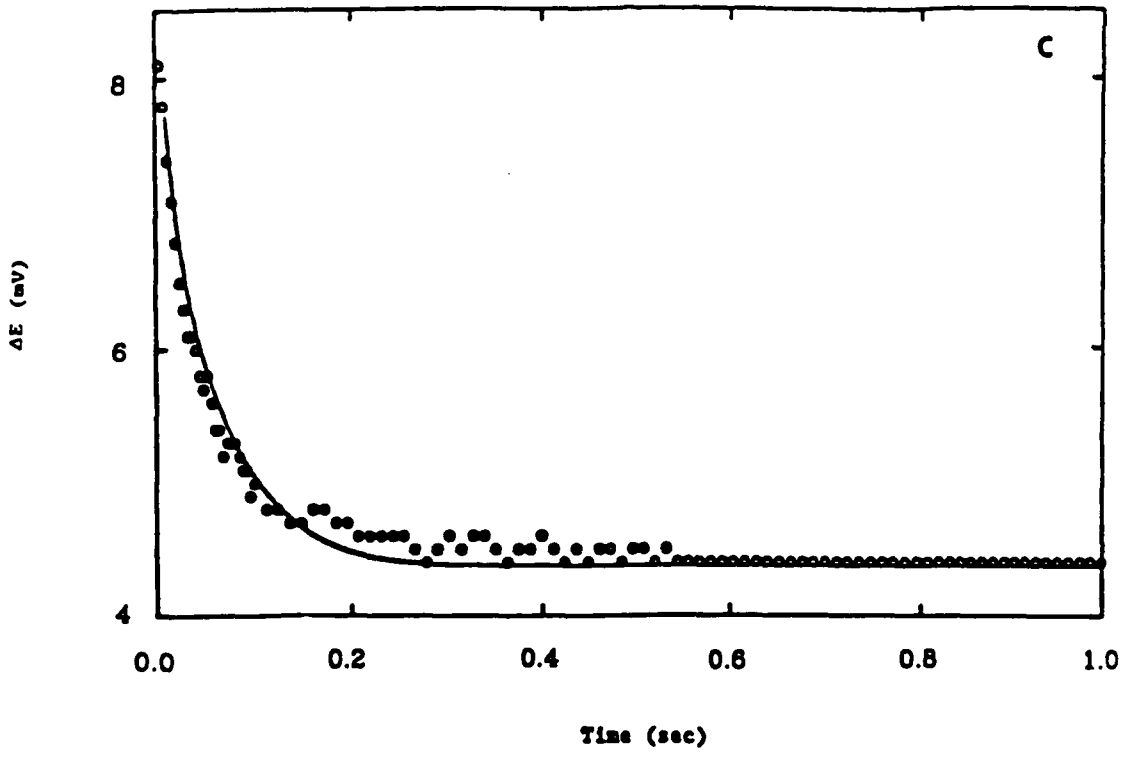
8. Simulated potential-time transients for the current-pulse experiment: Effect of film thickness on the transient. Simulation conditions as per Figure 7 except, D_{app} = 1×10^{-9} cm^2 sec^{-1} and film thicknesses as follows: A. 0.20 μm; B. 0.25 μm; C. 0.30 μm; D. 0.50 μm.



9. Comparisons of simulated (curve) and experimental (points) potential-time transients for the current-pulse experiment. Initial E = -0.4 V; i_p = 100 μA cm^{-2}; t = 50 msec; D_{app}'s are presented in Table III. Film thicknesses were as follows: A. 0.35 μm; B. 0.54 μm; C. 0.73 μm.



9B. (see page 129 for description)



9C. (see page 129 for description)

Simulated E_{oc} vs. Time Transients

Figure 7 shows the effect of D_{app} on the simulated E_{oc} vs. t transient. The values of i_p, τ and film thickness used in Figure 7 are typical of the experiments conducted here. These simulated curves predict that the rate of film equilibration should be very sensitive to the value of the apparent diffusion coefficient. Furthermore, these data suggest that the experimental transients should occur over an easily accessible time window.

The effect of film thickness on the simulated E_{oc} vs. t transient is illustrated in Figure 8. As might be expected, both the rate of relaxation and the value of the final equilibrium potential are strongly dependent on film thickness. While this sensitivity is good in the sense that it allows the effect of film thickness on D_{app} to be accurately assessed, it places a high premium on obtaining a reliable measure of the film thickness.

