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of the reduced PPy films doped with large anions was increased by the contact to the air. The charge transport for the reduced form of PPy film doped with large anions may be carried out by the hopping through the anion sites. The relation between the structure of this type of polypyrrole and conductivity is discussed.

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Electrochemical, In Situ Raman Spectroscopic, and Conductivity Studies of Polypyrrole Incorporating Large Anions: Conducting Nature of Reduced Form

by

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Abstract

Polypyrrole (PPy) thin films doped with large size anions, such as tetrasulfonated metallophthalocyanines, tetrasulfonated copper porphyrin, polyvinyl sulfate, and poly(p-styrenesulfonate), have shown electrochemical activities of redox pairs in both aqueous and nonaqueous solutions at the negative potentials where the PPy is reduced to a neutral form. In situ Raman spectroscopy showed that the charge transfer reactions of redox pairs took place at the surface of the reduced PPy thin films in the negative potential range. Cyclic voltammetric results indicated that the structurally rigid PPy films which were doped with large size anions demonstrated a considerable electrochemical conductivity when the PPy was reduced to a neutral form, although both ex situ and in situ conductivity measurements of these films indicated that the electronic conductivity of the reduced form is generally several orders of magnitude smaller than that of the oxidized form. Cyclic voltammetry also showed that the electrochemical activity at most of the reduced PPy films doped with large anions was increased by the contact to the air. The charge transport for the reduced form of PPy film doped with large anions may be carried out by the hopping through the anion sites. The relation between the structure of this type of polypyrrole and conductivity is discussed.

Introduction.

Polypyrrole films, which are electrically conducting,[1] have been widely investigated for their possible applications in the areas of catalysis,[2] electronic devices,[3] electrochromic displays,[4] battery electrodes,[5] and functional membranes.[6] The thin film of PPy can be prepared by electrochemical oxidation of the pyrrole monomer in both aqueous and nonaqueous media.[1] The PPy thin film electrode doped with inorganic anions, such as ClO_4^-, and BF_4^-, can be reversibly oxidized (conducting) and reduced (nonconducting).[1] On the other hand, in our previous report a PPy thin-film incorporating copper phthalocyanine tetrasulfonate (PPy-CuPcTs) was shown to be electronically conducting regardless of the oxidation state of the PPy.[7] The majority of the dopant (copper phthalocyanine tetrasulfonate) in the PPy-CuPcTs film remains in the film during the redox reaction of the PPy.[7,8] It has been found that the ion transport in the PPy-CuPcTs film during the redox reaction is carried out mainly by small cations from the supporting electrolytes.[7] Ion transport by cationic species during the redox reaction of the PPy has also been reported for the PPy thin films doped with anionic polyelectrolytes.[9]

Our previous finding about the conducting nature of the reduced PPy-CuPcTs film has raised a question about the charge-transport mechanism of the PPy film because there may not be a significant amount of PPy cations which are left in the reduced PPy film. The phenomenum was unexplainable based on the established theories for the electronic conductivity of the polypyrrole thin film. A couple of widely accepted explanations for the nature of electrical conductivity of the PPy are the charge transport by the diffusive motion of polypyrrole dications (bipolarons)[10] or by the hopping between localized sites associated with the counter anions.[11] Most of the experimental works for elucidating the charge-transport mechanism of PPy have been carried out for the PPy doped with smaller inorganic anions. In the oxidized PPy doped with inorganic anions both PPy cations and inorganic anions coexist in the film. When the PPy film is reduced (film is nonconducting), it is believed that the anions move out from the film. However, the relationship between the doping level of anions and conductivity is not quite linear. Pfhger et al.[12] have shown that the conductivity of the neutral PPy, which only has a conductivity of 10^{-6} S cm^{-1} level, increased several orders of magnitude by being exposed to the low concentration of oxygen. Only several percent of the maximum doping level is needed to obtain the highest conductivity. When the PPy is doped further with oxygen, the conductivity simply remains at the same level. A similar observation for the nonlinear nature of conductivity and anion doping level, although a different technique was used, was observed by Feldman et al.[13] Maddison et al.'s[11d] work which is based on both a PPy doped with p-tuluene-sulphonate (conductivity of 26 S cm^{-1}) and a dedoped PPy (conductivity of 8 S cm^{-1}) has shown that the dedoped PPy displayed more metallic nature than the doped PPy. Their work took advantage of the high conductive nature of the slightly doped PPy films and demonstrated the possible existence of two separate charge-transport pathways: (1) intrachain charge transport (show more metallic nature) and (2) interchain charge transport by hopping through the anionic sites.

In this paper the electrochemical conductivities of the polypyrrole thin films doped with large anions were investigated. The previously observed high conductivity of the reduced PPy-CuPcTs film would certainly suggest the existence of another charge transport besides the conductivity based on delocalized π electrons in the PPy backbones. We intend to create a condition for the polymer which may be suited for studying a charge-transport pathway other than the conductivity based on the PPy backbones. Electrochemical techniques can be used to create a neutral form of PPy by applying a very negative potential, yet almost all dopants (anions) were remaining in the PPy doped with large anions in the very negative potential range. As a result one can study the effects of dopants on conductivity independently.

Our previous studies on the PPy-CuPcTs film have also shown that the PPy cations remain unreduced in the film in the negative potentials in the (TBA)Cl solution because the size of TBA^+ is simply too large to be able to penetrate into the film in order to balance the charge of the PPy film. We tried to utilize this nature of the PPy-CuPcTs film and possibly of other PPy films doped with large anions for controlling the oxidation states of the PPy in the PPy films doped with large anions. This technique of controlling the oxidation state of the PPy by using electrolytes with different sizes of cations makes it easier for us to compare the conductive nature of both oxidized and reduced PPy films doped with large anions.

Besides the PPy-CuPcTs film, our studies are extended to cover wide range of systems and conditions in order to examine the possible conductivity of the reduced form of this type of PPy. The investigated systems include the PPy films doped with several metallophthalocyanine tetrasulfonates (PPy-MPcTs), copper phthalocyanine monosulfonate (PPy-CuPcS), copper porpyrin tetrasulfonate (PPy-CuPrTs), and a couple of anionic polyelectrolytes [polyvinyl sulfate (PPy-PVS) and poly(p-styrenesulfonate) (PPy-PSS)]. Structures of these anions are shown in Figure 1. Electrochemical conductivities of the PPy films are examined in both aqueous and nonaqueous solutions. An air free experimental condition was also used to investigate the possible contribution of polypyrrole oxide (PPy-O) to the conductive nature of the reduced PPy-CuPcTs film. Both ex situ and in situ conductivity measurements of the PPy films at different potentials are also carried out to see the conductivity change by the redox reaction of the PPy film and to relate with the cyclic voltammetric results. Those experiments described above are used to elucidate the charge-transport mechanism of the PPy thin films.

Experimental

The pyrrole (Aldrich) was purified by vacuum distillation after refluxing with zinc metal to remove the yellow-colored impurity. Acetonitrile (MeCN) was purified by the method reported by Forcier and Olver.[14] The copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt (Aldrich) was purified by recrystallization from the aqueous solution. All other metallophthalocyanine tetrasulfonic acid tetrasodium salts, copper phthalocyanine monosulfonic acid monosodium salt, and tetrasodium meso-tetrakis (p-sulfonato phenyl) copper porphyrin were obtained from Midcentury Chemicals. Poly(vinyl sulfate, potassium salt), poly(sodium p-styrenesulfonate), methyl viologen dichloride hydrate, nitrobenzene, and heptyl viologen dibromide hydrate were obtained from Aldrich Chemical Co., Inc. Sodium perchlorate (purified grade), sodium chloride, and sodium nitrate (certified ACS grade) were obtained from Fisher Scientific Co. Tetrabutylammonium chloride [(TBA)Cl], tetramethylammonium hexafluorophosphate [$(TMA)PF_6$], tetramethylammonium nitrate [$(TMA)NO_3$], tetraethylammonium perchlorate (TEAP), and tetrabutylammonium perchlorate (TBAP) were obtained from Southwestern Analytical Chemicals, Inc. The TBAP was recrystallized from the ethanol solution and dried under the vacuum before use. The TEAP was purified by the method of House et al.[15] Other chemicals were used without further purification.

The PPy thin-films were potentiostatically deposited on gold thin films (vacuum coated 1000 Å thick film on a 2.5 x 2.5 cm^2 x 1.5 mm glass plate) by applying +0.95 V vs. SCE in aqueous solutions containing both 0.1 M pyrrole and electrolytes of large anions. The concentration of the electrolytes was normally 0.05 M except for the CuPcTs (0.01 M), PSS (0.001 M), and PVS (0.001 M). The electrochemical deposition of the PPy film was carried out under N_2. The film thickness was controlled by the charge passed, and the thickness was estimated using 48 mc/cm^2 for a 1000-Å film. Measurements on 1000 Å dry PPy-CuPcTs films by a Ångstrom Technology Model 980-4020 Å-Scope Interferometer yielded values within ±20% of the estimated thickness.

For the electrochemical experiments, either an EG & G PARC Model 173 potentiostat/galvanostat with an EG & G PARC Model 175 signal generator, Model 179 digital coulometer, and a Houston Instrument Model 2000 X-Y recorder, or Bioanalytical Model BAS-100 electrochemical analyzer were employed. Electrochemical experiments in aqueous solutions were carried out in an one compartment cell containing a Pt helix as an auxilliary electrode and a SCE reference electrode. An undivided electrochemical cell which contained a Pt helix (auxilliary) and a $Ag/AgNO_3/MeCN$ (reference) electrodes was used for electrochemical experiments in acetonitrile solution. The supporting electrolytes were vacuum dried for two days, and the MeCN dried with CaH_2 was vacuum distilled into the above cell with the supporting electrolytes. The solution was deaerated by the freeze-pump-thaw method. The VAC Model glove box (Dri-Lab and Dri-Train) was used to provide the oxygen-free atmosphere when a PPy film electrode was transferred into the electrochemical cell after the preparation of the PPy film electrode.

Raman measurements were made using a system consisting of a homemade sample holder with optics, a Spex Model 1877 triplemate triple spectrometer, an EG & G PARC Model 1420 ISPD detector with an EG & G PARC Model 1218 controller and OMA2 console system, and a Tektronix Model 4662 interactive digital plotter. Details of the experimental set-up for in situ Raman spectroscopy is described elsewhere.[16] A Spectra-Physics Model 171-17 Ar^+ laser with an intensity of ~60 mW at the sample was employed as an excitation source. The excitation beam was brought onto the sample surface at a 60° angle from the horizontal. The final slit width of the triple spectrometer was set at 100 μm, and, normally, a 1800 grooves/mm grating was used. Calibration curves for the triple spectrometer were prepared by using the wavenumbers of Raman bands from metallophthalocyanine thin films. A Spex Model 1403 double spectrometer and a DM1B Datamate were used to record Raman spectra of the metallophthalocyanine thin films. The accuracy of measurements based on the triple spectrometer was estimated to be ±5 cm^{-1}. Raman spectra were collected in approximately 15-30 seconds with the triple spectrometer.

An EG & G PARC Model 273 potentiostat/galvanostat was used for the electrochemical polymerization and ex situ conductivity measurements of the PPy thin films. One compartment cell with three electrodes was used to prepare the PPy film on a small platinum disk electrode (1.77 mm^2). A platinum helix wire was used as an auxilliary electrode and the SCE was used as a reference. The preparation of the PPy films was carried out by the same manner as that for the deposition of the PPy films on the gold thin-film electrode. The conductivity measurements were carried out by using the two-electrode system by immersing polymer coated working electrode into mercury.[17] Prior to its electrochemical polymerization, the platinum surface was polished with 0.05 μ alumina (Buehler), and rinsed thoroughly with doubly distilled water. After the polymerization of PPy films, different potentials were applied in order to obtain the different oxidation states of PPy film. In the conductivity measurements, 10 to 40 mV were applied across the PPy film electrode (between platinum substrate and mercury). Current-voltage plots were linear for the applied potential of less than 100 mV.

In situ conductivity of both the PPy-CuPcTs and the PPy-PSS films was measured by an electrode which is described in Figure 2. Approximately 50 μm thick polymer film was electrochemically deposited by applying 0.95 V vs SCE to the gold thin film electrode (~2.5 x 4 mm^2). Two platinum wires (0.1 mm dia.) were placed approximately 0.25-0.65 mm apart. After the electrochemical formation of PPy films, those two platinum wires were totally covered by the PPy film. The resistance of the PPy film between the two platinum wires was measured by a Keithley Model 177 DMM, while the potential of the gold substrate was controlled by an EG & G PARC Model 273 potentiostat/galvanostat.

