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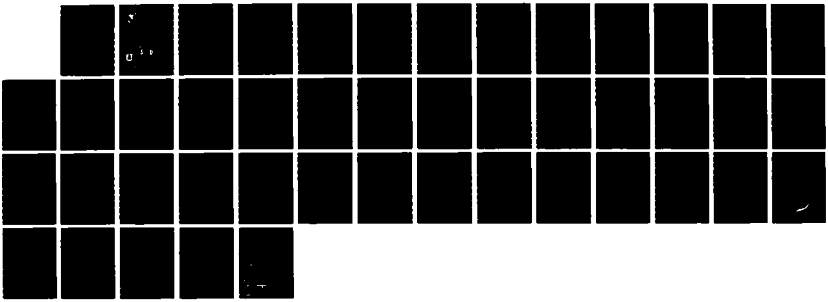

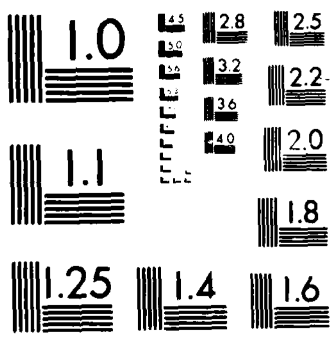
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AD-A172 401

FJSRL-TR-86-0009

FRANK J. SEILER RESEARCH LABORATORY

ELECTROCHEMISTRY OF SULFUR, Na_2S, S_2, S_2CL_2 AND CS_2 IN 1-METHYL-3-ETHYLIMIDAZOLIUM CHLORIDE-ALUMINUM CHLORIDE MELTS

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B. J. Piersma

J. S. Wilkes

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August 1986

AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE

FJSRL-TR-86-0009

This document was prepared by the Electrochemistry Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO. The research was conducted under Project Work Unit number 2303-F2-10. Dr. John S. Wilkes was the project scientist.

Inquiries concerning the technical content of this document should be addressed to the Frank J. Seiler Research Laboratory (AFSC), FJSRL/NC, USAF Academy, Colorado Springs, CO 80840. Phone AC 303-472-2655.

This report has been reviewed by the Commander and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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The electrochemical behavior of sulfur, sodium sulfide, sulfur monochloride and carbon disulfide was studied on a glassy carbon electrode at 25°C in 1-methyl-3-ethylimidazolium chloroaluminate melts in basic (excess organic chloride), neutral (1:1 mole ratio of organic chloride and $AlCl_3$) regions. Cyclic voltammetry, rotating disk electrode and steady-state potentiostatic techniques were used in the study. The literature on sulfur and sulfur compounds in $NaCl-AlCl_3$ melts is reviewed and comparisons are made with the room temperature melts.

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Electrochemistry of Sulfur, Na_2S, S_2, S_2CL_2 and CS_2 in 1-Methyl-3-Ethylimidazolium Chloride-Aluminum Chloride Melts

By

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SUMMARY

The electrochemical behavior of sulfur, sodium sulfide, sulfur monochloride and carbon disulfide was studied on a glassy carbon electrode at 25° C in 1-methyl-3-ethylimidazolium chloroaluminate melts in basic (excess organic chloride), neutral (1:1 mole ratio of organic chloride and $AlCl_3$) and acidic (excess $AlCl_3$) regions. Cyclic voltammetry, rotating disk electrode and steady-state potentiostatic techniques were used in the study. The literature on sulfur and sulfur compounds in $NaCl-AlCl_3$ melts is reviewed and comparisons are made with the room temperature melts.

PREFACE

The work described in the report was initiated in the Electrochemistry Division at FJSRL by Dr. Piersma, a visiting professor under the University Resident Research Program of the Office of Scientific Research, in 1981-82. This report was completed when B. J. P. participated in the Summer Faculty Research Program sponsored by the Air Force Office of Scientific Research/AFSC, United States Air Force, under contract F49620-85-C-0013.

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INTRODUCTION

The chemical properties and electrochemical behavior of sulfur and sulfur compounds have been studied in NaCl-$AlCl_3$ molten salts over the temperature range 150-250° C by several research groups within the past several years.(1-6) Depending on melt acidity and temperature, all of the following sulfur species have been proposed in chloroaluminate melts: S_8, S_{16}^{2+}, S_8^+, S_{12}^{2+}, S_2Cl^+, S_8^{2+}, S_4^+, S_4^{2+}, S_2^{2+}, S(II), SCl_3^+ and S(IV). It has been suggested that S_8^+ is the species of lowest valance, next to elemental sulfur, and that the existance of S_{16}^{2+} is unlikely (6). Fehrmann, et al. (6) also show that S_8^{2+} is not an important species in these melts. Sulfur can be reduced to S^{2-} and there is no evidence for the formation of polysulfides. (2,5) Mamantov (5) has suggested that in basic melt, the highest oxidation state for sulfur is the species S_2^{2+}, at least at lower temperatures. In acidic melts, the highest oxidation state is S(IV) (5,6). It has also been suggested that in these melts, sulfide interacts with chloroaluminate to form AlSCl in acidic melt and $AlSCl_2^-$ in basic melt (2). Reaction schemes have been suggested for the electrode reactions of sulfur in basic (1) and in acidic (5) melts.

In this paper we report our study of sulfur, Na_2S, S_2Cl_2 and CS_2 in a new room temperature chloroaluminate molten salt. We have observed significant differences in the reported behavior of sulfur compounds in NaCl-$AlCl_3$ melts and our results in room temperature 1-methyl-3-ethylimidazolium chloride(MeEtImCl)-$AlCl_3$ melts. In general, the electrochemical processes with sulfur compounds in room temperature melts are highly irreversible. We also observed that the presence of sulfur or sulfur compounds tends to extend the electrochemical windows, e.g., in acidic melts the overpotential for aluminum deposition is increased by up to 300mv.

EXPERIMENTAL

Aluminum chloride (Fluka, AG) was purified and MeEtImCl was synthesized and recrystallized following procedures established in this laboratory (7). S_2Cl_2 (Eastman), Na_2S (Baker), sulfur (Sargent-Welch) and CS_2 (Aldrich) were used, after drying, without further treatment. All melts were prepared and all experiments performed in a Vacuum Atmosphere Corp. controlled environment system in a dry argon atmosphere having <10 ppm water and oxygen. A simple pyrex glass cell with Teflon lid, containing a large tungsten foil counter electrode and a Pine Instruments glassy carbon working electrode (geometric area = 0.459cm2), was used for cylic voltammetric and rotating disc electrode voltammetric studies. Other measurements were carried out with a two-compartment cell having anode and cathode separated by a fine porosity glass frit. The reference electrode for all measurements was a coiled Al wire (Alfa) immersed in 0.6 melt (60 mole % $AlCl_3$/40 mole % MeEtImCl) contained in a separate pyrex glass tube with a fine porosity glass frit. Al wires were cleaned in aqueous 5% HF/15% HNO_3 for 5 seconds to remove oxide and rinsed with absolute ethanol just prior to being placed in the dry box. The temperature was maintained at 25 ± 1°C.

A PAR/EGG model 173 potentiostat was used with a PAR model 165 universal programmer and a Houston Omnigraphic model 2000 X-Y recorder. Dana model 5900 digital multimeters were used to measure potential and current and a Hewlett-Packard model 7100 BM strip chart recorder was used to record steady-state currents. A Pine Instrument Co. electrode rotator was used for rotating disc electrode (RDE) studies. Titration of the basic melt with $TiCl_4$ following the method of Osteryoung (8) indicated oxide levels in our melts on the order of 3-5 mM oxide.

RESULTS

Elemental sulfur is readily soluble up to 40 mM in basic and neutral melts at 25°C to give a clear, colorless solution. Higher sulfur concentrations in the melts are obtained at 25°C by stirring several hours. In acidic melts, sulfur dissolves more readily and gives a clear yellow solution. With heating to approximately 75°C, concentrations (based on monatomic sulfur) of greater than 0.4 molar were obtained. Sulfur appears to be stable in all melts examined, at least over a period of several days. Liquid S_2Cl_2 is readily soluble at 25°C yielding clear yellow solutions in basic and neutral melts. A dark reddish-brown solution results in acidic melt. S_2Cl_2 reacts chemically in acidic melt, e.g., the cathodic current peak observed with cyclic voltammetry for 35 mM S_2Cl_2 decreases with time and is absent after 4 hours. Na_2S is dissolved only with difficulty and only to the extent of about 30 mM at 25°C in acidic melt, but readily dissolves when the melt is heated to 60°C, and yields a clear, slightly yellow solution. The sulfide species formed by dissolving Na_2S in acidic melt reacts chemically with the melt, e.g., the change in anodic current peak shows a loss in oxidizable sulfide from 25mM to 10mM over a period of 72 hours. The solubility of Na_2S is much less in basic melt with less than 1mM solution resulting after 5 hours of stiring at 25°C. Na_2S is slightly more soluble at higher temperatures (60-70°C) (e.g., the increased solubility permits the observation of some redox behavior with cyclic voltammetry at higher temperatures), however the salt precipitates out as the melt is cooled to 25°C.

Liquid CS_2 dissolves slowly in basic melt, requiring about 30 min of stirring at 25°C to give a 75mM solution which is clear and colorless. CS_2 is immediately soluble in acidic melt at much higher concentrations yielding a clear slightly yellow solution that appears to be stable, at least, for 8-10 hours.

CYCLIC VOLTAMMETRY

Na_2S (Figs. 1 & 2)

CV curves for Na_2S in 0.4 melt show no redox activity of sulfide at 25°C, even after several days of stirring. When the melt is heated to 75°C (Fig 1 & 6), oxidation of sulfide is observed at +0.6V. The oxidation is irreversible and no evidence of reduction, other than of the melt, is observed. In 0.6 melt, where Na_2S is more soluble, an oxidation peak is observed at 25°C at about +2.0V. There are slight indications of reduction peaks on the cathodic sweep at 1.5V, 0.85V, 0.3V and -0.1V.

