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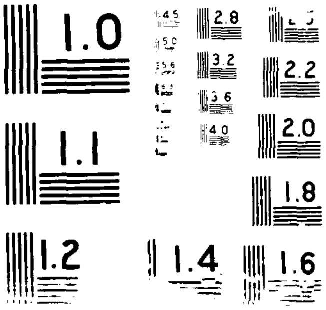
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The Electrochemical Behavior in Aqueous Media of Conducting Polymers: II: The Insoluble Fractions Obtained on the Cu(II) Catalyzed Polymerization of (2,5-Dibromo-3-Group IV Substituted) Thiophenes

By

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Substituted thiophenes are used as electrode material: the redox chemistry of copper containing polymer in contact with the electrolyte shows only internal copper chemistry.

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THE ELECTROCHEMICAL BEHAVIOR IN AQUEOUS MEDIA OF CONDUCTING POLYMERS: II; The Insoluble Fractions Obtained on the Cu(II) Catalyzed Polymerization of (2,5-DiBromo-3-Group IV Substituted) Thiophenes

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Abstract

The chemical polymerization of (2,5-dibromo-3-substituted) thiophenes utilizing $Cu(II)Cl_2$ as a copromoter yields an amorphous insoluble polymer fraction which exhibits a very high electronic conductivity varying between 10^{-1} to 10^{2} S-cm. These materials have been used as electrode materials. The redox chemistry of the Cu(II) containing polymer in contact with supporting electrolyte only shows a distinct internal (Cu(II)/Cu(I) cyclic voltammetric wave. No redox behavior for the thiophene ring system is observed. This material is very stable in aqueous media and appears to be conducting at positive and negative electrode potentials (contrary to the redox response of electrodeposited polythienylene films). The lack of 3-substituent steric effects is discussed. The similarities and, more important, the dissimilarities of the properties of these polymers and Cu(II)-dithiolate complexes are also discussed.

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Key Words: Conducting polymers, polythienylenes, polymer electrodes, aqueous media, 3-substituted 2,5-dibromothiophenes, Cu(II)/Cu(I), redox couple, substituent effects, and Cu(II)-dithiolate complexes.

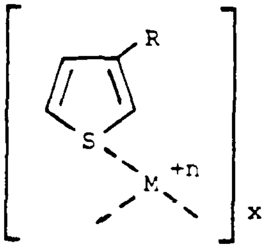
In recent years an extensive interest and research on the synthesis and electrochemical properties of macromolecules with extended π-electron systems has been reported (1). In particular, the majority of the research involved polymers with systems of conjugated π-electrons which, upon doping, form charge transfer complexes (2,3). These can exhibit semiconducting or metallic conducting properties (3-5).

The first well characterized conducting polymer system was poly(sulfur nitride), $(SN)_x$, (6-8) which was reported in the 1970's. The first conducting organic polymer system synthesized was poly(acetylene), $\leftarrow CH=CH \rightarrow_x$ which can undergo both n- and p-type doping. The conductivity of the poly(acetylenes) depends on the concentration and chemical nature of the dopant (9,10). Other conjugated π-electron systems with similar properties are poly(p-phenylene), $-(C_6H_4)_x-$ (11), and poly(p-phenylene vinylene), $\leftarrow C_6H_4CH=CH \rightarrow_x$ (12). These doped materials have limited stability (12). A very stable polymer film of poly(pyrrole), formed on electrooxidation of pyrrole on a platinum electrode, has been reported by Diaz et.al. (13). The neutral form of the polymer is an insulator, but on electrooxidation in nonaqueous media the film incorporates anions and exhibits high conductivity (14). Electrodeposited films of poly(thiophene) have electrical conductivity properties comparable to the poly(pyrrole) film. For polymerization and also for anion incorporation more positive potentials are required (15-17). However, when exposed to ambient conditions for a few weeks, these films lose their conductivity and electrode activity.

In connection of one of the results in this communication it is of interest to note that some reports indicate the inclusion of $CuCl_2$ in the electrolyte improves the electropolymerization of benzene and naphthalene (18,19).

Recently polymeric materials obtained by transition metal induced polymerization of the bis-Grignard compounds derived from 2,5-dibromothiophene and 2,5-dibromo-3-methyl thiophene have been reported by Yamamoto et al. (20,21). After iodine doping these poly(2,5-thienylenes), have been shown to exhibit significant conductivity. Interestingly, the polymers were very stable, and the authors commented that some of the transition metal catalyst incorporated in the polymer could not be removed or exchanged by chemical treatment. Zimmer et al. (22,23) devised a modification of the synthetic route by employing the 2,5-dilithiothiophenes in place of the bis-Grignard compounds. Subsequent anhydrous metal salts promoted polymerization producing materials which on iodine doping showed improved conductivity as compared to the materials prepared according to Yamamoto et al. In addition, these materials exhibited an extraordinary degree of stability.

In continuation of our interests in investigating conducting polymeric materials containing bonded redox centers for theoretical studies as well as potential electrocatalytic surfaces, we have synthesized a series of poly(3-substituted-2,5-thienylenes) containing various incorporated transition metals. The general unit monomer structure is:



Where R = -H, $-CH_3$, $-Si(CH_3)_3$, $-Ge(CH_3)_3$ and $-Sn(CH_3)_3$ for the Cu(II) containing polymers, and M = Cu(I), Cu(II), Mo(VI), Ru(III), Fe(III), Co(II), Ni(II), and Pt(IV) for 3-methyl-polymers. This paper, for reasons discussed below, deals principally with the Cu(II)-polymer series because of their unique electrochemical properties (24). Furthermore, this paper will deal only with the insoluble amorphous polymer fraction obtained from the synthesis. The electrochemical behavior of the methanol soluble Cu(II)-poly(3-methyl-2,5-thienylene) is different and is reported elsewhere (25). This paper will examine the redox behavior of incorporated Cu(II) upon electrochemical polarization in aqueous media; it also will demonstrate the electrical conductivity of this material by the cyclic voltammetry of the ferro/ferricyanide couple in the electrolyte phase. The effects of pH, potential sweep rate, prolonged electrolysis and storage conditions on stability, valence state of the incorporated copper, the nature of the 3-substituent, and the lability of the incorporated Cu(II) will be presented.

Experimental

The synthesis of the various 3-substituted-2,5-dibromothiophene monomers followed published procedures (26). The polymerization of the monomeric dibromo analogs utilizing n-butyllithium and transition metal catalysts and the isolation of the insoluble polymer fractions has also been previously reported (22,23).

The dried amorphous insoluble polymer fraction was pressed into pellets using a standard IR pellet dye under 5000 psi pressure. The polymer pellets were mounted in an electrode assembly system that has previously been described (27). All solutions were deaerated with argon unless otherwise specified. Potentials were measured at 20 ± 1 °C *vs* the saturated calomel electrode, SCE. For the i-E studies, a BAS model CV-1B-120 voltammetry controller and Hewlett-Packard model 136A x-y recorder were used.

Results and Discussion

In Figure 1 cyclic voltammograms for the insoluble polymer fraction of poly(2,5-thienylene) are shown. The material was obtained by using anhydrous $CuCl_2$ as the promoter in the polymerization of 2,5-dilithiothiophene (23). We shall demonstrate that the broad peaks are due to the redox reaction of the copper cations incorporated in the polymer matrix. The shape of the peaks also indicates a broad potential range of electrical conductivity in contrast to the polymer films produced on electrooxidation of thiophene (15-17). These curves were generated at two different sweep rates (10 mV/s and 100 mV/s). It is evident that at the lower sweep rate much higher amounts of charge are passed in the electrochemical reactions (Table 1). In Table 1 the amount of charge is listed also for various sweep rates. The supporting electrolyte in these experiments was 0.1 M $NaClO_4$. In addition this table contains the formal potentials, $E^{o'}$, calculated from cathodic and anodic peak potentials ($E^{o'} = (Epa+Epc)/2$). This data shows that the amount of charge involved in the redox reactions is very strongly dependent on the rate of potential polarization, whereas the $E^{o'}$ is relatively independent. The amount of charge and the dependence on sweep rate reveal that the copper, not only near the surface of the polymer, but some in the bulk of the polymer takes part in the redox reaction. It is interesting to note that the X-ray analysis (EDAX) of the surface of cycled electrodes actually showed a slightly increased copper concentration. The bulk copper concentration is about 30% by weight as measured by atomic absorption analysis.

It can be seen in Figure 1 that at the lower sweep rate more peaks or waves appear. These additional small peaks are generally at more negative potentials suggesting that they may be due to the reduction of Cu(I) to Cu(O). These peaks may represent a reduction of Cu(I), but it is not complete, meaning that only a small fraction of the Cu(I) is reduced to Cu(O) on the time scale of this experiment. It is important to note that the main current peaks represent a Cu(II)-Cu(I) redox reaction, and not the main oxidation of an extended π-electron system, such as occurs in electropolymerized poly(thienylenes) (13-17).

