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This report results from a contract tasking Principal Research Scientist,   Indian Institute of Science as follows: The contractor will investigate the influence of lithium and sodium cations on decomposition of dimethoxy ethane solvent employing cyclic voltametry as the essential experimental technique.

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11 September 1997

Dr. Charbel N. Raffoul
Chief, Aeronautical Engineering
E O A R D
223/231 Old Marylebone Rd
LONDON NW1 5TH U.K.

Dear Dr. Raffoul,

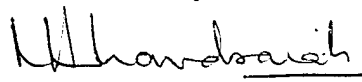Contract # F61708 - 97 - W0178
SPC 97 - 4057

Please find enclosed the final report on the research performed at Wright Laboratory during 4 through 29 August 1997 (Item # 2 of the contract schedule).

I request you to release the payment at an early date.

Thank you very much for your help during the course of this contract program.

Best regards.

Yours sincerely,

N. Munichandraiah

REPORT OF RESEARCH

INTRODUCTION

Yeager has discussed the importance of the lithium ion acting as a Lewis acid for increasing the reduction kinetics of propylene carbonate. In this case, it was suggested that the free energy of activation for the first electron transfer is lowered through interaction of the lithium ion with propylene carbonate. Scanlon has further illustrated the importance of the lithium ion during reductive decomposition of a non-aqueous medium through the use of computational chemistry. In this investigation, the calculated change in Gibbs energy for addition of an electron to tetrahydrofuran (THF) in the gas phase was +40.36 kcal/mole at 298K. However , the calculated change in Gibbs energy for the reaction of a lithium atom in the gas phase with THF in the gas phase to form a lithium ion stabilized THF anion radical was -1.94 kcal/mole at 298 K. The structure of lithium ion stabilized THF anion radical is a six membered ring with lithium ion bonded to both the anionic oxygen and methylene radical located at the terminal end of the alkyl chain. Further importance of the lithium ion was illustrated when sodium was substituted for lithium ion in the same reaction stated above. In this case the change in the Gibbs energy for the formation of sodium ion stabilized THFAR was +18.73 kcal/mole at 298 K. Cyclic voltammetric experiments comparing and contrasting the behavior of

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LiI to NaI in THF were consistent with the expected decomposition of THF when LiI was dissolved in THF. There was no evidence of THF decomposition when NaI was dissolved in THF.

In this investigation, we have used computational chemistry to investigate the cleavage of the carbon oxygen bond in dimethoxy ethane(DME). This was considered as a first approximation as to what may take place in a polyethylene oxide(PEO)-based polymer electrolyte since a separate alkyl radical and methoxy anion are formed during decomposition. The experimental phase of this work entails the comparison of LiI and NaI in DME as well as LiI and NaI in PEO-acetonitrile solvent system by using cyclic voltammetry.

EXPERIMENTAL

Gaussian 94 was used for all theoretical calculations. Single point energies for the lithium and sodium atoms, and geometry and frequency calculations for the DME were done using the unrestricted Hartree-Fock (UHF) method of calculation. For those chemical systems avoiding anion radicals, the restricted open-shell Hartree-Fock (ROHF) method of calculation was used. Scheme I illustrates the method for calculating the thermodynamic parameters used in this study.

For the purpose of supporting the theoretical predictions with experimental verifications, linear sweep and cyclic voltammetric techniques were employed. A three electrode cell containing platinum electrodes (area: 0.002 cm^2) was assembled in an electrolyte of 20 ml. Linear sweep voltammetry was conducted between 4.5 V and -4.5 V. The range of voltage with no current was estimated to be the stable voltage window of the taken electrolyte. The nature of the reactions at voltages above and below the stable voltage window were studied by using cyclic voltammetry.