Results and Discussion

1. Electrochemical Activity at the Reduced PPy Thin Film Electrodes.

Electrochemical behaviors of thin PPy films doped with large size anions were investigated in aqueous solutions. In order to test the electrochemical conductivity of the film electrodes in more negative potentials than the redox potential of PPy, methyl viologen dichloride [$(MV)Cl_2$] was added to the solutions as an electroactive species. Table I shows the list of large size anions which were used as dopants for preparing the PPy film electrodes. Table I also lists cyclic voltammetric data obtained from the PPy film electrodes: both cathodic and anodic peak potentials for the PPy redox reactions and those for the redox reaction of methyl viologen are shown. Supporting electrolytes which were used for the experiments are also listed in Table I. Thickness of the PPy films used for the electrochemical experiments was 1000 Å, except stated otherwise. Figure 3 shows the cyclic voltammograms of a PPy-PSS film electrode in 0.050 M NaCl (a) and in 0.050 M (TBA)Cl (b) in the presence of 0.0050 M $(MV)Cl_2$. Dotted curves in both Figure 3a and Figure 3b are CVs from the same electrode in the NaCl and the TBAP solutions without $(MV)Cl_2$. The CV from a gold electrode in the 0.001 M $(MV)Cl_2$ and 0.05 M (TBA)Cl solution is shown in Figure 3c as a reference. The observed redox currents ($\underline{E}_{pc}$ = -0.79 V, $\underline{E}_{pa}$ = -0.55 V) for the $MV^{2+}/MV^{\bullet+}$ pair in the cyclic voltammograms from the 0.05 M NaCl and 0.005 M $(MV)Cl_2$ solution (Figure 3a) indicated that the reduced PPy-PSS film was electrochemically conducting, even though the peak-to-peak separation ($\Delta\underline{E}_p$ = 240 mV) of the redox currents for the $MV^{2+}/MV^{\bullet+}$ pair at the PPy-PSS film electrode was much larger than that recorded at the gold electrode ($\Delta\underline{E}_p$ = 60 mV). The PPy-PSS film electrode also showed electrochemical conductivity in the 0.05 M (TBA)Cl solution in the presence of 0.005 M $(MV)Cl_2$. The PPy cations ($PPy^{\bullet+}$ or PPy^{2+}) were not reduced to the neutral form (PPy^0) in the 0.05 M (TBA)Cl and 0.005 M $(MV)Cl_2$ solution in the negative potential range because the size of TBA^+ was too large to be able to move into the film in order to balance the charge of the PPy-PSS film. The above results suggested that both oxidized PPy-PSS film (PPy exists as either $PPy^{\bullet+}$ or PPy^{2+}) and reduced PPy-PSS (PPy exists as PPy^0) were electrochemically conducting. All other PPy thin films doped with large anions including several metallophthalocyanine tetrasulfonates, copper porphyrin tetrasulfonate, and poly(vinyl sulfate) showed similar cyclic voltammograms of methyl viologen to those from the PPy-PSS film in both NaCl and (TBA)Cl solutions. It has been known that these large anions in the PPy films tend to remain in the film during the reduction of $PPy^{\bullet+}$ to PPy^0.[4a,7,9] Small cations, such as Na^+ and K^+, from the supporting electrolyte move into the film in order to balance the charge of the PPy film during the reduction of the PPy. The above results indicated that all of the PPy thin-films doped with large anions which are listed in Table I were electrochemically conducting in the aqueous solutions, whether the PPy in the films was oxidized or reduced to a neutral form.

Cyclic voltammetry of the PPy-CuPcTs film electrode was also carried out in the acetonitrile solution with 0.08 M (TMA)PF_6 as a supporting electrolyte. In order to examine the electrochemical conductivity of the reduced PPy film electrode, either 0.001 M or 0.005 M nitrobenzene (NB) was added to the solution as an electroactive species. As shown in Figure 4a, PPy (marked 1 and 1' in the CV) as well as CuPcTs (2 & 2' and 3 & 3') in the PPy-CuPcTs film can be reduced and reoxidized in the acetonitrile solution with 0.08 M (TMA)PF_6. The second redox peak currents ($\underline{E}_{pc}$ = -1.53 V and $\underline{E}_{pa}$ = -1.36 V at the scan rate of 50 mV/s) of the CuPcTs which were observed in the above CV were not seen in the CV recorded in the aqueous solution. Figure 4b shows CV recorded in the presence of 0.001 M NB. Both cathodic and anodic peak currents (3 and 3') for the redox reaction of $NB/NB^{\bullet -}$ were observed at -1.55 V and -1.37 V, respectively. The cathodic and anodic peak currents for the redox reactions of both PPy (1 and 1') and CuPcTs (2 and 2') were also observed. The second redox pair for the CuPcTs was covered by the large peak currents from the $NB/NB^{\bullet -}$ pair and was not clearly seen in the CV. The cyclic voltammogram of NB at a gold electrode is shown in Figure 4c. Even though the peak-to-peak separation for the redox reaction of NB was fairly large ($\Delta\underline{E}_p$ = 180 mV), the above results certainly indicated that the reduced PPy-CuPcTs film was electrochemically conductive in the acetonitrile solution. Cyclic voltammograms from a PPy film doped with BF_4^-($PPy-BF_4$) in the MeCN solution with (TEA)BF_4 have previously shown[18,19] the absence of electrochemical activity for the redox reaction of NB due to the nonconductive nature of the PPy-BF_4 film in the negative potential range where PPy existed as a neutral form.

2. __Effects of Cations on Ion Transport and on the Redox Reactions of PPy and Dopant__. The size of the cations from the supporting electrolytes was found to determine the feasibility of the redox reaction of PPy in the PPy film doped with large anions. Cyclic voltammograms of the PPy-CuPcTs film electrode were recorded in several supporting electrolytes with different cation sizes. Figure 5 shows the CVs in (a) NaCl, (b) $(TMA)NO_3$, (c) TEAP, and (d) (TBA)Cl. The order of the cation size is $TBA^+ > TEA^+ > TMA^+ > Na^+$. No significant cathodic currents which correspond to the reduction of $PPy^{\bullet +}$ to PPy^0 were observed in supporting electrolytes with larger cations (TBA^+ and TEA^+) due to the restricted movement of large cations. On the other hand, both Na^+ and TMA^+ were small enough to be able to move through the PPy-CuPcTs film when the negative potential was applied in order to reduce the PPy film.

The feasibility of the redox reaction of dopant (CuPcTs) in the PPy-CuPcTs film is also decided by the size of cation in the supporting electrolytes. Both anodic and cathodic currents (1 and 1′ in Figure 5a) which correspond to the redox reaction of CuPcTs in the film were observed in the 0.05 M NaCl solution. Small currents for the redox reaction of the CuPcTs were observed in the 0.05 M $(TMA)NO_3$. No significant current for the CuPcTs redox reaction was seen in both 0.01 M TEAP and 0.05 M (TBA)Cl.

We have previously reported that the MV^{2+} is small enough to be able to penetrate slowly into the PPy-CuPcTs film, and the MV^{2+} interacts with sulfonate groups.[7] The interaction between MV^{2+} and $-SO_3^-$ in the PPy-CuPcTs film was considered to be responsible for shifting the redox potential of PPy (~300 mV) to the more positive potential. When heptyl viologen (HV^{2+}), which is much larger in size than the MV^{2+}, was used as an electroactive species in 0.05 M NaCl to investigate the electrochemical conductivity of the PPy-CuPcTs film in the negative potential range, the shift of the reduction peak potential ($\underline{E}_{pc}$) of the PPy (marked 1) was very small (~30 mV), as shown in Figure 6a [curve a: without $(HV)Br_2$, curve b: with 0.005 M $(HV)Br_2$]. The CVs from the same electrode in 0.05 M (TBA)Cl are shown in Figure 6b [curve a: without $(HV)Br_2$, curve b: with 0.005 M $(HV)Br_2$]. The CV of the heptyl viologen at the gold electrode in the 0.05 M NaCl and 0.005 M $(HV)Br_2$ solution is shown in Figure 6c. The CVs which are shown in Figure 6a suggested that there may be a very little interaction between HV^{2+} and $-SO_3^-$ in the PPy-CuPcTs film. The HV^{2+} is too large to be able to move through the PPy-CuPcTs film. As a result, the interaction between HV^{2+} and $-SO_3^-$ may take place at the surface or very near the surface of the PPy-CuPcTs film. The observed redox currents for the $HV^{2+}/HV^{\bullet +}$ pair also strongly support our previous conclusion[7] that the PPy-CuPcTs is electronically conducting, even though the PPy mainly exists as a neutral form in the negative potential range. Because of the large size of HV^{2+}, one can rule out the possible contribution of the ion transport by HV^{2+} for the observed electrochemical activity at the PPy-CuPcTs film in the negative potential range.

In cyclic voltammograms from the PPy-PSS film electrode in the 0.05 M NaCl and 0.005 M $(HV)Br_2$ solution, the reduction peak potential ($\underline{E}_{pc}$) of the PPy shifted ~150 mV to the more positive potential compared to the $\underline{E}_{pc}$ of the PPy recorded in NaCl without $HVBr_2$. The results suggested the possible penetration of HV^{2+} into the film. Cyclic voltammograms of the PPy-CuPrTs film electrode also showed that the $\underline{E}_{pc}$ of the PPy shifted ~80 mV positively when the $(HV)Br_2$ was added to the NaCl solution.

3. **Effects of Oxygen**. Our experimental procedure involves washing of the PPy film electrode (ex. PPy-CuPcTs film) in the air after the preparation of the film electrode. Since some of the PPy may exist as a neutral form (PPy^{0}) in the as-polymerized PPy film,[7] the formation of PPy oxides (PPy-O) could take place during the film washing procedure in the air after the preparation of the film electrode. In order to eliminate the possible contribution of the PPy-O to the conducting nature of the PPy films, the PPy film electrodes which were prepared in the deoxygenated $Na_4CuPcTs$ solution were washed with water and placed in an air-tight electrochemical cell in a glove box with ultra high purity argon gas. The electrodes were never exposed to air during the entire procedure of experiments.

Cyclic voltammograms from a PPy-CuPcTs film electrode which was prepared under the air-free condition are shown in Figure 7. Figure 7a shows CVs recorded in the 0.05 M NaCl, 0.002 M $(MV)Cl_2$, and 0.002 M $K_4Fe(CN)_6$ solution. There are four redox pairs in the CV at the scan rate of 50 mV/s: $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ (1 and 1'), $PPy^{\bullet+}/PPy^{0}$ (2 and 2'), $MV^{2+}/MV^{\bullet+}$ (3 and 3'), and $MV^{\bullet+}/MV^{0}$ (4 and 4'). When the scan rate was slow (at 5 and 10 mV/s), there were two separate anodic peaks around -0.6 V. The first anodic peak ($\underline{E}_{pa}$ = -0.63 V at 5 mV/s) may be due to the oxidation of $MV^{\bullet+}Cl^{-}$ adsorbed on the PPy film electrode. Oxidation of $MV^{\bullet+}$ to MV^{2+} in the solution may be responsible for the second peak ($\underline{E}_{pa}$ = -0.55 V at 5 mV/s). Figure 7b shows a CV recorded from a PPy-CuPcTs film in the 0.05 M (TBA)Cl and 0.002 M $(MV)Cl_2$ solution. Two redox pairs are due to the redox reactions of both $MV^{2+}/MV^{\bullet+}$ (1 and 1') and $MV^{\bullet+}/MV^{0}$ (2 and 2'). The results showed that the PPy-CuPcTs film was electrochemically conductive in those two solutions at the negative potentials. However, it seems that the conductivity of the PPy-CuPcTs film in NaCl is much smaller than that in (TBA)Cl. Since the majority of the PPy in the PPy-CuPcTs film in the (TBA)Cl solution remains as the oxidized form even at the very negative potentials, the high conductive nature of the PPy-CuPcTs is expected to remain in the very negative potential range. The CV data in the NaCl solution confirmed that the PPy-CuPcTs certainly shows considerable conductivity at the negative potentials where the PPy exists as the neutral form. However, the broad and low current for the reduction of $MV^{\bullet+}$ to MV^0 at ~-1.1 V indicated that the conductivity of the PPy-CuPcTs film is low in the very negative potential range that is consistent with the results obtained by the conductivity measurements (see section 5).