Other investigators have reported an increased stability of Cu(I) ions in an electropolymerized poly(thienylene) matrix (28). In Table 2, the formal potential values for several copper catalyzed 3-substituted poly(thienylenes) are presented. Both, Cu(I) and Cu(II) were used to make poly(3-methyl-2,5-thienylene) and voltammograms of the former are shown in Figure 2. After extended cycling the redox couple of the more poorly conducting Cu(I) containing polymer gains definition and shifts to more negative potentials. This indicates a change in chemical environment or structure of the copper coordination geometry is taking place. From these data and the ones from Table 2 it becomes evident that the electrochemical behavior of polymers obtained with Cu(II) significantly differs from polymers obtained in the presence of Cu(I). The good mechanical and chemical stability of the electrodes during long cycling times suggests that Cu(II) as well as Cu(I) is strongly complexed by the polymer.

The polymers listed in Table 2 were designed so that the substituents had a systematic and large variation in size but, as small as possible differences in inductive properties. The only significant difference in inductive effects would occur in going from the 3-H to the 3-CH_3 group. Surprisingly, even the most bulky groups did not hinder the chemical polymerization or significantly affect the properties of the polymers. The lack of steric effects here is very surprising as bulky 3-substituents, -$C(CH_3)_3$ for example, prevent polymer film formation on electrooxidation (29), presumably because of steric hindrance of the 2-position. Also, substituents which varied in their ability to donate to or to withdraw electrons from the aromatic moiety of the polymer had strong effects on the redox potentials of electrooxidized poly(thienylenes) (2). With both steric and electronic effects of the chemically produced matrix being absent the evidence is that the thiophene ring system of chemically polymerized monomeric 3-substituted thiophenes does not undergo a redox reaction.

Figure 3 shows the voltammograms for Cu(II)-poly[3-(trimethylstannyl)-2,5-thienylene] when successively more negative switching potentials are employed. It appears that the oxidation peak cannot be observed without a prior negative scan first. This required first reduction once again supports the opinion that Cu(II) cations are initially incorporated in the polymer and are responsible for the main redox couple.

In Figure 4 data are representative of experiments in which some environmental conditions are varied. It appears that oxygen lowers the redox currents. The redox currents in deaerated solutions are also slightly lower if the electrolyte is stirred. This phenomonon is not understood, however one explanation might be explained by assuming that stirring may stimulate faster diffusion of the Cu(II) cations on or near the surface into the bulk of the solution.

In Figure 5 the concentration of copper leached into the bulk electrolyte is plotted as a function of time. The rate of leaching slows after ca. 30 hr. The total amount of copper leached into solution is only a fraction fraction of the copper incorporated in the polymer, and the polymer can be cycled for several weeks ($\sim 10^5$ cycles) without changing the shape of the voltammogram or the magnitude of the peak currents. This material may be stored in air for several weeks and used again. Also, no observable swelling of the polymer disk was observed on cycling the potential.

It is very characteristic for all of the Cu(II) containing polymers to exhibit increasing redox current peaks during the first few cycles. This phenomena is shown for two polymers in Figure 6. It is thought that this peak growth is due to the time necessary for water to penetrate and saturate the polymer matrix and, perhaps, also to some structural changes. That this is a reversible process becomes evident by the fact that the cyclic voltammograms of a used and dried polymer needs a few cycles before returning to steady state. Thus, emphasizing the fact that water plays a very important role in the conductivity of these polymers. As a matter of fact, water changes the dried polymer from virtually non-conductors to good conductors as was reported by us in a previous paper (24) when it was found that poly(3-substituted-2,5-thieylenes) incorporating Cu(II) exhibit a huge increase in conductivity on "doping" with water going from 10^{-7}S-cm^{-1} to greater than almost 40 S-cm^{-1} in some cases.

It is well known that some transition metal dithiolate complexes exhibit semi-conducting properties (30,31). The 1,2-dicyanoethylene-1,2-dithiolate complexes are a particularly well studied system and it is interesting to note that the copper complex not only has the highest electrical conductivity but it is also found with solvent molecules of crystallization (30).

In order to further study solvent effects in our polymers the following experiments were carried out. Pressed polymer disks were exposed to different constant humidity environments by suspension above sulfuric acid-water mixtures. The conductivity, as measured by the four point probe method, incresed proportionally with relative humidity, and droplets of moisture actually formed on the pellet surfaces at 100% humidity. This unusual water nucleating property is not understood at this time. At present we cannot distinguish whether the water is coordinated, or is in an environment comparable to hydrophilic ionomers, where there is a separate phase containing water molecules and ions within a matrix of nonionic units (32).

Voltammograms were taken in H_2O and D_2O (0.1 M $NaClO_4$) solutions and are shown in Figure 7. It can be seen that the main redox peaks are separated by an additional

40 mV in the deuterated solvent. Isotope effects considered for other electrochemical systems (33) include: 1) 20% lower diffusion coefficients in the more viscous D_2O, 2) slight differences in the double layer capacity, 3) increased pH (0.41 pH units due to lower auto dissociation) and associated equilibria changes, and 4) large thermodynamic effects due to the stronger deuterium bonds. A 40 mV change is relatively large suggesting a primary isotope effect (34). At present it is not known which of the above effects or, perhaps a combination, predominate.

Voltammograms taken in mixed solvent solutions containing different amounts of water are shown in Figure 8. It can be seen that in the electrolyte which contains smaller amounts of water (75% t-butanol) the redox peaks decrease. In water/acetonitrile solutions (Figure 8) much higher currents and sharper peaks appear which suggests that the internal redox couple is more reversible in water/acetonitrile electrolyte than in water.

In Figure 9 voltammograms in solutions of different pH (0.1 M NaOH and 0.1 M $HClO_4$) are presented. In basic solution (pH=13) the native reduction peak observed in neutral solutions has disappeared. An explanation might be that the Cu(II) cations are coordinated to OH^- anions causing a drastic shift of the redox potential or it could mean that the copper-sulfur bonds have been broken. In pH=1 $HClO_4$ electrolyte it appears that the bulk polymer is irreversibly oxidized.

If the voltammograms are taken in a 0.1 N $NaClO_4$ solution containing 10^{-2} N $K_3Fe(CN)_6$ (Figure 10, curve 1). Two pairs of redox peaks are observed. The more negative pair is typical with respect to peak potentials and shapes of a solution phase ferri/ferrocyanide couple at any solid electrode such as platinum. The more positive couple is at potentials similar to that observed for the internal Cu(II)/Cu(I) couple as would be expected. On removing the same electrode from the 10^{-2} N ferri/ferrocyanide-0.1 N $NaClO_4$ solution, washing it repeatedly with distilled water and immersing it in a 0.1 M $NaClO_4$ electrolyte, the cyclic voltammogram showed only the internal Cu(II)/Cu(I) couple (curve 2). Curve 2 is identical to that of the same electrode initially cycled in supporting electrolyte only. It is obvious that the current peaks for the internal copper(II/I) couple is reduced when a solution phase redox couple is present. Thermodynamically no such reduction in the peak currents for the Cu(II)/Cu(I) couple should occur. However, if the redox process for the internal Cu(II)/(I) couple is rate limited by anion counterion diffusion and slow compared to electron transfer through the polymer to the solution interface the above results would be expected.

Conclusions

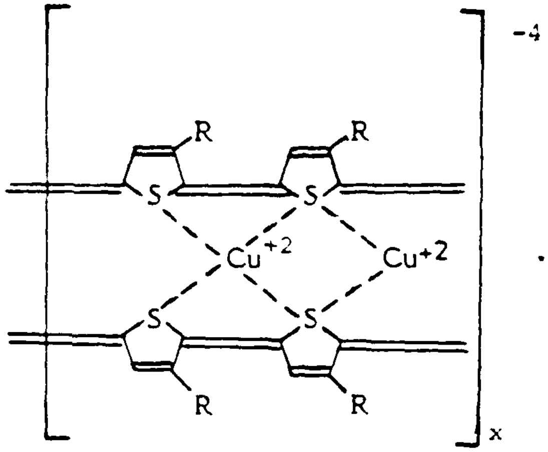
The electronic conducting polymer incorporating Cu(II) produced on the chemical polymerization 3-substituted-2,5-dilithiothiophenes are remarkably good conductors after being "doped" with water (up to 40 S-cm^{-1} for some batches). The same polymers containing other transition metal ions relatively remain, even after "doping" with water poor electronic conductors ($\sim 10^{-7}$ S-cm^{-1}). Their conductivity however, did not increase by incorporation of water (24), which is a big factor in the increase of conductivity of the Cu(II) promoted poly(3-substituted-2,5-thienylenes).

The cyclic voltammograms of the highly conducting polymer exhibit an internal Cu(II)/Cu(I) redox couple and no redox couple for the thiophene ring system. The lack of ring electrochemistry in these polymers may account for the great stability of these materials in aqueous media and even in the presence of oxygen. Presumably the Cu(II) is coordinated to the sulfurs and also acts to crosslink the polymer chains. This probably also contributes to their stability. Surprisingly, there are no significant inductive and steric effects as the 3-substituent on the thiophene moiety is varied. In contrast to electrochemically produced poly(thienylenes), these materials conduct over the entire potential window (about +1.5 to -1.0 V vs SCE).