Sulfur (Figs. 3-6)

In 0.4 melt, sulfur has a large irreversible reduction peak at about -0.67V, and oxidation appears to occur at the melt limit. When the anodic limit is extended (Fig 3b) several additional reduction peaks are observed, i.e., at 0.55V, 0.45V, 0.2V, -0.55V, along with the major peak at -0.67V. In 0.6 melt, no reduction is observed until after sulfur is first oxidized. Details of the redox process (Fig 4b) give evidence for a single quasi-reversible oxidation and a single reduction peak on the reverse sweep following oxidation. Fig (4a) shows that the presence of sulfur in the melt increases the overpotential for aluminum deposition by about 300mV. In a much more concentrated sulfur solution (at 75°C), three oxidation peaks and two reduction peaks are evident (cf. Fig. 5 and Table I). In 0.5 melt (Fig 6), three oxidation peaks are clearly seen with a broad peak at 1.54V and sharper peaks at 2.04 and 2.15V. On the reverse sweep, reduction occurs with a minor peak at 0.6V and a large peak at 0.2V.

S_2Cl_2 (Figs 7 & 8)

In basic melt (Fig 7a), no oxidation apart from the anodic melt limit was observed for S_2Cl_2. Four reduction peaks, with the major peak at -1.07V, were obtained in 0.4 melts (of Table I). In neutral melt (actually slightly acidic), a reduction peak at 0.3V increases by a factor of 4 following oxidation and a larger cathodic peak at -0.55V is not influenced by prior oxidation. The reduction product formed at potentials negative to -0.5V remains on the electrode surface and successive cycles show the decrease and disappearance of the -0.55 cathodic peak. Repeated cycling up to a cathodic limit of -0.5V has no effect on the other peaks. A large oxidation peak is observed in 0.5 melt at 1.45V, but is not present without prior reduction. Figure 8 for acidic melt shows an anodic peak of 2.10V, which is not present without prior reduction and a single large cathodic peak at 1.3V. The cathodic peak disappears after 2-3 hours indicating chemical interaction with the melt. The anodic peak remains after the cathodic peak has disappeared but is much smaller, e.g., after 2 hours the current is less than one-half its original value.

CS_2 (Fig 10)

The CV for CS_2 in basic melt shows a cathodic peak at 1.23V and a broad anodic peak following reduction, beginning at about 0.0V. In acidic melt, a sharp anodic peak is observed at about 2.2V and no reduction is evident.

CV behavior for the 3 sulfur compounds and sulfur are summarized in Tables I-III. The differences observed for the anodic and cathodic peaks for S, Na_2S and S_2Cl_2 tend to suggest that the species resulting in the melts are not the same. The effects of sulfur species in increasing the overpotential for aluminum deposition are summarized in Table II. Kinetic parameters that could be derived from variation of sweep rates are summarized in Table III.

RDE VOLTAMMETRY

Systems for which rotating disk electrode studies could be conducted and corresponding results are summarized in Table IV. For the other systems studied, no current plateaus, from which data could be obtained, were observed. Pure diffusion control was not obtained for any of the systems studied. S_2Cl_2 in basic melt provided interesting results which are shown in Fig 9. The potential at which the second current plateau begins is dependent on electrode rotation rate and is proportional to $\omega^{-1/2}$ (cf. Fig. 11). The limiting currents for the two processes are proportional to $\omega^{1/2}$, however, the i vs $\omega^{1/2}$ plots do not extrapolate through zero, indicating mixed kinetic and diffusion control. Diffusion coefficients were not calculated for most sulfur species since diffusion control was not obtained. For S in 0.5 melt and S^{2-} in 0.6 melt the diffusion coefficients (see Table IV) are on the same order of magnitude as those for Fe^{3+} and Cu^{2+}.(9,10) A value of $D = 3 \times 10^{-6} cm^2 sec^{-1}$ has been reported for sulfide in $PbCl_2$ - KCl melt at 440°C.(11)

The standard heterogeneous rate constants were determined as previously (9,10), by extrapolating plots of ln k_f vs E to $E_{p/2}$, with the assumption that the reactions are first order. Where comparisions can be made (i.e., for sulfur and Na_2S in acidic melt and for sulfur and S_2Cl_2 in neutral melt) the significant differences in values for k_s are another indication that the species formed by dissolving sulfur, Na_2S and S_2Cl_2 in the various melts are probably not the same.

STEADY STATE

The only system which gave reasonable steady state behavior with a reasonable Tafel slope was sulfur in acidic melt (of Fig 12). In neutral melt, the Tafel slope observed for oxidation of sulfur indicated that probably the product of oxidation was remaining on the electrode surface to some extent and the current appears to be limited by kinetic rather than diffusion control (Fig 13). No steady-states could be obtained with S_2Cl_2 as Na_2S. While the data is very limited, determination of the reaction order from the slope of ln i vs ln C at a constant potential could be made for sulfur in neutral and acidic melts. The steady-state results can be summarized as follows:

System	b_{anodic}	n_s
sulfur/0.6 melt	RT/F	1
sulfur/0.5 melt	2RT/F	1

DISCUSSION

To understand the nature of the sulfur species and their redox behavior in room temperature melts, it will be helpful to briefly summarize that results reported for $NaCl-AlCl_3$ melts. A summary of CV results is presented in Table V.

Basic $NaCl-AlCl_3$ Melt

Sulfide reacts with the melt

$$S^{2-} + AlCl_4^- \rightarrow AlSCl_2^- + 2Cl^- \quad (1)$$

$$AlSCl_2^- \rightarrow Al_2SCl_6^- \quad \text{(solvation)}$$

and as $[S^{2-}]$ is increased, a chain-like structure is formed (13):

$$[Al_nS_{n-1}Cl_{2n+2}]^{n-}$$

where n=3,4 in dilute melts but approaches infinity as the $[AlSCl_2^-]$ is increased. From analysis of $CsCl-AlCl_3$ melts, Bjerium, et al. (13) found that

$$(n-1)[Al_2SCl_6]^{2-} \rightarrow [Al_nS_{n-1}Cl_{2n+2}] + (n-2)\ AlCl_4^- \quad (2)$$

when 20% of the Al was in $AlCl_4^-$ and 80% was $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$. Osteryoung (2,3) suggested that

$$S_2 + 2AlCl_4^- + 4e^- \rightarrow 2AlSCl + 6Cl^- \qquad (3)$$

with no evidence for polysulfide ions and that sulfur is oxidized to S_2^{2+}. Mamantov, et al. (1) summarize their studies of sulfur in basic melt as:

$$\left.\begin{array}{l} 2S_n \rightleftharpoons \text{sulfur chain} \rightleftharpoons nS_2 \quad \xrightarrow{-2ne^-} \\ 2S_n \rightleftharpoons 2S_n^+ \rightleftharpoons \text{sulfur chain} \quad \xrightarrow{-ne^-} \end{array}\right\} nS_2^{2+} \qquad (4)$$

and

$$S_2^{2+} \overset{AlCl_4^-}{\rightleftharpoons} S_2Cl^+ \overset{AlCl_4^-}{\rightleftharpoons} S_2Cl_2 \qquad (5)$$

where n is most likely 8.

For oxidation of sulfide at lower temperature (175° C)

$$\left.\begin{array}{l} S^{2-} \rightarrow S + 2e^- \\ S \rightarrow 1/2\ S_2^{2+} + 2e^- \end{array}\right\} \qquad (6)$$

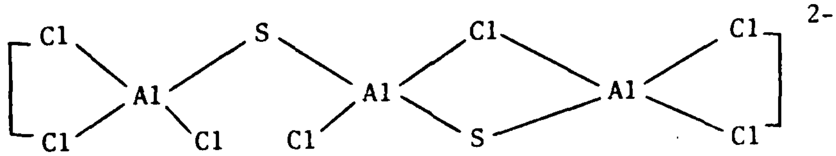
and at higher temperature (250° C)

$$\left.\begin{array}{l} S^{2-} \rightarrow S + 2e^- \\ S \rightarrow S^{2+} + 2e^- \end{array}\right\} \qquad (7)$$

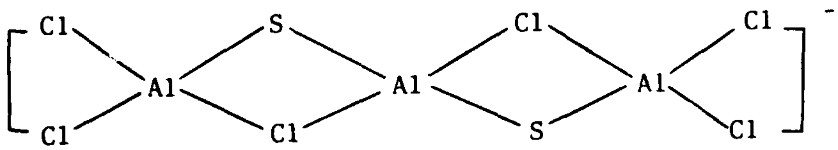
In neutral melt, Bjerium, et al. (13) propose that:

$$[Al_nS_{n-1}Cl_{2n+2}]^{n-} \rightleftharpoons [Al_nS_{n-1}Cl_{2n+2-m}]^{(n-m)-} + mCl^-$$
$$\uparrow\downarrow \qquad (8)$$
$$[Al_nS_{n-1}Cl_{n+3}]^- + (n-1)Cl^-$$

For example, when n = 3, m = 1, the structure is



and when n = 3, m = 2



As the melt acidity is increased, n increases and the species approaches AlSCl, however, it was considered unlikely that isolated AlSCl molecules exist.

ACIDIC NaCl-$AlCl_3$ MELT

The following reactions are suggested for sulfur species in acidic melt, primarily from the work of Mamantov, et al. (5) and Bjerium, et al.(6):

$$S_8 \overset{-e^-}{\rightleftharpoons} S_8^+ \overset{-e^-}{\rightleftharpoons} S_8^{2+} \qquad (9)$$

$$S^{2+}{}_8 + 8AlCl_4^- \rightleftharpoons 4S_2Cl^+ + 4Al_2Cl_7^- + 6e^- \qquad (10)$$

$$S_2Cl^+ + 10AlCl_4^- \rightarrow 2SCl_3^+ + 5Al_2Cl_7^- + 6e^- \qquad (11)$$

Bjerium, et al. (6) argue that besides elemental sulfur, only the species S_8^+, S_{12}^{2+} and S_4^+ exist in acidic NaCl-$AlCl_3$ melt at 150°C.

MeEtImCl-$AlCl_3$ MELTS

Sulfur species in MeEtImCl melts are, in general, not well behaved and the electrode reactions are highly irreversible. Our data permit only limited mechanism discussions for sulfur and sulfur monochloride in acidic and neutral melts.

