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Cyclic Voltammetry and In Situ Raman Spectroscopic Investigation

by

Chan S. Choi and Hiroyasu Tachikawa

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Jackson State University  
Department of Chemistry  
Jackson, Mississippi

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Electrochemical Behavior and Characterization of Polypyrrole Copper  
Phthalocyanine Tetrasulfonate Thin Film:  
Cyclic Voltammetry and In Situ Raman Spectroscopic Investigation

Chan S. Choi and Hiroyasu Tachikawa\*

Department of Chemistry  
Jackson State University  
1400 Lynch Street  
Jackson, Mississippi 39217-0510

\*To whom correspondence can be directed.

September 7, 1989

## ABSTRACT

Cyclic voltammetry has shown that polypyrrole thin films (200-5000 Å thick) doped with copper phthalocyanine tetrasulfonate (PPy-CuPcTs) are electrochemically conducting in the negative potential range where polypyrrole (PPy) in the PPy-CuPcTs film exists as a neutral form. In situ Raman spectroscopy showed that ion transport in the PPy-CuPcTs film was carried out by small cations from the supporting electrolytes during the redox reaction of the PPy. Majority of the CuPcTs of the original doping level still remains in the film after the reduction of the PPy. Large cations, such as tetrabutylammonium and methyl viologen, showed strong effects on shifting the redox potential of the PPy thin film electrodes. A very strong resonance Raman band at  $1556\text{ cm}^{-1}$ , which is due to the symmetric stretching of the C=C bond in the neutral form of PPy, disappeared when a PPy thin film electrode was oxidized. Redox potentials of several PPy thin films formed with different anions were calculated by monitoring the intensity change of the  $1556\text{ cm}^{-1}$  Raman band when the electrode potential was changed. The redox potentials obtained by this method are very close to those by cyclic voltammetry. In situ Raman spectroscopy also showed that the ring portion of CuPcTs in the thinner PPy-CuPcTs film (200-1000 Å thick) is reduced and reoxidized in the negative potential range. A huge anodic current observed at the PPy-CuPcTs thin film electrode in the presence of methyl viologen in the  $\text{NaClO}_4$  solution is due to the catalytic oxidation of a methyl viologen polymer (or MVC10 film) by an oxidized form of PPy.

### Introduction

Electrically conducting organic polymers have received a good deal of interest in the last decade or so for their possible technical applications as well as for the fundamental standpoint.<sup>1</sup> Polypyrrole (PPy), one of the most well studied conducting polymers, can be prepared by both chemical and electrochemical oxidation of pyrrole monomer in aqueous and nonaqueous media.<sup>2</sup> In the electropolymerized thin film PPy which is doped with inorganic anions, such as  $\text{ClO}_4^-$  and  $\text{BF}_4^-$ , PPy itself exists as oxidized forms (cation radical and dication). The doped PPy film exhibits high electrical conductivity, but it becomes nonconducting upon electrochemical reduction. Spectroscopic studies<sup>3,2(c)</sup> have shown that the neutral form of PPy has mostly  $\alpha$ ,  $\alpha'$  linked planar structure and an extended conjugated  $\pi$ -system. Elemental analyses<sup>4</sup> of the electropolymerized PPy suggest that every three to four pyrrole rings in the polymer carry a single positive charge and form a complex with an anion (dopant). The PPy film can also be prepared by incorporating organic macrocycles; PPy film incorporating tetrasulfonated iron phthalocyanines (PPy-FePcTs) has been prepared, and its catalytic nature for the oxygen reduction has been investigated.<sup>5</sup> Other sulfonated phthalocyanines, such as tetrasulfonated or monosulfonated cobalt phthalocyanines (CoPsS), have been used as anions forming PPy-CoPcS film electrodes.<sup>6</sup> Such conducting polymers showed higher stability than the PPy incorporating inorganic counter ions. Similar types of PPy have been prepared by incorporating metalloporphyrins.<sup>7</sup> These conducting polymers formed with macrocycles are eventually very important in the area of catalysis.<sup>5,7</sup> Other potentially important applications for the polymers include electrochromic devices<sup>6</sup> and battery electrodes.<sup>8</sup>

Electrochemical behavior of thin film electrodes of PPy incorporating organic macrocycles is normally more complex because there may be redox reactions of the doped species as well as the redox reactions of the PPy itself. Rosenthal, *et al.*<sup>6(a)</sup> reported that the doped CoPcS formed a complex with the PPy and remained in the PPy-CoPcS polymer matrix during the redox reactions. Electrochemical behavior of the PPy-CoPcTs film reported by those authors indicated the presence of cathodic currents in the negative potential range. Recently, we have made oral reports<sup>9</sup> of a conducting nature of PPy thin film incorporating tetrasulfonated copper phthalocyanine (PPy-CuPcTs) in the negative potential range. The PPy polymers incorporating inorganic anions have a conductive nature only in the oxidized form, and this phenomenon has been explained by a theory based on the polymeric cations and dications (polarons and bipolarons).<sup>10</sup> The observed conductivity of the PPy-CuPcTs in the negative potential range could be explained by the polaron theory only if the PPy cations remained in the film during the application of the reduction potential. We will demonstrate in this paper that the PPy-CuPcTs film certainly conducts in the negative potential range (PPy is in neutral form), and a possible structure for this film electrode will be proposed in order to explain the conductive nature.

Raman spectroscopic investigations of PPy thin films have recently been reported<sup>11</sup> for the characterization of PPy during the redox reaction and also during the electropolymerization reactions. The major concern in these works is the observation of structural change of the PPy during the redox reactions. Assignments of major Raman bands have also been carried out. The main purpose of our work is to use Raman spectroscopy for the determination of redox potentials of PPy and the elucidation of ion transport mechanism in the film

electrodes as well. It has been generally understood that the anionic species in PPy incorporating inorganic anions move (in and out) from the polymer matrix during the redox reaction of PPy.<sup>2</sup> Ion transport mechanism in PPy incorporating organic macrocycles is quite an interesting subject because the counter anions are likely to be remaining in this type of polymer during the redox reactions. We will present in situ Raman spectroscopic data which support the ion transport by cationic species.

Spectroelectrochemical techniques<sup>12</sup> have been used for elucidating the charge transfer reaction mechanism of conducting polymers because the presence of high capacitive charge tends to create problems for obtaining accurate redox potential by electrochemical methods. This paper demonstrates that in situ Raman spectroscopy is useful for obtaining the redox potential of PPy itself in several PPy thin film polymers with various counter anions. In situ Raman spectroscopy is also utilized to explain the redox reaction mechanism for the catalytic behavior of the PPy-CuPcTs thin film electrode in the presence of methyl viologen.

#### Experimental

Pyrrole (99% purity), copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt (appr. 85% purity), and methyl viologen dichloride hydrate were obtained from Aldrich Chemical Co., Inc. Sodium perchlorate (purified grade) and sodium nitrate (certified A.C.S. grade) were obtained from Fisher Scientific Co. Tetrabutylammonium chloride (TBACl) and tetrabutylammonium perchlorate (TBAP) were obtained from Southwestern Analytical Chemicals, Inc. Copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt ( $\text{Na}_4\text{CuPcTs}$ ) was purified by dissolving it in water, filtering out insoluble impurities, evaporating the  $\text{Na}_4\text{CuPcTs}$  solution to a minimum volume of water, and cooling the evaporated solution in the ice bath



to recrystallize  $\text{Na}_4\text{CuPcTs}$ . The crystals were thoroughly washed with acetone and dried in the oven at  $70^\circ\text{C}$ . Pyrrole was first refluxed with zinc metal to remove yellow colored impurity, then vacuum distilled. All other chemicals were used as received.

The substrate for polymer film deposition for both cyclic voltammetry and Raman spectroscopy was a gold film (thickness of  $1000 \text{ \AA}$ , geometric area of  $\sim 0.2 \text{ cm}^2$ ) with a Cr intermediate layer (thickness of  $70 \text{ \AA}$ ) vacuum-deposited onto a glass plate ( $2.5 \text{ cm} \times 2.5 \text{ cm} \times 0.16 \text{ cm}$  thick) by using a Varian Model 3118 vacuum bell jar system. The edge portion of Au surface was covered with Scotch-Weld 1838 B/A epoxy adhesive (3M) to avoid any possible contact of Cr with the solution. A platinum helix was used as an auxiliary electrode. The reported potentials were measured with respect to a saturated calomel electrode (SCE). The substrate for UV-visible spectroscopy was either a tin oxide coated glass electrode (PPG glass Co.) or a gold film (thickness of  $200 \text{ \AA}$ ) with a Cr intermediate layer (thickness of  $40 \text{ \AA}$ ) which was vacuum deposited onto a glass plate. The electrochemical cell for the in situ UV-visible spectroscopy was a  $1 \text{ cm} \times 1 \text{ cm} \times 5 \text{ cm}$  quartz cuvette with platinum foil as an auxiliary electrode and silver wire as a quasi-reference electrode. The PPy-CuPcTs films were potentiostatically deposited on a substrate by stepping the potential to  $+0.95 \text{ V}$  vs. SCE under  $\text{N}_2$  (ultra high purity) in the aqueous solution containing  $0.05 \text{ M Na}_4\text{CuPcTs}$  and  $0.1 \text{ M pyrrole}$ . The film thickness was controlled by the charge passed and was estimated using  $48 \text{ mc/cm}^2$  for a  $1000 \text{ \AA}$  film.<sup>13</sup> Measurements on  $1000 \text{ \AA}$  dry films with a Ångstrom Technology Model 980-4020 Å-Scope Interferometer yielded values within  $\pm 20\%$  of the estimated thickness. The PPy film doped with  $\text{ClO}_4^-$  (PPy- $\text{ClO}_4$ ) was deposited in the same way as above from the aqueous solution containing  $0.05 \text{ M NaClO}_4$  and  $0.1 \text{ M pyrrole}$ . The PPy film doped with  $\text{NO}_3^-$  (PPy- $\text{NO}_3$ ) was prepared from an

aqueous solution containing 0.05 M  $\text{NaNO}_3$  and 0.1 M pyrrole. The film electrode was washed thoroughly with distilled water before carrying out electrochemical and spectroscopic experiments.

For the electrochemical experiments, an EG & G PARC Model 173 potentiostat/galvanostat with an EG & G PARC Model 179 digital coulometer, a PARC Model 175 signal generator, and a Houston Instrument Model 2000 X-Y recorder were employed. Beckman Model 5230 spectrophotometer was used for recording UV-visible absorption spectra. 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.<sup>14</sup> As an excitation source, either a Spectra-Physics Model 171-17  $\text{Ar}^+$  laser or Model 171-01  $\text{Kr}^+$  laser with an intensity of 15-60 mW at the sample was employed. The excitation beam was brought onto the sample surface at a 60 degree angle from the horizontal. The final slit width of the triple spectrometer was set at 100  $\mu\text{m}$ , and normally a 1800 grooves/mm grating was used. Calibration curves for the triple spectrometer were prepared by using the wavenumbers of metallophthalocyanine thin film electrodes recorded by a system consisting of a Spex Model 1403 double spectrometer and DM1B datamate. The accuracy of measurements was estimated to be  $\pm 5\text{cm}^{-1}$ . Raman spectra were collected in approximately 30 seconds with the triple spectrometer. For a better resolution of Raman spectrum ( $\pm 2\text{cm}^{-1}$ ), a Spex Model 1403 double spectrometer, a DM1B datamate, and a Houston Instrument DMP-40 digital plotter were employed.

## Results and Discussion

A. PPy thin film doped with inorganic anions. Cyclic voltammetric experiments (A.1) of a couple of well studied polypyrrole thin films, PPy-ClO<sub>4</sub> and PPy-NO<sub>3</sub> film electrodes (1000 and 5000 Å), were carried out in order to present data which can be compared with the results of the PPy-CuPcTs thin film electrode. In situ Raman spectroscopy (A.2) of these film electrodes were performed to establish our Raman technique which can be used for the understanding of more complexed PPy-CuPcTs films.

A.1. Electrochemistry. Figure 1(a) shows a cyclic voltammogram (CV) of a 1000 Å PPy-ClO<sub>4</sub> film electrode in an aqueous solution of 0.05 M NaClO<sub>4</sub>. A cyclic voltammogram recorded in an aqueous solution containing 0.05 M NaClO<sub>4</sub> and 0.005 M MVCl<sub>2</sub> at the same electrode is shown in (b). Figure 1(c) is a CV for a solution containing 0.005 M MVCl<sub>2</sub> in 0.05 M NaClO<sub>4</sub> at the gold electrode. A CV with a dotted line in Figure 1(c) was recorded at the gold electrode in 0.05 M NaClO<sub>4</sub> solution. Redox potential of the PPy-ClO<sub>4</sub> film electrode which was calculated by averaging both anodic and cathodic peak potentials ( $E_{pa} = -0.02$  V,  $E_{pc} = -0.13$  V) was -0.08 V at the scan rate of 50 mV/s. A small second cathodic peak of PPy was seen at -0.42 V. The cathodic peak potential for the reduction of MV<sup>2+</sup> to MV<sup>+</sup> at the gold electrode was -0.72 V at the scan rates of 5 mV/s - 20 mV/s. A small cathodic peak current in Figure 1(b) around -0.72 V was due to the reduction of MV<sup>2+</sup> to MV<sup>+</sup>. The peak current was low compared with that in the CV at the gold electrode because the PPy film doped with ClO<sub>4</sub><sup>-</sup> had very low conductivity, which was of semiconducting or almost insulating nature, in the negative potential range. No cathodic current for the reduction of MV<sup>2+</sup> to MV<sup>+</sup> was observed at a 5000 Å PPy-ClO<sub>4</sub> film electrode.