Table I. Apparent Diffusion Coefficients for Polypyrrole Films

Film Thickness	D_{app}
μm	$\times 10^9$ cm^2 sec^{-1}
0.35	8.3 ± 0.3
0.54	6.2 ± 0.3
0.73	4.2 ± 0.5

Apparent Diffusion Coefficients Values

Experimental E_{oc} vs. t transients were obtained for three different polypyrrole film thickness and for four different values of the current pulse. These curves were matched to simulated curves using D_{app} as the *only adjustable parameter*. Typical data are shown in Figures 9. Excellent fits between the experimental and simulated data were obtained; this gives us some confidence in the veracity of the theoretical model.

The model can be further tested by evaluating the effect of the magnitude of the current pulse on the value of D_{app} obtained. The theory predicts that D_{app} should be independent of i_p, provided, of course, that i_p is not so large that the film is converted to an electronic conductor. To assess the effect of i_p, current pulses of 100, 200, 300 and 400 μA cm^{-2} were applied to a 0.54 μm-thick film. D_{app}'s were obtained from the best match between experimental and simulated transients. An average value of 6.2 ($\pm$0.2) x 10^{-9} cm^2 sec^{-1} was obtained. Since this standard deviation is identical to the standard deviation for replicate measurements at a single value of i_p, there is clearly no dependence of D_{app} on i_p.

D_{app} values for three different polypyrrole film thicknesses are shown in Table I. Each D_{app} represents an average of eight determinations (two films, four different current densities for each film). Note first that the D_{app} values reported in Table I are as much as an order of magnitude larger than values reported by Diaz et al. (25) and Osaka et al. (29). Because these previously reported data were obtained using large amplitude chronoamperometric methods, we believe (see Theory Section) that these D_{app} values are suspect.

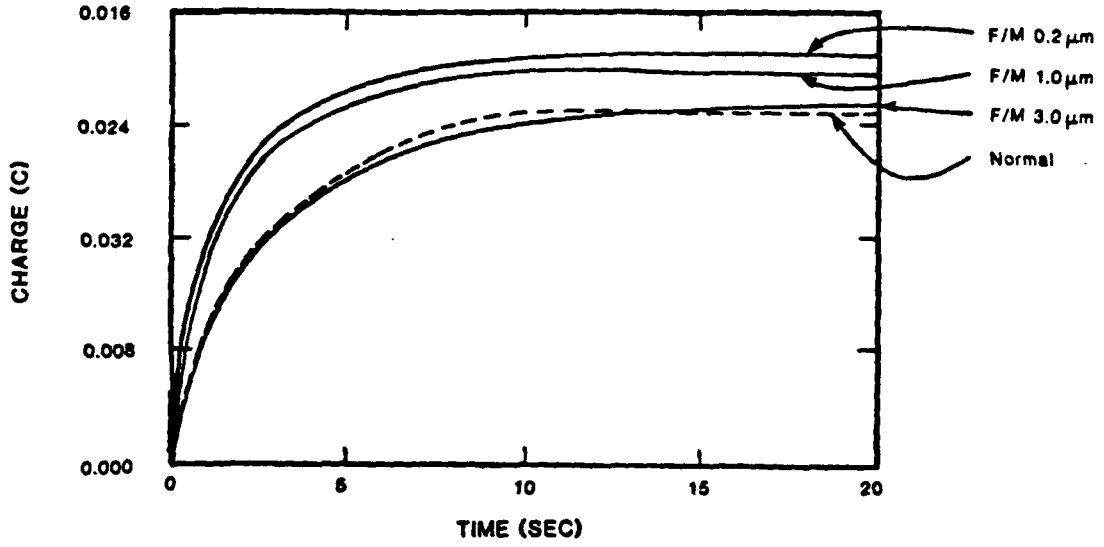
The theory developed here predicts that, if thin films have the same chemical and morphological composition as thick films, D_{app} should be independent of film thickness. In contrast, while excellent matches between experimental and simulated transients were obtained for all of the film thickness reported here (Figure 9), D_{app} clearly decreases with film thickness (Table I). These data are in agreement with the often reported qualitative observation that charge transport rates decrease with film thickness (45). Furthermore, Osaka et al. observed a similar trend in their data (29).

Fibrillar/Microporous Polypyrrole Promotes Higher Rates of Charge-Transport Than Conventional Polypyrrole Films

An electron micrograph of typical polypyrrole fibrils prepared via the microporous membrane-coated electrode technique, is shown in Figure 4. We prepared such fibrillar/microporous films because we believed that the rate of charge-transport in these films would be faster than in conventional polypyrrole. We postulated that the fibrillar/microporous films would support higher rates of charge-transport because 1) The micropores, when filled with solvent, would become fast ion-conducting channels into the film, 2) While counterions would ultimately have to enter or exit the polymer phase (Equation 1), these ions would only have to traverse the radius of the narrow fibril, and 3) Transport into the polymer phase would be changed from a linear diffusion process (conventional polypyrrole film) to a cylindrical diffusion process (fibrous film).