RESULTS AND DISCUSSION

The purpose of the theoretical investigation was to compare and contrast the ability of lithium and sodium ions to stabilize an anion radical intermediate product. The general reaction considered in these calculations was either a lithium atom or sodium atom in the gas phase reacting with DME in the gas phase to form a cation stabilized DME anion radical (DMEAR). The results of the *ab initio* calculations involving three species are shown in Table1. The change in Gibbs energy at 298 K for lithium reacting with DME to form Li$^+$-DMEAR is -5.267 kcal/mole. Fig.1 shows the optimized geometry for Li$^+$-DMEAR. It can be seen that lithium is bonded to both the methoxy anion and the alkyl cation radical. The lithium ion -radical bond distance is 2.45 A, while the lithium ion- methoxy anion bond distance

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is 1.60 A. It has been shown through separate calculations that the addition of an electron to DME in the gas phase results in cleavage of the carbon-oxygen bond to form two chemical fragments. This is shown in Fig.2. The change in Gibbs energy at 298 K for this reaction is +36.58 kcal/mole.

The final reaction considered was between a sodium atom in the gas phase reacting with DME in the gas phase to form the sodium ion-stabilized DMEAR (Na^+-DMEAR). The change in Gibbs energy for this reaction is 8.52 kcal/mole at 298 K. Fig. 3 shows the optimized geometry for Na^+-DMEAR. The main distinction between Na^+-DMEAR and Li^+-DMEAR is that the sodium ion is bonded to the neutral oxygen donor atom and does not bond with free-radical. This is the preferred configuration as shown by the geometry optimization process. The sodium ion-methoxy anion bond distance is 1.99 A. The sodium ion-neutral oxygen donor atom bond distance is 2.34 A.

Experiments were conducted under identical conditions to compare and contrast the linear sweep voltammograms of LiI and NaI dissolved in DME. The voltammograms are shown in Figs. 4a and b. The stable voltage window of DME containing LiI is 1.74 V, which is lower than that of DME containing NaI by about 1.36 V.The currents for LiI are higher in magnitude than for NaI.

The linear sweep voltammograms recorded for LiI and NaI in acetonitrile containing polyethylene oxide are shown in Figs.5a and b. In this case also , the

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stable voltage window for LiI is 3.07 V which is lower than that of NaI by about 0.53 V. The cyclic voltammograms (for LiI) recorded between -1.5V and -4.5 V are shown in Fig. 6 and the voltammograms between 0 V and 2.0 V are shown in Fig. 7. The cathodic voltammograms (Fig. 6) are found to have multiple peaks and they are irreversible. The voltammograms recorded for different concentrations of LiI showed that the peak currents increase with concentration. These results suggest that the reactions corresponding to these peaks are related to decomposition of the solvent molecules in presence of lithium cation.

Thus, the electrochemical experimental results are consistent with role of the lithium ion being important for making a decomposition process thermodynamically allowed.

SCHEME I

$$\Delta E^{298} = \Delta E_e^{\,o} + \Delta E_v^{\,o} + [\Delta(\Delta E_v)^{298} + \Delta E_r^{\,298} + \Delta E_t^{\,298}] = \text{Thermal Energy}$$

$$\Delta H^{298} = \Delta E^{298} + \Delta(PV)$$

$$\Delta G^{298} = \Delta H^{298} - T\,\Delta S$$

Definition of Terms:

$\Delta E_e^{\,o}$ Electronic energy difference between products and reactants at 0 K.

$\Delta E_v^{\,o}$ Difference between the zero-point vibrational energies of the products and reactants (0 K).

$\Delta(\Delta E_v)^{298}$ Change in the vibrational energy difference between 0 K and 298 K.

$\Delta E_r^{\,298}$ Difference in the rotational energies of products and reactants at 298 K.

$\Delta E_t^{\,298}$ Difference in the transitional energy change between products and reactants at 298 K.

$\Delta(PV)$ PV work term $= \Delta nRT$, where Δn is equal to the difference in moles between products and reactants.