The cyclic voltammogram of a 1000 Å PPy-NO<sub>3</sub> film electrode in 0.05 M NaNO<sub>3</sub> at the scan rate of 50 mV/s was similar to that of the PPy-ClO<sub>4</sub> film, as shown in Figure 2(a). The second cathodic peak of PPy at -0.42 V was more pronounced than that in the CV of the PPy-ClO<sub>4</sub> film electrode. The CV of the same electrode in the presence of MV<sup>2+</sup> (electrolytes of 0.05 M NaNO<sub>3</sub> and 0.005 M MVCl<sub>2</sub>) showed a sharp anodic current at -0.40 V along with a low broad cathodic current around -0.70 V which are due to the redox reaction of MV<sup>2+</sup>/MV<sup>+</sup> pair (see Figure 2(b)). Since the reduced form of the PPy-NO<sub>3</sub> film is known to be electronically nonconductive,<sup>2</sup> the redox reaction of MV<sup>2+</sup>/MV<sup>+</sup> must take place at the surface of the gold substrate. The MV<sup>2+</sup> which penetrated slowly through the pinholes during the potential scan to -1.2 V was probably reduced at the gold surface to form MV<sup>+</sup>. Consequently, the sharp anodic current at -0.40 V is likely due to the oxidation of MV<sup>+</sup> in the film. Our results in cyclic voltammetric experiments for both PPy-ClO<sub>4</sub> and PPy-NO<sub>3</sub> thin films are certainly consistent with the previous reports that PPy thin film doped with inorganic anions can be switched between electronically conducting and insulating states.<sup>2</sup>

**A.2. Raman spectroscopy.** In situ Raman spectra of a 1000 Å PPy-ClO<sub>4</sub> film electrode recorded in 0.05 M NaClO<sub>4</sub> solution are shown in Figure 3. The spectra were recorded by first setting the potential at -1.0 V, then moving it every 100 mV until 0.4 V. The potential was reversed at +0.4 V and moved to the negative direction completing the cycle at -1.0 V. Several selected spectra which are shown in Figure 3 represent general trends of spectral change during the redox reactions. In the spectrum recorded at -1.0 V, a couple of strong bands were observed at 1556 and 1037 cm<sup>-1</sup> which had been assigned as a symmetric stretching vibration of C=C<sup>11(d,e),17</sup> and the CH in-plane deformation in the PPy.<sup>15</sup> Intensities of these bands were potential

dependent, and the Raman scattering disappeared almost entirely at +0.4 V. The relationship between Raman intensity of the  $1556\text{ cm}^{-1}$  band and potential is shown in Figure 4. The potential at a half intensity for the forward (- to + direction) step ( $E_{1/2}(F)$ ) was -0.09 V and that for the reversed step ( $E_{1/2}(R)$ ) was -0.36 V. The redox potential ( $E_{\text{redox}}$ ) was calculated by averaging the  $E_{1/2}(F)$  and  $E_{1/2}(R)$ . The averaged value (-0.23 V) is close to the redox potential (-0.22 V) obtained by averaging  $E_{\text{pa}}$  and  $E_{\text{pc}2}$  in the cyclic voltammogram of the same system. The redox potentials of both the PPy-ClO<sub>4</sub> and the PPy-NO<sub>3</sub> film electrodes by using cyclic voltammetry and in situ Raman spectroscopy are listed in Table I.

Raman intensities of both  $1556$  and  $1037\text{ cm}^{-1}$  bands were also quite high when other excitation sources such as 457.9 nm and 488 nm of Ar<sup>+</sup> laser were used. However, they were barely seen when the 647.1 nm line of Kr<sup>+</sup> laser was used as the excitation source. The results suggest that those Raman bands are the resonance Raman scattering. The neutral form of PPy (PPy<sup>o</sup>) has a strong absorption band at ~372 nm (3.3 eV) due to  $\pi$ - $\pi^*$  transition<sup>16</sup> which tails off after ~550 nm as shown in the curve (-1.2 V) in the inset of Figure 5. One could certainly observe the resonance Raman scattering of the PPy by using the 514.5 nm line as the excitation source. The Raman spectra in Figure 3(b) showed that the frequency of the C-C stretching band shifted to higher wavenumbers as the potential was moved to the positive direction. The  $1556\text{ cm}^{-1}$  band recorded at -1.0 V shifted to  $1582\text{ cm}^{-1}$  at 0.0 V, but the exact amount of the shift was obscured by the continuous drop of band intensity at the positive potential. The observed intensity drop must be related to the resonance nature of Raman scattering of the  $1556\text{ cm}^{-1}$  band because the absorbance of the 372 nm band dropped sharply as the PPy film was oxidized (see inset of Figure 5). The shifted band frequency may reflect the formation

of both radical cation and dication during the oxidation of the PPy. Furukawa *et al.*<sup>11(e)</sup> observed the shift of C-C stretching band position from 1564  $\text{cm}^{-1}$  to 1581  $\text{cm}^{-1}$  during the oxidation of the PPy-ClO<sub>4</sub> film in the acetonitrile solution. The former band was assigned to the neutral form of PPy and the latter was assigned as overlap bands originating from the radical cation and dication by the same authors.

In situ Raman spectra of a 1000 Å PPy-NO<sub>3</sub> film electrode were recorded in aqueous 0.05 M NaNO<sub>3</sub>. The Raman spectrum change of the PPy-NO<sub>3</sub> film electrode in NaNO<sub>3</sub> solution was similar to that of the PPy-ClO<sub>4</sub> film in NaClO<sub>4</sub> solution. Raman intensities from the oxidized PPy-NO<sub>3</sub> film were generally higher than those of the oxidized PPy-ClO<sub>4</sub> film. Redox potential of the electrode in NaNO<sub>3</sub> solution by the Raman method (-0.29 V) was slightly more cathodic than that of PPy-ClO<sub>4</sub> (-0.23 V) (see Table I). Major bands for both oxidized and neutral PPy in the PPy-NO<sub>3</sub> film electrode are listed in Table II. Our results for the band shifts by the oxidation are very similar to those reported by Virdee and Hester.<sup>11(d)</sup> Two strong bands for the skeletal vibrational modes<sup>15</sup> of the PPy (1043 and 1568  $\text{cm}^{-1}$ ) showed sharp drops in their intensities by the oxidation, but the Raman band due to C-N stretching vibration (1320  $\text{cm}^{-1}$ ) maintained its intensity, even though its frequency shifted to 1335  $\text{cm}^{-1}$ . Also notable was the appearance of a 923  $\text{cm}^{-1}$  band (C-H stretching vibration<sup>17</sup>) by the oxidation.

**B. PPy thin film doped with CuPcTs.** PPy-CuPcTs thin films (200-5000 Å) were studied by cyclic voltammetry, and in situ Raman and in situ UV-visible spectroscopies. Results in this section are described for 1000 Å films, unless stated otherwise. Effects of film thickness are described separately.

**B.1. Electrochemistry.** Cyclic voltammetric studies on the PPy-CuPcTs film electrodes were carried out in several supporting electrolytes including  $\text{Na}_4\text{CuPcTs}$ ,  $\text{NaClO}_4$ ,  $\text{NaNO}_3$ , TBAP, and TBACl. Concentration of the supporting electrolyte was normally 0.05 M. In order to test the conductivity of the electrodes in the negative potential range,  $\text{MVCl}_2$  (0.005 M) was added to the solutions. There were generally two redox pairs in CV's without  $\text{MVCl}_2$ : one for the PPy redox reaction and another for the redox reaction of dopants (CuPcTs). Cyclic voltammograms of PPy-CuPcTs film electrodes in 0.05 M  $\text{NaClO}_4$  solution with (b) and without (a)  $\text{MVCl}_2$  are shown in Figure 6. The first pair in Figure 6(a) (1 and 1') is related to the redox reaction of CuPcTs in the film<sup>18</sup>. The second pair (2 and 2') is due to the redox reaction of polypyrrole, even though the redox potential (-0.45 V) of the PPy-CuPcTs shifted approximately 200 mV toward more negative potential compared with that of the PPy- $\text{ClO}_4$  film in the same solution. By adding 0.005 M  $\text{MVCl}_2$  to the solution, the cyclic voltammogram in Figure 6(b) showed well defined peaks ( $E_{a1} = -0.52$  V,  $E_{c1} = -0.71$  V) which corresponded to the redox reaction of  $\text{MV}^{2+}/\text{MV}^+$  pair mainly in the solution. A portion of the currents is also due to the redox reaction of CuPcTs. A small pair of redox currents at -0.92 V ( $E_{a3}$ ) and -1.12 V ( $E_{c3}$ ) is due to the redox reaction of  $\text{MV}^+/\text{MV}^0$  pair. A sharp, very high anodic current ( $E_{a2} = 0.0$  V) and a broad cathodic current ( $E_{c2} = -0.19$  V) were also observed. Although the redox potential (-0.10 V) of this pair shifted toward the positive direction in the presence of  $\text{MVCl}_2$ , it is likely that the redox reaction of the PPy itself was responsible for the current. Our Raman spectroscopic investigation indicated that the sharp anodic peak current at 0.0 V was due to the catalytic oxidation of methyl viologen polymer film (or  $\text{MVClO}_4$  film) on the PPy-CuPcTs electrode (see section B.6).

The cyclic voltammogram of the same electrode in 0.05 M NaNO<sub>3</sub> (Figure 7(a)) was basically the same as that in 0.05 M NaClO<sub>4</sub>. Very dramatic changes in CV were observed when 0.005 M MVCl<sub>2</sub> was added to the solution. Cyclic voltammograms recorded at scan rates of 5, 10, and 20 mV/s are shown in Figure 7(b). Several anodic peaks were seen at -0.60 V (1), -0.50 V (2), -0.23 V (3), and -0.10 V (4) at the scan rate of 10 mV/s. Also, a shoulder at -0.80 V (5) was observed at the same scan rate. Three cathodic peaks at -0.28 V (4'), -0.75 V (1'), and -1.2 V (5') were also seen at the same scan rate. Peaks (4) and (4') should correspond to the redox reaction of the PPy, even though the redox potential of the PPy was shifted more anodic than that of the PPy in the NaNO<sub>3</sub> solution without MVCl<sub>2</sub> (see Figure 7(a)). One can easily assume that a cathodic peak (1') is primarily due to the reduction of MV<sup>2+</sup> to MV<sup>+</sup>. The cathodic peak current (5') and a shoulder (5) should be related to the MV<sup>+</sup>/MV<sup>0</sup> redox reaction. The reason why the cyclic voltammogram of the PPy-CuPcTs film electrode in NaClO<sub>4</sub> solution is different from that in NaNO<sub>3</sub> and the origin of anodic currents observed in the potential range from -0.5 to -0.6 V will be discussed in a later section (see section B.6.). Cyclic voltammograms of the PPy-CuPcTs film electrode in 0.05 M Na<sub>4</sub>CuPcTs solution showed both anodic and cathodic peak currents which were due to the redox reaction of PPy (see Table I). When MVCl<sub>2</sub> (0.005 M) was added to the solution, a sharp cathodic peak current was observed at ~-0.8 V which was due to the reduction of MV<sup>2+</sup> to MV<sup>+</sup>.

A cyclic voltammetric curve of the PPy-CuPcTs film electrode recorded in 0.01 M TBAP was quite different from those observed in the above described three supporting electrolytes: There was no clear cathodic peak in the curve, although only a slight hump was seen around -0.3 V. A broad low anodic current ( $E_{pa} = -0.0$  V) was seen in the CV, and the current level was less than 25% of the peak current observed in the CV of the same electrode in 0.05 M



NaClO<sub>4</sub> solution. The voltammetric behavior of the PPy-ClO<sub>4</sub> film electrode in TBAP was quite different from that of the PPy-CuPcTs in the same supporting electrolyte: the CV of the 1000 Å PPy-ClO<sub>4</sub> film electrode in 0.01 M TBAP showed a normal level of both anodic and cathodic peak currents. Cyclic voltammograms were also recorded at the PPy-CuPcTs film electrode in 0.05 M tetrabutylammonium chloride solution with 1.0 mM MVCl<sub>2</sub>. Normal level of anodic and cathodic currents for the redox reactions of MV<sup>2+</sup>/MV<sup>+</sup> pair was seen, but a very low level of currents was observed for the PPy redox reactions. The redox currents observed for Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup> pair (E<sub>redox</sub> = 0.03 V) at the same electrode confirmed the electrochemical conductivity of the PPy-CuPcTs film in the positive potential range.

In summary, the electrochemical activities were observed at the PPy-CuPcTs thin film electrodes in both positive and negative potential ranges. This means that the PPy-CuPcTs thin film is electrochemically conductive in the negative potential range which is clearly different from the conductive nature of thin film polypyrrole doped with inorganic anions such as PPy-ClO<sub>4</sub> and PPy-NO<sub>3</sub>.

**B.2. Raman spectroscopy.** In situ Raman spectra of the PPy-CuPcTs film electrode were recorded in 1.0 mM Na<sub>4</sub>CuPcTs solution by using 488 nm line of Ar<sup>+</sup> laser as the excitation source.<sup>19</sup> Several selected spectra recorded in the potential range between -1.0 V and +0.2 V in two regions ((a) 550-1300 cm<sup>-1</sup> and (b) 1100-1700 cm<sup>-1</sup>) are shown in Figure 8. They were similar to the spectra of the PPy-ClO<sub>4</sub> thin film electrode recorded in the NaClO<sub>4</sub> solution by using 514.5 nm line of Ar<sup>+</sup> laser as the excitation source (see Figure 3). A couple of strong resonance Raman bands were observed at 1555 cm<sup>-1</sup> and 1042 cm<sup>-1</sup> when the electrode potential was set at -1.0 V. In the studies of PPy-ClO<sub>4</sub>, these two bands were assigned as a symmetric stretching vibration of

C=C and a ring breathing of polypyrrole<sup>15</sup>, respectively. However, the intensities of those bands in the spectra of the PPy-ClO<sub>4</sub> film were much lower than those in the spectra of the PPy-CuPcTs film. This difference of Raman intensities might be caused by the difference of energy involved in the  $\pi$ - $\pi^*$  transition in those two films: 3.3 eV for PPy-ClO<sub>4</sub> and 3.1 eV for PPy-CuPcTs.<sup>20</sup> The shift of several major bands in the Raman spectrum of the PPy-CuPcTs film in NaClO<sub>4</sub> solution during the redox reaction is summarized in Table II. A change in Raman spectrum of the PPy-CuPcTs film during the oxidation of PPy is very similar to that for the PPy-NO<sub>3</sub> film electrode. The results suggest that the structural change of the PPy during the redox reaction is basically unaffected by the dopants (either inorganic anions or macrocycles).

The redox potential of PPy in the PPy-CuPcTs film electrode was obtained from Raman intensity vs. potential curve. The redox potential obtained by cyclic voltammetry and in situ Raman spectroscopy are summarized in Table I. The redox potential of the PPy-CuPcTs film in Na<sub>4</sub>CuPcTs solution by the "Raman method" (-0.54 V) is somewhat more cathodic than that by the CV method (-0.43 V). Changes in the Raman spectrum clearly indicated that the PPy in the PPy-CuPcTs film was reduced by applying the negative potential ( $E_{\text{redox}} = -0.54$  V) and was reoxidized by reversing the potential. Other than the results for the PPy-CuPcTs electrode in Na<sub>4</sub>CuPcTs solution, redox potentials obtained by the cyclic voltammetry and the "Raman method" are very close to each other. It was found that the in situ Raman technique for the determination of redox potentials of the film electrode was very useful, particularly, for an electrode such as PPy-CuPcTs, which shows more than one pair of redox currents in the CV. This technique also eliminates the complication of determining the redox potentials in the presence of large capacitive currents.