OXIDATION OF SULFUR SPECIES

Similarities in the CV behavior of sulfur and S_2Cl_2 suggest a common species., Following the proposal of Bjerium (13), we assume a species of the form AlSCl. The anodic oxidation appears to be first order in sulfur for both acidic and neutral melts, thus for a Tafel slope of 2 RT/F, the first electron transfer is the rate limiting step:

$$AlSCl \rightarrow AlSCl^+ + e^- \qquad (12)$$

The Tafel slope determined from steady-state potentiostatic measurements for sulfur in acidic melt is RT/F and appears to be a real difference from the transient Tafel slope. In this case it would appear that a chemical step following eq. 12 is the rate limiting step, for example:

$$AlSCl + AlSCl^+ \rightarrow (AlSCl)_2^+ \qquad (13)$$

A second electron transfer is indicated by the presence of a 2nd anodic CV peak, thus:

$$(AlSCl)_2^+ \rightarrow S_2^{2+} \text{ species} + e^- \qquad (14)$$

REDUCTION OF SULFUR SPECIES

For both sulfur and S_2Cl_2, reduction in acidic melt appears to have a different rate determining step than reduction in neutral melt. A Tafel slope of 2RT/F in acidic melt suggests that the first election transfer is the rate limiting step, i.e.:

$$Al_2S_2Cl_2^{2+} + e^- \rightarrow Al_2S_2Cl_2^+ \qquad (15)$$

In neutral melt, the RT/F slope suggests a chemical step following eq. 15 is rate limiting:

$$Al_2S_2Cl_2^+ \rightarrow AlSCl + AlSCl^+ \qquad (16)$$

This process is then followed by a faster electron transfer step.

$$AlSCl^+ + e^- \rightarrow AlSCl \qquad (17)$$

CONCLUSIONS

1. The electrochemical behavior of sulfur and sulfur compounds is significantly different in room temperature MeEtImCl/$AlCl_3$ melts than in

$NaCl/AlCl_3$ melts. Important differences are lack of solubility of Na_2S and marked irreversibility of redox behavior in the room temperature melts.

2. The presence of sulfur species in the melts extends the electrochemical windows, particularly by increasing the overpotential for Al deposition in acidic melt.

3. Mechanisms for oxidation and reduction of sulfur and monochloride sulfur have been proposed for neutral and acidic melts. Sulfur and S_2Cl_2 probably form similar species in the melt and undergo similar electrochemical processes.

4. Diffusion coefficients and standard hetrogenous rate constants were determined for some of the sulfur species and for different melt compositions.

5. Sulfur and the sulfur compounds examined here are probably not suitable as battery cathodes in $MeEtImCl-AlCl_3$ melts.

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ILLUSTRATIONS

Fig 1: C V of 7 mM Na_2S in 0.4 melt

(a) at 25°C

(b) at 75°C

Fig 2: C V of 25 mM Na_2S in 0.6 melt at 25°C

(a) melt without Na_2S

(b) melt with Na_2S

Fig 3: C V of 36 mM sulfur in 0.4 melt

(a) anodic sweep to +0.9v

(b) anodic sweep to +1.3v

Fig 4: C V of 0.6 melt saturated with sulfur at 25°C

(a) cathodic sweep showing Al depositions

(b) details of redox behavior

Fig 5: C V of 0.4 M sulfur in 0.6 melt at 75°C

Fig 6: C V of 24 mM sulfur in 0.5 melt

Fig 7: C V of $S_2 Cl_2$

(a) 31 mM $S_2 Cl_2$ in 0.4 melt

(b) 22 mM $S_2 Cl_2$ in 0.5 melt

Fig 8: C V of 35 mM $S_2 Cl_2$ melt

Fig 9: RDE Curves for 3 mM $S_2 Cl_2$ in 0.4 melt

Fig 10: C V of CS_2

(a) 0.4 melt

(b) 0.6 melt

Fig 11: Dependence of potential at beginning of second current plateau on electrode rotation rate.

Fig 12: Study-state log i vs E behavior for sulfur in 0.6 melt at 25°C.

(Δ) 36 mM sulfur

(•) 72 mM sulfur

Fig 13: Steady-state log i vs E behavior for sulfur in 0.5 melt.

(Δ) 9.8 mM sulfur

(•) 48 mM sulfur

Table I
Potentials of CV Current Peaks

System		Reduction	Oxidation
NA_2S	0.4 melt	-------	0.69V (1)
	0.6 melt	1.52V, 0.85V, 0.31V, -0.10V	2.02V
Sulfur	0.4 melt	0.55, 0.45, 0.20, -0.55, -0.67(2)	at anodic melt limit
	0.5 melt	0.57, 0.20	1.54, 2.04, 2.15
	0.6 melt	1.39 (3)	2.11, 2.24
0.4m S in 0.6 melt/75°C		1.90, 1.45	2.03, 2.22, 2.39
S_2Cl_2	0.4 melt	-0.75, -0.95, -1.07, -1.45	at anodic melt limit
	0.5 melt	0.30(4), -0.55	1.45(5)
	0.6 melt	1.30	2.10(5)
$C S_2$	0.4 melt	-1.23(3)	0.45, 0.63
	0.6 melt	----------	2.19

(1) only observed at higher temperatures where NA_2S becomes soluble
(2) major peak and only peak present for lower anodic sweep limits
(3) Present only after prior oxidation
(4) Peak greatly increased after oxidation
(5) not present without prior reduction

Table II
Effect of Sulfur Compounds on Electrochemical Windows

System	0.4 (basic) Melt	0.5 (neutral) Melt	0.6 (acidic) Melt	Al dep.	Al reoxid.
MEIC/$AlCl_3$	+0.97 to -1.60V	+1.20 to -1.20 V	+2.35 to -0.050V	-0.075V	+0.220V
with .30mM S	0.90 to -1.70	2.30 to -0.43*	2.52 to -0.33	-0.330	+0.210
with .30mM S_2Cl_2	0.95 to -1.95	1.90 to -0.60*	2.30 to -0.20	-0.200	+0.120
with .30mM NA_2S	0.90 to -1.75	1.20 to -1.50	1.90 to -0.235	-0.235	+0.175

* on acidic side of neutral

Table III
Kinetic Parameters Derived from CV

System	$E_{p/2}$	$E_{p,c}$	$E_{p,a}$	$i_{p,a}/i_{p,c}$	b_c	b_a	$\alpha_c n_c$	$\alpha_a n_a$	$\frac{i_{p,c}}{\nu 1/2}$	$\frac{i_{p,a}}{\nu 1/2}$
10 mM S in 0.6 Melt	1.75	1.37V	2.11V	3.3	-135MV	119 mV	0.52	0.48	max at ν=10	dec with inc ν
24 mM S in 0.5 Melt	0.88	0.21	1.54	2.0	-72	123	0.57	0.43	~ const.	~ const.
35 mM S_2Cl_2 in 0.6 Melt	1.68	1.28	2.09	1.2	-200	170	0.52	0.48	const.	max for $5 \leqq \nu \leqq 10$
22 mM S_2Cl_2 in 0.5 Melt	0.91	0.31	1.49	3.9	-70	140	0.67	0.33	~ const.	~ const.

Table IV
Parameters Derived from RDE Voltammetry

System	i v_s $W^{1/2}$	D_O(cm^2/sec)	D_R(cm^2/sec)	k_s(cm/sec)	α_n	n
0.6 Melt 100 mM S	Kinetic Control	--	--	1.24×10^{-5}	0.42	--
0.5 Melt 25 - 50 nM S	Kinetic Control for E = 1.8 - 2.2V Diffusion Control for E > 2.2V	--	2.7×10^{-7}	$k_s(1) = 6.2 \times 10^{-7}$ $k_s(2) = 1.1 \times 10^{-5}$	0.47 0.42	-- --
0.5 Melt 22 mM S_2Cl_2	Kinetic Control	--	--	k_s (oxid) = 2.3×10^{-7} k_s (oxid) = 1.9×10^{-3}	0.43 0.42	-- --
0.4 Melt 31 mM S_2Cl_2	Mixed Kinetic and diffusion Control	-- --	--	$k_s(1) = 4.5 \times 10^{-5}$ ks(2) = 6.3×10^{-5}	0.45	1
0.6 Melt 25 mM NA_2S	Kinetic Control diffusion Control at E = 2.1V	--	7.0×10^{-8}	3.2×10^{-7}	0.31	--

Table V
Summary of CV Results in $NaCl/AlCl_3$ Melts

System	t		cathadic peaks	anodic peaks	rev. couple	secure
S/basic $NaCl/AlCl_3$	175C	Pt	1.85V, 0.92V, 0.50V	1.930, 1.25V	(1.85/1.93)	Mamantov (1975)
S/acidic $NaCl/AlCl_3$	175C	Pt	1.88, 1.78, 0.81, 0.47	1.98, 1.51	(1.88/1.98)	Mamantov (1975)
S/basic $NaCl/AlCl_3$	175C	glassy C	1.80, 0.6	2.02, 1.42	querirri	Mamantov (1976)
Na_2S/basic $NaCl/AlCl_3$	257C	W	1.83, 1.05	1.91, 121	(1.83/1.91) (1.05/1.21)	Mamantov (1976)
Na_2S/acidic $NaCl/AlCl_3$	175C	glassy C	2.39, 2.26, 1.38	2.53, 1.92	(2.39/2.53)	Osteryoung (1976)
S/basic $NaCl/AlCl_3$	175C	glassy C	1.79, 0.60	2.13, 1.53	inev	Osteryoung (1976)
Na_2S/basic $NaCl/AlCl_3$	175C	glassy C	1.95, 0.55	2.10, 1.58	very small redn pks	Osteryoung (1976)
S_2Cl_2/basic $NaCl/AlCl_3$	175c	W	1.93, 0.94	2.02, 1.48	(1.93/2.02)	Osteryoung (1976)
S/acidic $NaCl/AlCl_3$	250c	W	1.86, 1.75 1.08 minor peak at 1.45	1.95, 1.83 1.28 minor peak at 1.55	(1.86/1.95) (1.75/1.83)	Mamantov (1974)