The microstructure of these polymers and the nature of the copper coordination is not known at this time. The fact that they are extremely stable and not soluble in anything has made it impossible to study them by the usual techniques. However, an interesting comparison of the divalent transition metal dithiolate system and our analogous coordinated polymer systems shows structural, electrical, and physical similarities (30). The sulfur-double bond-sul structural element common to the best conducting materials (30,31,35), perhaps, is also possible in the poly(thienylene) π-system if the resonance structure with double bonds between the rings would be the predominate one. That this structural element may be important to conductivity of the polymer is corroborated that by the fact that the 1,2-dicyanoethylene-1,2-dithiolates are 10^5 times more conducting than the 2,2-dicyannoethylene-1,1-dithiolate metal salts in which such structure elements cannot occur (30). A frequently observed geometry found for conducting charge transfer salts involves flat complexes stacking one upon another, forming a two dimensional conducting lattice, with the counter ions between parallel planes (36,37,2). All the conducting Cu(II) thiolate complexes are planar, again suggesting the importance an the inter-ring double bonded resonance form of poly(thienylene), which also would be planar.

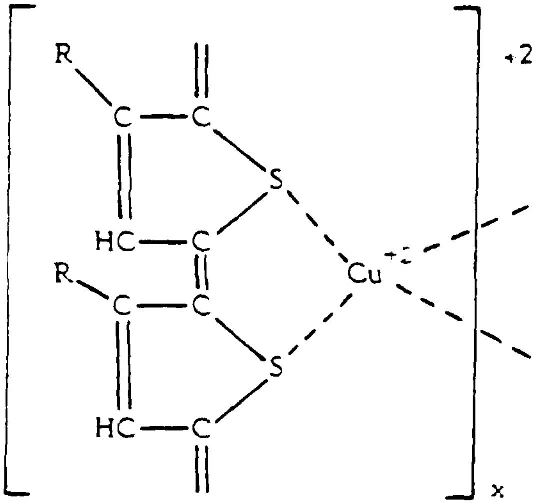
Our results which show copper superior to other transition metals parallel the findings for the 1,2-dithiolates, where the conductivity for divalent transition metals decreased in the order: $Cu^{+2} > Co^{+2} > Ni^{+2} > Fe^{+2}$. In similar coordinated polymeric systems the copper complexes exhibited the highest electrical conductivities, up to 40 S-cm^{-1} (31,34). Generally, the dithiolate complexes and coordinated polymers were darkly colored and insoluble in organic solvents and water; thus, their appearance resembles physically the Cu(II)-poly(thienylenes), which even after exhaustive solvent extraction, retain a very high copper content. Two postulated structures are discussed below. One possibility is that copper is both coordinated to the sulfur in an anionic polymer complex and is also ionically situated "outside" the polymer chain, balancing the charge. Water or polar solvent molecules are associated with the cations sited outside the polymer chain facilitating charge-transfer, thereby, increasing the conductivity. This also accounts for the very high Cu(II)-thiophene ring ratio. Also, it is important to note that water content has been shown to have a significance on the electron conductivity for similar $K_2Pt(CS)$,

$Br_{0.8}\cdot x\,H_2O$ systems (38).



$\cdot\ 2\,Cu^{+2}, m\,H_2O$ I

However, in spite of this attractive analogy, several experimental facts seem to contradict it. First of all, the model contains chemically bound Cu(II) as shown above. These copper ions would be expected to be readily, if only partially, exchange when the polymer is in contact with electrolyte solutions, such as 0.1 M $LiClO_4$, etc. No such cation exchange or leaching to any extent is observed. Secondly, on variation of the anion of the solution supporting electrolyte, even with the large $Fe(CN)_6^{-3}$ anion, it was shown that the polymer exchanges the anion (29), which indicates that the Cu(II) polymer matrix is positively charged. Thus, it is more likely that the basic resonance structure in the polymer is:



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Although somewhat analogous to the dithiolate salts, there is another distinct difference. This could, therefore, account for the fact that the Cu(II) polymer has at least a 10^5 S-cm^{-1} better conductivity than the Cu(II) dithiolates. The extended π-system of the amorphous polymer is probably more important with respect to electron conductivity than two dimensional copper-copper interaction. Furthermore, the lack of steric hindrance on chemical polymerization, again in contrast to the electrooxidation polymerization method, indicates that the chemical polymerization proceeds in such a way or rate to yield an organized polymer that does not yield sterically hindered 3,4-substituent units in the polymer (see structure II). This would permit the formation of an extended planar π-system in the polymer itself. It is well known that extended π-system polymers cease to exhibit red shift of optical absorbance beyond about 8 to 9 unit oligomers (39,40). The same is true of the negative shift of oxidation potential for about 5 to 6 unit oligomers(40). The thermal motion of the chain at this point overcomes the stability of the conjucation (39) and larger oligomers exhibit the same optical and electrochemical properties. However, the Cu(II) crosslinking could "freeze" the thermal motion of the polymer and enhance the electron conductivity in the polymer. Separate studies of the electrooxidation of various methyl substituted thiophene oligomers in nonaqueous media have shown that restricted rotation about the 2-5-polymer linkage drastically effect the morphology and electrochemistry of the conducting polymer film (40). Thus, if Cu(II) has a specific orientation effect on the extended π-system, the above results could be expected.

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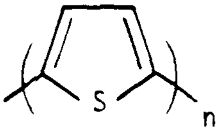
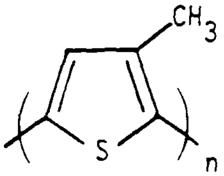
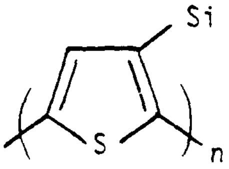
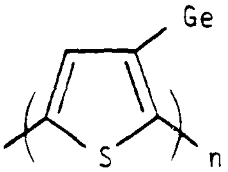
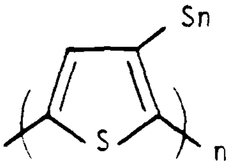
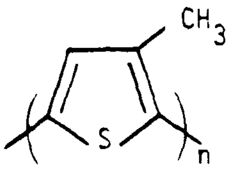
Table I: Amounts of Anodic Charge and Formal Potentials at Various Scan Rates for Cu(II)-poly(2,5-thienylene)

ν, mV s^{-1}	Q, μ C cm^{-1}	$E^{0'}$mV
2	3000	7
5	2430	-3
10	1840	-3
20	1225	7
50	1125	-36
100	900	-28
200	770	-23
500	450	-27

Table II: Formal Potential Values for Poly(thienylene) and Its Derivatives. Scan rate 100 mVs^{-1}.

Polymer	Catalyst	$E^{0'}$ mV
	$CuCl_2$	-28
	$CuCl_2$	-56
	$CuCl_2$	-24
	$CuCl_2$	-33
	$CuCl_2$	-23
	CuCl	-185

Figures

Figure 1: Cyclic voltammograms of Cu(II)-poly(2,5-thienylene) in 0.1 N $NaClO_4$ at different polarization rates: 10 $mV{\cdot}s^{-1}$ (1) and 100 $mV{\cdot}s^{-1}$ 92).

Figure 2: Cyclic voltmmograms of Cu(I)-poly(2,5-thienylene) in 0.1 N $NaClO_4$: (1) after 2 sweeps (2) after 66 hr of cyclic polarization. Sweep rate 100 $mV{\cdot}s^{-1}$.

Figure 3: Cyclic voltammograms of Cu(II)-poly(3-$Sn(CH_3)_3$-2,5-thienylene) in 0.1 N $NaClO_4$. Sweep rate 100 $mV{\cdot}s^{-1}$.

Figure 4: Cyclic voltammograms of Cu(II)-poly(3-$Si(CH_3)_3$-2,5-thienylene in 0.1 N $NaClO_4$: (1) unstirred, deaerated solution; (2) stirred, deaerated solution; (3) presence of O_2 in solution. Sweep rate 100 $mV{\cdot}s^{-1}$.

Figure 5: Concentration of copper in solution (0.1 N $NaClO_4$) vs time of cyclic polarization from poly(2,5-thienylene). Sweep rate 100 $mV{\cdot}s^{-1}$.

Figure 6: Cyclic voltammograms of polythienylenes in 0.1 $NaClO_4$: Cu(II)-poly(3-$Ge(CH_3)_3$-2,5-thienylene), (1) first sweep, (2) third sweep, (3) after 14 hours of cycling. Cu(II)-poly(3-$Sn(CH_3)_3$-2,5-thienylene), (1) first sweep, (2) third sweep, (3) eighth sweep, (4) eleventh sweep. Sweep rate 100 $mV{\cdot}S^{-1}$.