B.3. Effects of cations and anions on ion transport and the redox potentials. Because of the inability of the doped anions to move out from the PPy-CuPcTs film, balancing the charge of the film during the reduction may be accomplished by the transport of cations from the solution to the film. The stability of the reduced form of PPy-CuPcTs film electrode was examined in 1.0 mM Na<sub>4</sub>CuPcTs solution by recording Raman spectra after cutting off the applied negative (-1.0 V) potential. The intensity of the 1555 cm<sup>-1</sup> band was dropped to a level of less than 50% of the original intensity within two minutes and disappeared entirely in 12 minutes. The results suggest that the oxidized form of PPy-CuPcTs is thermodynamically much more stable than the reduced form of PPy-CuPcTs. The results also demonstrated that the sodium ions which had moved into the film during the reduction process moved out from the film as soon as the applied negative potential was cut off (there was little chance that the film was oxidized by oxygen, since the solution was deoxygenated thoroughly with the ultra high purity nitrogen gas).

In situ Raman spectra of the PPy-CuPcTs film electrodes were recorded in other solutions including 0.05 M NaClO<sub>4</sub>, 0.05 M NaNO<sub>3</sub>, and 0.01 M TBAP by using the 514.5 nm line of Ar<sup>+</sup> laser as the excitation source. The results in both NaClO<sub>4</sub> and NaNO<sub>3</sub> solutions were very similar to those recorded in Na<sub>4</sub>CuPcTs solution (see Figure 8). Redox potentials obtained by the "Raman method" in both NaClO<sub>4</sub> and NaNO<sub>3</sub> solutions were -0.49 V and -0.45 V, respectively (see Table I). However, in situ Raman spectra of the same electrode in 0.01 M TBAP was quite different from the above results; Raman intensity for the reduced form of the electrode was much lower than that recorded in either NaClO<sub>4</sub> or NaNO<sub>3</sub> solution. Figure 9 shows spectra for both the oxidized and the reduced forms of the electrode in 0.01 M TBAP (a) and those recorded in 0.05 M NaClO<sub>4</sub> solution (b). When the PPy-CuPcTs film was

reduced at -1.0 V in the TBAP solution, the intensity of the  $1555\text{ cm}^{-1}$  band was only less than 20% of the band intensity observed in the 0.05 M  $\text{NaClO}_4$  solution at the same potential. The redox potential of the PPy-CuPcTs electrode in the 0.01 M TBAP obtained by the "Raman method" was -0.37 V. The redox potential apparently shifted more than 100 mV toward the positive direction in the TBAP solution. In situ Raman spectra of the PPy- $\text{ClO}_4$  film electrode were also recorded in 0.01 M TBAP, and the results are basically identical to those recorded in the  $\text{NaClO}_4$  solution. The only difference was that the redox potential of the PPy was slightly more negative (-0.36 V) than that in the  $\text{NaClO}_4$  solution (-0.23 V) (see Table III which lists the redox potential of PPy recorded in the presence of large cations in the solution).

These results suggest that a small portion of the CuPcTs (probably less than 20%) in the PPy-CuPcTs thin film electrode is replaced by  $\text{ClO}_4^-$  during the oxidation of the film. When the reduction potential was applied, only the  $\text{ClO}_4^-$  ion in the film moved into the solution, but the CuPcTs anions were still remaining in the film. As a result, a small portion of the PPy in the film was reduced in order to balance the charge. Because the size of  $\text{TBA}^+$  is too large to be able to move into the film quickly, it does not contribute to the ion transport (not like  $\text{Na}^+$ ) during the reduction reaction. However, a slight shift of the redox potential of PPy in the TBAP solution from that in  $\text{NaClO}_4$  solution suggests that a small number of  $\text{TBA}^+$  may penetrate slowly into the film and interact with  $\text{SO}_3^-$  in the CuPcTs. The above results certainly suggest that the PPy-CuPcTs film cycled in the  $\text{NaClO}_4$  solution actually consists of both PPy-CuPcTs (over 80%) and PPy- $\text{ClO}_4$  (less than 20%), and only the PPy- $\text{ClO}_4$  portion of the film electrode is reduced by the application of

the negative potential in the TBAP solution. The redox potential of the PPy-CuPcTs film electrode (-0.37 V) in TBAP is basically the same as that of the PPy-ClO<sub>4</sub> film electrode (-0.36 V) in the same medium (see Table III).

The redox potentials of the PPy-CuPcTs film electrodes are 160-260 mV more negative than those of PPy film electrodes doped with inorganic anions (see Table I). Formation of the complex between PPy and CuPcTs in the film could certainly affect the redox reaction of the PPy-CuPcTs due to the presence of four sulfonated groups. Those negative charges in the complex would contribute to moving the redox potential of the PPy-CuPcTs to the more negative potential. On the other hand, the redox potential of the PPy-CuPcTs film electrode was shifted toward the positive direction by the addition of large cations in the solution (see Table III). It is very likely that cations, particularly MV<sup>2+</sup>, interact with SO<sub>3</sub><sup>-</sup> in the PPy-CuPcTs film and help the redox potential move to more positive value.

**B.4. Redox reaction of doped species (CuPcTs).** In the cyclic voltammetric studies of the PPy-CuPcTs film electrode, the presence of cathodic and anodic currents for the redox reaction of CuPcTs has been described (see Figure 6(a).  $E_{pc} = -0.92$  V and  $E_{pa} = -0.62$  V). In situ UV-visible spectra of a PPy-CuPcTs film electrode which are shown in Figure 5 certainly support the conclusion derived from electrochemical data. There were three absorption bands at 336, 630, and 677 nm at 0.0 V where PPy was oxidized and CuPcTs existed as a neutral form. When only the PPy was reduced at -0.8 V, a new shoulder appeared around 400 nm, which was due to the neutral form of PPy. The observed three bands, which are due to the neutral CuPcTs, remained at -0.80 V. However, the absorption at both 630 and 684 nm (shifted from 677 nm) bands decreased because of the decreased background which was due to the reduction of PPy. When the electrode was further reduced at -1.2 V,

three bands at 336, 630, and 684 nm almost disappeared, and a couple of new peaks appeared at 400 nm and 586 nm. The results suggest the formation of the reduced CuPcTs in the film at -1.2 V. It is interesting to note that the band at 400 nm which is due to the neutral form of PPy in the PPy-CuPcTs film is red-shifted approximately 30 nm compared with the band (372 nm) observed from the PPy-ClO<sub>4</sub> film at the same potential (see the inset of Figure 5).

In situ Raman spectrum of a PPy-CuPcTs film electrode which was recorded in 0.05 M NaClO<sub>4</sub> solution using Kr<sup>+</sup> laser (647.1 nm) as the excitation source showed resonance Raman bands mainly from CuPcTs that include 503, 594, 689, 747, 1358, and 1559 cm<sup>-1</sup>. The intensity of the bands decreased to a very low level when the PPy-CuPcTs film was reduced at -1.1 V. The change of the Raman spectrum which was recorded in 1200-1700 cm<sup>-1</sup> region during the redox reaction of the PPy-CuPcTs film is shown in Figure 10. This change may be related to the reduction of CuPcTs, which is most likely the reduction of ligand portion of the molecule.<sup>21</sup>

**B.5. Effects of film thickness.** Concentration of the CuPcTs in the PPy-CuPcTs films ranging from 200-5000 Å was determined by absorption spectroscopy (absorbance at the 630 nm band was used). The mole fraction of CuPcTs was the highest (0.075) in 200 Å film and the lowest (0.013) in 5000 Å film, as shown in Table IV. A similar decrease in concentration with increased film thickness for polypyrrole thin films doped with tetrasulfonated cobalt phthalocyanine has been reported.<sup>6(b)</sup> Considering that approximately 12-16 pyrrole monomers are attracted to 4 sulfonated groups<sup>22</sup> in a CuPcTs molecule, the mole fraction of CuPcTs in the PPy-CuPcTs film should be in 0.077-0.059 range. As a result of this consideration, one realizes that the PPy may not be totally oxidized in thicker films which are just prepared by the electrochemical oxidation of pyrrole monomers. It is conceivable in our

experiment that the neutral PPy in the electropolymerized PPy-CuPcTs film was oxidized quickly to form a polypyrrole oxide (PPy-O) when it was exposed to the air immediately after the preparation of the film.<sup>4(a)</sup>

For cyclic voltammetric experiments, electrodes with three different thicknesses<sup>23</sup> (200, 1000, and 5000 Å) were chosen. Cyclic voltammograms of 1000 Å film in 0.05 M NaClO<sub>4</sub> solution have already been shown in Figure 6. In the CV the peak currents for the PPy redox reactions were much higher than those for the CuPcTs. However, the CV of a 200 Å film electrode showed that the current levels for the redox reactions of both PPy and CuPcTs were comparable to each other because of the higher mole fraction value of CuPcTs in the 200 Å film electrode. The CV for a 5000 Å film showed both cathodic and anodic peak currents for the redox reaction of PPy. On the other hand, no peak current was observed for the redox reaction of CuPcTs. The CV's for all three electrodes in the NaClO<sub>4</sub> solution with MVCl<sub>2</sub> showed both cathodic and anodic peak currents for the methyl viologen redox reactions.

Both UV-visible and Raman spectroscopic data for those three film electrodes are consistent with the electrochemical observations. In situ UV-visible spectra for the 200 Å film showed basically the same spectral changes as those observed for the 1000 Å film (see Figure 5) when the potential was stepped from 0.0 V to -0.8 V, then to -1.2 V. In comparison, the CuPcTs in the 5000 Å film was not reduced by stepping the potential to -1.2 V since the three absorption bands (336, 630 and 684 nm) which are characteristic of the neutral CuPcTs remained the same at -1.2 V. In situ Raman spectra (1200-1700 cm<sup>-1</sup> region) of the 200 Å film by using 647.1 nm excitation source showed that the intensity of the major bands including 1358 and 1559 cm<sup>-1</sup> disappeared almost entirely at -1.0 V which indicates almost

complete reduction of the CuPcTs.<sup>24</sup> Intensity of those bands in the spectrum for the 5000 Å film remained the same when the potential was stepped to -1.2 V.

The charge transfer reaction of CuPcTs in the 5000 Å film may be blocked by the formation of some unknown species near the CuPcTs. These species could be generated after the Na<sup>+</sup> ions moved into the film during the reduction of PPy oxide (PPy-O). Another possible explanation for the absence of the redox reaction of CuPcTs in the 5000 Å film is that the film structure with a high mole fraction of PPy, particularly near the film surface, does not favor the charge transport around the CuPcTs molecules.

In summary, (1) concentration of CuPcTs was found to be high in the thinner film and low in the thicker film, (2) PPy-CuPcTs films ranging from 200 Å to 5000 Å were electrochemically conducting in the negative potential range (PPy exists as a neutral form), (3) the PPy in all three films, ranging from 200 to 5000 Å, was fully reduced by the application of negative potential at -0.8 V, and (4) CuPcTs was reduced at -1.2 V in the thinner films (200 and 1000 Å), but was not reduced in the thicker film (5000 Å) by applying the same potential.

**B.6. Effects of methyl viologen.** It has already been described that there are sharp and high currents (mostly anodic) in the CV's of the PPy-CuPcTs thin film electrodes in the presence of MVCl<sub>2</sub> in both NaClO<sub>4</sub> and NaNO<sub>3</sub> solutions (see Figure 6(b) and 7(b)). The CV of the PPy-CuPcTs film electrode in the 0.05 M NaClO<sub>4</sub> solution containing 0.005 M MV<sup>2+</sup> showed a six times larger amount of charge for the anodic peak at -0.02 V (10 mV/s scan rate) than that in the solution without MV<sup>2+</sup>. In situ Raman spectra of the PPy-CuPcTs film electrode were recorded in the 0.05 M NaClO<sub>4</sub> and 0.005 M MVCl<sub>2</sub> solution. Measurements were made in 1100-1700 cm<sup>-1</sup> region starting at -1.2 V.



As shown in Figure 11, there were initially two significant bands at 1530 and 1551  $\text{cm}^{-1}$  when recorded at -1.2 V, but the 1551  $\text{cm}^{-1}$  band which is due to the C=C symmetric stretching vibration of PPy disappeared at -1.0 V. The 1551  $\text{cm}^{-1}$  band reappeared at -0.5 V, but its intensity gradually decreased when the PPy was oxidized by stepping the potential to more positive potentials. The intensity change of the 1551  $\text{cm}^{-1}$  band with potentials ranging from -1.2 V to +0.4 V for both forward and reversed directions is shown in Figure 12. The formation of film substances on the surface of the PPy-CuPcTs thin film electrode at more cathodic potentials than -0.6 V was responsible for the drop of the 1551  $\text{cm}^{-1}$  band intensity. The appearance of the band at 1530  $\text{cm}^{-1}$  in the same potential range also suggests the formation of film substance on the PPy-CuPcTs electrode surface. These results indicated the charge transfer reaction of  $\text{MV}^{2+}$  to  $\text{MV}^+$ , which was followed by the formation of  $\text{MVClO}_4$  film, took place at the surface of the PPy-CuPcTs film electrode.