Cyclic voltammograms from the PPy-PSS film electrodes were also recorded under the air-free condition. Figure 8a shows CVs recorded in the 0.05 M NaCl, 0.002 M $K_4Fe(CN)_6$, and 0.002 M $(MV)Cl_2$ solution. Peak currents for the redox reaction of the $MV^{2+}/MV^{\bullet+}$ pair (1 and 1') were very small and there was no current for the $MV^{\bullet+}/MV^0$ pair. On the other hand, the CVs recorded in the (TBA)Cl solution (Figure 8b) showed both cathodic and anodic currents for the redox reactions of $MV^{2+}/MV^{\bullet+}$ (1 and 1') and $MV^{\bullet+}/MV^0$ (2 and 2'). Again, the conductivity of the PPy-PSS film was high in the (TBA)Cl solution in the negative potential range because the PPy remained as the oxidized forms even at the very negative potentials. On the other hand, the PPy-PSS film showed a very small electrochemical activity in the NaCl solution at the negative potentials where the $PPy^{\bullet+}$ was reduced to the neutral form. When one compares the above results with those observed from the PPy-PSS film which was exposed to the air after the preparation of the film, the electrochemical conductivity of "oxygen free" PPy-PSS was much smaller (see Figures 3a and 8a). Contrary to the PPy-PSS film, no significant oxygen effect on the conductivity was observed for the PPy-CuPcTs film. It seems that the exposing the film to the air during the washing procedure increases the conductivity of the PPy-PSS film, even though it is not clear at this point how it would influence the nature of the PPy-PSS film. It has been reported[12] that a small amount of oxygen increases the conductivity of neutral PPy. Although the majority of the $PPy^{\bullet +}$ is reduced to the PPy^0 at the negative potentials, a small amount of O_2 may still remain in the PPy film. This oxygen or some unknown species formed by the interaction with O_2 may be responsible for the fairly high conductivity of the film at the negative potentials.

4. Raman Spectroscopy. In situ Raman spectra of the PPy-PVS film electrode were recorded in the 0.05 M $NaClO_4$ aqueous solution in the potential range between -1.1 V and +0.5 V. Figure 9 shows selected spectra of the PPy-PVS film recorded in two regions [(a) 600-1200 cm^{-1} and (b) 1200-1700 cm^{-1})]. A couple of strong resonance Raman bands were observed at 1562 and 1042 cm^{-1}. Basically, the same bands have previously been observed from the PPy-CuPcTs film.[7] These two bands have been assigned as a symmetric stretching vibration of C=C[20] and a ring breathing [7,20c] of the neutral form of PPy, respectively. A couple of medium intensity bands were also observed at 1005 and 1317 cm^{-1} from the reduced PPy-PVS film. The intensity of the Raman bands decreased as the potential was stepped to the positive direction, and the Raman intensity was very low when the potential reached to +0.3 V. The 1562-cm^{-1} band, which was observed at -1.1 V, shifted to the higher wavenumber as the potential was moved to the positive direction, and the peak wavenumber increased to 1585 cm^{-1} at 0.1 V. Basically, the same frequency shift has been observed for the PPy-CuPcTs film.[7] The 1562- and 1585-cm^{-1} bands may be assigned[20b] to the neutral form of PPy and overlap bands originating from the radical cation and dication, respectively. From the relationship between the intensity change of the 1562 cm^{-1} band and the applied potential, the redox potential of the PPy-PVS film was calculated[7]

(E_{redox} = -0.50 V). The obtained redox potential by the Raman method was ~200 mV more cathodic than that by the CV (see Table I). At any rate the above results showed that the PPy in the PPy-PVS film was certainly reduced to form a neutral PPy in the negative potential range.

In situ Raman spectra of the PPy-PVS film were also recorded in the presence of MV^{2+} in the $NaClO_4$ solution. Figure 10 shows several selected spectra recorded at potentials ranging from -1.1 V to +0.3 V. Raman spectra recorded at -1.1 V showed several bands at 996, 1028, 1041, 1350, 1530, 1556, and 1647 cm^{-1}. Both 1041- and 1556-cm^{-1} bands are due to the neutral form of PPy in the PPy-PVS film. All other bands except the 996-cm^{-1} band are originated from the $MV^{\bullet+}ClO_4^-$ film formed on the PPy-PVS film. The 996-cm^{-1} band may be due to the neutral form of PPy, but it is also possible that the MV^0 formed on the PPy-PVS film is responsible for the same band. Raman spectroscopic studies of methyl viologen on a thin film gold electrode[7] have previously shown that a medium intensity band at 992 cm^{-1} is due to the MV^0 which is formed at the very negative potential (-1.2 V). A CV of a 1000 Å PPy-PVS film in the 0.05 M $NaClO_4$ and 0.005 M $(MV)Cl_2$ solution showed a very small cathodic current (E_{pc} = -1.1 V) for the reduction of the $MV^{\bullet+}$ to MV^0 at the PPy-PVS film. All of the bands from the $MV^{\bullet+}ClO_4^-$ film (1025, 1350, 1530, 1647) disappeared when the potential was stepped to more positive than -0.5 V because the $MV^{\bullet+}ClO_4^-$ was oxidized to MV^{2+} at the potential.

It is interesting to note that the 1556-cm^{-1} band as well as other bands from the neutral form of PPy were still observed when the potential was stepped from -1.1 to -1.0 V. However, these bands were not seen at the same potential at the PPy-CuPcTs film electrode.[7] This phenomenum has previously been interpreted as evidence for the formation of the thick MV^0 film on the PPy-CuPcTs film electrode at the very negative potential. It is clear from the above results that both $MV^{\bullet+}ClO_4^-$ and MV^0 were formed on the PPy-PVS film at the negative potentials,[7,21] but the MV^0 film was not as thick as that formed on the PPy-CuPcTs film in the same potential range. The above results suggested that the charge-transfer reaction for the reduction of MV^{2+} to $MV^{\bullet+}$ and the further reduction to MV^0 took place at the surface of the PPy-PVS film electrode. The results also indicated that the rate of the second charge-transfer reaction, which formed MV^0 on the surface of the PPy-PVS film, was not quite as high as that of the PPy-CuPcTs film because of the low conductive nature of the PPy-PVS film at the very negative potentials.

5. Conductivity Measurements.

a. Ex Situ Conductivity Measurements. Conductivities of several PPy films doped with large anions including CuPcTs, PSS, and PVS were measured. The conductivity of a PPy-ClO_4 film was also measured in order to compare with those of the PPy films doped with large anions. The accuracy of this technique was examined by observing the conductivities of 1000 Å PPy films, and the error of the measurement was within ±20%.

Figure 11a shows the conductivity curves of PPy films recorded between 0.95 V and -1.0 V. Measurements were carried out after applying a potential for 2 min. After cutting off the applied potential, the film was dried for 10 min at 50°C before the measurement. It can be seen that the conductivity is greatly related to the applied potential. The conductivities of PPy-ClO_4, PPy-PVS, and PPy-PSS films started to drop as the PPy was reduced to the neutral form. However, the conductivity of the PPy-CuPcTs film dropped slightly after an extremely negative potential (-1.0 V) was applied. In order to examine the conductivity difference between the wet and dry films, the conductivity of a PPy-CuPcTs film (1 μm thick) was measured after drying it at 80°C for different time lengths. Figure 11b shows the conductivity change with drying time for both oxidized (0.95 V) and reduced (-1.0 V) films. The conductivity at t = 0 means that the measurement was made quickly (less than 1 min) after cutting off the applied potential. Before the measurements at t=0, the water on the electrode surface was removed by blowing nitrogen gas. The conductivity of the oxidized PPy-CuPcTs film (1 μm thick) was approximately 10^{-2} S cm^{-1} and was not affected by the drying time except the conductivity at t = 0 which was slightly low. The results suggest that the conductivity of the dry oxidized PPy-CuPcTs film may be slightly higher than that of the wet film. The conductivity of the reduced PPy-CuPcTs was low (~10^{-4} S cm^{-1}) when the film was not dried (t = 0). After drying the film in the oven for 2 min, the conductivity increased to ~10^{-3} S cm^{-1}. This increased conductivity of the dried film may be mainly due to the unstable nature of the reduced PPy-CuPcTs film rather than the possible high conductivity of the dry film. We have previously observed that a resonance Raman band at 1555 cm^{-1} from the reduced PPy-CuPcTs in the aqueous Na_4CuPcTs solution was dropped to a level of less than 50% of the original intensity within 2 min.[7] It is quite likely that the reduced PPy-CuPcTs film was quickly oxidized in the air during the drying procedure. These consideration would suggest that the conductivity of the reduced PPy-CuPcTs may be around 10^{-4} S cm^{-1} or slightly lower than this value.

The effect of the film thickness on the conductivity of both PPy-CuPcTs and PPy-PSS films was also examined. Table II lists the conductivities of both PPy-CuPcTs and PPy-PSS films of which the thickness is between 0.1 and 2.0 μm. The measured resistance values for the oxidized PPy-CuPcTs films of different thicknesses were almost the same within the experimental deviation. The results suggested that the observed resistance was mainly due to the contact resistance rather than the actual resistance of the PPy-CuPcTs film.

Consequently, the actual conductivity of the oxidized PPy-CuPcTs should be higher than that of the obtained value (1.5×10^{-2} S cm^{-1}) from the 2μm thick film. On the other hand, the obtained conductivity values ($1\text{-}2 \times 10^{-3}$ S cm^{-1}) for the oxidized PPy-PSS films of several different thicknesses were basically in the same range and can be considered to be close to the actual conductivity of the PPy-PSS film. It is interesting to note that the conductivity ($1\text{-}2 \times 10^{-3}$ S cm^{-1}) of the oxidized PPy-PSS obtained by our method was approximately two orders of magnitude smaller than a reported conductivity for a thick (100 μm) PPy-PSS film which was measured by the four-terminal Van Der Pauw method.[9] It has been known that the reported conductivity values for free standing PPy films, which were normally measured by the four-point probe method, were several orders of magnitude greater than the conductivity values measured by other methods.[13]

b. <u>In Situ Conductivity Measurements</u>. Figure 12 shows plot of the log of the in situ conductivity (σ) of the PPy films (PPy-PSS and PPy-CuPcTs) vs. the applied potential. The resistance of the PPy-PSS film was recorded at each potential after applying the potential for 2 min in the 0.001 M poly(sodium p-styrenesulfonate) and 0.1 M pyrrole solution. The same solution was used for forming the PPy-PSS film. The conductivity of the PPy-PSS film at 0.4 V was 6.3×10^{-3} S cm^{-1} and the same conductivity level was maintained until the potential reached to -0.5 V where the conductivity suddenly started to drop and reached to 3.7×10^{-5} S cm^{-1} at -0.7 V. The observed conductivity decrease should be related to the reduction of the PPy cations to the neutral form of PPy. The potential for the observed conductivity change (~-0.55 V at half drop of conductivity) is ~160 mV more negative than the redox potential of the PPy in a 1000 Å PPy-PSS film by the cyclic voltammetry. The potential difference may be caused by the slow reduction process of the thick PPy film which was used in the in situ conductivity measurements.

The resistance of the PPy-CuPcTs film was measured at each potential after applying the potential for 10 min in the 0.05 M $Na_4CuPcTs$ and 0.1 M pyrrole solution. The obtained conductivity for the oxidized form of the PPy-CuPcTs film (at 0.4 V) was 6.9×10^{-1} S cm^{-1}. The conductivity dropped sharply between -0.4 V and -0.6 V. That potential was almost same as the redox potential measured by both the CV and the Raman method.[7] When the potential was moved further to the negative direction, the conductivity dropped continuously but less sharply and finally reached to $\sim 10^{-4}$ S cm^{-1} level at -1.0 V. When the potential was reversed and stepped backed to the positive direction, the conductivity of the PPy film failed to come back to the original high conductivity level of the oxidized form. This results may be due to the deterioration of the film which was caused by the extended exposure to the very negative potentials. Contrary to the above results, the conductivity measurements of a PPy-CuPcTs film which was carried out by 2 min interval between potentials showed a complete recovery of the conductivity as the potential moved back to the positive direction, as shown in Figure 12. However, the conductivity vs. potential relationship obtained by the above method (2 min interval) could be slightly distorted due to the somewhat incomplete oxidation and reduction of the film.