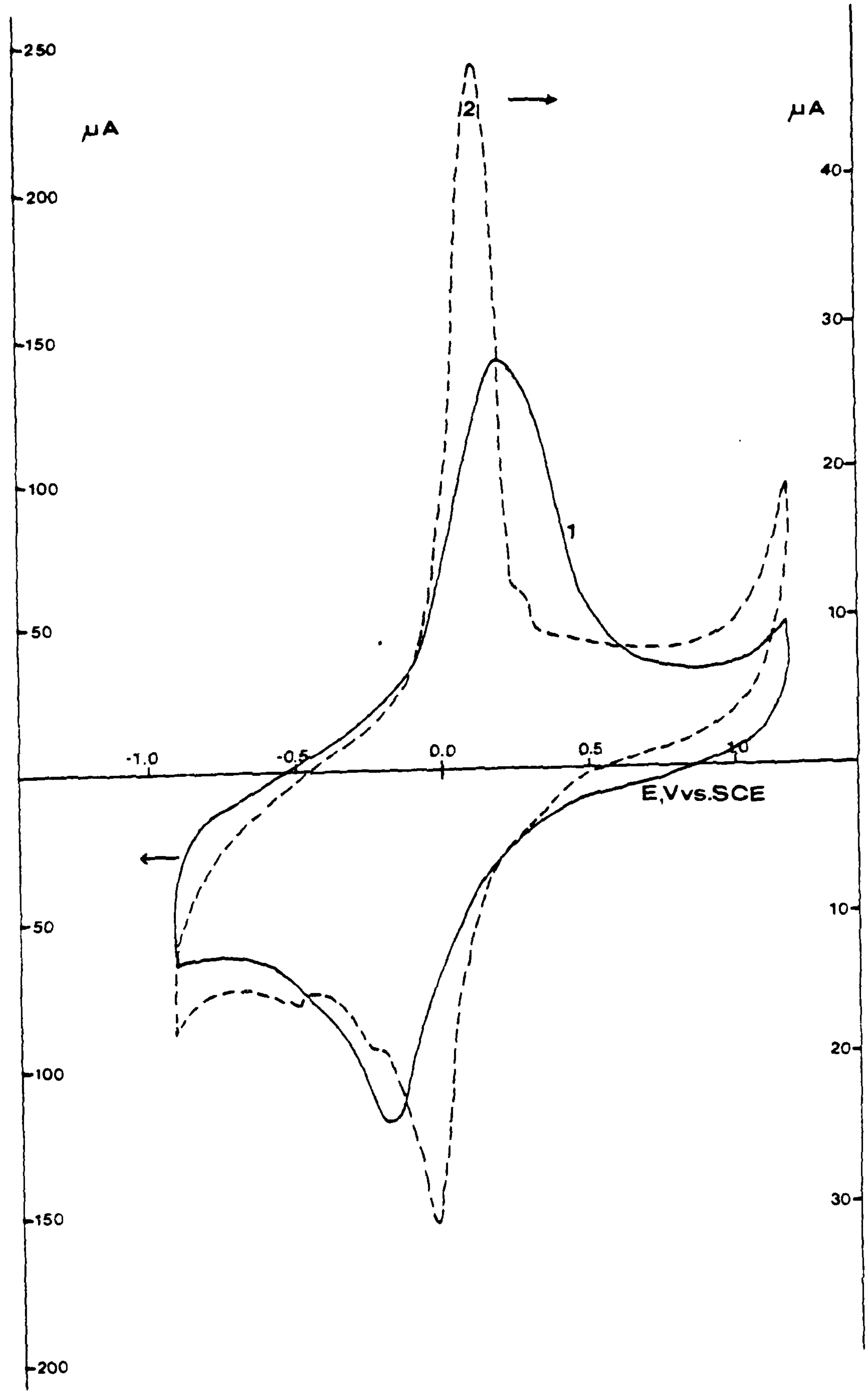
Figure 7: Cyclic voltammogram of Cu(II)-poly(2,5-thienylene) in 0.1 N $NaClO_4$ solutions: (1) H_2O, (2) D_2O. Sweep rate 100 $mV{\cdot}s^{-1}$.

Figure 8: Cyclic voltammograms of polythienylenes in 0.1 N $NaClO_4$: (a) Cu(II)-poly(3-$Si(CH_3)_3$-2,5-thienylene) in 75% t-butanol-25% water; (b) Cu(II)-poly(3-methyl-2,5-thienylene) in CH_3CN solution. Sweep rate 100 $mV{\cdot}s^{-1}$.

Figure 9: Cyclic voltammograms of Cu(II)-poly(3-$Si(CH_3)_3$-2,5-thienylene) in (1) 0.1 N NaOH, (2) 0.1 N $HClO_4$. Sweep rate 100 $mV{\cdot}s^{-1}$.

Figure 10: Cyclic voltammograms of Cu(II)-poly(3-$Si(CH_3)_3$-2,5-thienylene) in 0.1 N $NaClO_4$:

(1) Solution contains 10^{-2} N $K_3Fe(CN)_3$.
(2) After washing procedure -- in background solution (0.1 N $NaClO_4$).