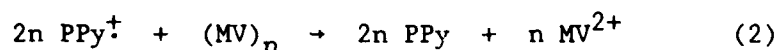
In order to further investigate the nature of the film formed on the PPy-CuPcTs electrode, *in situ* Raman spectra were recorded in the same solution at a thin film gold electrode. As seen in Figure 13 ((a) 600-1200  $\text{cm}^{-1}$ , (b) 1100-1700  $\text{cm}^{-1}$ ), several strong bands including 1025, 1358, and 1534  $\text{cm}^{-1}$  appeared at -0.665 V. A strong, new band appeared at 992  $\text{cm}^{-1}$  when the potential was further moved to -1.2 V. The potential was reversed at -1.2 V, and the band at 992  $\text{cm}^{-1}$  disappeared when the potential was stepped to -0.9 V. The gold electrode surface which had no deposit at the positive potential became brown when the potential was set at  $\sim$ -0.6 V, and it became colorless at more negative potentials than -1.0 V. Raman spectrum recorded at the gold electrode in the same solution at -0.72 V showed several broad, low intensity bands in 690-920  $\text{cm}^{-1}$  region. Those bands might suggest the formation of polymeric film of methyl viologen in the negative potential range. The above

observations indicate that at least two different films (possibly three) may be formed on the gold electrode in the  $\text{NaClO}_4$  solution with  $\text{MVCl}_2$  at the negative potentials: The first film formed at  $-0.665$  V was  $\text{MVClO}_4$ , and the second film formed at  $-1.2$  V was  $\text{MV}^\circ$ . The third film, methyl viologen polymers (PMV), might be formed after the production of  $\text{MV}^\dagger$  in the negative potential range. One would also notice the possible formation of PMV in the cyclic voltammogram which was recorded at the gold electrode in the  $0.05$  M  $\text{NaClO}_4$  and  $0.005$  M  $\text{MVCl}_2$  solution (Figure 1(c)). An anodic current observed at  $-0.6$  V was likely due to the oxidation of  $\text{MV}^\dagger$  to  $\text{MV}^{2+}$ ; a portion of the current may be due to the oxidation of  $\text{MVClO}_4$  to  $\text{MV}^{2+}$ . There was also a low anodic current which remained in the entire potential range until  $0.4$  V. This may reflect the slow oxidation of the PMV (or  $\text{MVClO}_4$ ) in this potential range. Several Raman bands, including those at  $1358$  and  $1534$   $\text{cm}^{-1}$ , remained even at  $+0.6$  V. However, they were not seen when the spectrum was recorded after washing the electrode with distilled water (Figure 13(b)). Formation of a polymeric form of methyl viologen has previously been reported by Landrum, *et al.* at gold minigrad electrodes.<sup>25</sup>

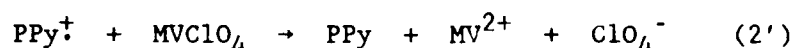
Raman spectra at the gold electrode in the  $0.05$  M  $\text{NaNO}_3$  and  $0.005$  M  $\text{MVCl}_2$  solution were similar to those in the  $\text{NaClO}_4$  and  $\text{MVCl}_2$  solution. However, no broad bands were seen in the  $690$ - $920$   $\text{cm}^{-1}$  region at  $-0.72$  V. The intensity of the  $992$   $\text{cm}^{-1}$  band, which is due to the  $\text{MV}^\circ$ , was not as strong as that recorded in the  $\text{NaClO}_4$  and  $\text{MVCl}_2$  solution. The color at the gold electrode surface in the  $\text{NaNO}_3$  and  $\text{MVCl}_2$  solution was rather purple than brown in the  $-0.6$  V to  $-1.0$  V range. A part of the purple colored substance ( $\text{MV}^\dagger$ ) which was generated at the electrode surface at  $-0.665$  V diffused into the bulk of the solution instead of forming  $\text{MVNO}_3$  film. These results indicated that the solubility of  $\text{MVNO}_3$  was much higher than that of  $\text{MVClO}_4$  which seemed to remain

on the electrode surface as a film. Raman spectra of  $MV^{2+}$ ,  $MV^{\dagger}$ , and  $MV^{\circ}$  at a silver electrode have been reported.<sup>26</sup> The observed Raman spectra of both  $MVC10_4$  and  $MVNO_3$  are similar to the reported spectrum of  $MV^{\dagger}$  in the solution rather than that of  $MV^{\dagger}$  adsorbed on the silver electrode.

The sharp anodic current (at -0.0 V) which was observed in the CV of the PPy-CuPcTs film electrode in the  $NaClO_4$  and  $MVCl_2$  solution (see Figure 6(b)) may be interpreted as the catalytic oxidation of polymerized methyl viologen (or  $MVC10_4$ ) film by the oxidized form of PPy. The catalytic oxidation may be explained by the following reactions:



or



The reactions will be completed when both the PPy in the PPy-CuPcTs and the PMV (or  $MVC10_4$ ) on the PPy-CuPcTs film electrode are totally oxidized.

The electrochemical behavior of the PPy-CuPcTs film electrode in the 0.05 M  $NaNO_3$  and 0.005 M  $MVCl_2$  solution seems more complicated than that in the perchlorate solution. A sharp anodic current at -0.6 V (1 in Figure 7(b)) is due to the oxidation of  $MVNO_3$  on the PPy-CuPcTs film because the current-scan rate relationship is almost linear. Another sharp anodic current (2 in the same figure) is due to the oxidation of  $MV^{\dagger}$  to  $MV^{2+}$  in the solution because it shows nearly a linear relationship between the peak current and the square root of the scan rate. The anodic current at -0.10 V (4 in the same figure) is primarily due to the oxidation of the PPy itself in the PPy-CuPcTs film. However, the total charge for the peak current is almost twice as large as

that observed in the  $\text{NaNO}_3$  solution without  $\text{MVCl}_2$ . A portion of the current may be due to the catalytic oxidation of PMV (or  $\text{MVNO}_3$ ). A much thinner PMV film (or  $\text{MVNO}_3$ ) must be formed on the PPy-CuPcTs film during the reduction of  $\text{MV}^{2+}$  to  $\text{MV}^+$  in the  $\text{NaNO}_3$  and  $\text{MVCl}_2$  solution than that formed in the  $\text{NaClO}_4$  and  $\text{MVCl}_2$  solution. The origin of the anodic current (3) is not certain, but it could be the oxidation of the PPy which does not form a complex with the CuPcTs in the film.

Although it is not certain whether the polymeric methyl viologen or a methyl viologen salt (such as  $\text{MVClO}_4$  and  $\text{MVNO}_3$ ) is responsible for the observed catalytic current, above results certainly indicate that the solubility of methyl viologen salts ( $\text{MV}^+\text{X}^-$ ) formed in different electrolytes plays an important role for the unusual electrochemical behavior at the PPy-CuPcTs film electrode. Since the solubility of  $\text{MVNO}_3$  is much higher than that of  $\text{MVClO}_4$ , the catalytic current was much smaller in the  $\text{NaNO}_3$  solution than that in the  $\text{NaClO}_4$  solution. The solubility of methyl viologen salts must be important for the polymer formation, if the PMV film is responsible for the catalytic current.

**B.7. Conducting nature of PPy-CuPcTs thin film.** Cyclic voltammetric experiments (see section B.1) showed that the PPy-CuPcTs thin film electrode is electrochemically conducting in both positive and negative potential ranges between +0.4 V to -1.2 V. Both in situ Raman and in situ UV-visible spectroscopies (see sections B.2. and B.5.) indicated that the polypyrrole cations were reduced to the neutral form of PPy in the negative potential range ( $E_{\text{redox}}$  of  $\text{PPy}^+/\text{PPy}^\circ$  is -0.54 V). The observed electrochemical behaviors could be explained by (1) ionic conductivity, (2) porous nature (pinholes and channels), and/or (3) the electronic conductivity of the PPy-CuPcTs film electrode. One expects that the PPy-CuPcTs thin film has a

reasonably high ionic conductivity (small cations can move through the film easily) in the negative potential range because the PPy-CuPCTs film probably behaves as a cation exchange membrane<sup>27</sup>. On the other hand, the PPy-CuPcTs film electrode appears to be structurally more rigid than the PPy doped with inorganic anions, and it is unlikely that the porous nature of the film contributes significantly to the observed electrochemical activities at the PPy-CuPcTs film electrode. If the ionic conductivity must play the major role for the observed redox reaction of methyl viologen at the electrode, the charge transfer reaction of methyl viologen must take place on the surface of the gold substrate. However, our Raman spectroscopic investigations of the PPy-CuPCTs film electrode in the presence of  $MVCl_2$  (see B.6) indicated that the redox reaction of  $MV^{2+}/MV^{\dagger}$  pair took place at the surface of the film electrode instead of at the surface of the gold underlayer. These results strongly suggest that the reduced PPy-CuPcTs thin film has a characteristic of electronic conductor, even though the majority of the PPy exists as a neutral form.

If the electronic conductivity instead of the ionic conductivity of the reduced PPy-CuPcTs film mainly contributes to the observed electrochemical activities, one cannot rely on the polaron theory for explaining the above results because the concentration of the PPy cations must be negligible in the negative potential range where the PPy cations can be reduced to a neutral form of PPy. It has been suggested that the structure of PPy may resemble the ring structure of phthalocyanine.<sup>2(c)</sup> It is conceivable that each ring structure consists of 12-16 pyrrole rings. During the polymer formation process, oxidized forms of 3-4 pyrrole rings could be attracted by each sulfonated group in the CuPcTs. Stacked forms of the CuPcTs and the polypyrrole rings could be formed. This arrangement could lead to the

possibility of electron delocalization by the  $\pi$ - $\pi$  overlap of the macrocycles and the polypyrrole rings<sup>21</sup> which would establish a conduction pathway. A high degree of crystallinity for PPy-CoPcTs film has been confirmed by X-ray diffraction studies by Rosenthal, *et al.*<sup>6(b)</sup> The proposed stacked form structure would provide a high degree of crystallinity for the PPy-CuPcTs film. It is interesting to note that the PPy-CuPcTs thin films show conductivity whether the PPy exists as an oxidized form or a neutral form. This suggests that doped anions may play a major role in order to decide if the PPy film is conductive.

There are still a few unknown factors which might contribute to the observed conductivity of the PPy-CuPcTs thin film electrode when the PPy is in a neutral form. The role of cations, such as  $MV^{2+}$  and  $Na^+$ , for the conductive nature of the film is not known at this stage. Also unknown is the behavior of the PPy-O during the reduction reaction of the PPy-CuPcTs film, but it is quite unlikely that the PPy-O would play the major role for the conductive nature of the PPy-CuPcTs electrode. Although the high oxygen content in the PPy film doped with inorganic anions has been reported,<sup>28</sup> this type of PPy film behaves as an insulator when it is reduced.

#### Acknowledgment

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19. The  $\text{Na}_4\text{CuPcTs}$  solution has a very high extinction coefficient in the broad spectral range and the minimum absorbance was observed at near 488 nm. The concentration of the  $\text{Na}_4\text{CuPcTs}$  solution (1.0 mM) used in this experiment was almost the threshold that one can carry out the above experiment with our cell which has a gap of -2 mm between the window and the electrode surface. The cyclic voltammogram recorded in the same solution at the scan rate of 10 mV/s showed  $E_{\text{pa}} = -0.25\text{ V}$ ,  $E_{\text{pc}} = -0.61\text{ V}$  ( $E_{\text{redox}} = -0.43\text{ V}$ ).
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Table I. The redox potentials of PPY based upon cyclic voltammetric and in situ Raman spectroscopic data

| Electrode/Electrolyte                           | Cyclic voltammetry <sup>a</sup> |               |                    | Raman method <sup>b</sup> |                  |                    |
|---|---------------------------------|---------------|--------------------|---------------------------|------------------|--------------------|
|   | $E_{pa}$ (V)                    | $E_{pc1}$ (V) | $E_{redox}$ (V)    | $E_{1/2}(F)$ (V)          | $E_{1/2}(R)$ (V) | $E_{1/2}(Ave)$ (V) |
| PPY-ClO <sub>4</sub> /0.05 M NaClO <sub>4</sub> | -0.02                           | -0.13         | -0.08 <sup>c</sup> | -0.09                     | -0.36            | -0.23              |
| PPY-NO <sub>3</sub> /0.05 M NaNO <sub>3</sub>   | -0.02                           | -0.08         | -0.05 <sup>d</sup> | -0.24                     | -0.33            | -0.29              |
| PPY-CuPcTs/0.001 M Na <sub>4</sub> CuPcTs       | -0.25                           | -0.61         | -0.43              | -0.48                     | -0.60            | -0.54              |
| PPY-CuPcTs/0.05 M Na <sub>4</sub> CuPcTs        | -0.30                           | -0.48         | -0.39              |                           |                  |                    |
| PPY-CuPcTs/0.05 M NaClO <sub>4</sub>            | -0.33                           | -0.53         | -0.43              | -0.45                     | -0.52            | -0.49              |
| PPY-CuPcTs/0.05 M NaNO <sub>3</sub>             | -0.34                           | -0.49         | -0.42              | -0.44                     | -0.46            | -0.45              |

a:  $E_{redox}$  was obtained by averaging the anodic and cathodic peak potentials. The scan rate was 50 mV/s.

b:  $E_{1/2}$ , the potential at a half Raman intensity, was obtained from the relative Raman intensity vs. potential curve. F and R denote the forward and reverse directions, respectively.  $E_{1/2}(Ave)$  was obtained by averaging the  $E_{1/2}(F)$  and  $E_{1/2}(R)$ .

c:  $E_{redox}$  using  $E_{pc2}$  is -0.22 V

d:  $E_{redox}$  using  $E_{pc2}$  is -0.22 V

Table II. Shifts of major band positions ( $\text{cm}^{-1}$ ) in the Raman spectra of PPy during the redox reactions.  $\lambda_{\text{exc}} = 514.5 \text{ nm}$ .

| 1000 Å PPy-NO <sub>3</sub> film in 0.05 NaNO <sub>3</sub> |                   | 1000 Å PPy-CuPcTs film in 0.005 M NaClO <sub>4</sub> |                   |
|---|-------------------|--|-------------------|
| Neutral (-1.0 V),   | Oxidized (+0.4 V) | Neutral (-1.2 V),                                    | Oxidized (+0.2 V) |
|   | 923 (W)           |  | 924 (W)           |
|   |                   | 996 (W)  |                   |
| 1043 (S)  | 1050 (W)          | 1043 (S)   | 1053 (W)          |
| 1320 (M)  | 1335 (M)          | 1316 (M)   | 1329 (M)          |
|   |                   |  | 1359 (M)          |
|   | 1424 (W)          |  | 1432 (W)          |
| 1568 (VS)   | 1601 (M)          | 1559 (VS)  | 1591 (M)          |

Table III. Effects of large cations on the redox potential of PPy

| Electrode/Electrolyte   | $E_{\text{redox}}$ (V) | $\Delta E$ (mV) <sup>b</sup> |
|---|------------------------|------------------------------|
| PPy-CuPcTs/0.001 M Na <sub>4</sub> CuPcTs                               | -0.54 <sup>a</sup>     |                              |
| PPy-CuPcTs/0.05 M Na <sub>4</sub> CuPcTs<br>+ 0.005 M MVC1 <sub>2</sub> | -0.27                  | 270                          |
| PPy-CuPcTs/0.05 M NaClO <sub>4</sub>                                    | -0.43                  |                              |
| PPy-CuPcTs/0.05 M NaClO <sub>4</sub><br>+ 0.005 M MVC1 <sub>2</sub>     | -0.11                  | 320                          |
| PPy-CuPcTs/0.05 M NaNO <sub>3</sub>                                     | -0.42                  |                              |
| PPy-CuPcTs/0.05 M NaNO <sub>2</sub><br>+ 0.005 M MVC1 <sub>2</sub>      | -0.20                  | 220                          |
| PPy-CuPcTs/0.01 M TBAP  | -0.37 <sup>a</sup>     | 60 <sup>c</sup>              |
| PPy-ClO <sub>4</sub> /0.05 M NaClO <sub>4</sub>                         | -0.23 <sup>a</sup>     |                              |
| PPy-ClO <sub>4</sub> /0.01 M TBAP                                       | -0.36                  |                              |

a:  $E_{1/2}$ (Ave) by Raman method

b:  $\Delta E$  is the potential shift caused by the addition of a large cation

c: This  $\Delta E$  value (60 mV) was obtained with respect to the  $E_{\text{redox}}$  value (-0.43 V) of PPy-CuPcTs/0.005 M NaClO<sub>4</sub>

Table IV. Effects of film thickness on the mole fraction of CuPcTs in the PPy-CuPcTs films.

| film thickness ( $\text{\AA}$ ) | 200   | 300   | 500   | 800   | 1000  | 2000  | 5000  |
|---------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Mole fraction of CuPcTs         | 0.075 | 0.058 | 0.034 | 0.034 | 0.039 | 0.024 | 0.013 |