The slow conductivity decrease which was observed by the 10 min interval method between -0.7 V and -1.0 V (Figure 12) may be due to the slow ion transport in the PPy-CuPcTs film. For the reduction of the PPy-CuPcTs film, small cations (Na^+) in the supporting electrolyte must move into the film in order to balance the charge of the film. Since the structure of the

PPy-CuPcTs film may be more rigid than that of the PPy-PSS, the rate of the ion transport in the PPy-CuPcTs film is slower than that in the PPy-PSS film. Because of the high ion-transport rate in the PPy-PSS film, the conductivity vs. potential relationship for the PPy-PSS film showed a sharp decrease of the conductivity when the very negative potentials were applied (see Figure 12). It is also interesting to note that the conductivity of the PPy-CuPcTs film decreases almost four orders of magnitude when the PPy cation radicals were reduced to the neutral form (at -1.0 V), yet; the remaining conductivity (10^{-4} S cm^{-1}) is enough to be able to observe electrochemical activity for the redox reactions of methyl viologen (see Figure 7a).

6. Charge-Transport Mechanism. Even though the PPy thin-films doped with large size anions showed electrochemical conductivity in the negative potentials, both the cyclic voltammetric and conductivity data indicated that the conductivity of the oxidized form of PPy films is always much higher than that of the reduced form. We have previously proposed a stacked form as a possible structure for the PPy-CuPcTs thin film[7] in order to explain the conductive nature of the reduced PPy-CuPcTs film. Mitchell et al.[11e] recently observed in their X-ray scattering studies that the PPy doped with toluene sulphonate has an anisotropic structure with the planes of the aromatic rings aligned paralell to the film surface. This suggests that it is quite possible that the PPy incorporating large anions with benzene rings could have the stacked-form structure. This structure has the PPy chains and large size anions chains alternately stacked paralell to the surface of the electrode. The structures of both PPy-CuPrTs and PPy-PSS could also be the stacked form, since the aromatic rings are present in both CuPrTs and PSS. Another possible structure for the PPy-PSS is that the PSS is incorporated into the PPy matrix with entanglement.[16] The observed shifts of the redox potential of PPy in

those films in the presence of 0.005 M $(HV)Br_2$ in the solution (see section 2; 30 mV for PPy-CuPcTs, 80 mV for PPy-CuPrTs, 150 mV for PPy-PSS), suggested that the penetration of HV^{2+} (or $HV^{\bullet +}$) into both PPy-CuPrTs and PPy-PSS films was more significant than that in the PPy-CuPcTs film. The results also suggest that the structures of both PPy-CuPrTs and PPy-PSS are less rigid than that of PPy-CuPcTs. The expected structural difference would certainly affect the conducting nature of the PPy films. The structure of the PPy-PVS film may be different from the above described stacked form because the aromatic rings are not present in the PVS molecule. A possible structure for the PPy-PVS film could be similar to the one proposed by Kuivalainen et al.[22] for the PPy doped with inorganic anions (the structure as metallic fibrils separated by thin potential barriers). The PPy chains and the PVS chains may be entangled together.

In situ Raman spectroscopic data of the PPy-PVS film showed that the reduced form of the PPy-PVS film is electronically conducting. Even though the structure of the PPy-PVS film may be less rigid than that of the PPy-CuPcTs film, the Raman data suggested the charge-transfer reaction of the MV^{2+} to $MV^{\bullet +}$ took place at the surface of the PPy-PVS film instead of at the gold underlayer. The results certainly indicated the presence of electronic conductivity when the PPy doped with large anions are in the neutral form, although the level of conductivity in the very negative potential range is quite different between PPy-CuPcTs and PPy-PVS.

Electronic conductivity of the oxidized PPy films has been mainly explained by either a theory based on the diffusive motion of PPy bipolarons through the film[10] or a charge transport due to the hopping of charge carriers.[11] The charge transport across the PPy film can be carried out by at least two processes: intrachain and interchain charge transports.[11e] The intrachain charge-transport in PPy chains (PPy backbone conductivity) could be carried out through the delocalized π systems of these PPy chains. The interchain charge transfer on the other hand, may be carried out by the hopping through the sites of large anions.

When the PPy is reduced to the neutral form, the conductivity of the PPy chains drops. Based on the results from both ex situ and in situ conductivity measurements, the order of the conductivity for the reduced PPy films is PPy-CuPcTs > PPy-PSS > PPy-PVS > PPy-ClO_4. It is obvious that the reduced PPy-ClO_4 film has the lowest conductivity among those PPy films because it lacks any significant number of anions in the film. The observed low conductivity of both the reduced PPy-PSS and PPy-PVS films indicated that the main source of the conducting nature of the oxidized form of these films was the oxidized PPy chains (intrachain charge transport in the PPy backbone). Both the PSS and the PVS anions should remain in the film when the two PPy films are reduced,[9] but results showed that these two anions did not help to maintain high conductivity. The electronic conductivity of the reduced PPy-CuPcTs was observed to be higher than that of the reduced PPy-PSS. The difference of conductivity between these two films may be related to the degree of the rigidity of the stacked form structure of the PPy films. When a PPy chain and a large anion chain are separated by short distance, interchain charge transport could take place easily through the anion sites. We have previously proposed electron delocalization by the π-π overlap of the CuPcTs and the PPy rings as a possible charge-transport mechanism for the PPy-CuPcTs film.[7] However, the proposed mechanism must require a very close interaction between the PPy chains and CuPcTs, but this arrangement may not allow the penetration of MV^{2+}. Our previous observation of the shifted redox potential (~300 mV) of the PPy in the PPy-CuPcTs film in the presence of MV^{2+} in the solution[7] suggested the interaction between $-SO_3^-$ (in the PPy-CuPcTs film) and the MV^{2+}, which was penetrated into the film. Because of the forgoing reasons, it is more likely that the interchain charge transport takes place through the anion sites rather than π-π overlap of the PPy chains and the large anion chains, even though one can not totally rule out the possible contribution of the π-π overlap for the charge transport.

The conductive nature of PPy films as a whole could be explained by the charge-transport mechanism based on the hopping through the anionic sites. The PPy films may be classified into four types based on the oxidation state and the size of the anions: (1) oxidized PPy films doped with either small anions or large anions, (2) oxidized PPy films with very small number of anions (dedoped PPy), (3) reduced PPy films with large anions, and (4) reduced PPy films with small anions (very small number of anions in the film). Type 1 PPy films normally show high conductivity because electrons could hop between anion sites through the PPy chains which may posses metallic conductivity. This arrangement simply shortens the hopping distance. Type 2 PPy films are also highly conductive, but the conductivity of this type of film may be still a little lower than that of type 1 because of the lack of the large number of anion sites. Charge transport in type 3 PPy films can be carried out through the hopping between anionic sites. Since there is no high conductive PPy chains available in the reduced form, the hopping distance between anions is totally dependent on the actual distance between anionic sites: this hopping distance is much larger than that in the type 1 films. So, if the structure of the PPy film is rigid, the anion sites may be close enough, and this fairly short hopping distance should lead to a considerably high conductivity. If the structure is less rigid, the hopping distance should be large, and conductivity must be very low. Type 4 PPy films simply do not have enough number of anions, and the hopping distance must be extremely large.

One, also, should not neglect the possible contribution from the intrachain charge transport in the large anion chains, in order to explain the fairly good conductivity of the PPy-CuPcTs film in the negative potential range. The electrons might move through the delocalized π systems of the CuPcTs molecules and this charge-transport pathway helps to shorten the hopping distance. However, the suggested charge transport through the π systems of the large dopants (CuPcTs) may become inefficient when the dopant is reduced at the very negative potential, which eventually leads to the drop of conductivity.

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19. Our cyclic voltammetric investigations showed that there was no significant peak currents for the redox reaction of the NB at the PPy-BF_4 film electrode in the wet acetonitrile solution (1% H_2O) with $(TEA)BF_4$, as reported by Diaz and Castillo (see ref 18). However, the CVs recorded from a 1000 Å PPy-BF_4 film electrode in the dry acetonitrile solution with $(TEA)BF_4$ showed both cathodic and anodic currents which corresponded to the redox reaction of the NB (manuscript in preparation).

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Table I. Cyclic Voltammetric Data from PPy Films Doped with Large Size Anions

dopant	peak potentials for $PPy^{\cdot +}/PPy^{0}$ [a]		peak potentials for $MV^{2+}/MV^{\cdot +}$ [a]		solvent/supporting electrolyte
	E_{pc}(V)	E_{pa}(V)	E_{pc}(V)	E_{pa}(V)	
PSS	-0.45	-0.32	-0.79 [b]	-0.54 [b]	$H_2O/NaCl$
			-0.76 [b]	-0.54 [b]	$H_2O/(TBA)Cl$
PVS	-0.32	-0.26	-0.81 [b]	-0.60 [b]	$H_2O/NaClO_4$
CuPcTs	-0.51	-0.31	-0.71	-0.60	$H_2O/NaCl$
			-0.72	-0.62	$H_2O/(TBA)Cl$
	-0.40 [c]	-0.28 [c]	-0.96 [c,d]	-0.66 [c,d]	$MeCN/(TMA)PF_6$
FePcTs	-0.45	-0.29	-0.74	-0.55	$H_2O/NaClO_4$
CoPcTs	-0.42	-0.24	-0.75	-0.59	$H_2O/NaClO_4$
NiPcTs	-0.46	-0.26	-0.88 [b]	-0.50 [b]	$H_2O/NaClO_4$
MnPcTs	-0.45	-0.30	-0.71	-0.54	$H_2O/NaClO_4$
H_2PcTs	-0.50	-0.41	-0.79	-0.57	$H_2O/NaClO_4$
CuPrTs	-0.48	-0.35	-0.73	-0.54	$H_2O/NaClO_4$
	-0.44	-0.30	-0.74 [b]	-0.58 [b]	$H_2O/NaCl$
CuPcS [e]	-0.51	-0.25			$H_2O/NaCl$

[a] The scan rate was 20 mV/s.

[b] The scan rate was 10 mV/s.

[c] The potentials were measured with respect to a silver wire.

[d] Peak potentials of $NB/NB^{\cdot -}$.

[e] PPy-CuPcS film electrode (1000 Å) showed electrochemical activities in the negative potential with $(HV)Br_2$.

Table II. Thickness Effect on Conductivities of PPy Films Doped with Large Anions

PPy-CuPcTs (oxidized)[a]			PPy-CuPcTs (reduced)[b]		
thickness (Å)	resistance (Ω)	conductivity (S cm^{-1})	thickness (Å)	resistance (Ω)	conductivity (S cm^{-1})
1000	0.50	0.12×10^{-2}	1000	14	4.2×10^{-5}
5000	0.49	0.58×10^{-2}	5000	70	4.1×10^{-5}
12000	0.67	1.0×10^{-2}			
20000	0.78	1.5×10^{-2}			
PPy-PSS (oxidized)[a]			PPy-PSS (reduced)[b]		
2600	1.3	1.1×10^{-3}			
5000	1.27	2.2×10^{-3}	5000	38×10^{3}	7.5×10^{-8}
12000	5.0	1.4×10^{-3}	12000	111×10^{3}	6.1×10^{-8}
20000	10.5	1.3×10^{-3}			

a: Resistivity was measured just after preparation of the film by applying +0.95 V.

b: Measurements were made after applying -1.2 V for 2 min.

FIGURE CAPTIONS

Figure 1. Structure of large anions which were used as dopants for preparing polypyrrole films. 1: metal phthalocyanine tetrasulfonate, 2: copper porphyrin tetrasulfonate, 3: poly(p-styrenesulfonate), 4: polyvinyl sulfate.

Figure 2. Schematic illustration of an electrode used for in situ conductivity measurements.

Figure 3. Cyclic voltammograms at: (a) a PPy-PSS film electrode (1000 Å thick) in 0.05 M NaCl [curve a: with 0.005 M $(MV)Cl_2$, curve b: without $(MV)Cl_2$], (b) a PPy-PSS film electrode (1000 Å thick) in 0.05 M (TBA)Cl [curve a: with 0.005 $(MV)Cl_2$, curve b: without $(MV)Cl_2$], and (c) a gold electrode in the 0.05 M (TBA)Cl and 0.001 $(MV)Cl_2$ solution.