μA
250
200
150
100
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50
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150
200
2
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μA
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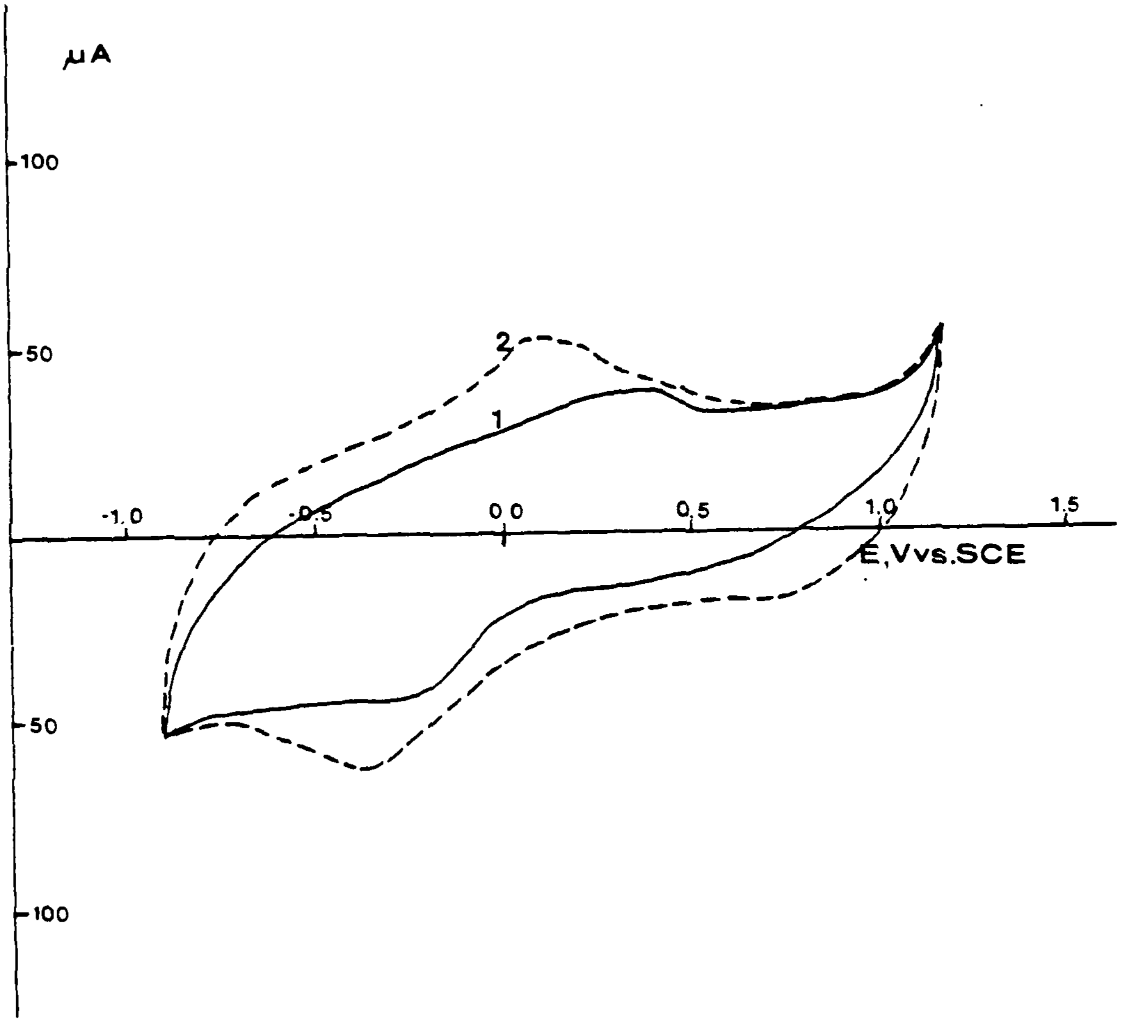
E,V vs.SCE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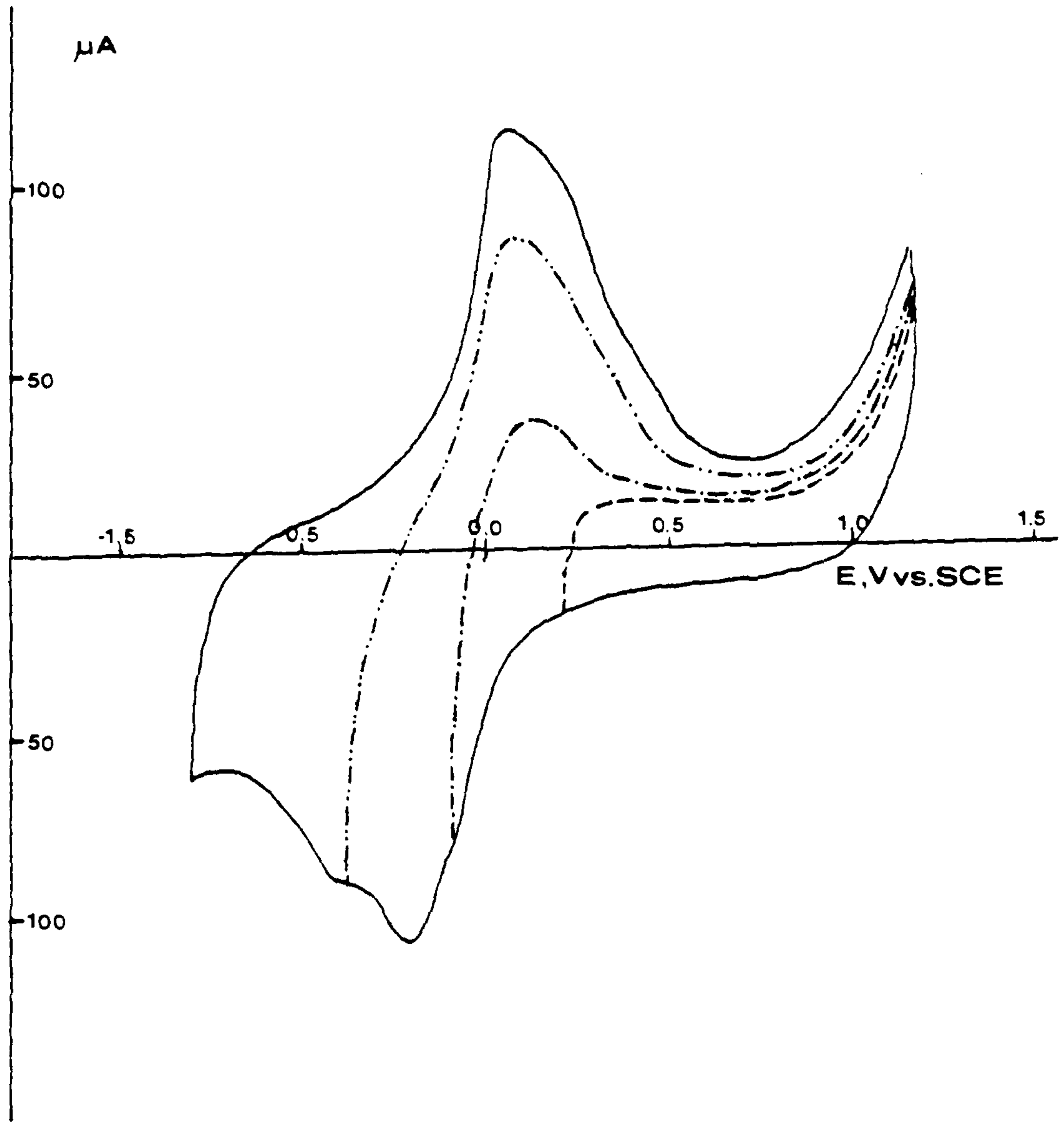
1.0
1.5
E,Vvs.SCE
1
2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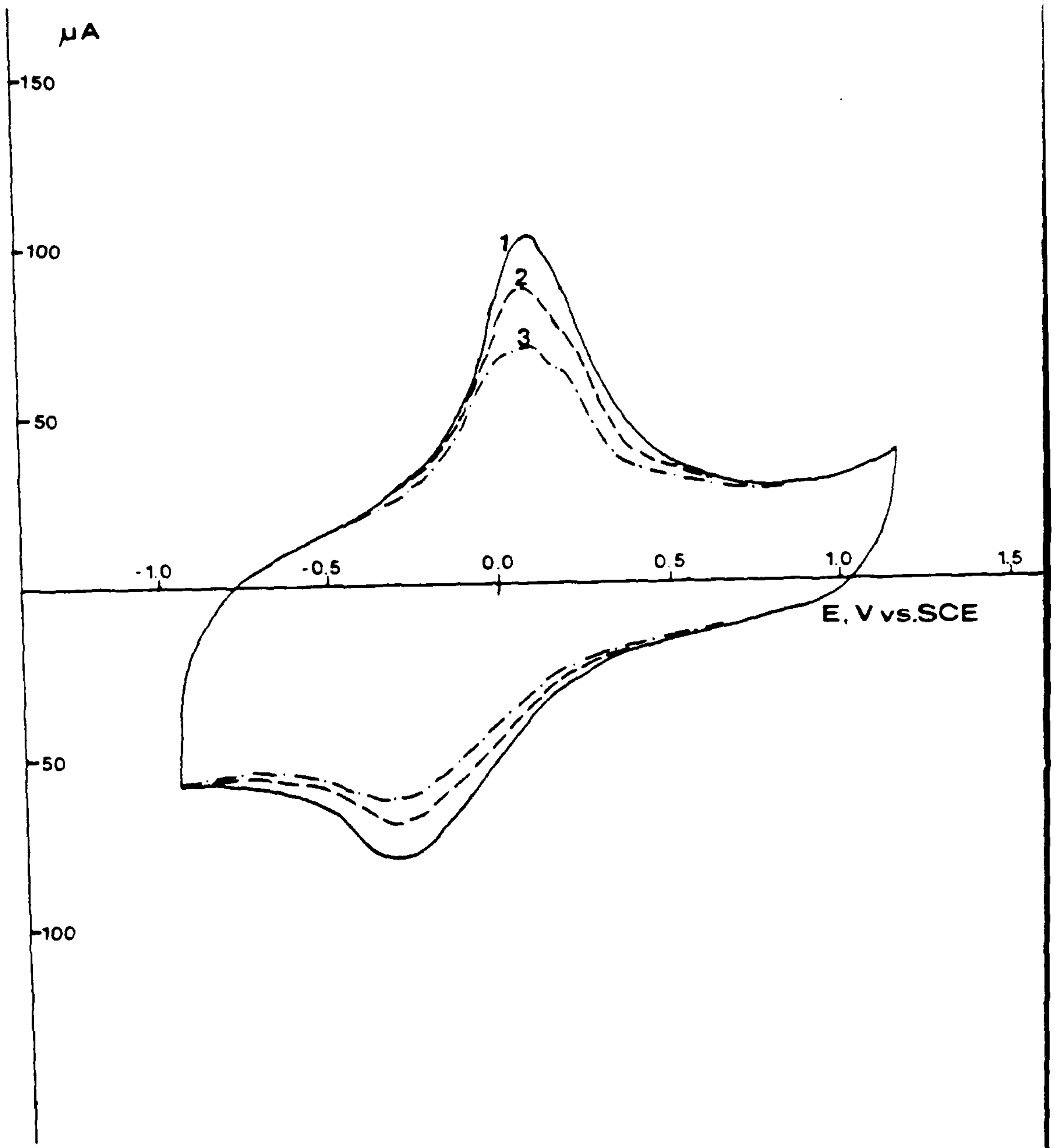
E,V vs.SCE