## FIGURE CAPTIONS

- Figure 1. Cyclic voltammograms at: (a) PPy-ClO<sub>4</sub> film electrode (1000 Å) in 0.05 M NaClO<sub>4</sub>, (b) the same electrode in 0.05 M NaClO<sub>4</sub> and 0.005 M MVCl<sub>2</sub>, (c) thin film gold electrode in 0.05 M NaClO<sub>4</sub> and 0.005 M MVCl<sub>2</sub> and in 0.05 M NaClO<sub>4</sub> (dotted curve).
- Figure 2. Cyclic voltammograms at: (a) PPy-NO<sub>3</sub> film electrode (1000 Å) in 0.05 M NaNO<sub>3</sub>, (b) the same electrode in 0.05 M NaNO<sub>3</sub> and 0.005 M MVCl<sub>2</sub>, (c) thin film gold electrode in 0.05 M NaNO<sub>3</sub> and 0.005 M MVCl<sub>2</sub>.
- Figure 3. In situ Raman spectra of a PPy-ClO<sub>4</sub> film electrode (1000 Å) in 0.05 M NaClO<sub>4</sub> at different potentials for: (a) 600-1200 cm<sup>-1</sup> range, (b) 1100-1700 cm<sup>-1</sup> range.  $\lambda_{\text{exc}} = 514.5 \text{ nm}$ .
- Figure 4. Relative Raman intensity of 1556 cm<sup>-1</sup> band vs. potential. Spectra recorded for a 1000 Å PPy-ClO<sub>4</sub> film in the 0.05 M NaClO<sub>4</sub> solution were used to calculate relative intensity values.
- Figure 5. In situ UV-visible absorption spectra of a PPy-CuPcTs film electrode (1000 Å) in the 0.05 M NaClO<sub>4</sub> aqueous solution at 0.0, -0.8, and -1.2 V. The inset shows absorption spectra of a PPy-ClO<sub>4</sub> film electrode (1000 Å) in the same solution at 0.2 and -1.2 V.
- Figure 6. Cyclic voltammograms at a PPy-CuPcTs film electrode (1000 Å) in: (a) 0.05 M NaClO<sub>4</sub>, (b) 0.05 M NaClO<sub>4</sub> and 0.005 M MVCl<sub>2</sub>.
- Figure 7. Cyclic voltammograms at a PPy-CuPcTs film electrode (1000 Å) in: (a) 0.05 M NaNO<sub>3</sub>, (b) 0.05 M NaNO<sub>3</sub> and 0.005 MVCl<sub>2</sub>.

- Figure 8. In situ Raman spectra of a PPy-CuPcTs film electrode (1000 Å) in 0.001 M Na<sub>4</sub>CuPcTs at different potentials for: (a) 550-1250 cm<sup>-1</sup> range, (b) 1100-1700 cm<sup>-1</sup> range.  $\lambda_{\text{exc}} = 488 \text{ nm}$ .
- Figure 9. In situ Raman spectra of a PPy-CuPcTs film electrode (1000 Å) at both -1.0 and 0.4 V vs. SCE in: (a) 0.01 M TBAP, (b) 0.05 M NaClO<sub>4</sub>.  $\lambda_{\text{exc}} = 514.5 \text{ nm}$ .
- Figure 10. In situ Raman spectra of a PPy-CuPcTs film electrode (1000 Å) in 0.05 M NaClO<sub>4</sub> at no applied potential (NAP), -1.1 and -0.6 V vs. SCE.  $\lambda_{\text{exc}} = 647.1 \text{ nm}$ .
- Figure 11. In situ Raman spectra of a PPy-CuPcTs film electrode (1000 Å) in the 0.05 M NaClO<sub>4</sub> and 0.005 M MVCl<sub>2</sub> solution at different potentials.  $\lambda_{\text{exc}} = 514.5 \text{ nm}$ .
- Figure 12. Relative Raman intensity of 1551 cm<sup>-1</sup> band vs. potential, for the PPy-CuPcTs film electrode (1000 Å) in the 0.05 M NaClO<sub>4</sub> and 0.005 MVCl<sub>2</sub> solution.  $\lambda_{\text{exc}} = 514.5 \text{ nm}$ .
- Figure 13. In situ Raman spectra at a thin film gold electrode in 0.05 M NaClO<sub>4</sub> and 0.005 MVCl<sub>2</sub> at: (a) 0.4, -0.665, -1.2, -0.9, -0.2, and 0.4 V vs. SCE for 600-1200 cm<sup>-1</sup> range, (b) at 0.4, -0.665, -0.9, -0.2, and 0.6 V vs. SCE, and after washing the electrode, for 1100-1700 cm<sup>-1</sup> range.  $\lambda_{\text{exc}} = 514.5 \text{ nm}$ .



Figure 1

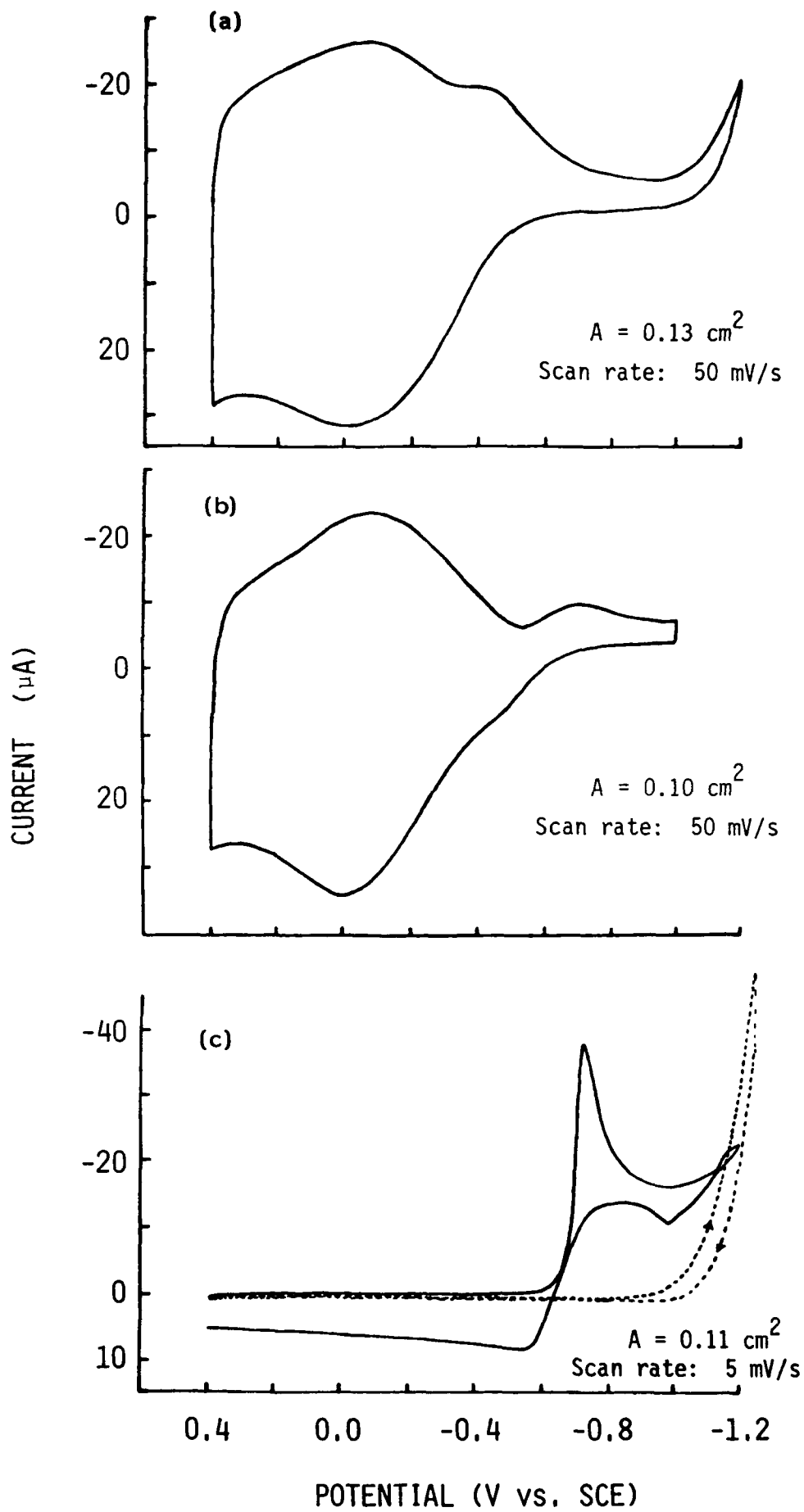


Figure 2

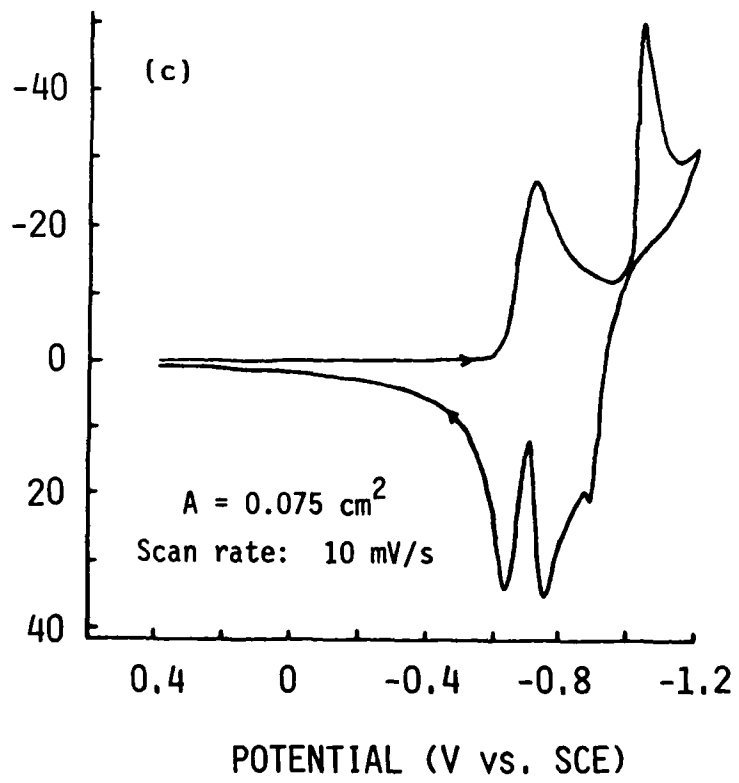
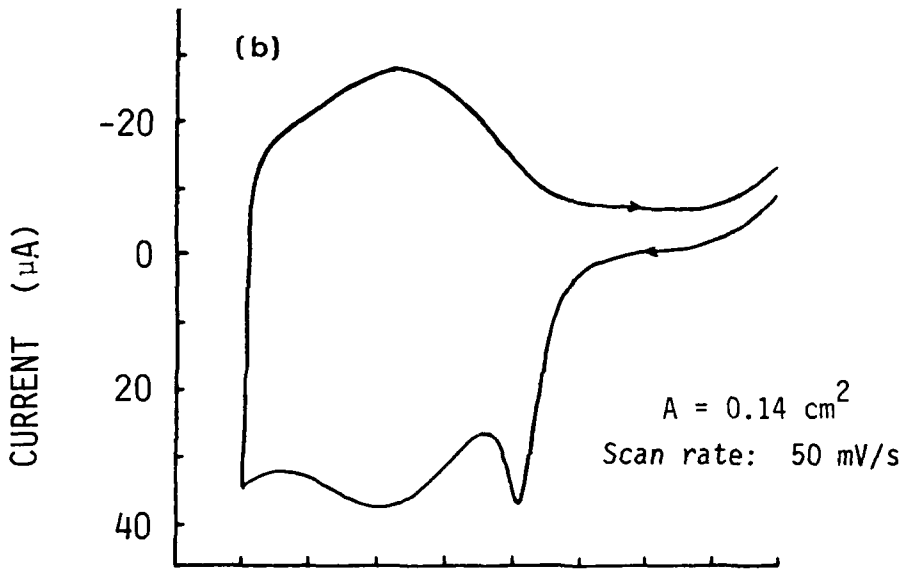
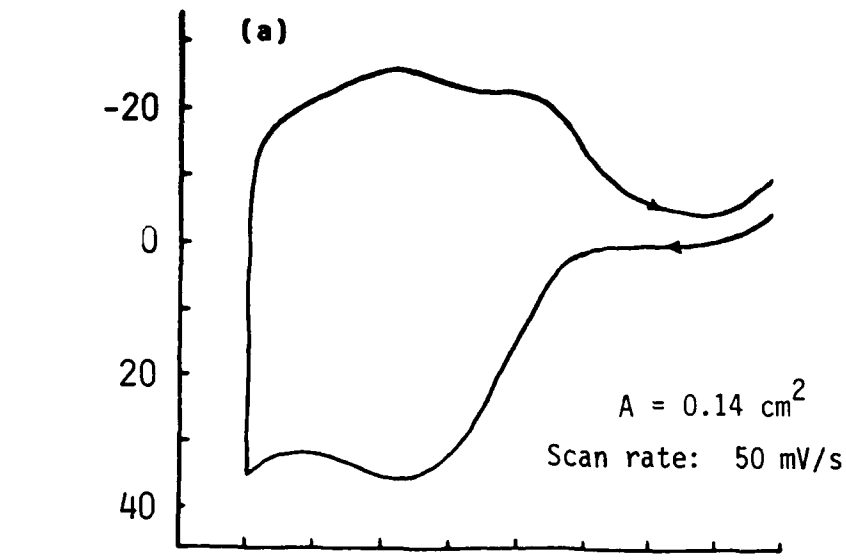