Figure 4. Cyclic voltammograms at: (a) a PPy-CuPcTs film electrode (1000 Å thick) in the acetonitrile solution with 0.08 M $(TMA)PF_6$, (b) a PPy-CuPcTs film electrode (1000 Å thick) in the acetonitrile solution with 0.08 M $(TMA)PF_6$ and 0.001 M nitrobenzene, and (c) a gold electrode in the acetonitrile solution with 0.08 M $(TMA)PF_6$ and 0.005 M nitrobenzene.

Figure 5. Cyclic voltammograms at PPy-CuPcTs film electrodes (1000 Å thick) in: (a) 0.05 M NaCl, (b) 0.05 M $(TMA)NO_3$, (c) 0.01 M TEAP, and (d) 0.05 M (TBA)Cl.

Figure 6. Cyclic voltammograms at: (a) a PPy-CuPcTs film electrode (1000 Å thick) in 0.05 M NaCl [curve a: without $(HV)Br_2$, curve b: with 0.005 M $(HV)Br_2$], (b) a PPy-CuPcTs film electrode in 0.05 M (TBA)Cl

[curve a: without $(HV)Br_2$, curve b: with 0.005 M $(HV)Br_2$], and (c) a gold electrode in the 0.05 M NaCl and 0.005 M $(HV)Cl_2$ solution.

Figure 7. Cyclic voltammograms recorded under the oxygen-free condition at a 1000 Å PPy-CuPcTs film electrode in: (a) 0.05 M NaCl, 0.002 M $(MV)Cl_2$, and 0.002 M $K_4Fe(CN)_6$ solution, and (b) 0.05 M (TBA)Cl and 0.002 M $(MV)Cl_2$ solution.

Figure 8. Cyclic voltammograms recorded under the oxygen-free condition at a 1000 Å PPy-PSS film in: (a) 0.05 M NaCl, 0.002 M $(MV)Cl_2$, and 0.002 M $K_4Fe(CN)_6$ solution, and (b) 0.05 M (TBA)Cl and 0.002 M $(MV)Cl_2$ solution.

Figure 9. In situ Raman spectra of a PPy-PVS film electrode (1000 Å thick) in 0.05 M $NaClO_4$ at different potentials for: (a) 600-1200 cm^{-1} range, (b) 1200-1700 cm^{-1} range. $\lambda_{exc} = 514.5$ nm.

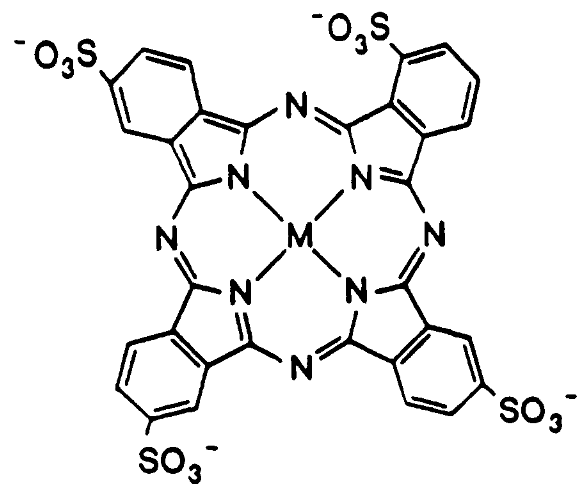
Figure 10. In situ Raman spectra of a PPy-PVS film electrode (1000 Å thick) in the 0.05 M $NaClO_4$ and 0.005 M $(MV)Cl_2$ solution at different potentials for: (a) 600-1200 cm^{-1} range, (b) 1200-1700 cm^{-1} range. $\lambda_{exc} = 514.5$ nm.

Figure 11. (a) Plot of the log of ex situ conductivity (σ) of the PPy films vs. the applied potentials: (⊡) PPy-CuPcTs (1000 Å), (●) PPy-PSS (5000 Å), (▲) PPy-PVS (5000 Å), and (▼) PPy-ClO_4 (1000 Å).
(b) Plot of the log of the conductivity (σ) of the PPy-CuPcTs film (1 μm thick) vs. drying time at 80°C: (▼) oxidized film (at 0.95 V), and (⊙) reduced film (-1.0 V).

Figure 12. Plot of the log of in situ conductivity (σ) of the PPy films vs. the applied potentials: (●) PPy-CuPcTs, the potential was moved

from positive to negative (Ox → Rd), 10 minutes interval between measurements, (▲) PPy-CuPcTs, Ox → Rd, 2 min interval, (⊡) PPy-CuPcTs, Rd → Ox, 2 min interval, and (▼) PPy-PSS, Ox → Rd, 2 min interval.

Fig. 1



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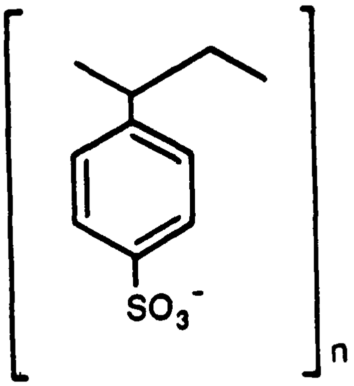

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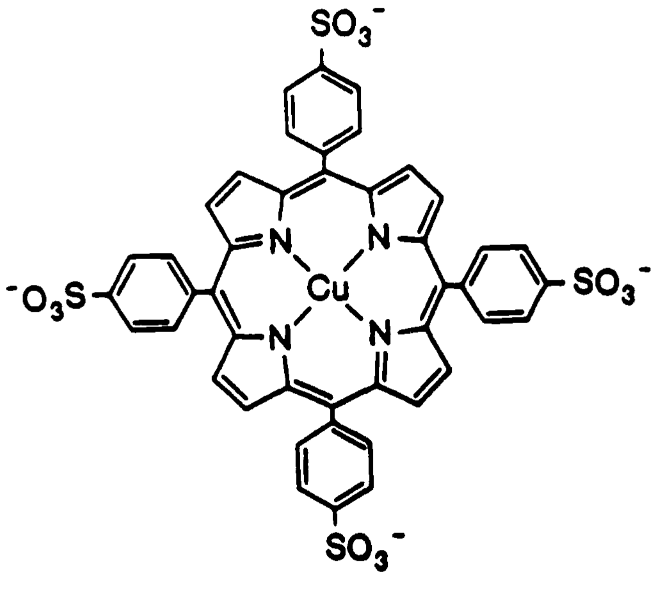

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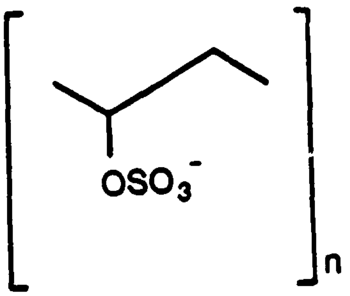


4

Fig. 2

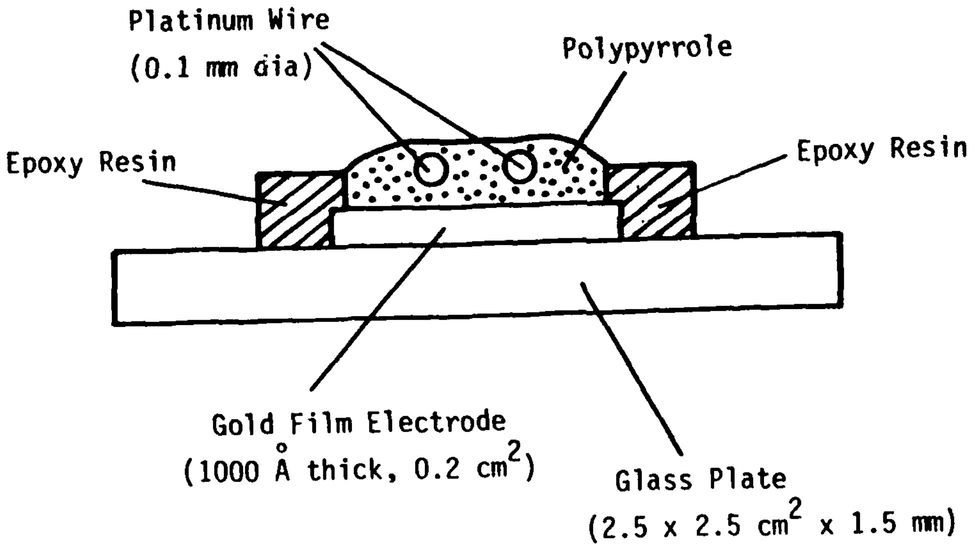
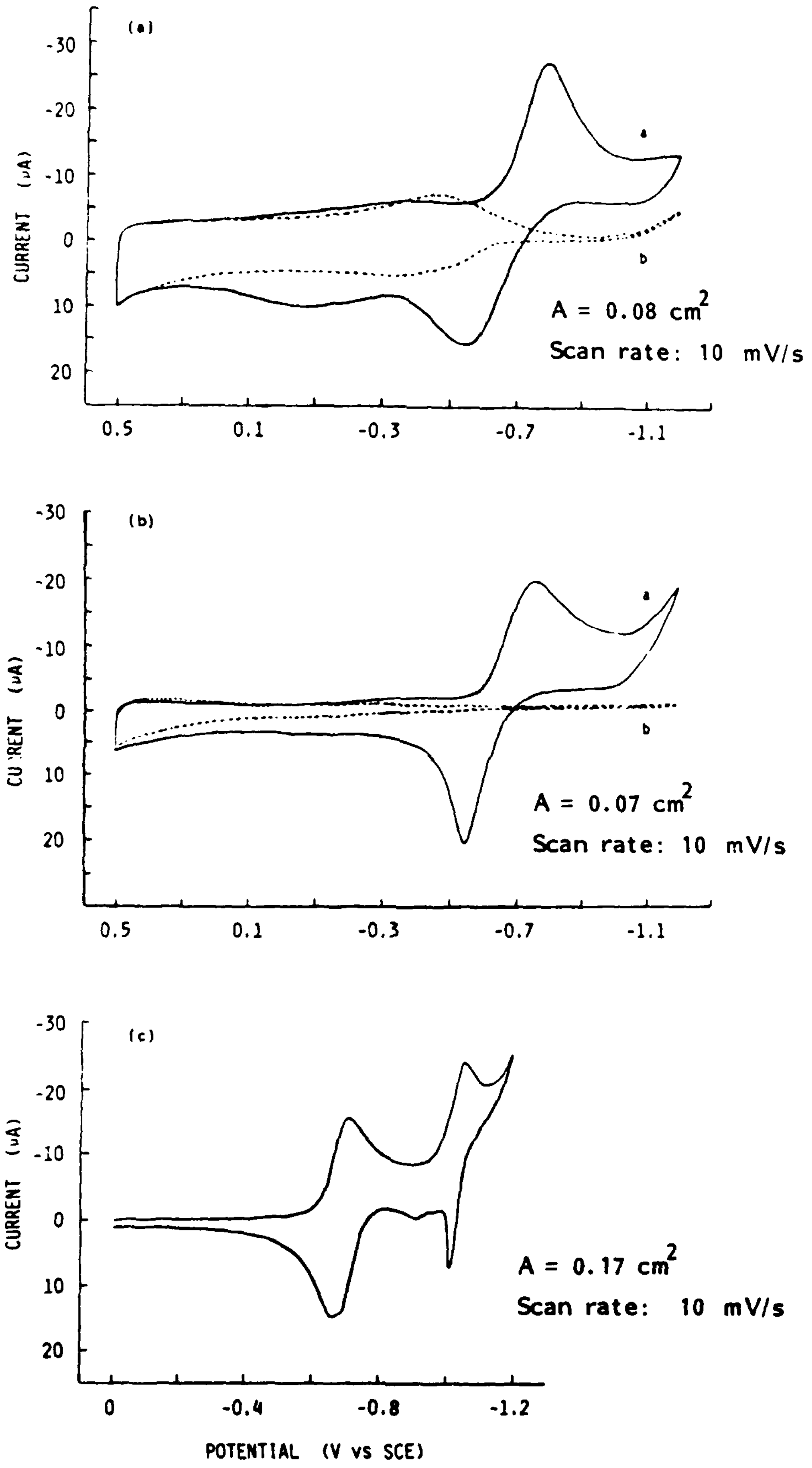
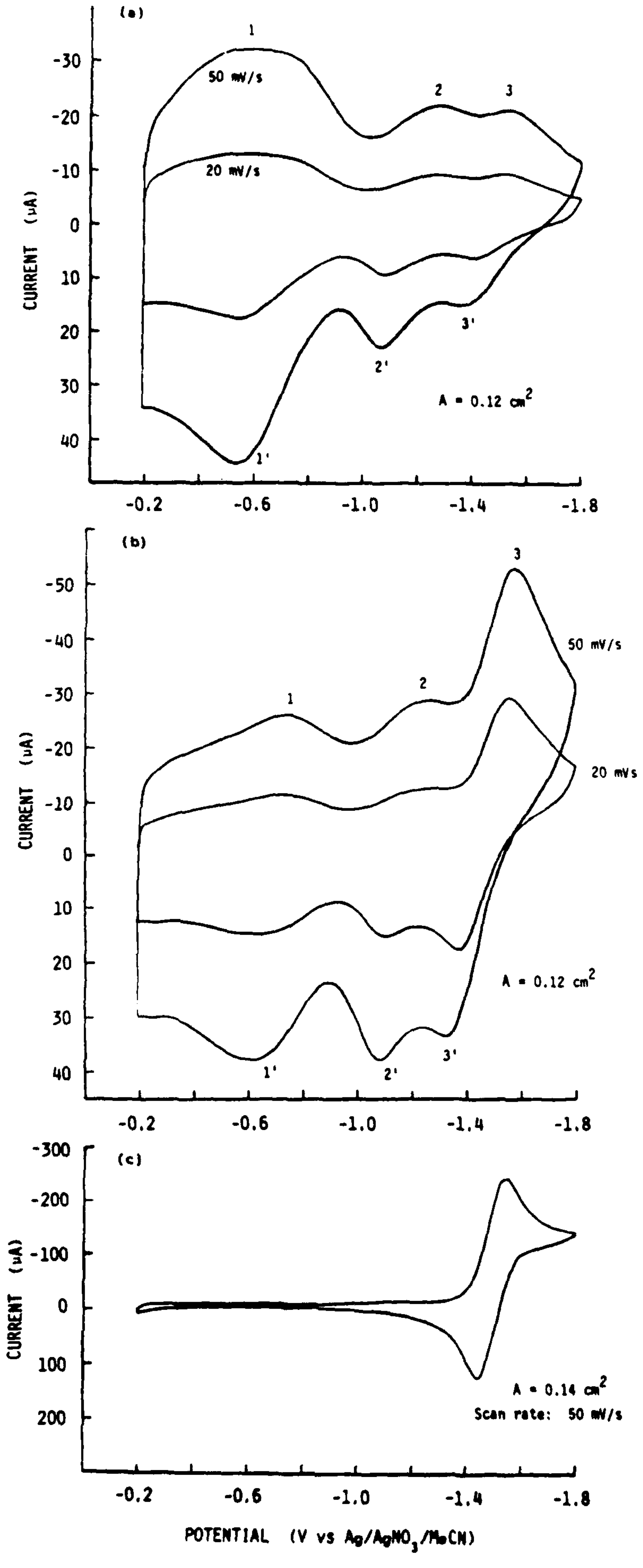