FIG 1(a) CV OF Na2S IN 0.4 MELT AT 45 C

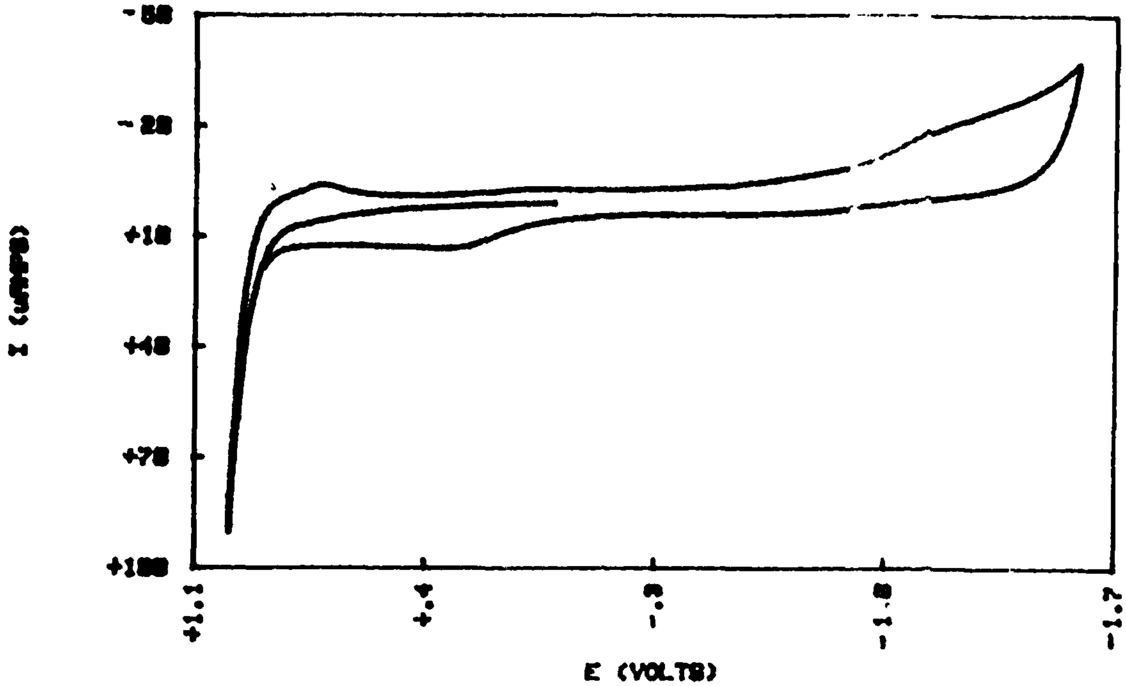


FIG 1(b) CV OF Na2S IN 0.4 MELT AT 75 C

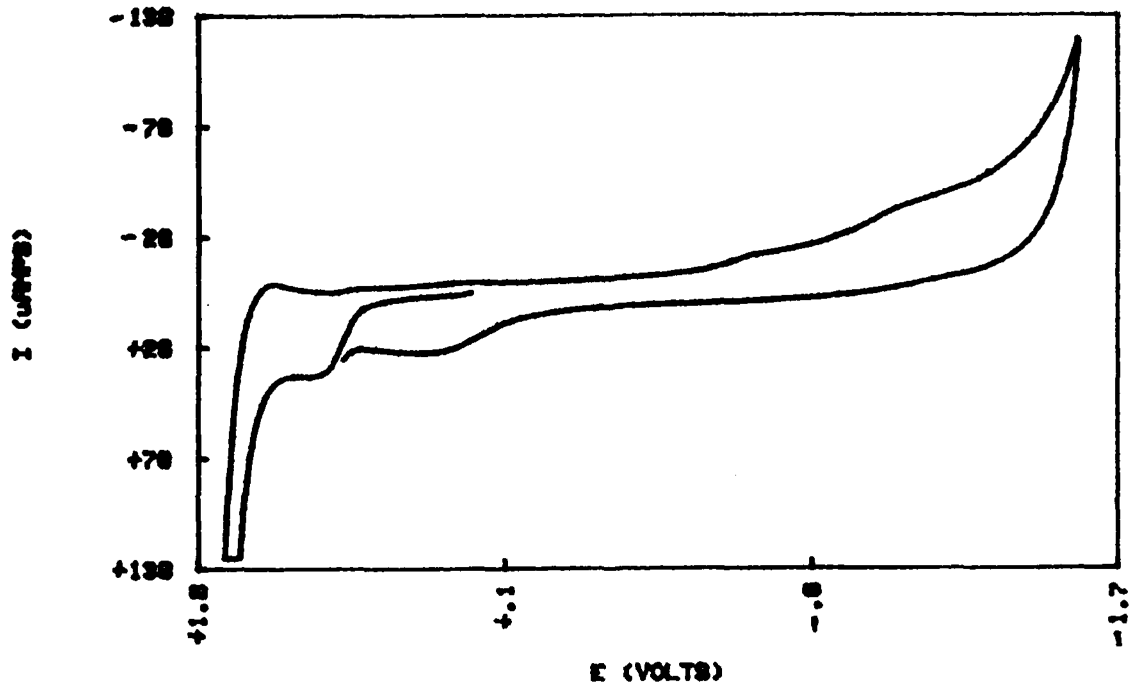


FIG 2(a) CV OF 8.8 MELT

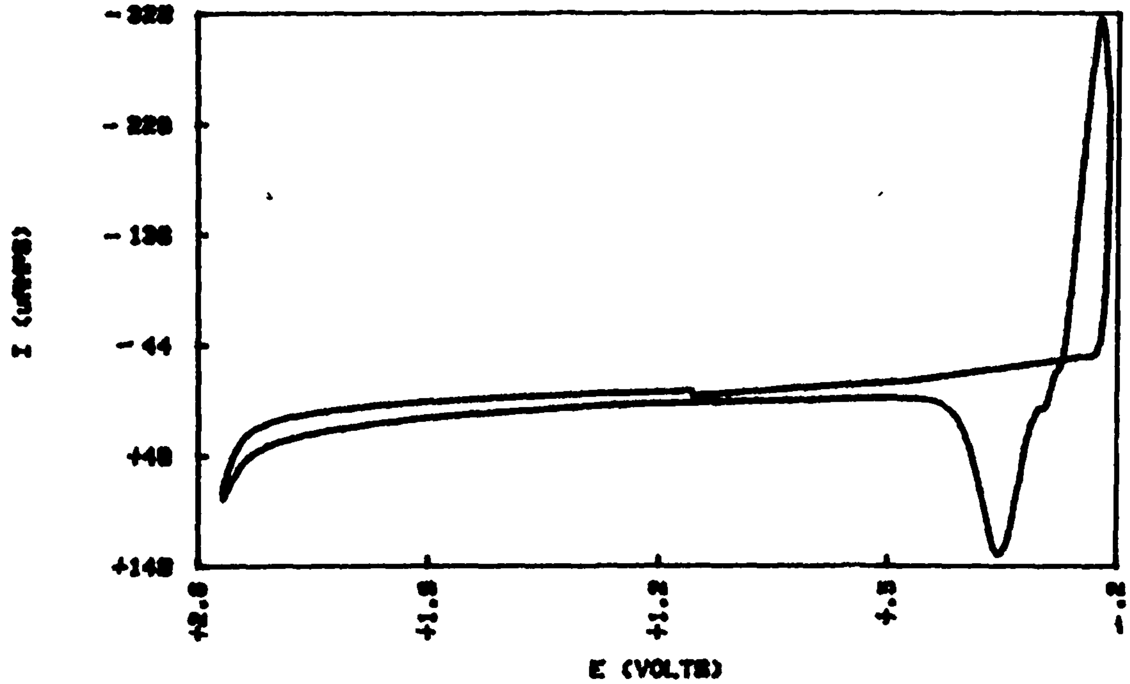


FIG 2(b) CV OF Na_2S IN 8.8 MELT