To test whether the fibrous versions of polypyrrole supported higher rates of charge-transport than conventional polypyrrole films, charge-time transients were obtained for both types of polypyrrole. These charge-time transients were associated with the reduction of the polymer. The polymer films were first quantitatively oxidized at +0.2 V vs. SCE. The potential was then stepped to -0.6 V where the reduction of the polymer proceeds at the diffusion-controlled rate. The corresponding charge vs. time transients were recorded using the X-Y recorder.

Reductive charge-time transients were obtained for a conventional (amorphous) polypyrrole film and for fibrillar/microporous films having fibril diameters of 3, 1 and 0.2 μm. It is important to point out that



10. Charge-time transients associated with the reduction of a conventional polypyrrole film (1.6 μm thick; dashed curve labeled "Normal") and three fibrillar/microporous polypyrrole films (labeled "F/M"; fibril diameters as shown.

all four of these films contained the same quantity of polypyrrole. This was assured by using 1.2 C of charge during the synthesis of all of the films.

The charge-time transients are shown in Figure 10 ("normal" in this figure refers to the conventional polypyrrole film; this film was ca. 1.6 μm thick; the designator F/M refers to the fibrillar/microporous membranes). Note first that the charge-time transients for the conventional (normal) film and for the fibrillar/microporous film with 3.0 μm-diameter fibrils are essentially identical. This is not surprising since the radii of these fibrils are essentially identical to the thickness of the conventional film.

Note, however, that at any time, the 0.2 and 1.0 μm fibril-diameter films deliver more charge than the conventional films. This is very clear evidence that these narrow fibril-diameter films promote faster rates of charge-transport than conventional polypyrrole. Furthermore, the total amount of charge delivered by these fibrous versions of polypyrrole is greater than the charge delivered by the conventional polypyrrole film. This observation has important implications to possible battery applications of these polymers.

There is, however, one disappointing feature about the data in Figure 10. While the rate of charge-transport for the 1.0 μm fibril-diameter film is substantially higher than for the normal film, the 0.2 and 1.0 μm fibril-diameter films support very similar rates of charge-transport. We had predicted (and hoped) that the rate of charge-transport would become faster and faster as the fibril diameter was decreased; the data in Figure 10 suggest that this is not happening.

Careful electron microscopic investigation of the bases of the polypyrrole fibers studied here revealed that these fibers do not grow directly from the substrate Pt electrode. Rather, a very thin base layer of conventional polypyrrole forms first; the fibrils grow out of this base layer. This base layer undoubtedly results from the fact that there is always a thin layer of solution between the membrane and the substrate electrode surface. This base layer undoubtedly retards the rate of charge-transport in the fibrous versions of the polymer.

The above discussion suggests that superior fibrillar/microporous films would be obtained if the base layer of conventional polypyrrole could be eliminated. We have recently shown that this can be accomplished by sputtering the electrode directly onto the back of the host membrane (55); we will report the results of these studies in a forthcoming manuscript (55).

CONCLUSION

We have developed a new small amplitude electrochemical method for determination of apparent diffusion coefficients associated with charge-transport in electronically conductive polymers. For the reasons noted in the Theory Section, this method is ideally suited for investigations of such polymers. In a more general sense, this method should also be a convenient and powerful tool for studying transport in nearly any type of electroactive polymer film. Some of the features which make this an attractive and powerful method for analysis of transport in polymer films are discussed below.

First, because this is a small amplitude method, the electrochemical, chemical and morphological properties of the film are not greatly perturb by the analysis. Because electroactive polymer films may show dramatic changes in solvent content, ionic character, morphology, etc. upon oxidation or

reduction, the minimally invasive character of this method is an attractive feature. Second, and also related to the small amplitude nature of this method, by starting at different values of initial applied potential, the effects of the extent of oxidation or reduction on charge transport in the film can be assessed. Thus, for example, the effects of redox-induced changes in solvent content or morphology can be quantitatively evaluated using this method. This is not possible with large amplitude methods.

Third, unlike conventional methods for evaluating charge transport in polymer films on electrode surfaces (19-24), there is no current flow during the data acquisition period. Thus, effects of migration and uncompensated film resistance are minimized or completely eliminated. Fourth, the theoretical model for obtaining D_{app} is applicable to both the semi-infinite and finite diffusion cases. Thus, unlike many other methods (19-24), it is not necessary to adjust the experimental conditions such that the semi-infinite case is obtained.

We have also shown that fibrillar/microporous versions of polypyrrole support faster rates of charge-transport than conventional polypyrrole films.

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