Platinum Wire
(0.1 mm dia)
Polypyrrole
Epoxy Resin
Epoxy Resin
Gold Film Electrode
(1000 Å thick, 0.2 cm2)
Glass Plate
(2.5 x 2.5 cm2 x 1.5 mm)

Fig. 3



(a)
-30
-20
-10
0
10
20
CURRENT (μA)
a
b
A = 0.08 cm2
Scan rate: 10 mV/s
0.5
0.1
-0.3
-0.7
-1.1
(b)
-30
-20
-10
0
10
20
CURRENT (μA)
a
b
A = 0.07 cm2
Scan rate: 10 mV/s
0.5
0.1
-0.3
-0.7
-1.1
(c)
-30
-20
-10
0
10
20
CURRENT (μA)
A = 0.17 cm2
Scan rate: 10 mV/s
0
-0.4
-0.8
-1.2
POTENTIAL (V vs SCE)

Fig. 4



(a)
1
2
3
50 mV/s
20 mV/s
1'
2'
3'
A = 0.12 cm²
-30
-20
-10
0
10
20
30
40
CURRENT (µA)
-0.2
-0.6
-1.0
-1.4
-1.8
(b)
1
2
3
50 mV/s
20 mVs
1'
2'
3'
A = 0.12 cm²
-50
-40
-30
-20
-10
0
10
20
30
40
CURRENT (µA)
-0.2
-0.6
-1.0
-1.4
-1.8
(c)
-300
-200
-100
0
100
200
CURRENT (µA)
A = 0.14 cm²
Scan rate: 50 mV/s
-0.2
-0.6
-1.0
-1.4
-1.8
POTENTIAL (V vs Ag/AgNO3/MeCN)

Fig, 5

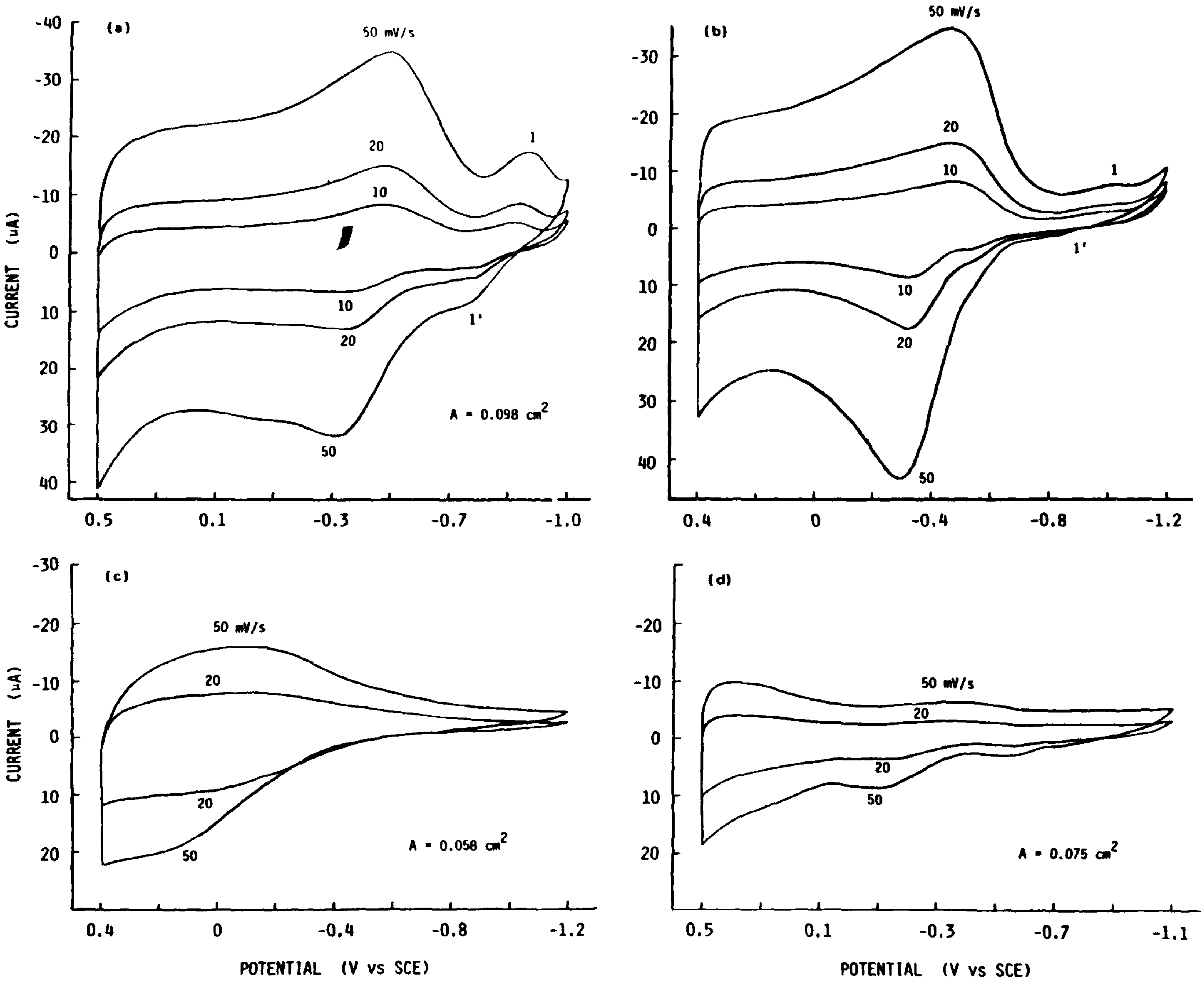

(a)
50 mV/s
20
10
1
10
20
1'
50
A = 0.098 cm^2
CURRENT (uA)
-40
-30
-20
-10
0
10
20
30
40
0.5
0.1
-0.3
-0.7
-1.0
(b)
50 mV/s
20
10
1
1'
10
20
50
-30
-20
-10
0
10
20
30
40
0.4
0
-0.4
-0.8
-1.2
(c)
50 mV/s
20
20
50
A = 0.058 cm^2
CURRENT (uA)
-30
-20
-10
0
10
20
0.4
0
-0.4
-0.8
-1.2
POTENTIAL (V vs SCE)
(d)
50 mV/s
20
20
50
A = 0.075 cm^2
-20
-10
0
10
20
0.5
0.1
-0.3
-0.7
-1.1
POTENTIAL (V vs SCE)

Fig. 6

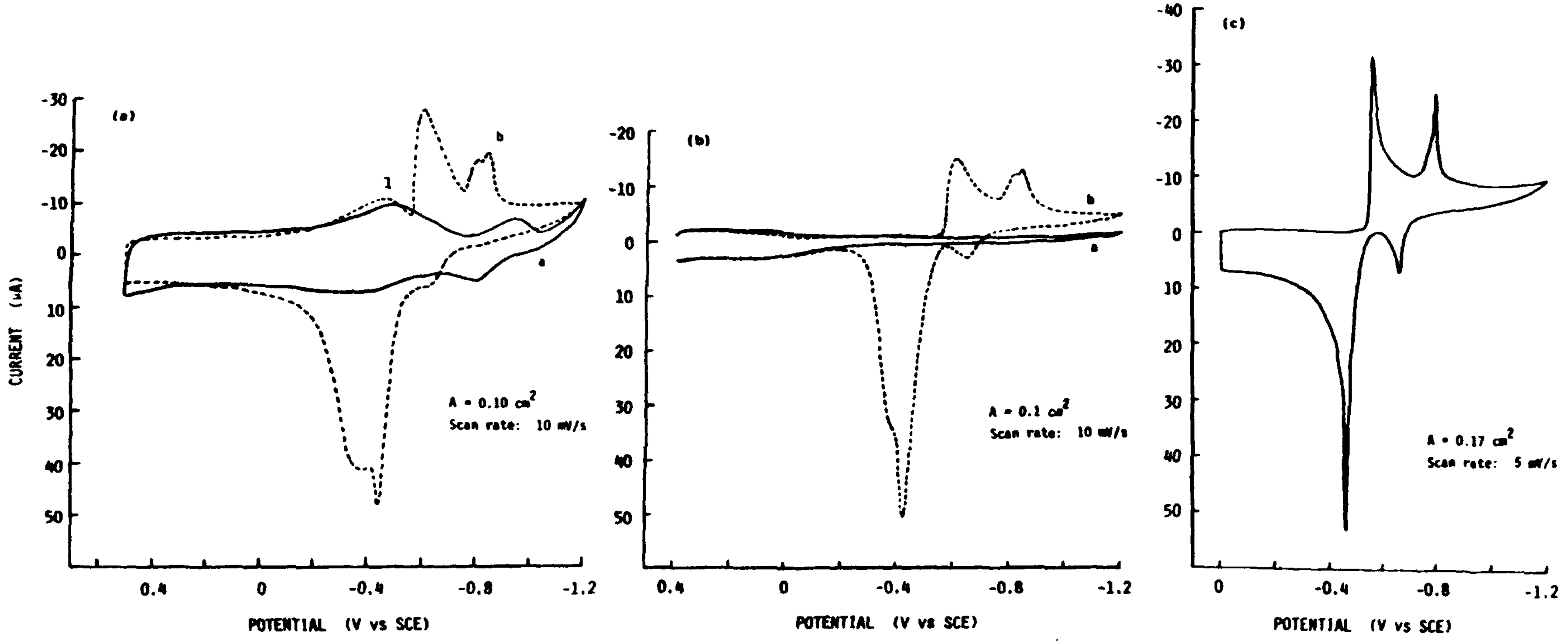

(a)
(b)
(c)
CURRENT (µA)
-30
-20
-10
0
10
20
30
40
50
-40
0.4
0
-0.4
-0.8
-1.2
POTENTIAL (V vs SCE)
1
a
b
A = 0.10 cm^2
Scan rate: 10 mV/s
A = 0.1 cm^2
Scan rate: 10 mV/s
A = 0.17 cm^2
Scan rate: 5 mV/s