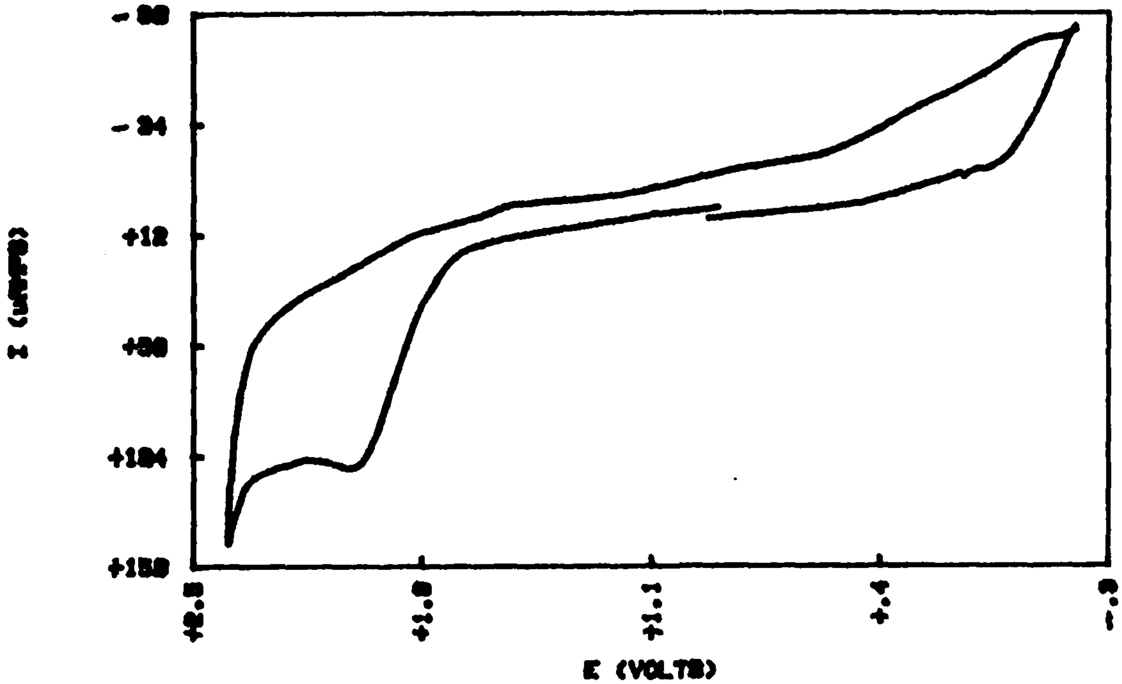


FIG 3(a) CV OF SULFER IN 0.4 MELT

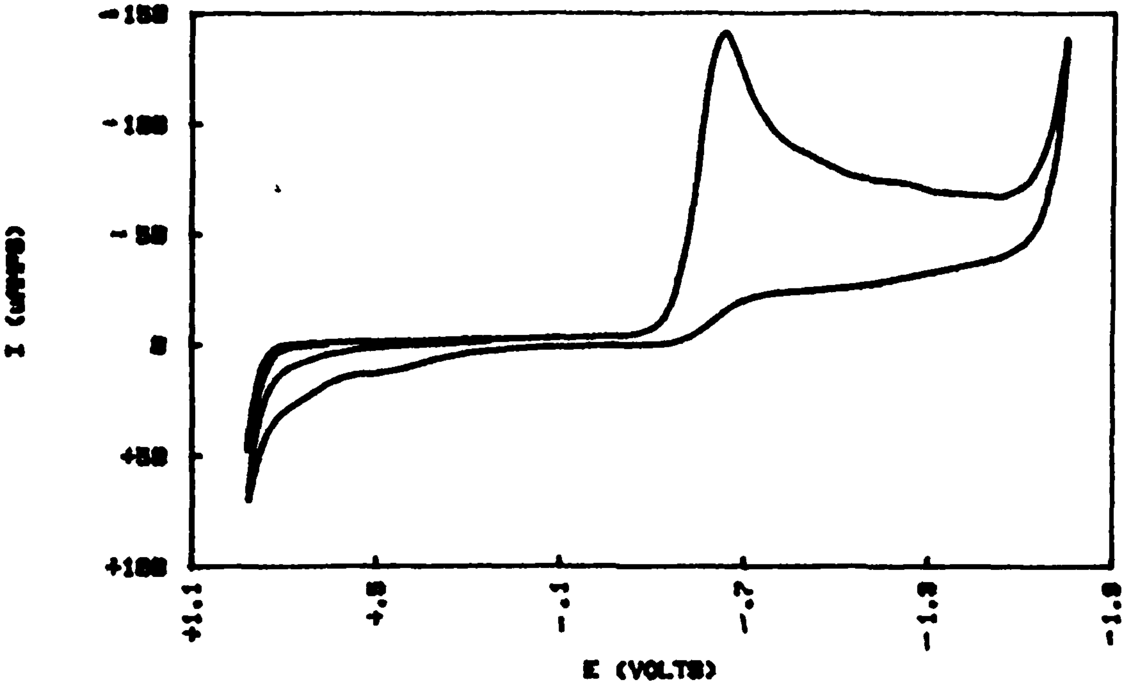


FIG 3(b) CV OF SULFER IN 0.4 MELT

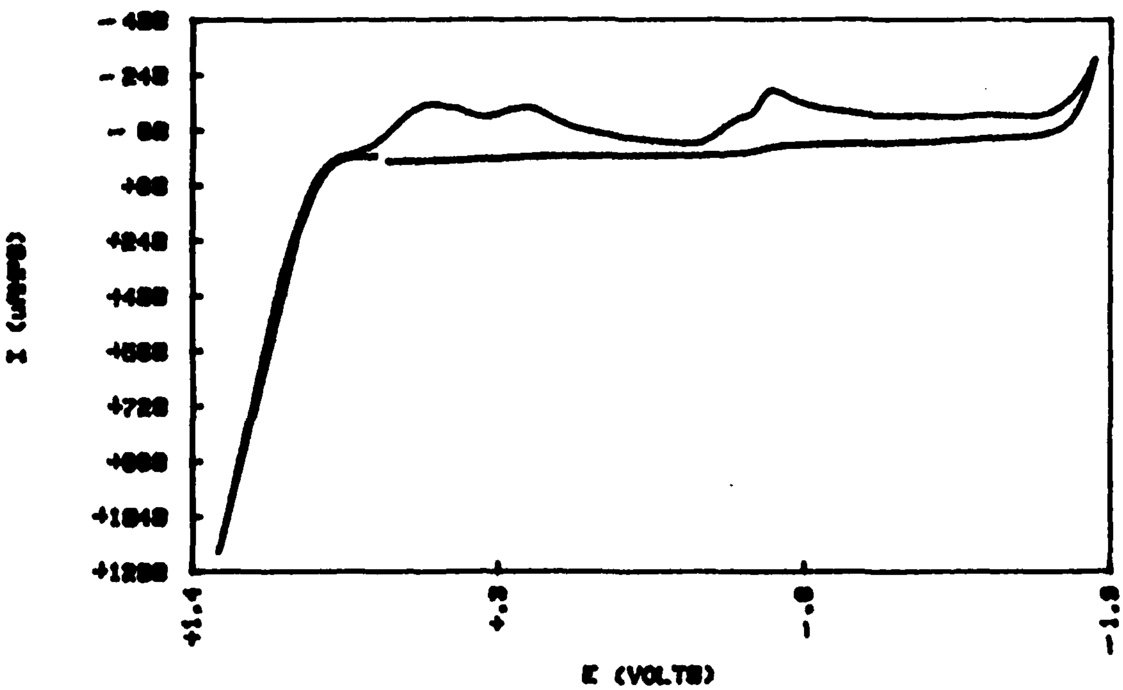


FIG 4(a) CV OF SULFER IN 0.8 MELT

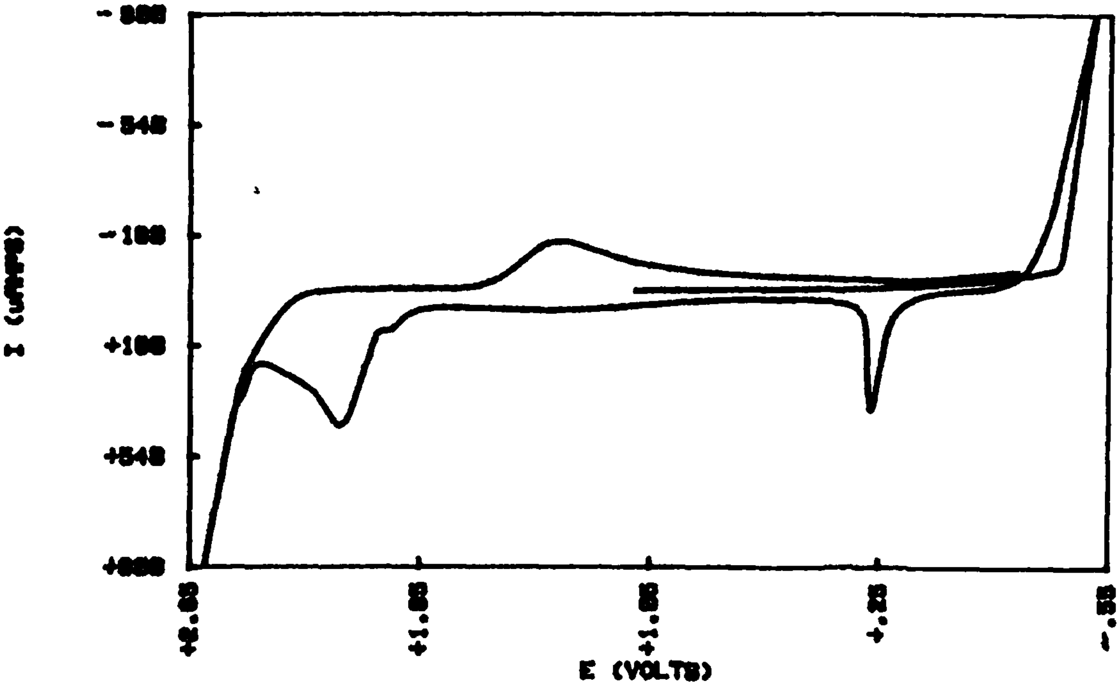


FIG 4(b) CV OF SULFER IN 0.8 MELT