Figure 2

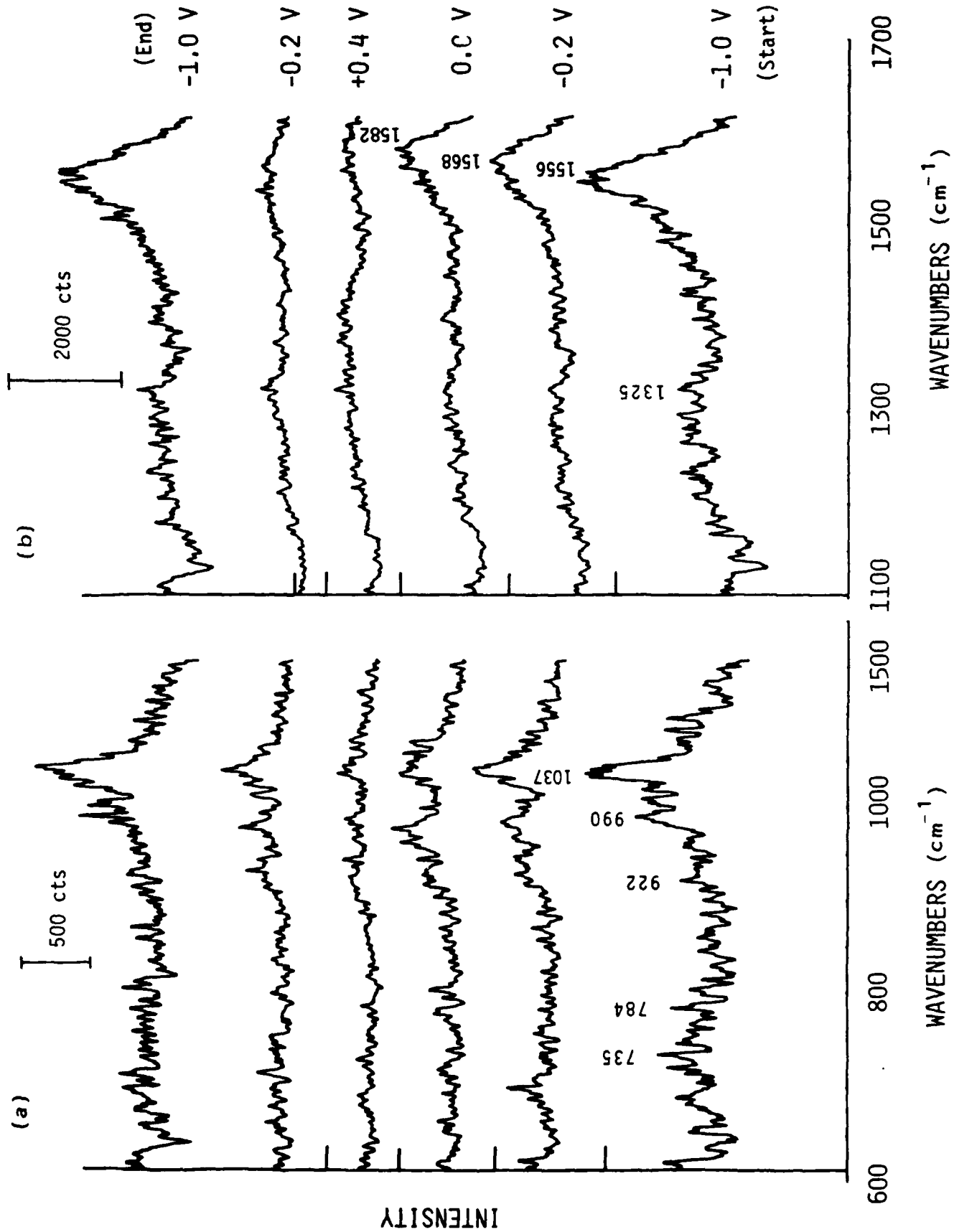


Figure 4

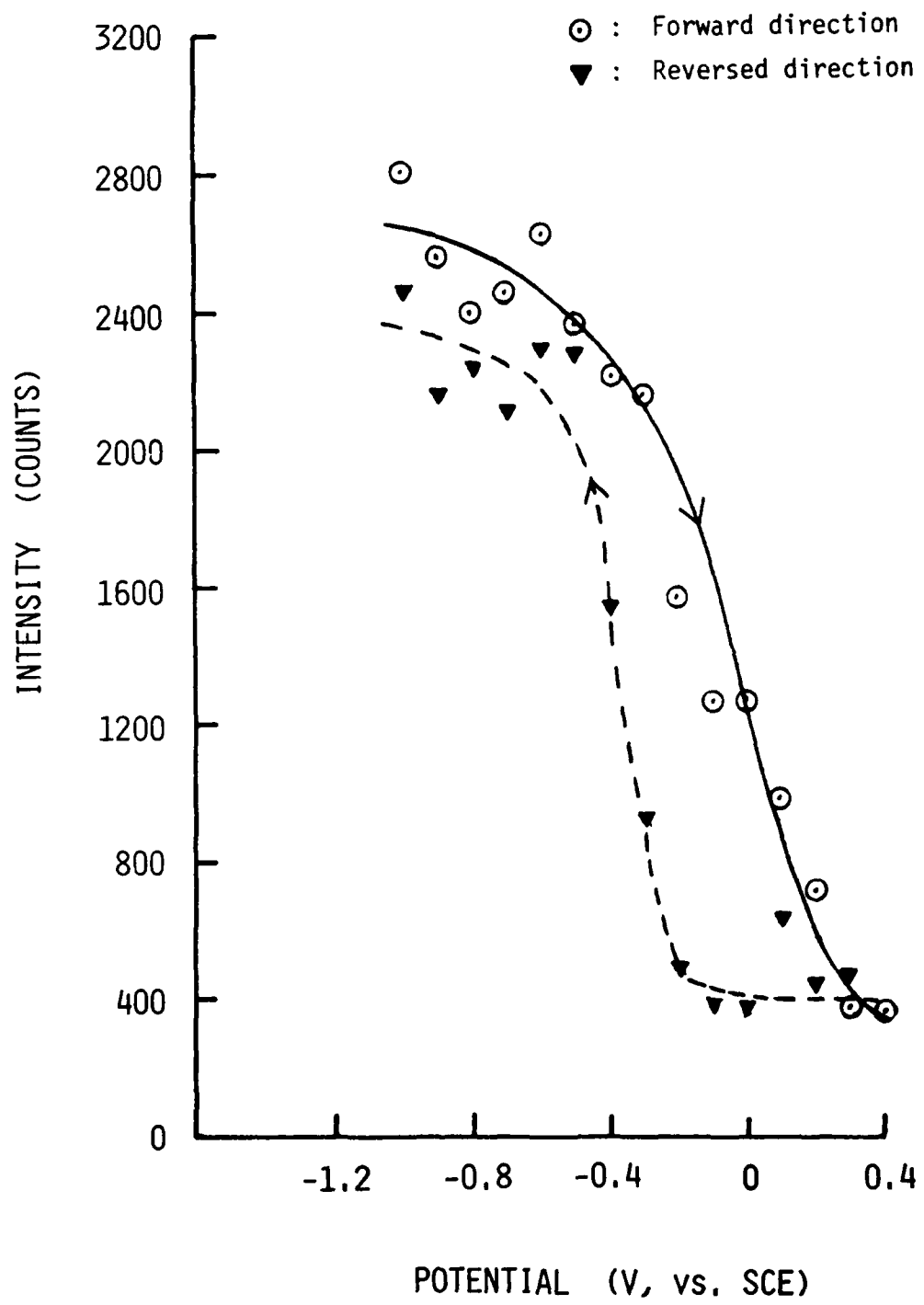


Figure 5

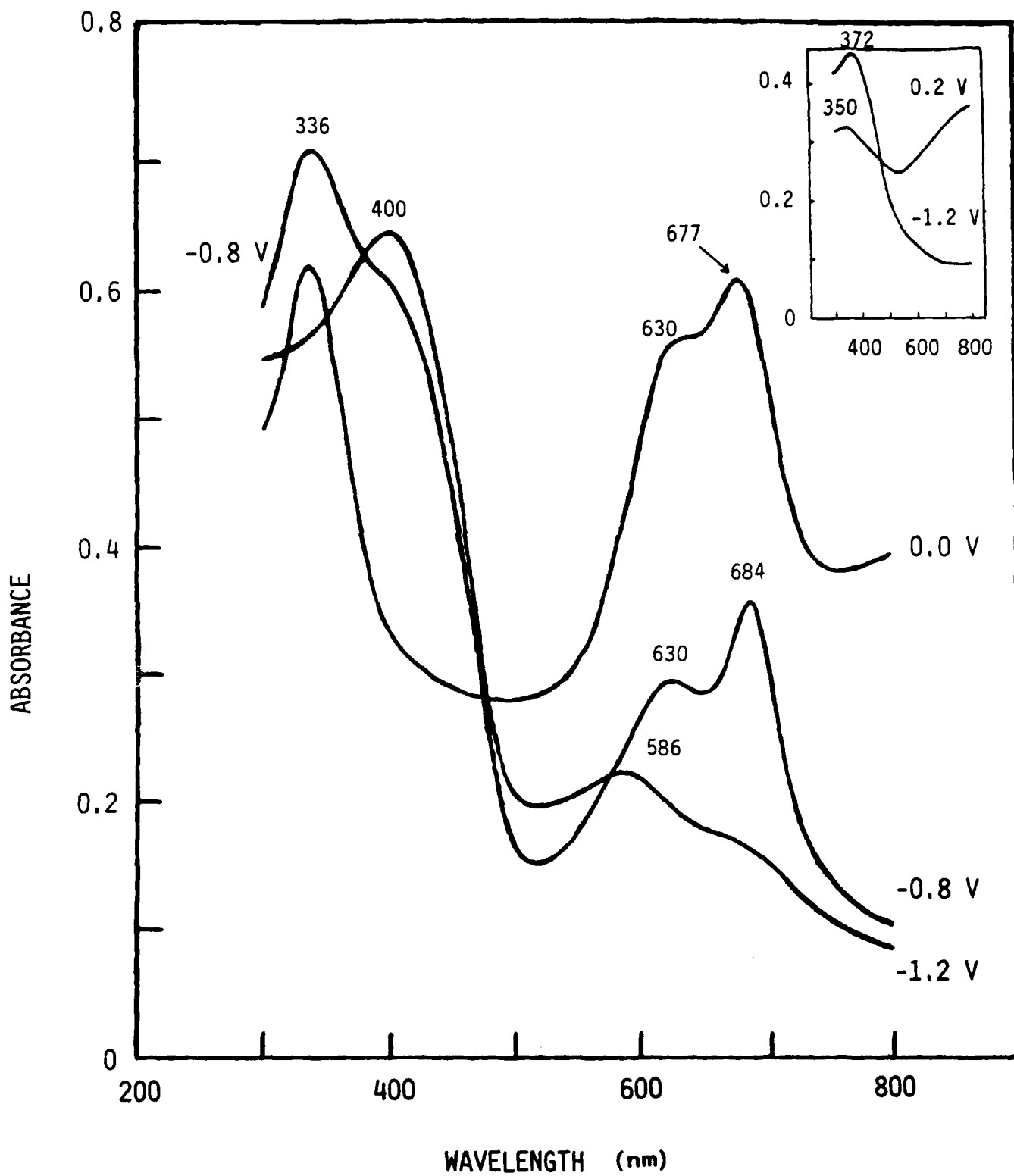


Figure 6(a)

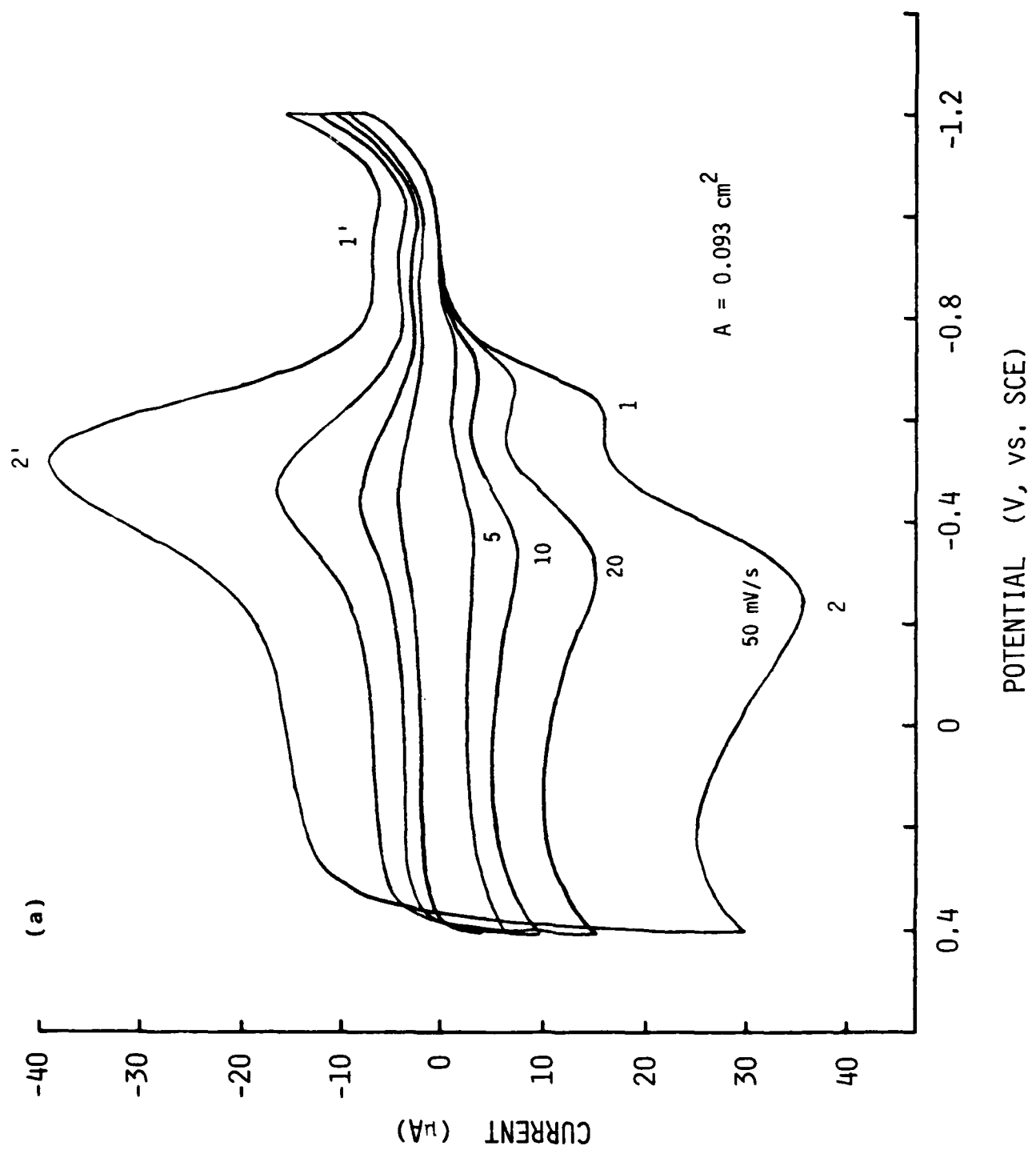


Figure 6(b)