μA
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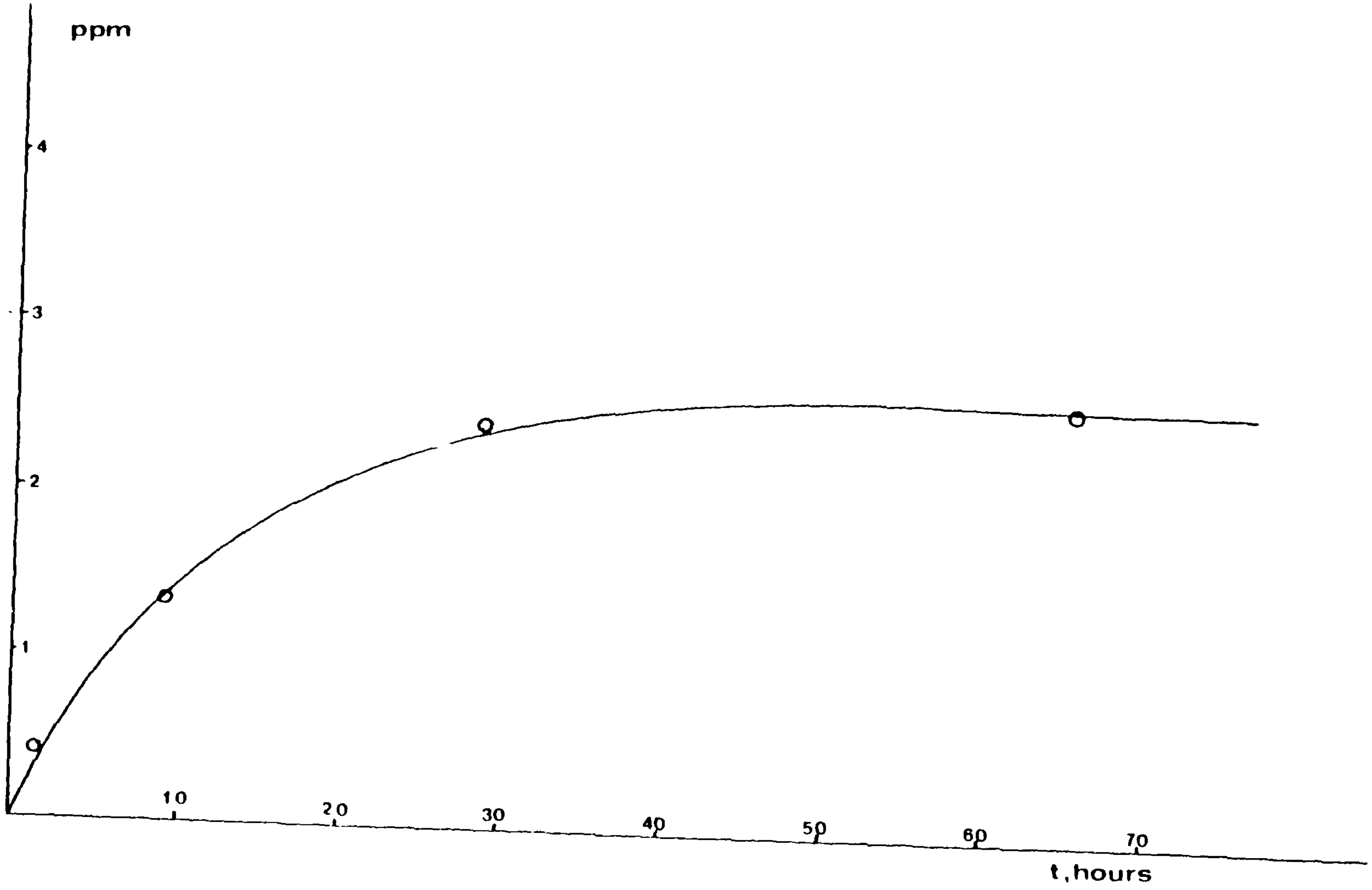
E, V vs.SCE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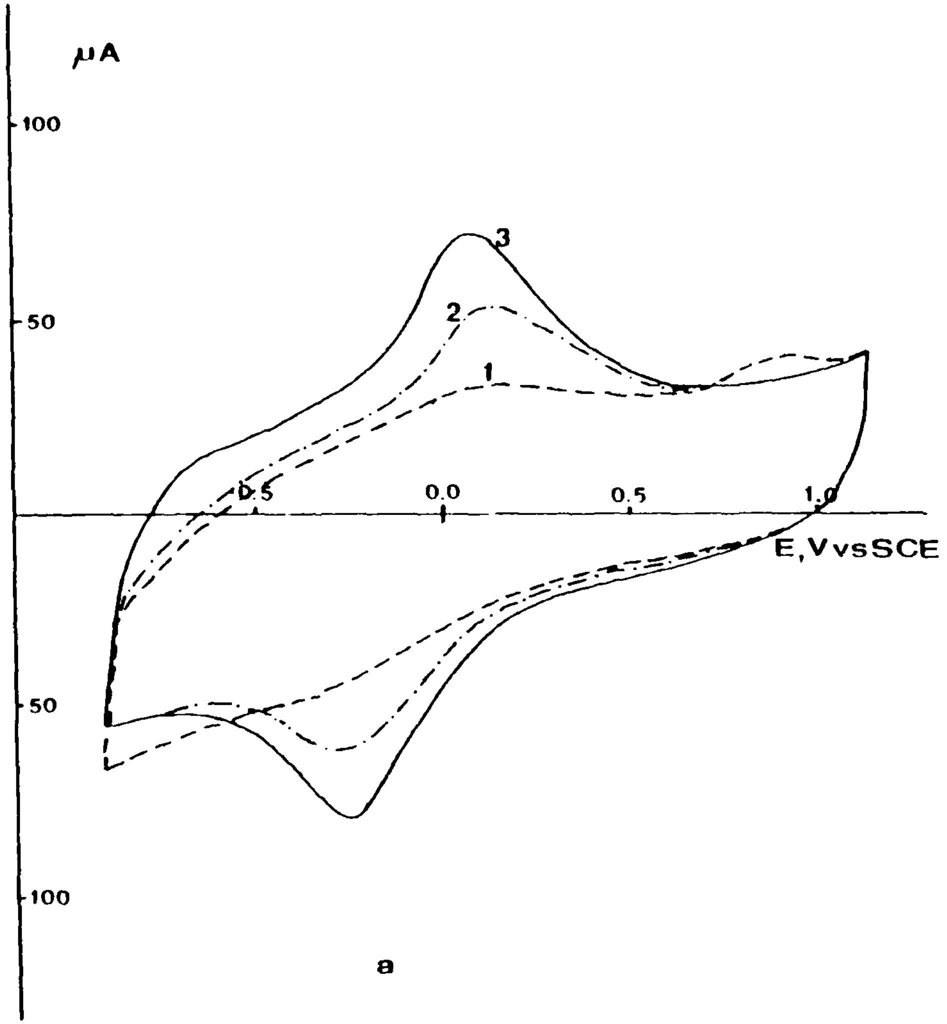
t,hours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E,VvsSCE
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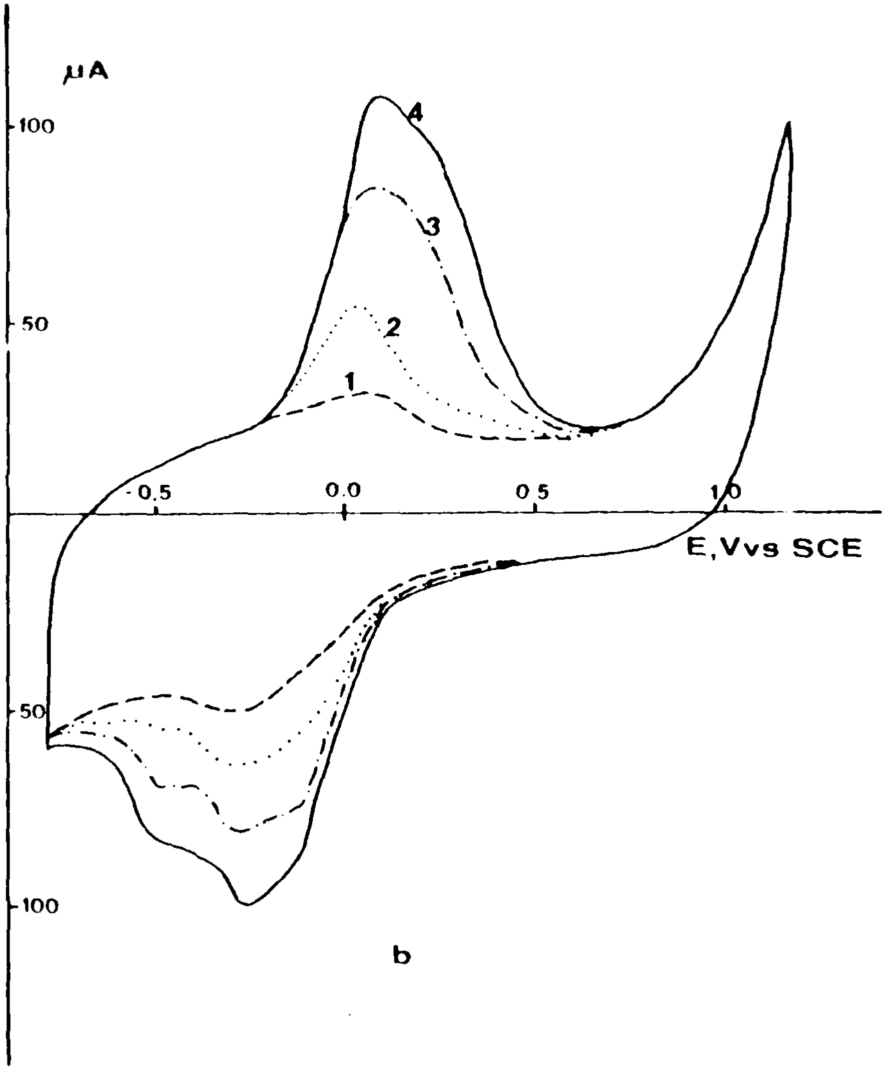
a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E,Vvs SCE
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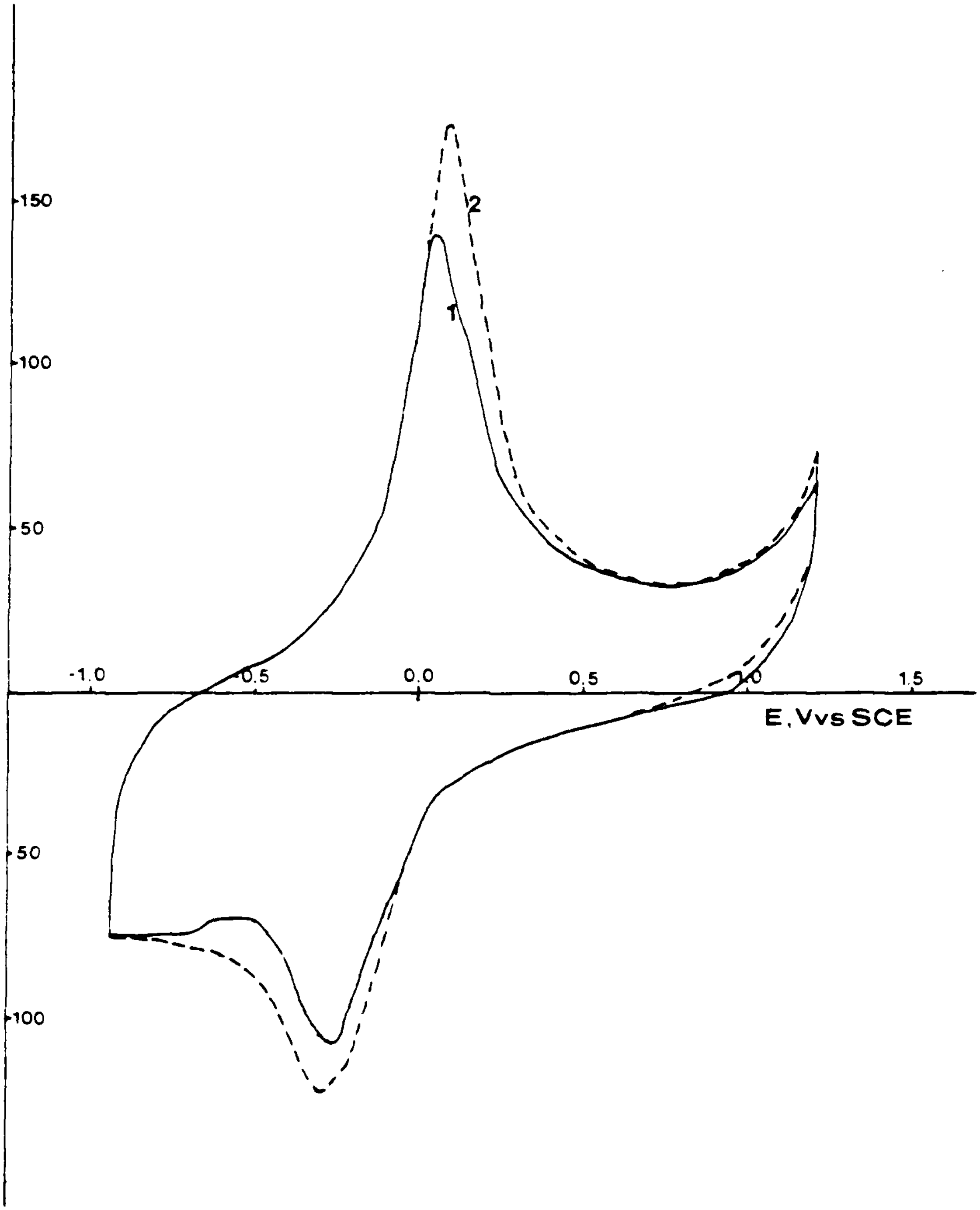
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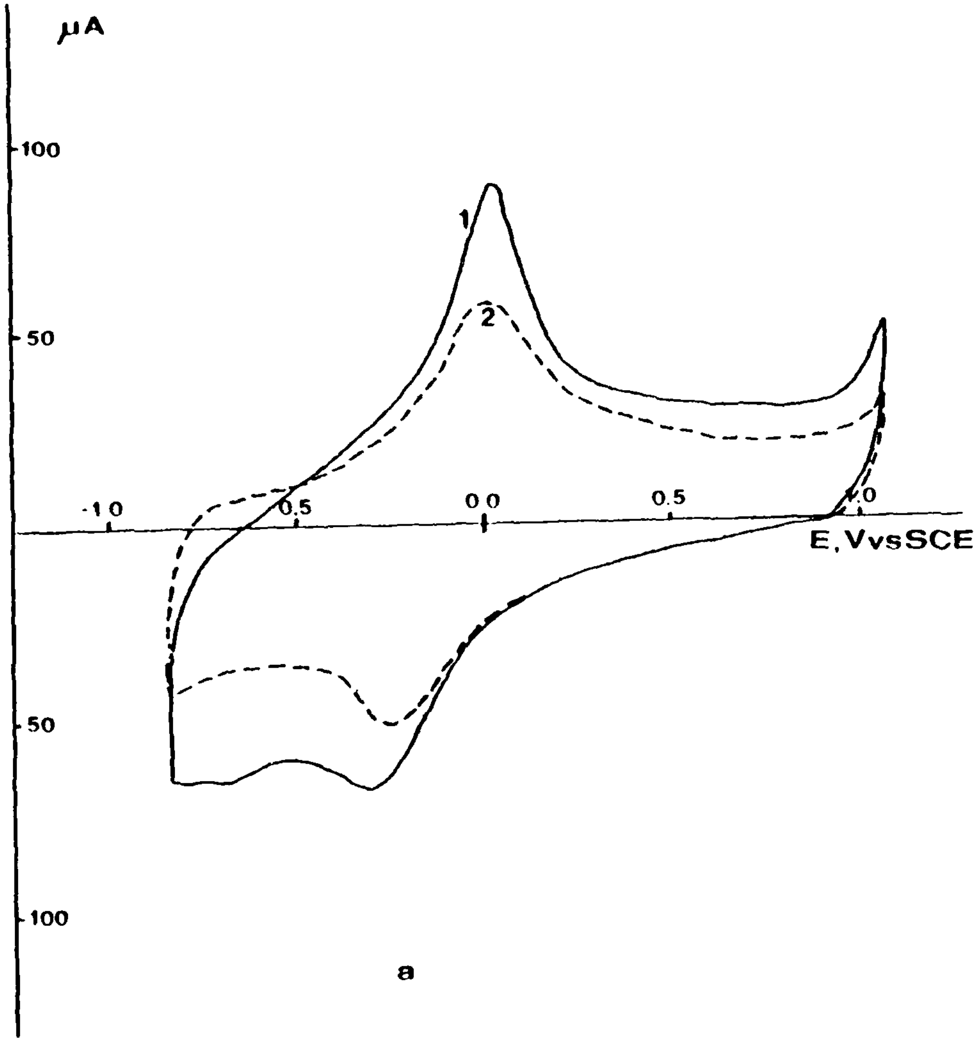
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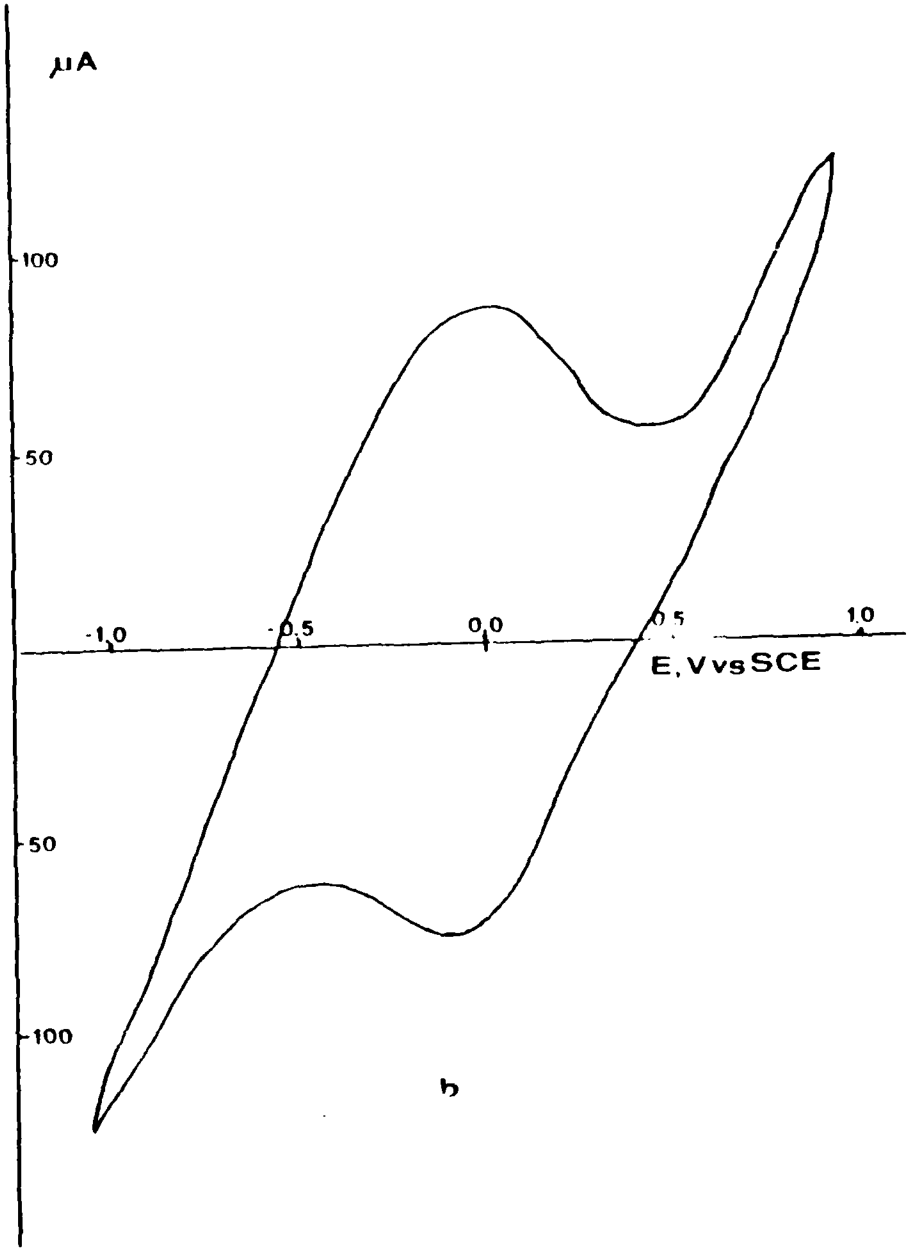
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E, V vs SCE