Fig. 7

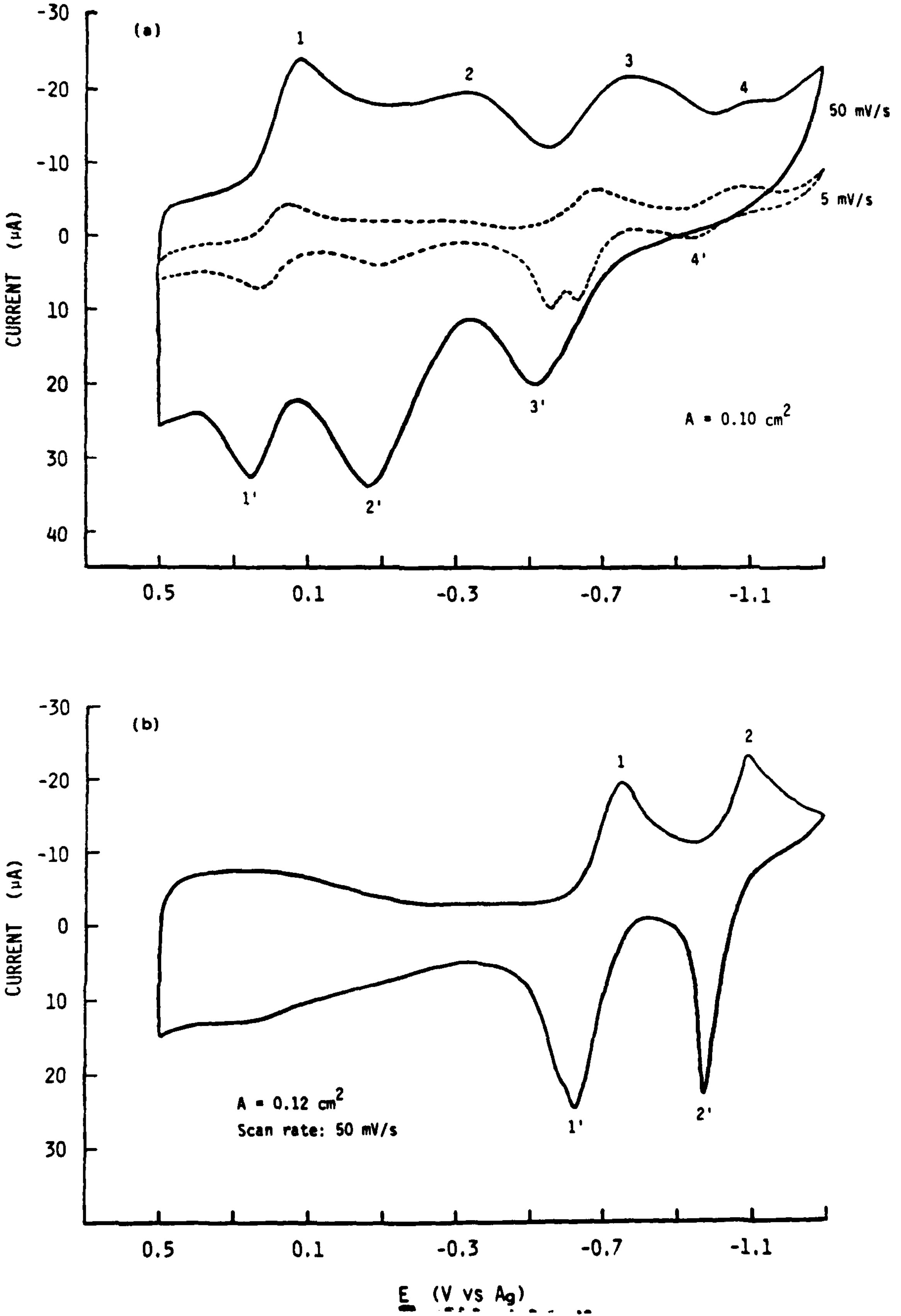

(a)
-30
-20
-10
0
10
20
30
40
CURRENT (μA)
1
2
3
4
50 mV/s
5 mV/s
4'
3'
1'
2'
A = 0.10 cm²
0.5
0.1
-0.3
-0.7
-1.1
(b)
-30
-20
-10
0
10
20
30
CURRENT (μA)
1
2
1'
2'
A = 0.12 cm²
Scan rate: 50 mV/s
0.5
0.1
-0.3
-0.7
-1.1
E (V vs Ag)

Fig. 8

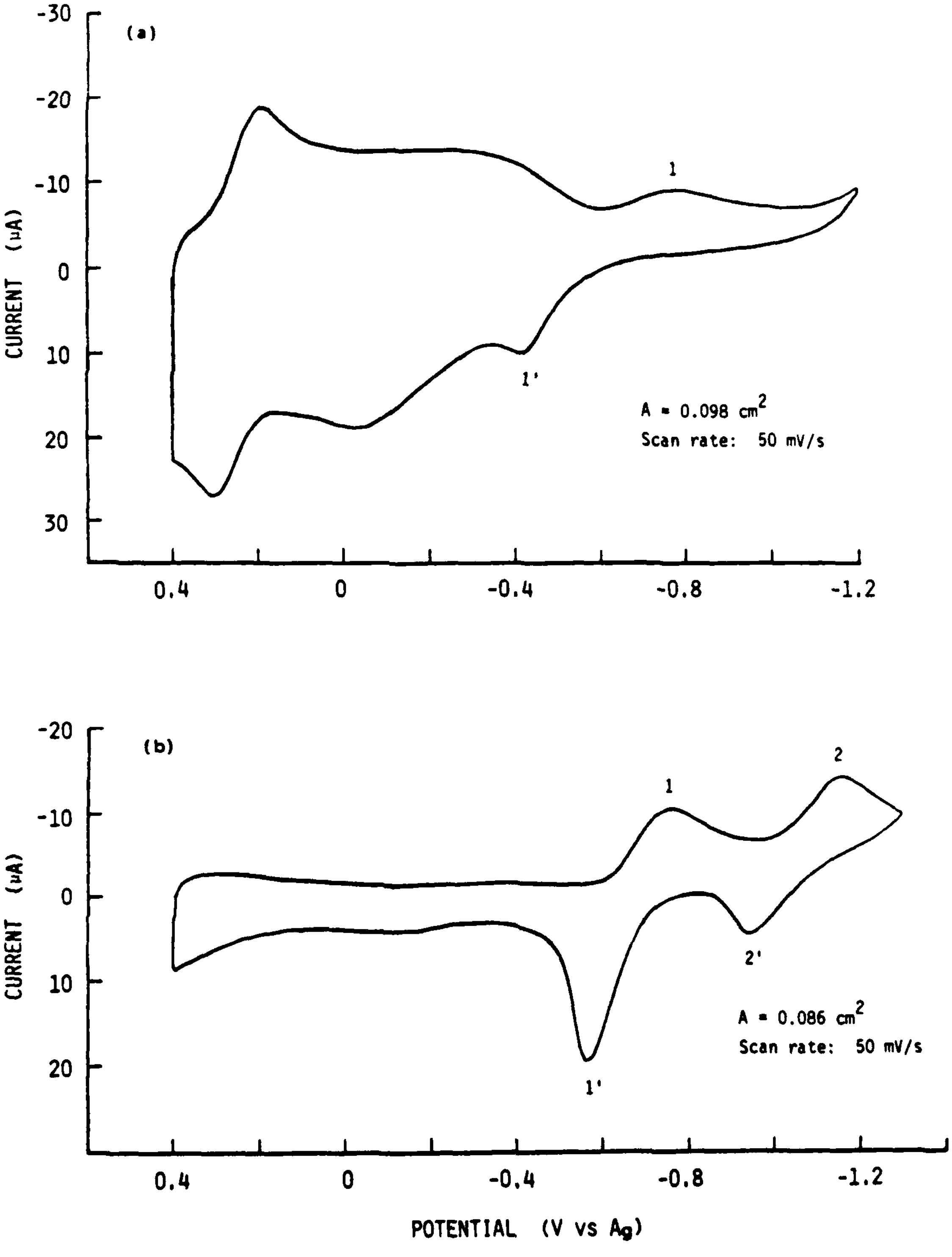

(a)
-30
-20
-10
0
10
20
30
CURRENT (μA)
1
1'
A = 0.098 cm²
Scan rate: 50 mV/s
0.4
0
-0.4
-0.8
-1.2
(b)
-20
-10
0
10
20
CURRENT (μA)
1
2
2'
1'
A = 0.086 cm²
Scan rate: 50 mV/s
0.4
0
-0.4
-0.8
-1.2
POTENTIAL (V vs Ag)

Fig. 9

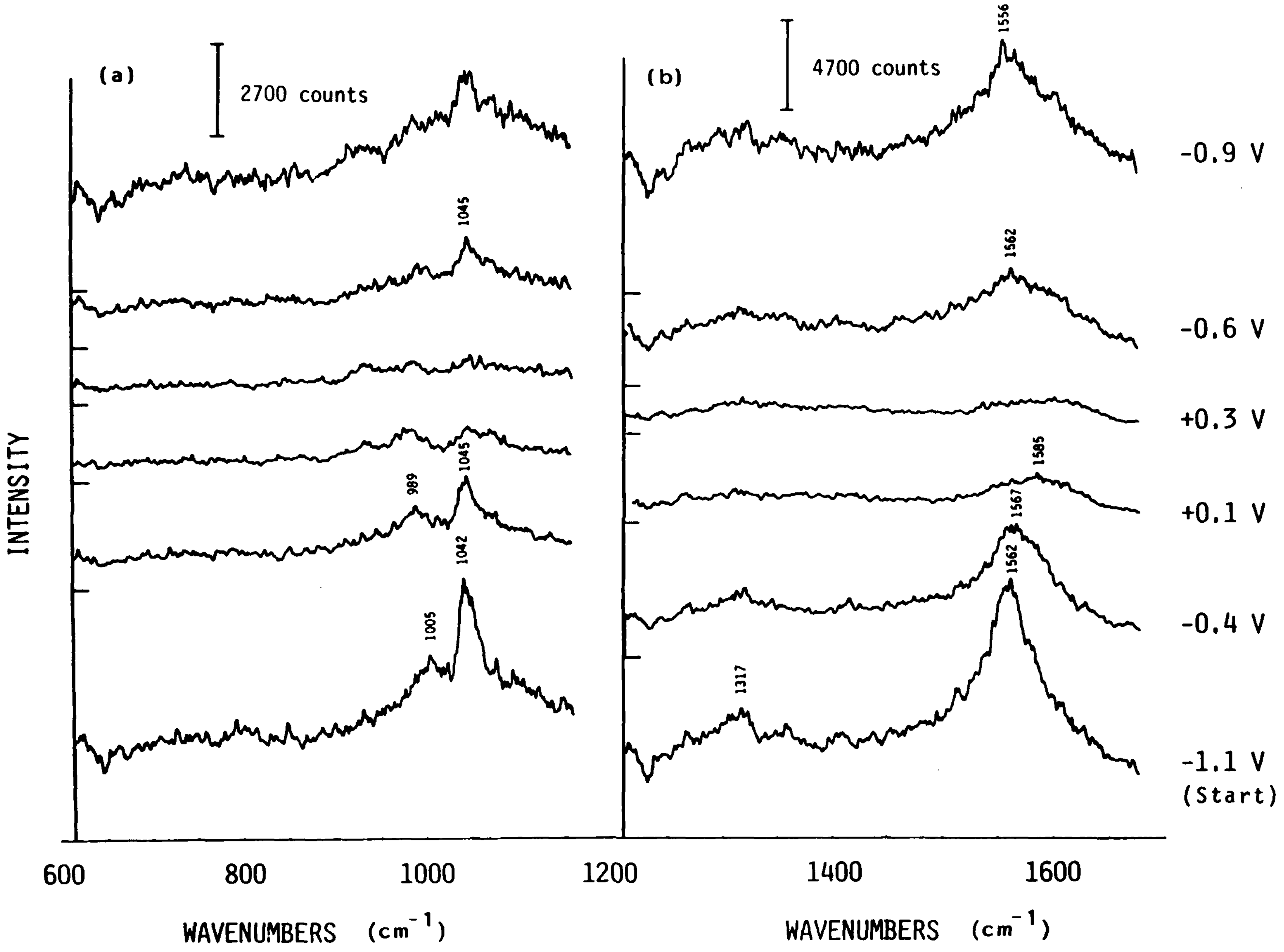

(a)
2700 counts
1045
989
1045
1005
1042
INTENSITY
600
800
1000
1200
WAVENUMBERS (cm^{-1})
(b)
4700 counts
1556
1562
1585
1567
1562
1317
1400
1600
WAVENUMBERS (cm^{-1})
-0.9 V
-0.6 V
+0.3 V
+0.1 V
-0.4 V
-1.1 V
(Start)