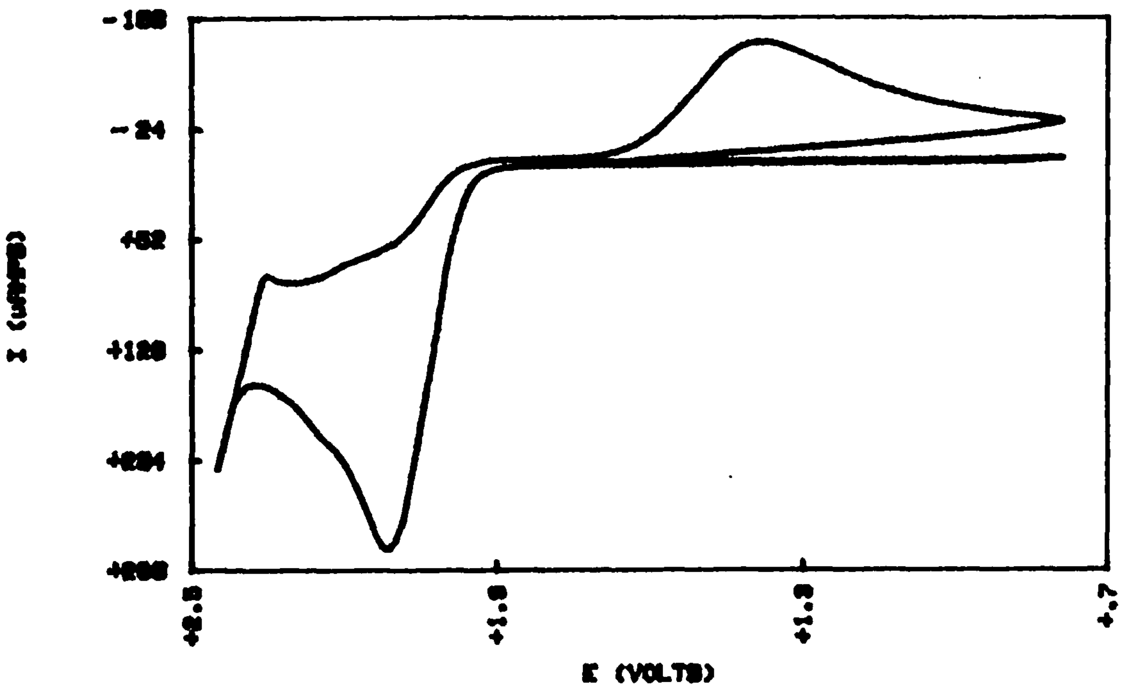


FIG 5 CV OF SULFER IN 0.6 MELT AT 70 C

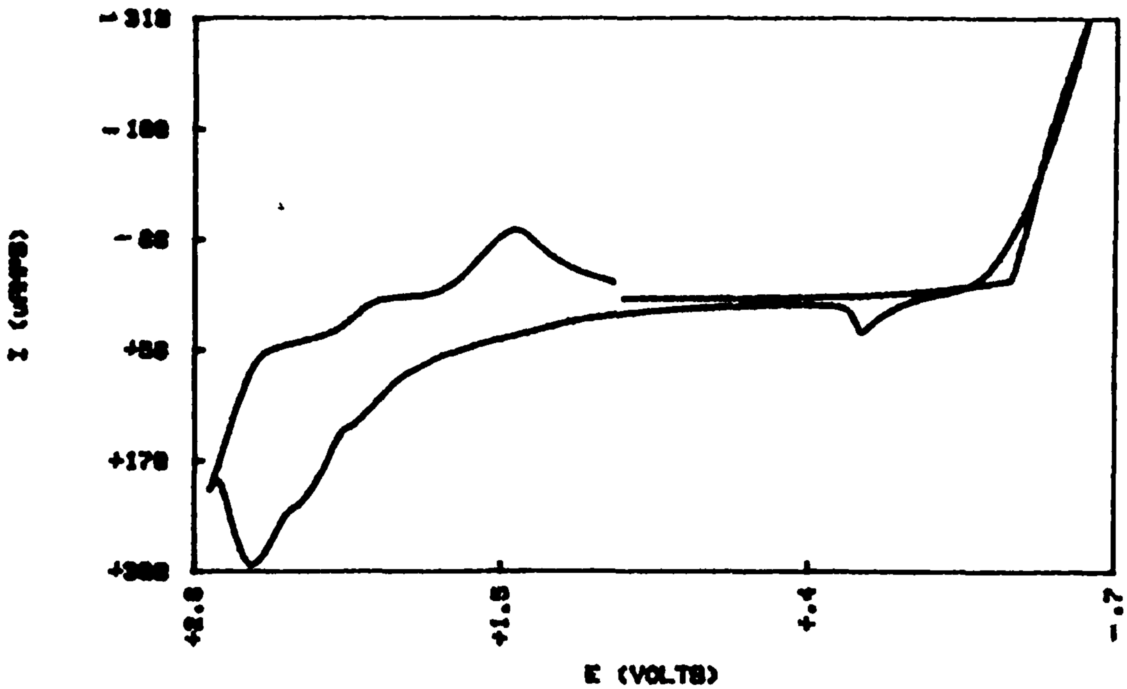


FIG 6 CV OF SULFER IN 0.5 MELT

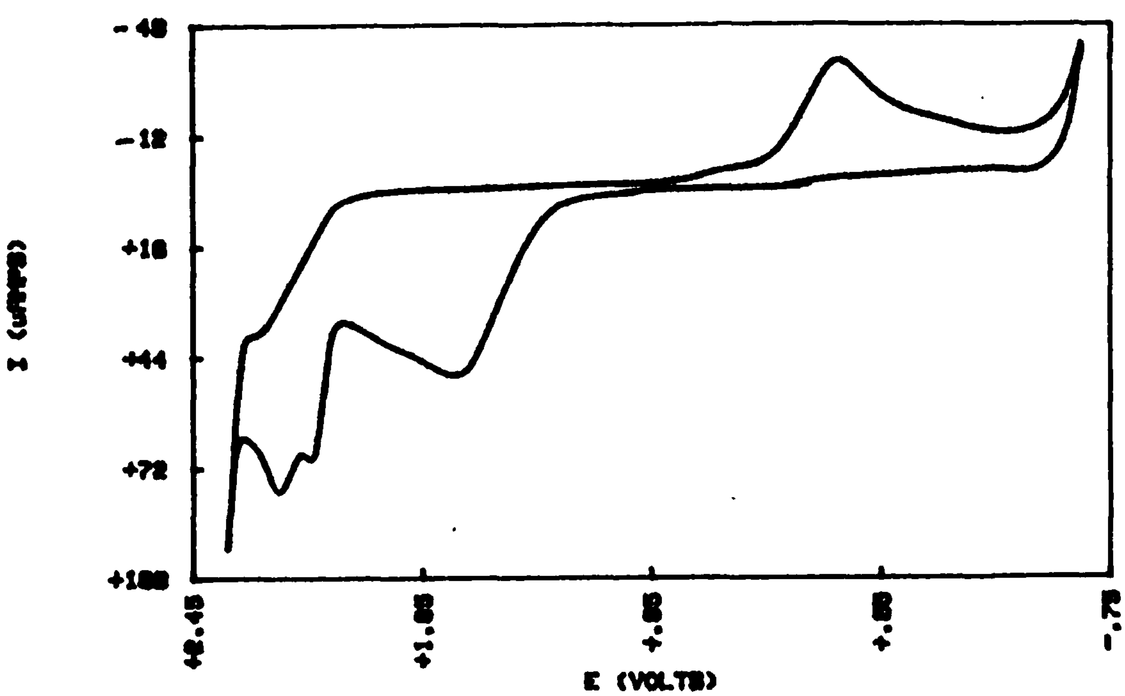


FIG 7(a) CV OF S2Cl2 IN 0.4 MELT

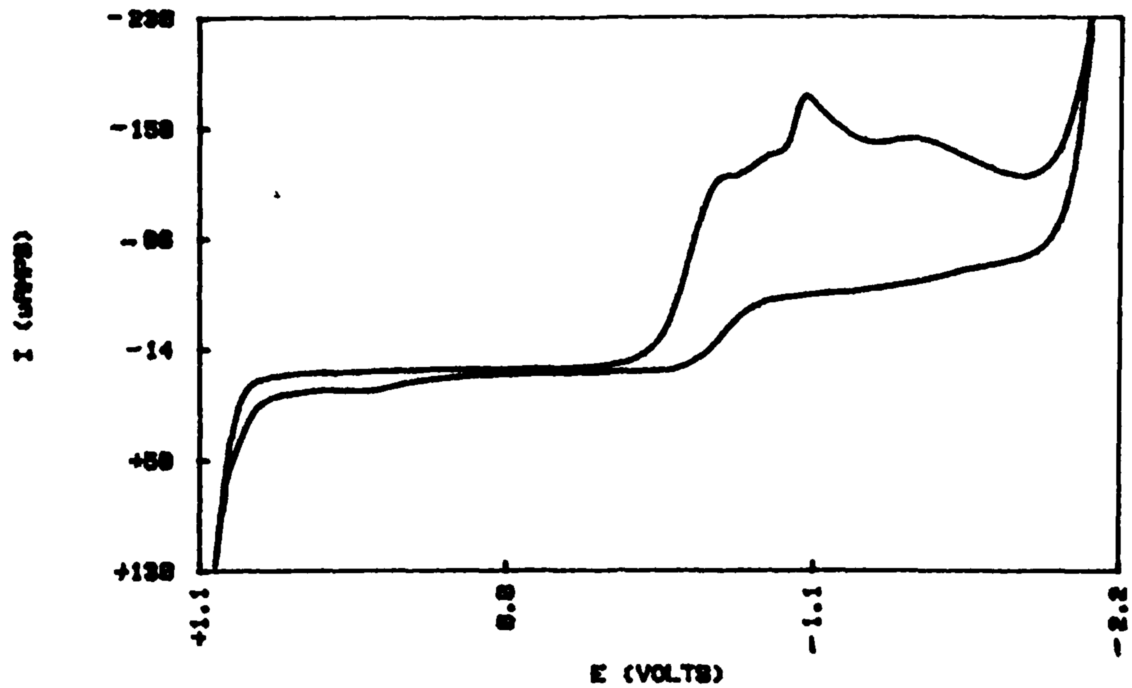