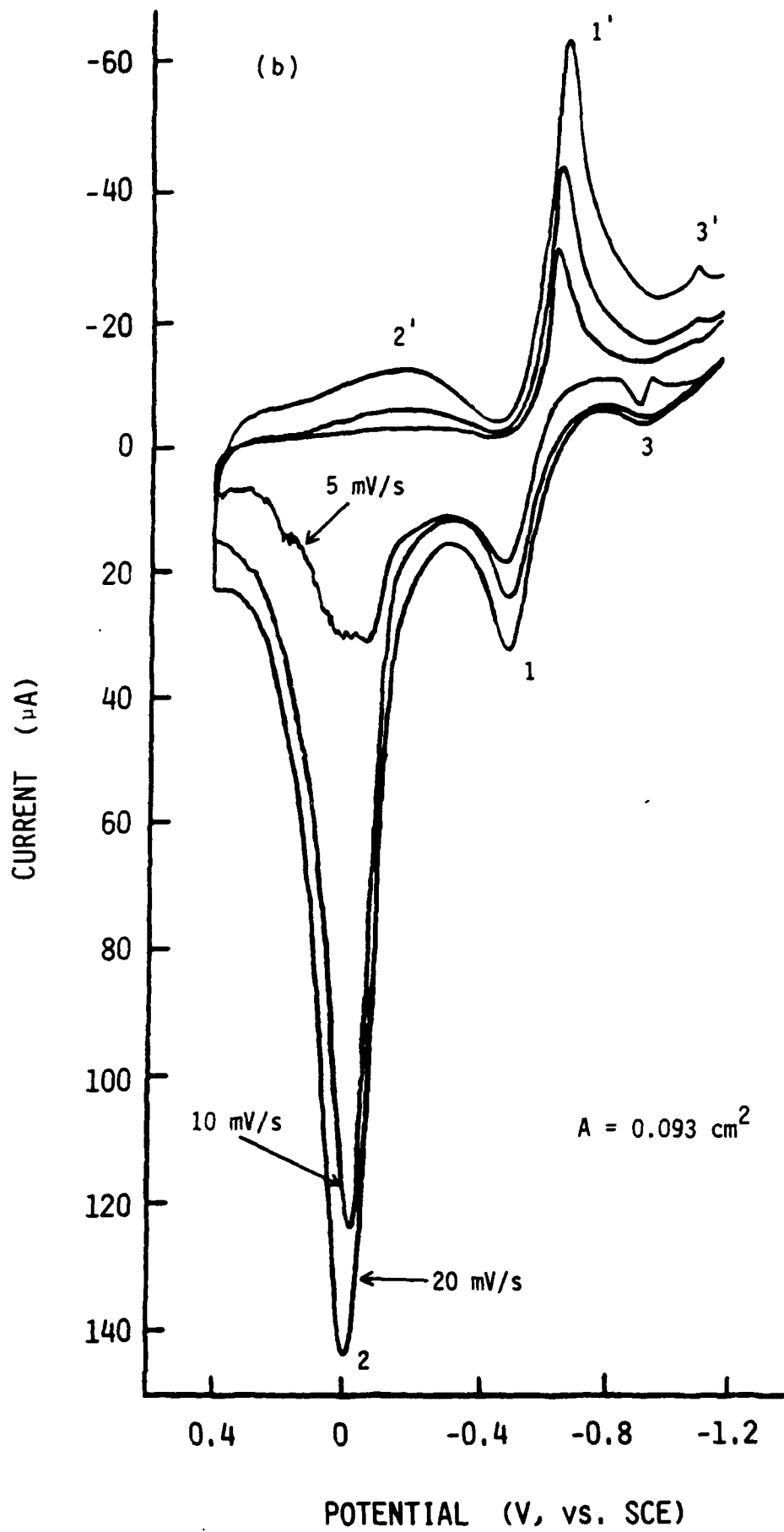


Figure 7(a)

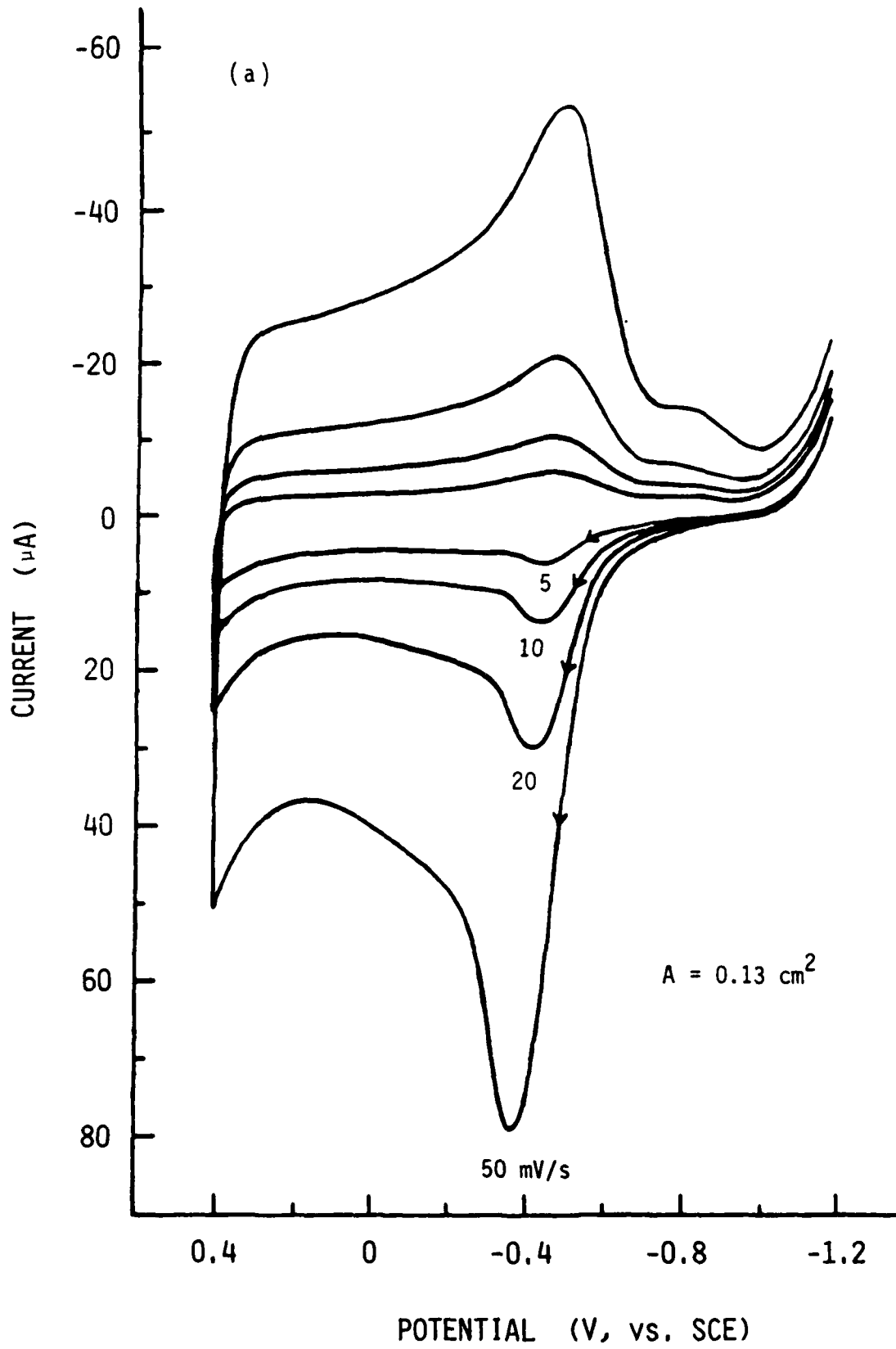




Figure 7(b)