Fig.10

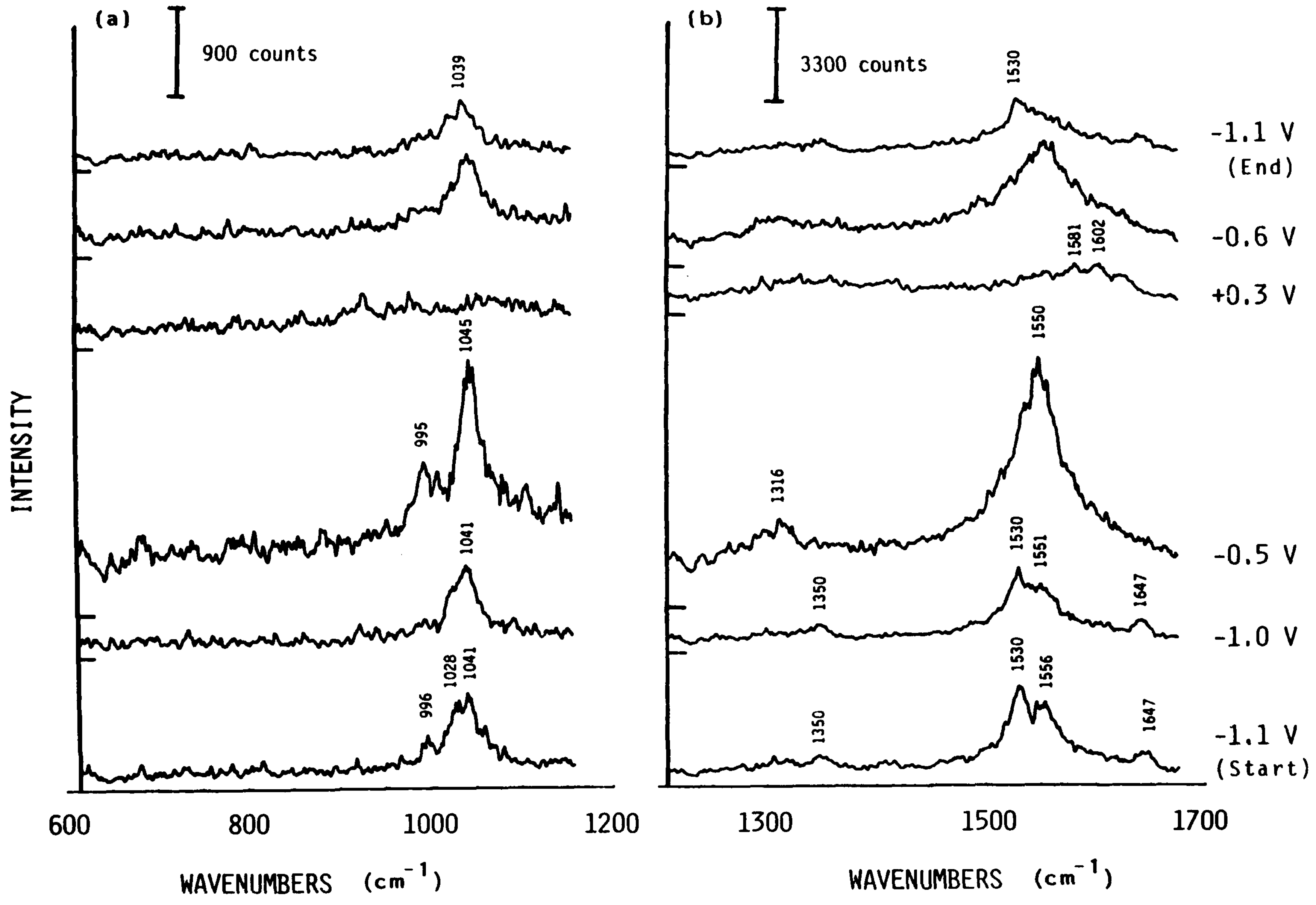

(a)
900 counts
1039
995
1045
1041
996
1028
1041
INTENSITY
600
800
1000
1200
WAVENUMBERS (cm-1)
(b)
3300 counts
1530
1581
1602
1550
1316
1530
1551
1350
1647
1530
1556
1350
1647
1300
1500
1700
WAVENUMBERS (cm-1)
-1.1 V (End)
-0.6 V
+0.3 V
-0.5 V
-1.0 V
-1.1 V (Start)

Fig. 11

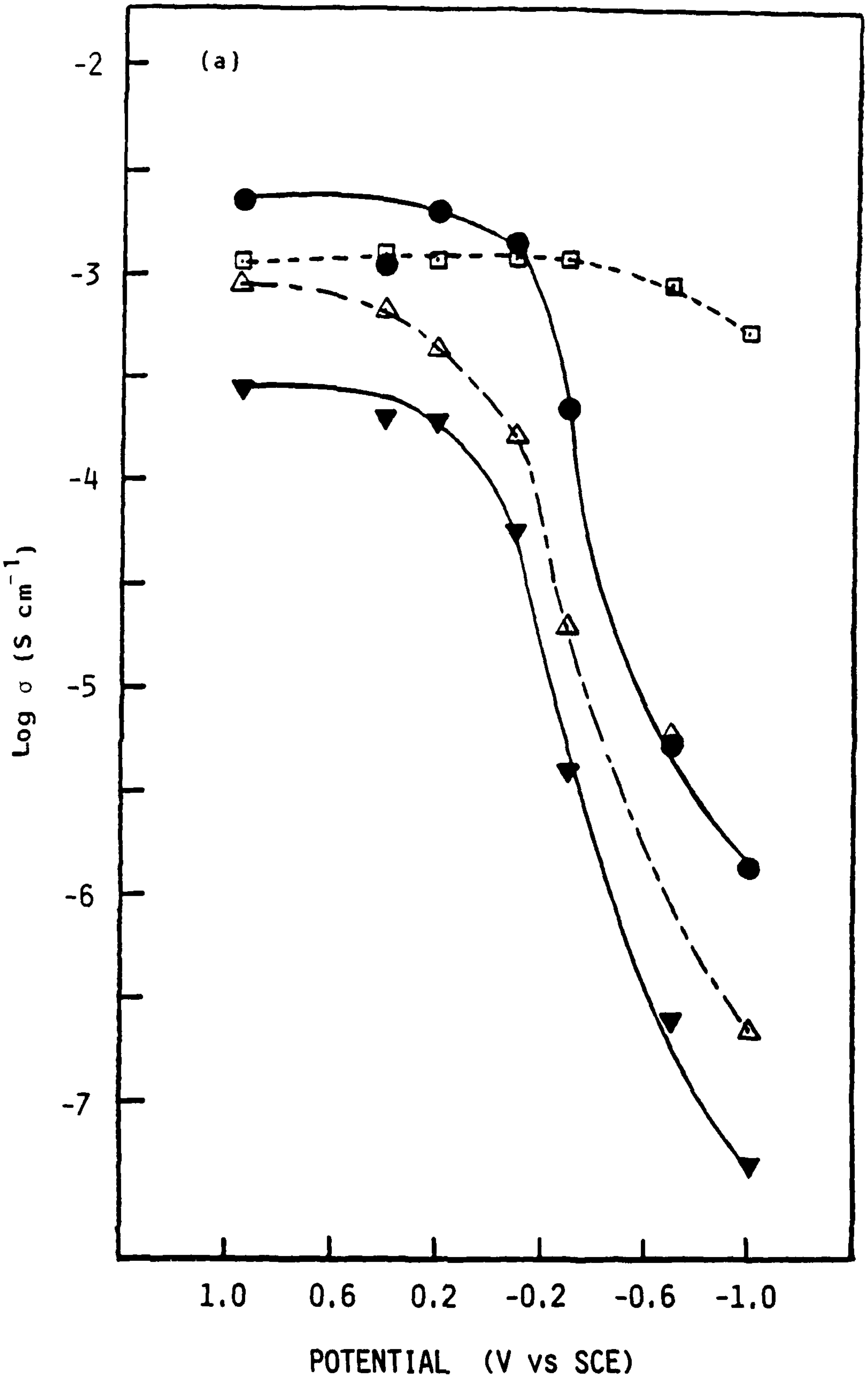


Fig. 11

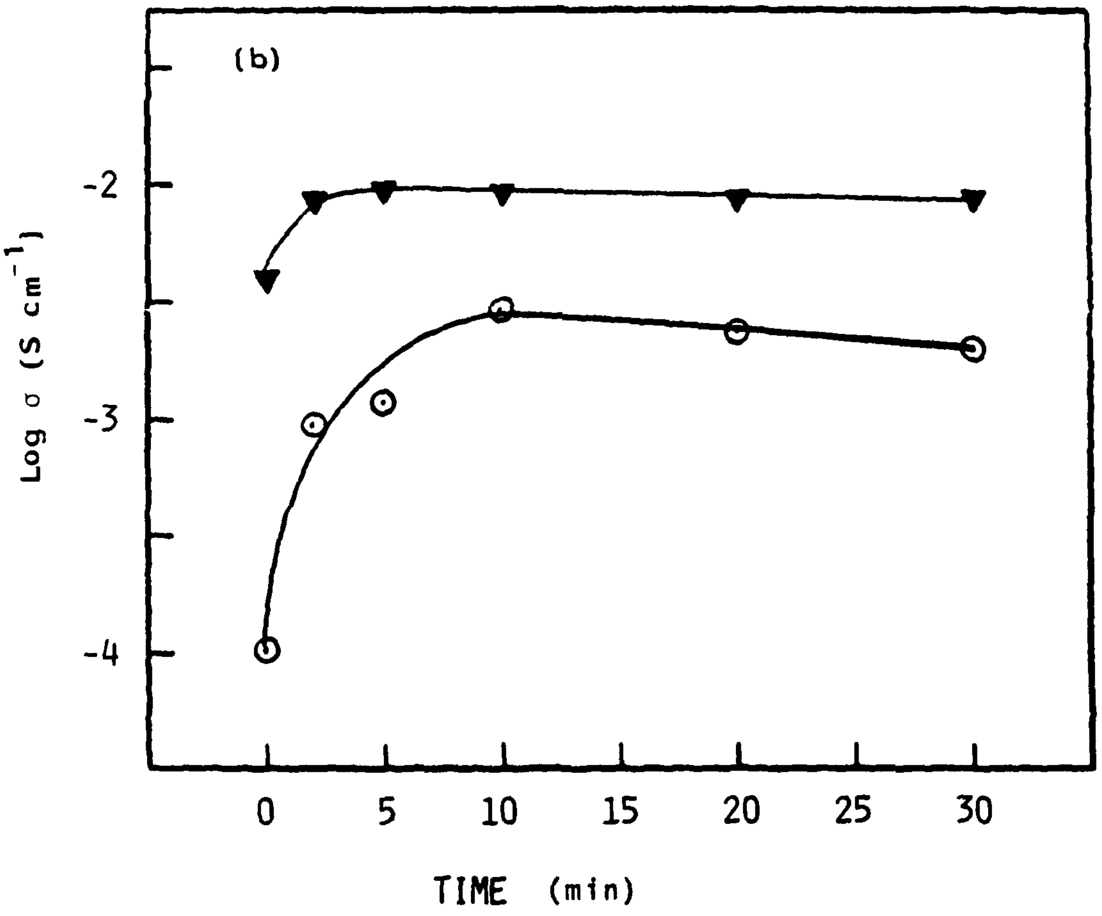


Fig. 12