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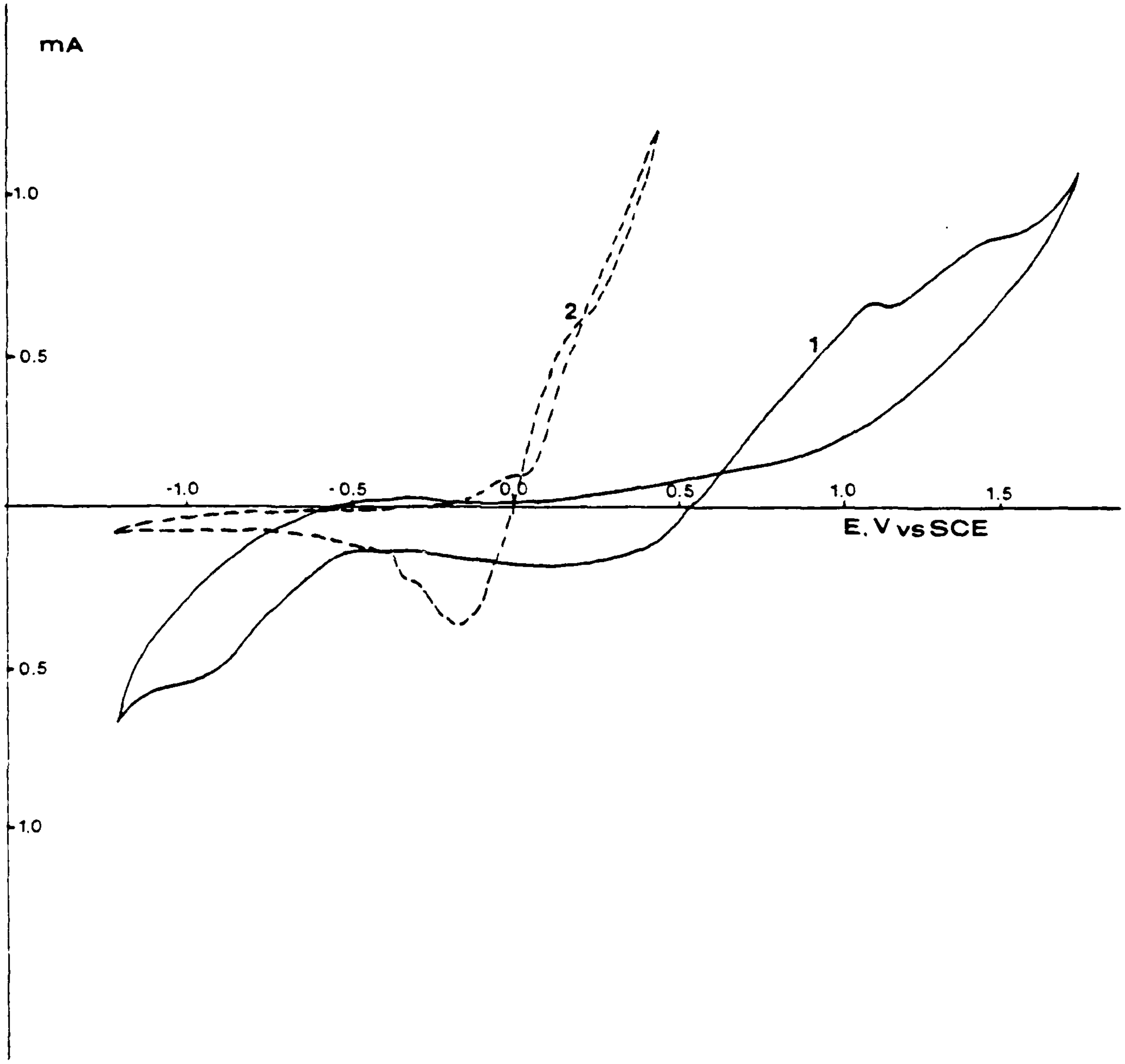