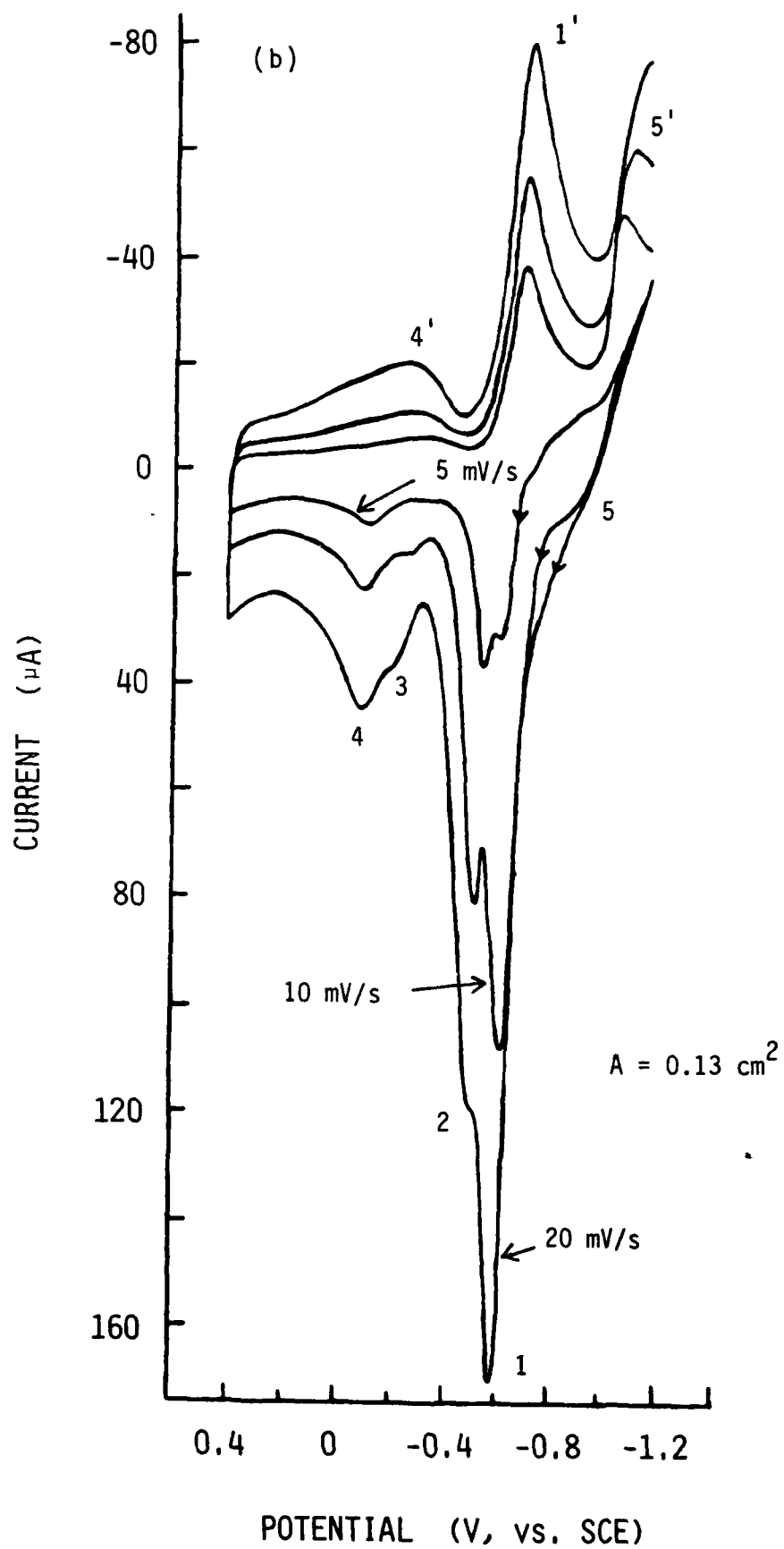


Figure 8

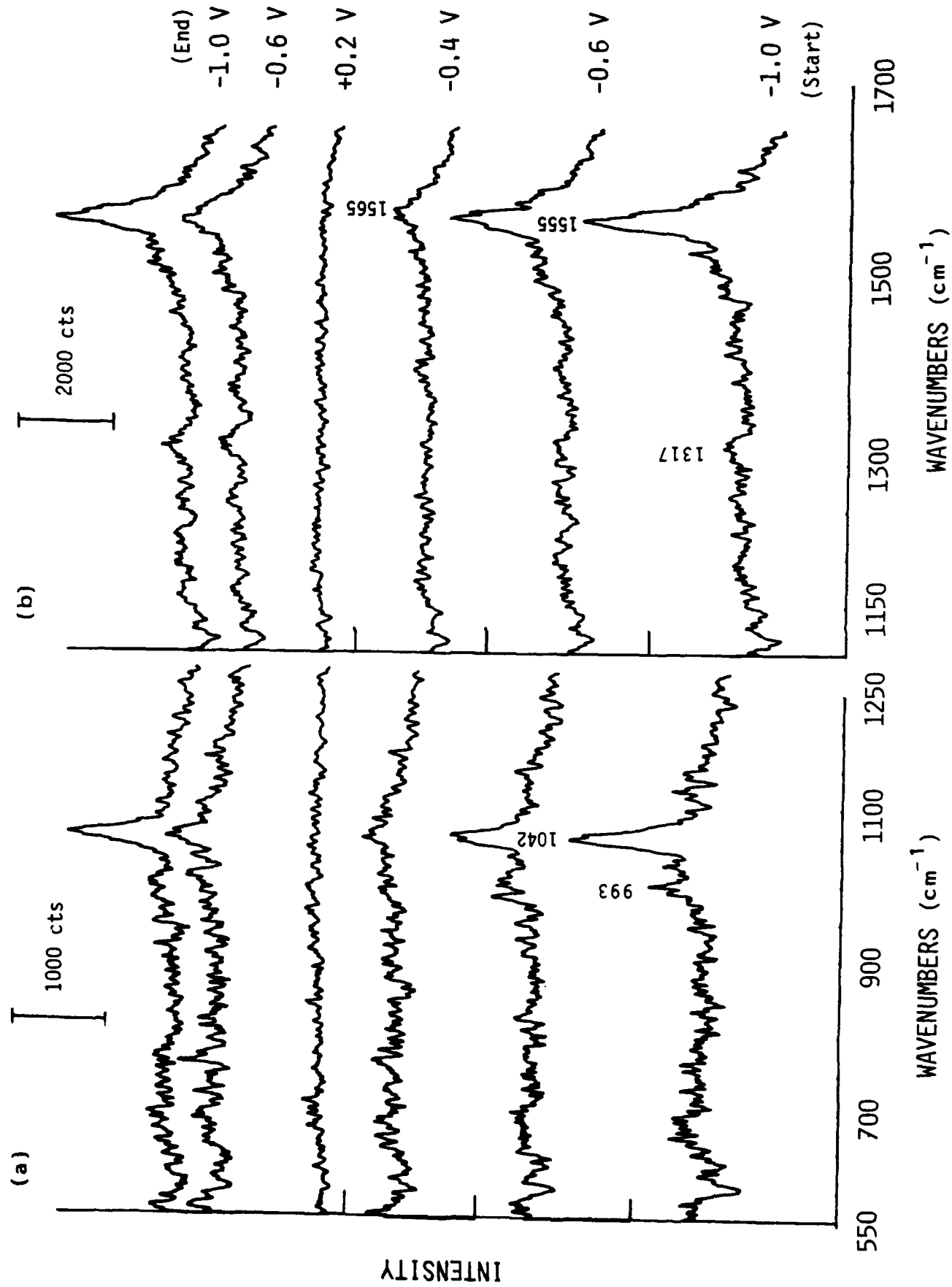


Figure 9

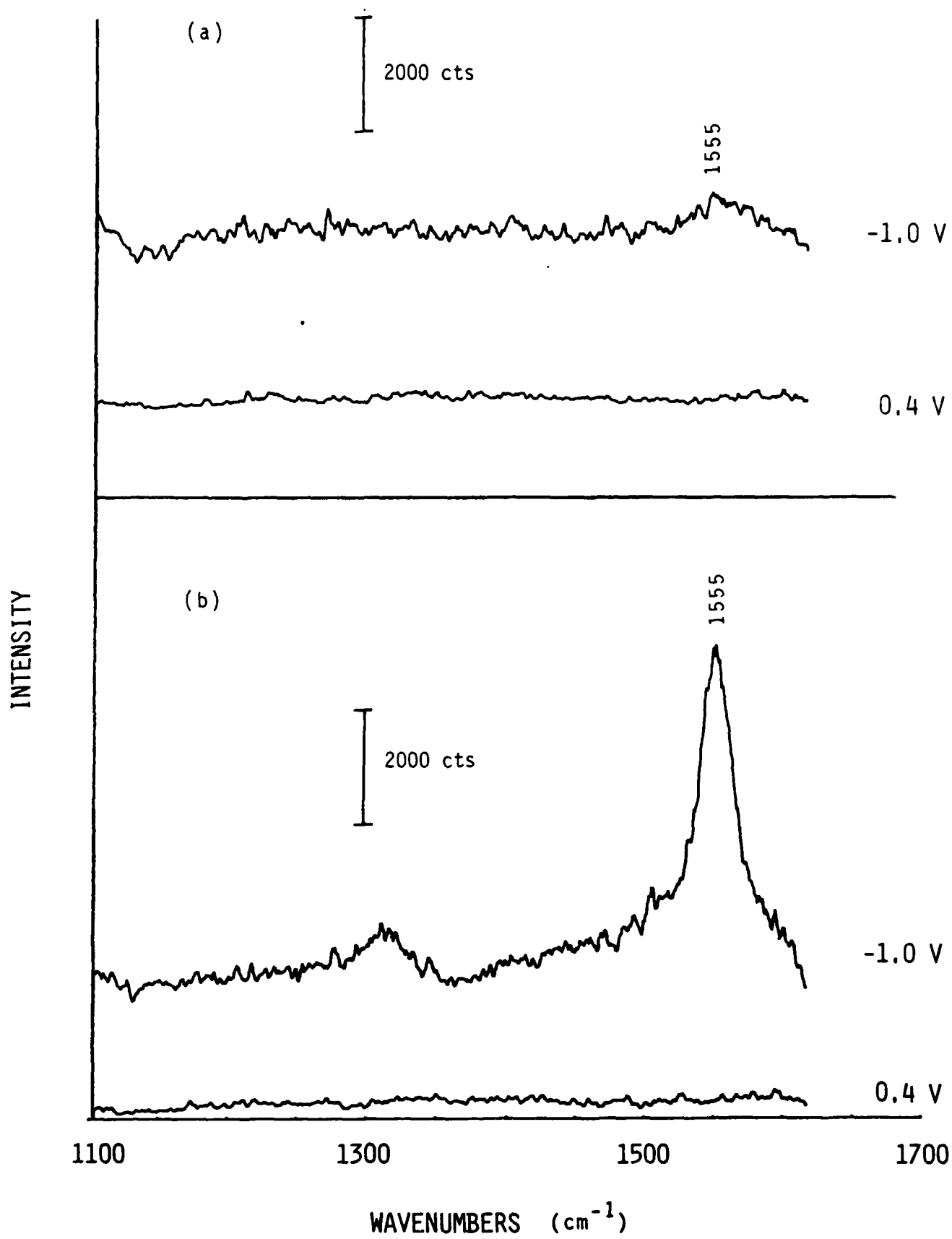


Figure 10

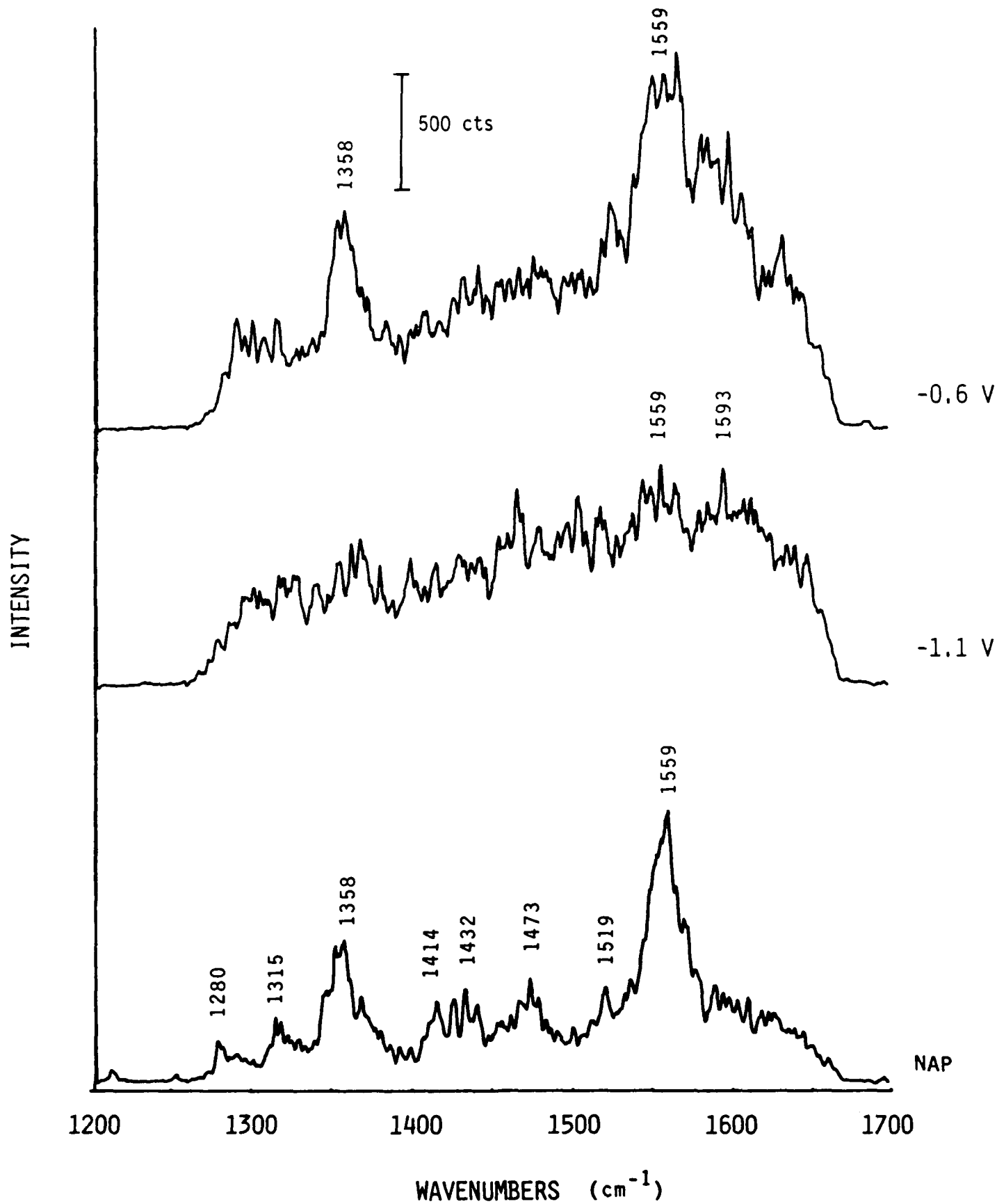


Figure 11

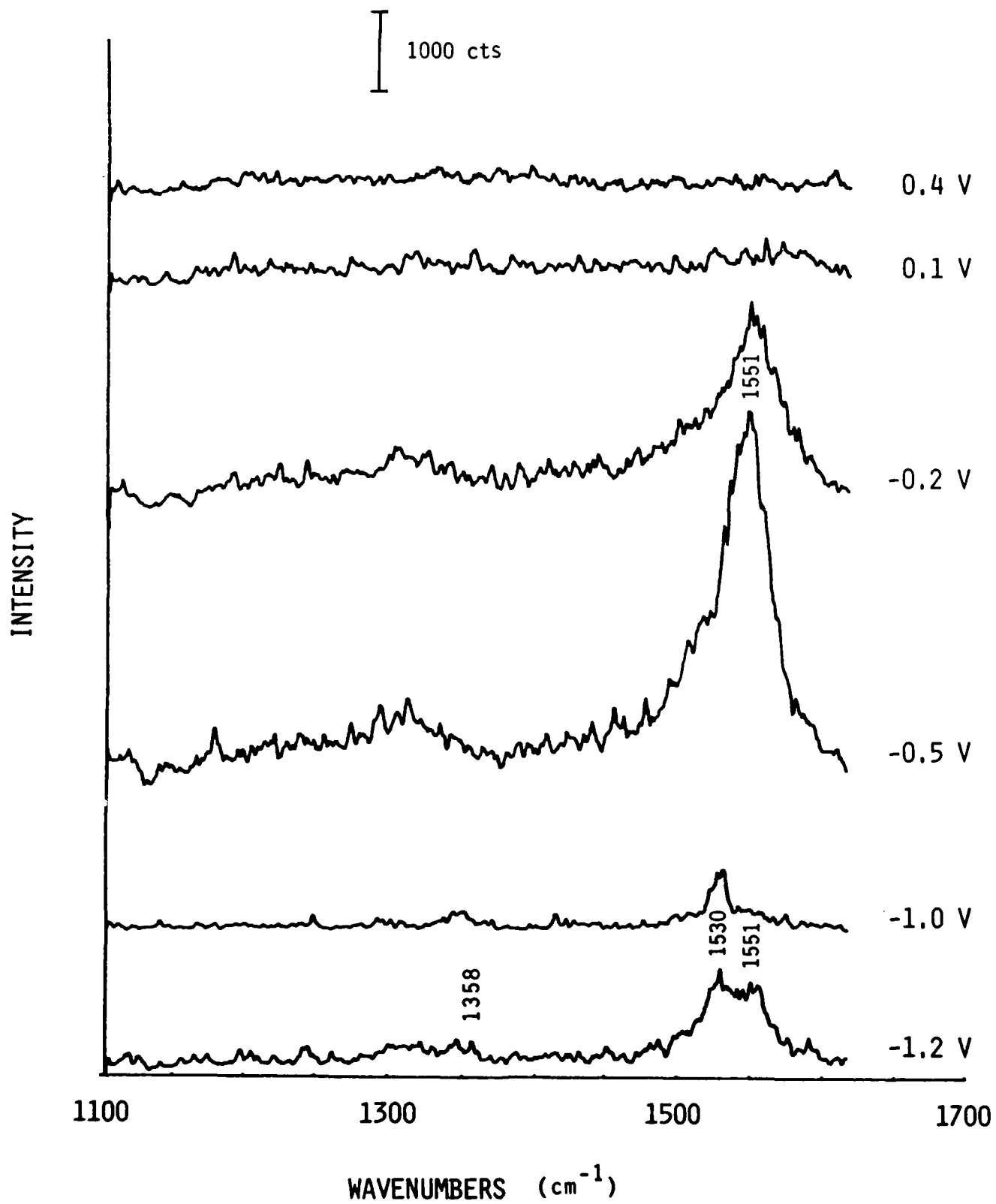


Figure 12

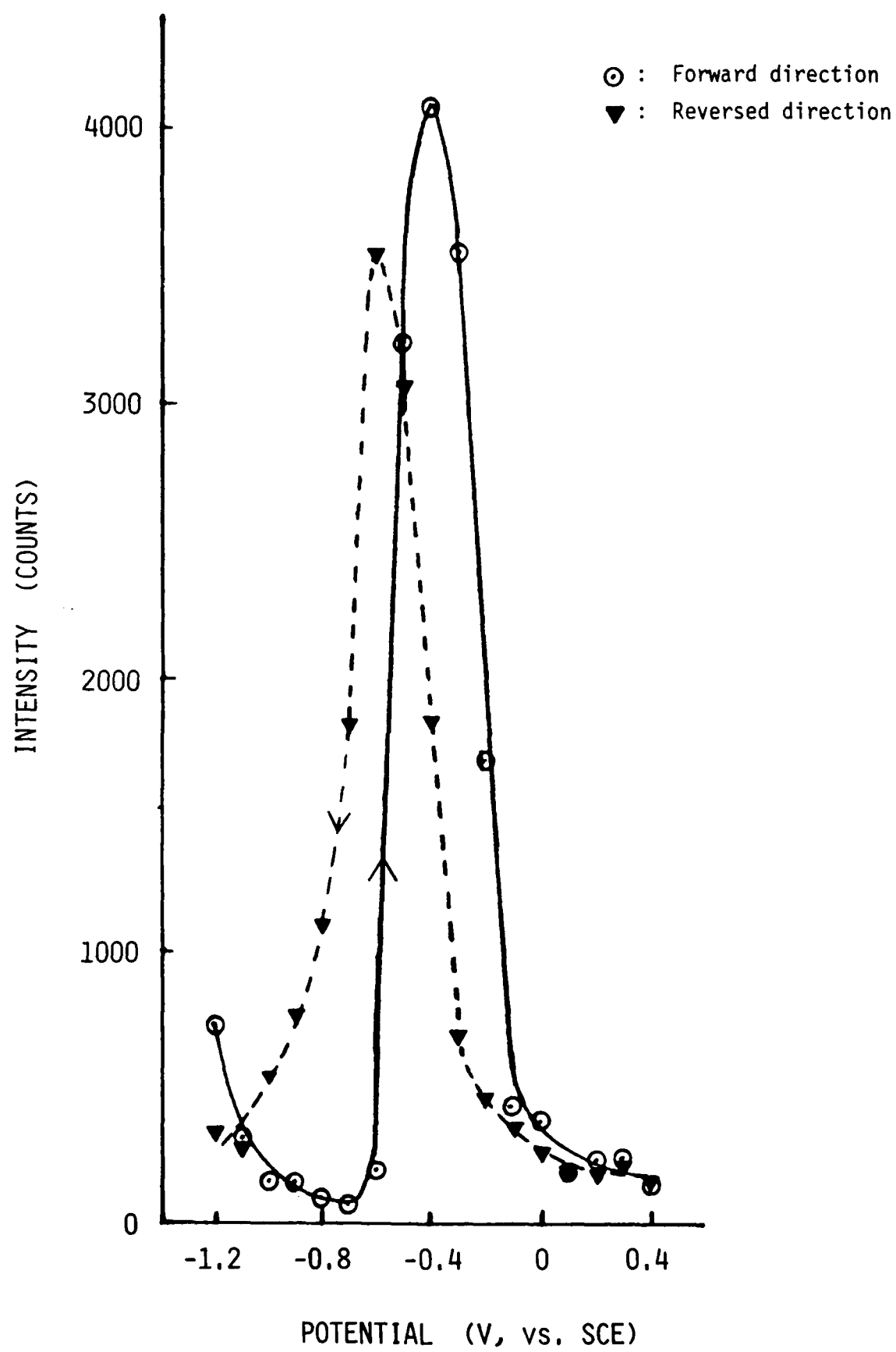


Figure 13