FIG 7(b) CV OF S2Cl2 IN 0.5 MELT

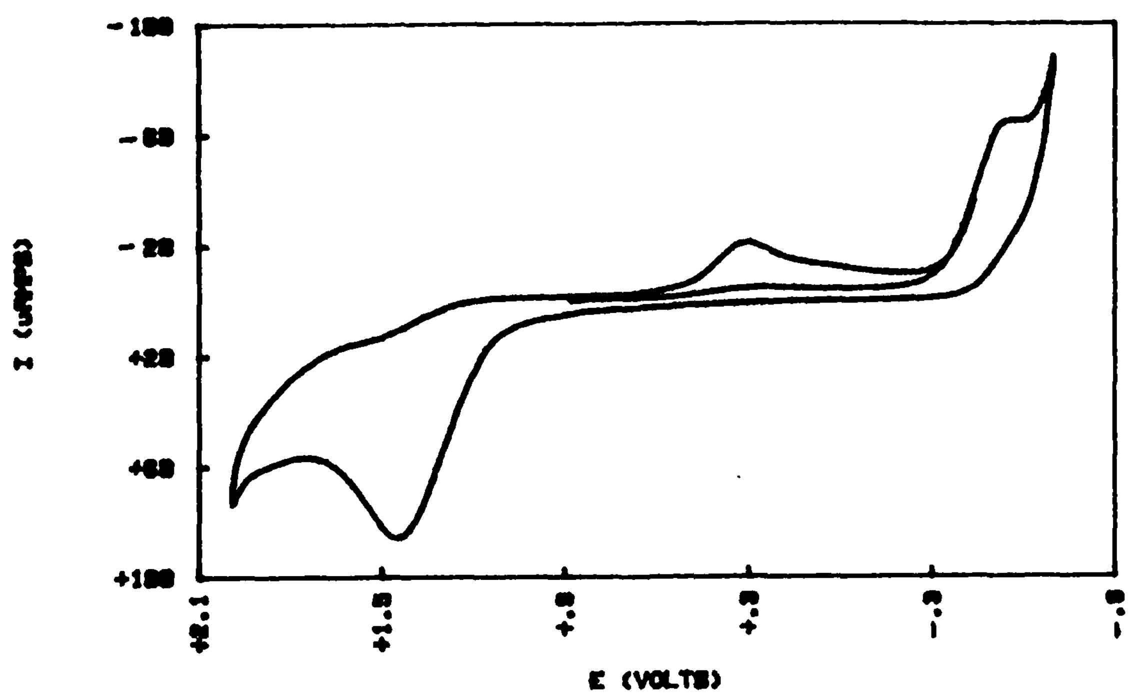


FIG 8 CV OF S2C12 IN 0.6 MELT

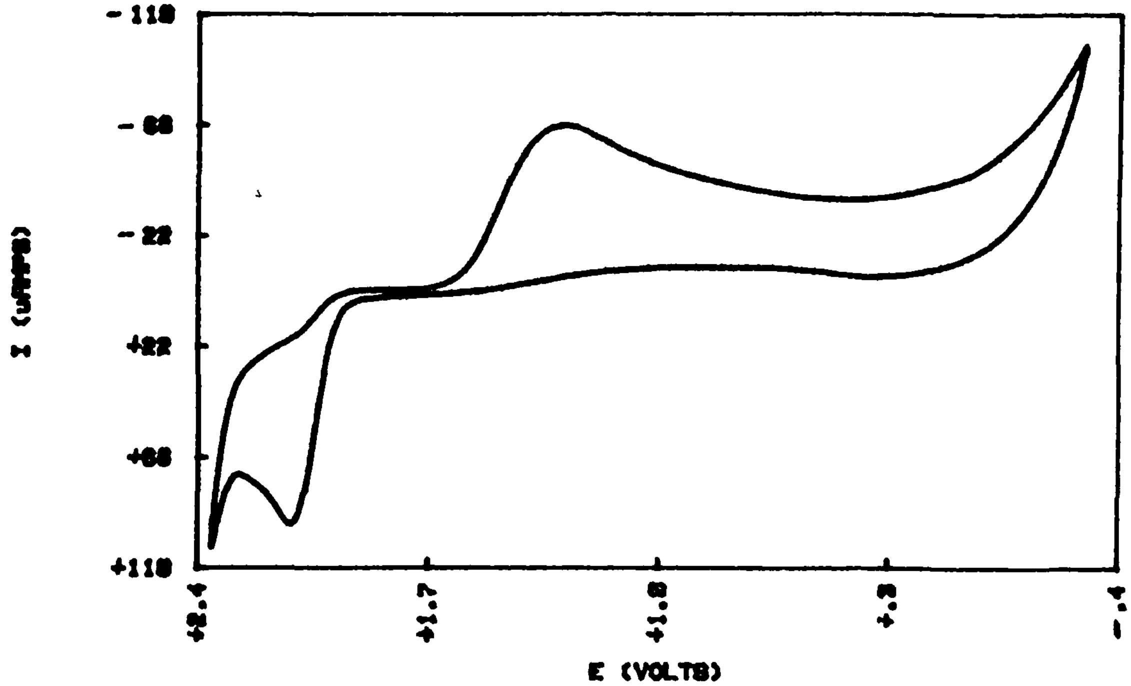


FIG 9 RDE OF S2C12 IN 0.4 MELT

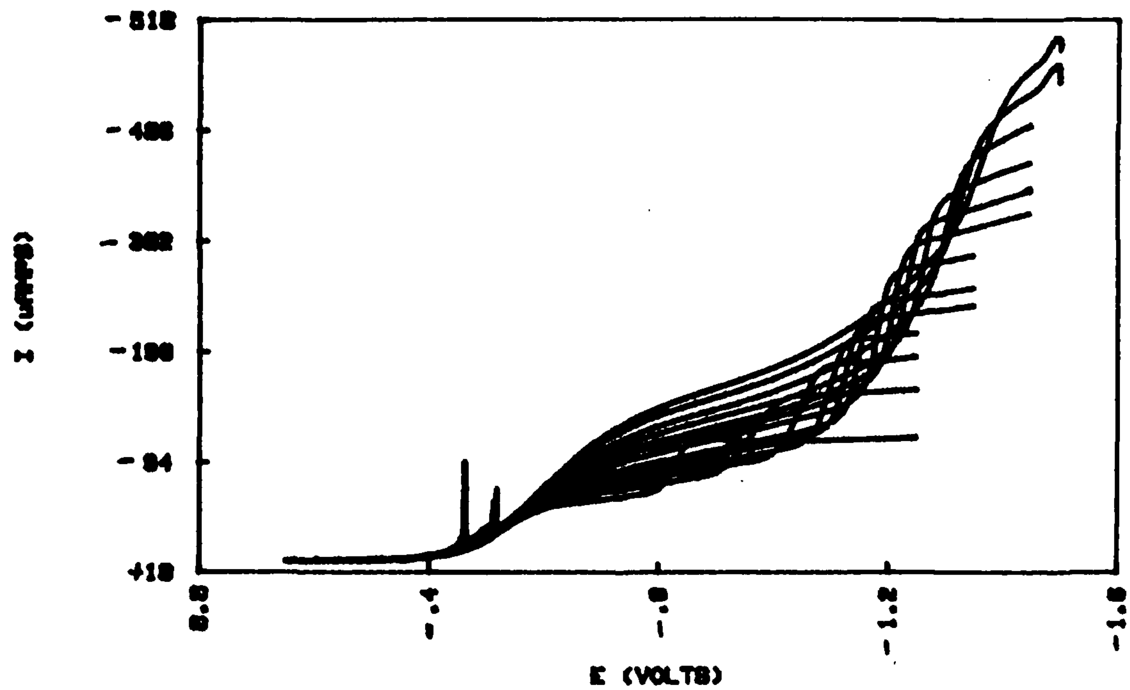


FIGURE 11

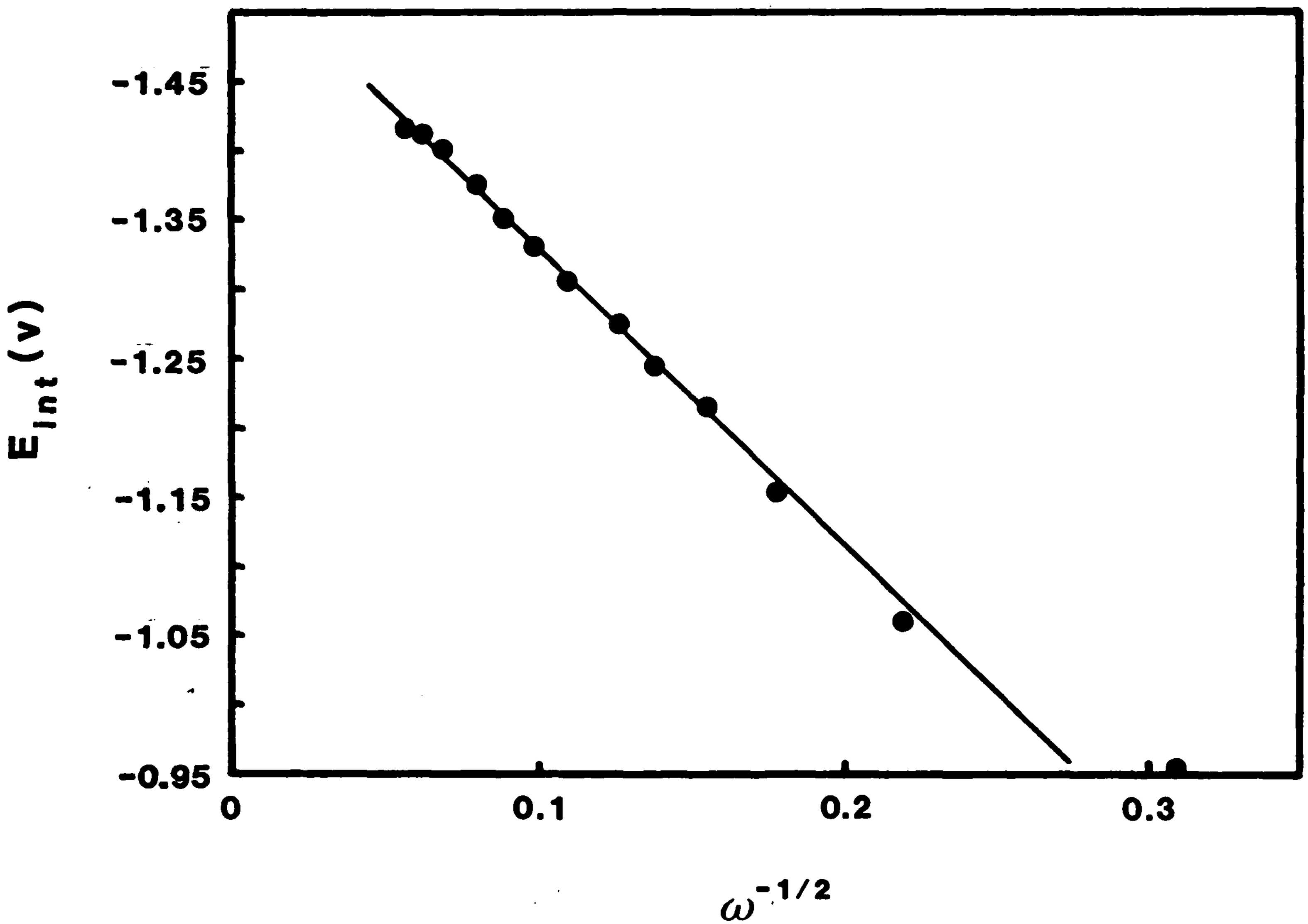


FIG 18(a) CV OF CB2 IN 8.4 MELT