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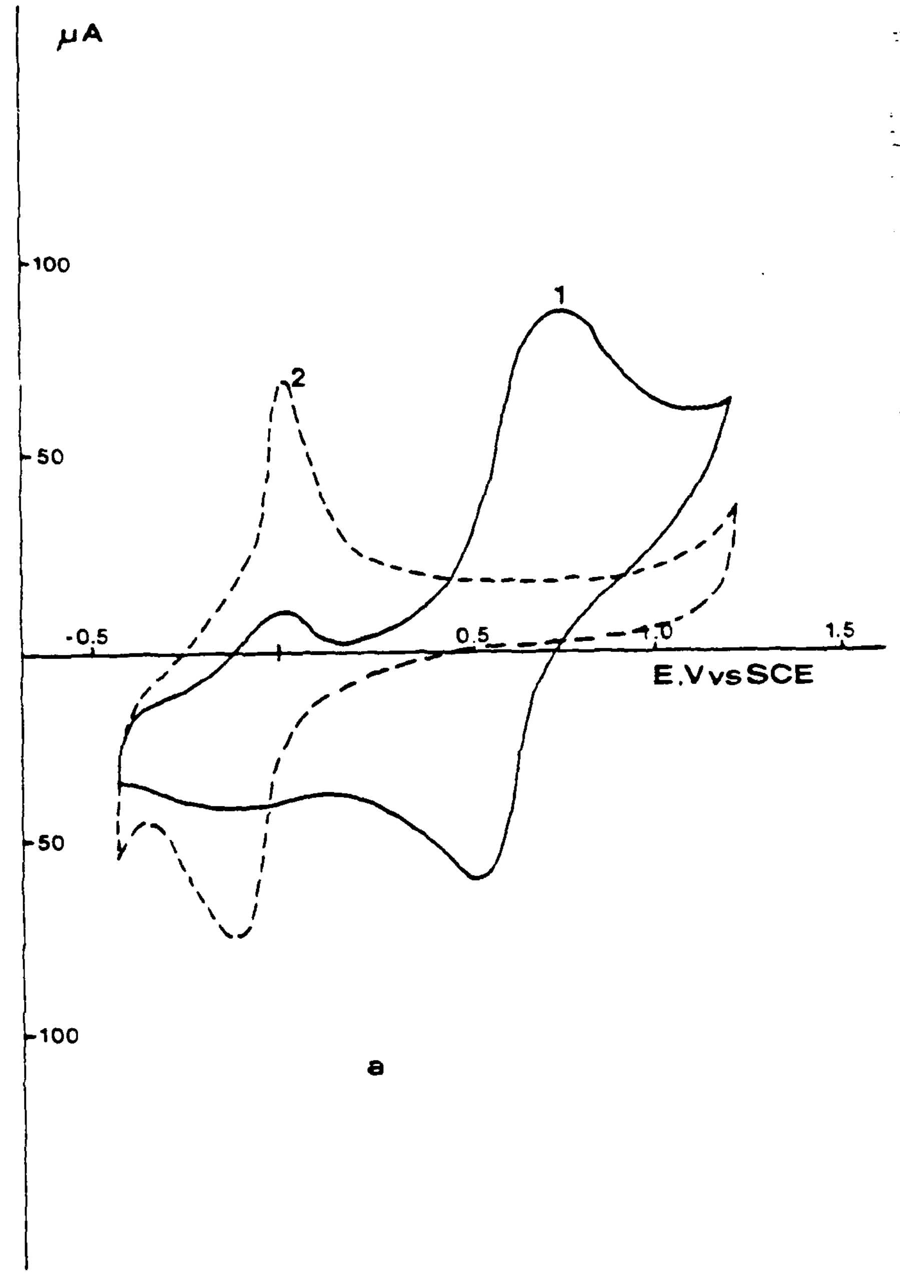
E, V vs SCE
1
2



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