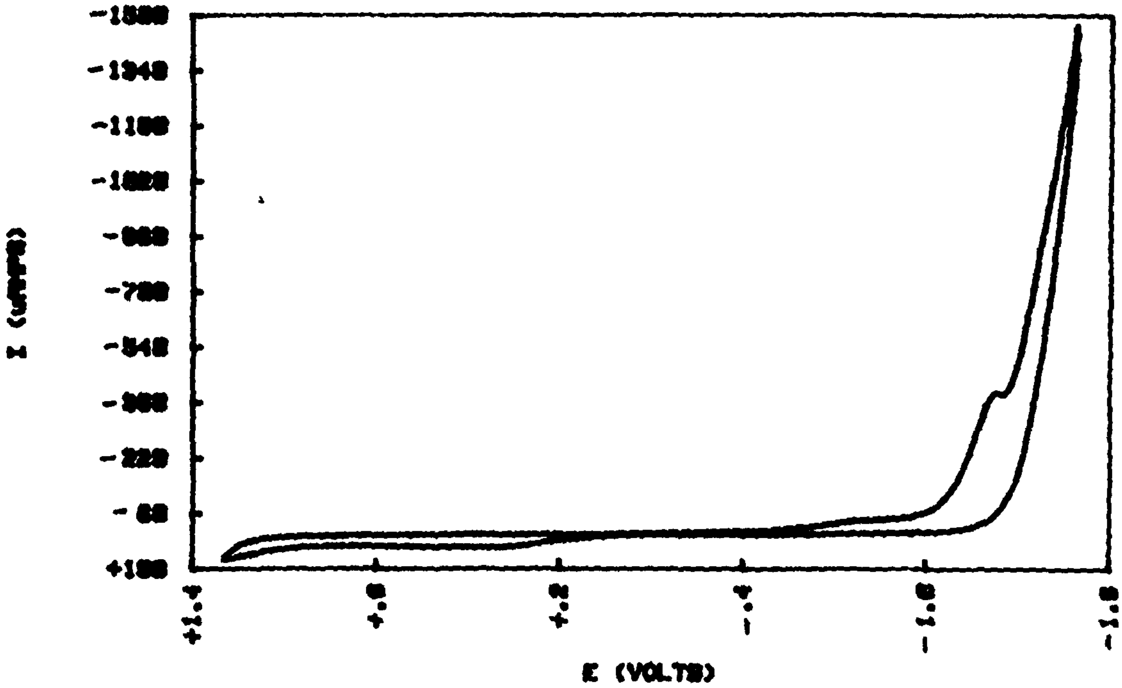


FIG 18(b) CV OF CB2 IN 8.8 MELT

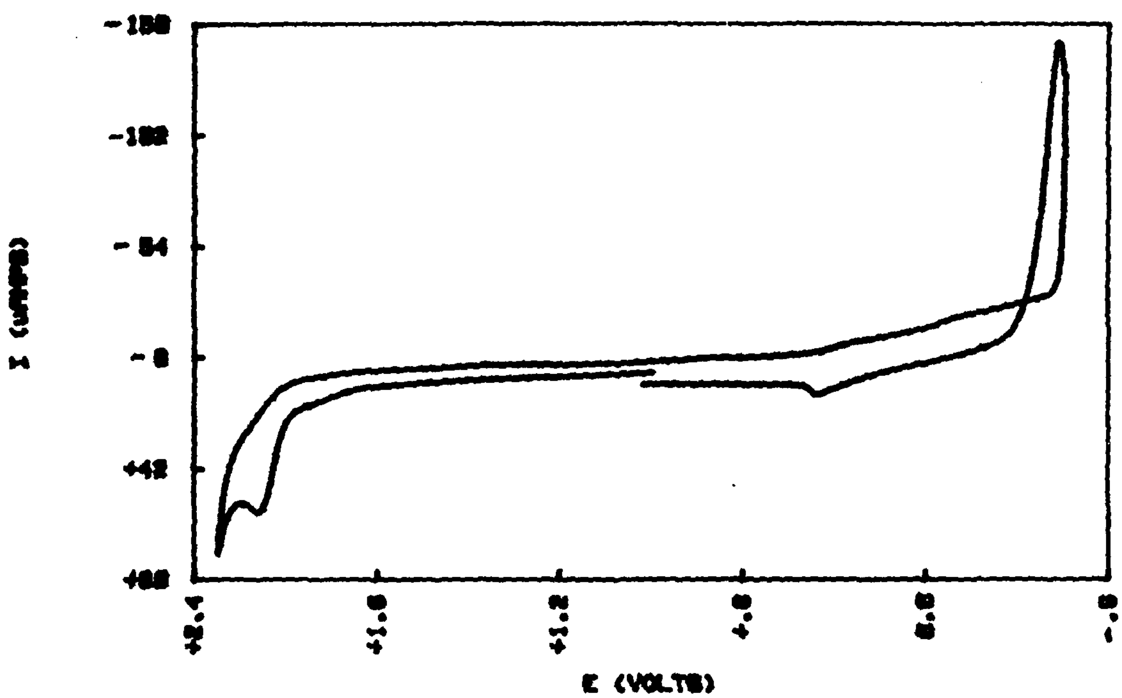


FIGURE 12

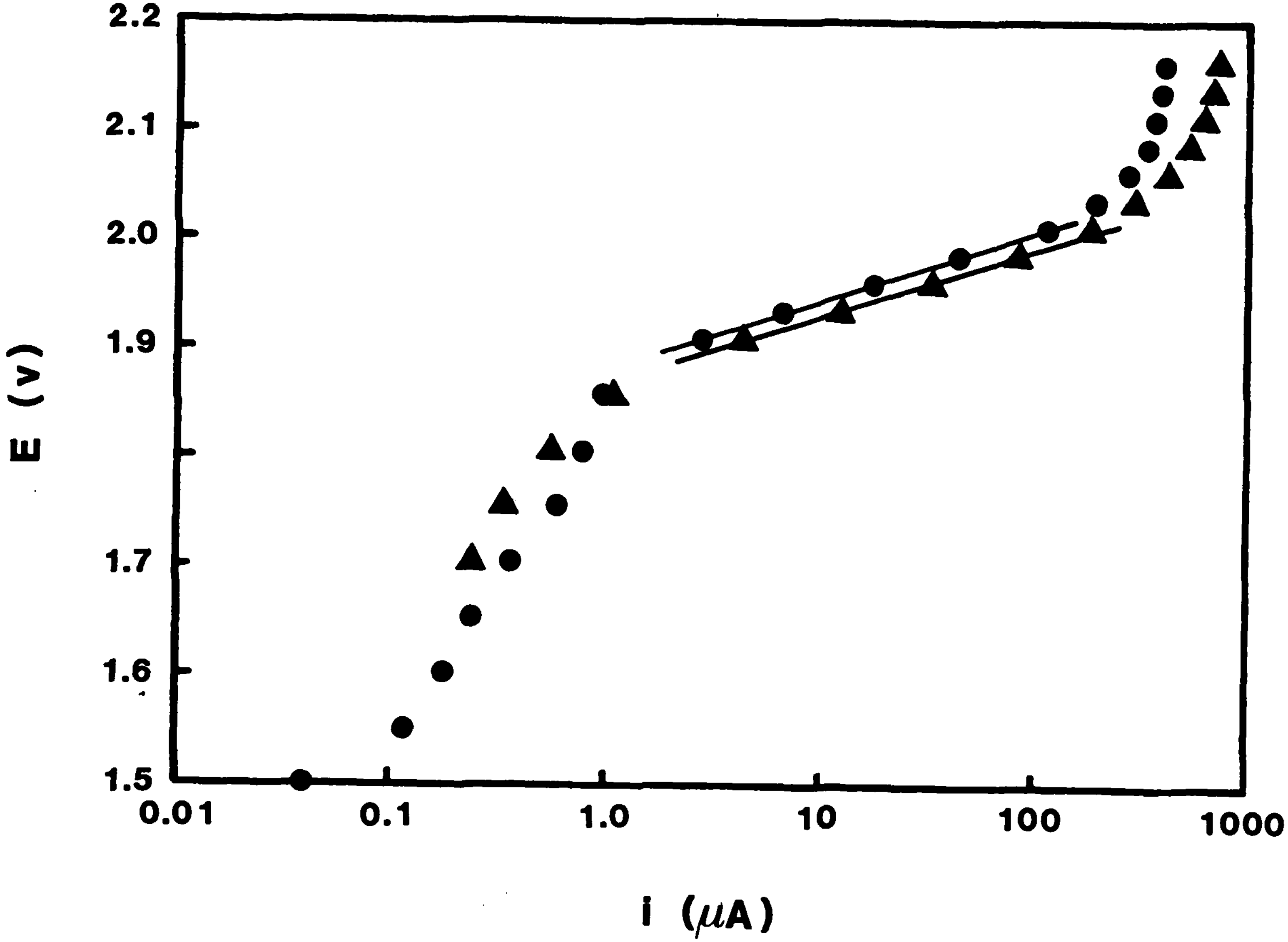
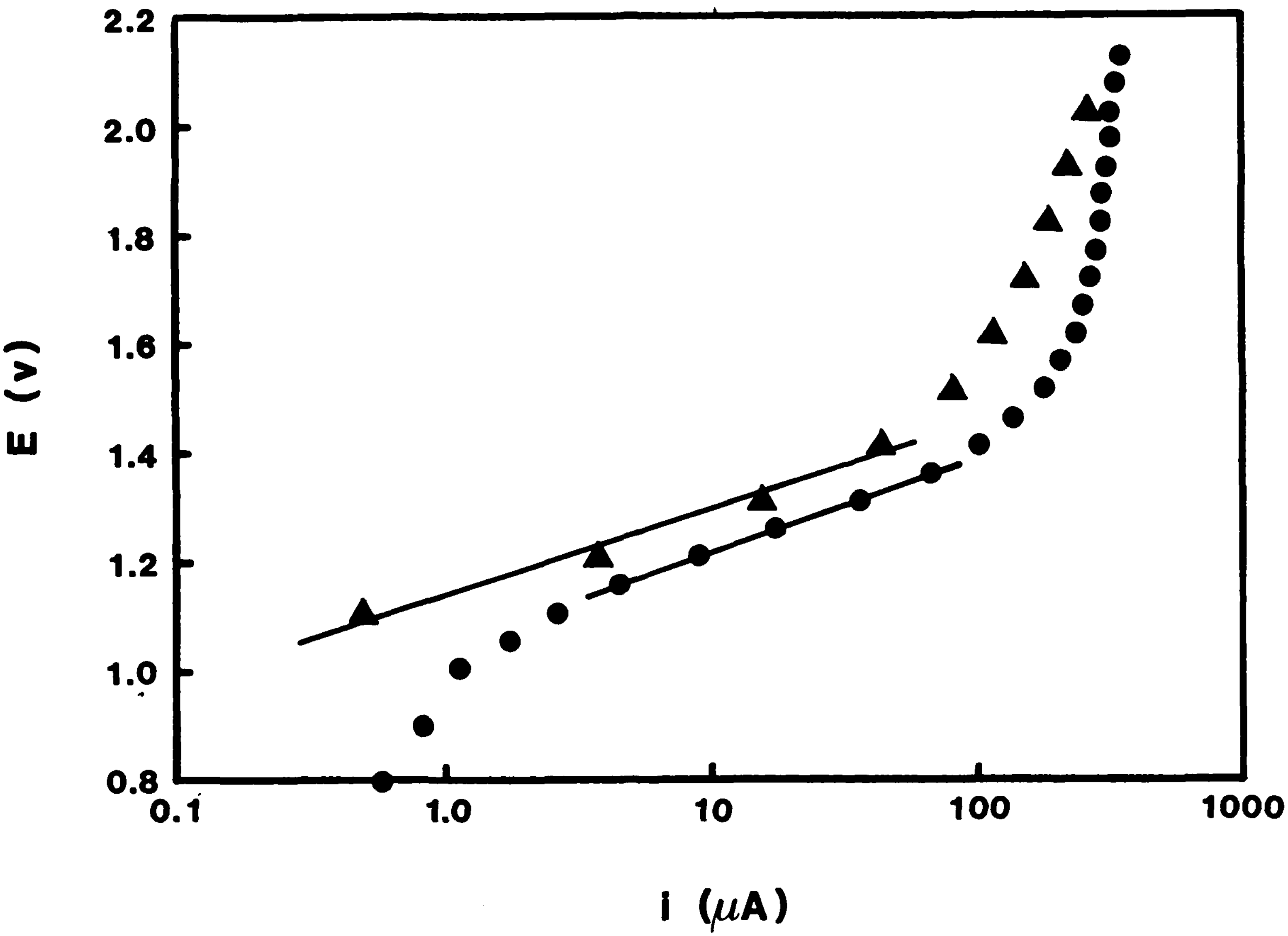


FIGURE 13



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