TABLE I

Molecule	Method/Basis Set	E_e^o (Hartree)	E_v^o (kcal/mole)	E_{therma}^{1298} (kcal/mole)	S^{298} (cal/mole K)
Li^o	UHF/6-31+G(d,p)	-7.4315628	-	0.889	33.17
Na^o	UHF/6-31+G(d,p)	-161.8414428	-	0	36.17
DME	UHF/6-31+G(d,p)	-307.0041406	95.138	99	85.638
DMER	ROHF/6-31+G(d,p)	-306.916972	87.659	93.6	100.082
Li$^+$-DMEAR	ROHF/6-32+G(d,p)	-314.4362845	91.024	97.718	108.891
Na$^+$-DMEAR	ROHF/6-31+G(d,p)	-468.824148	90.149	96.962	107.086
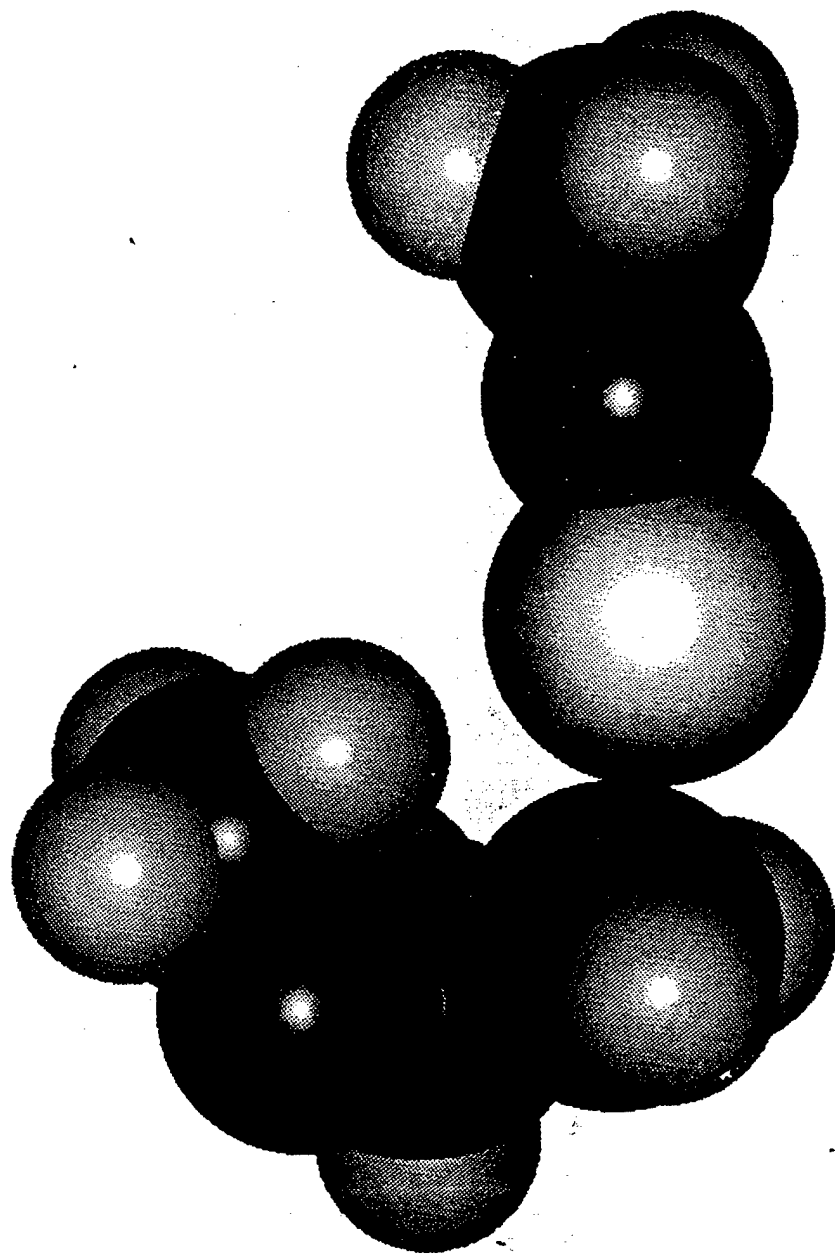
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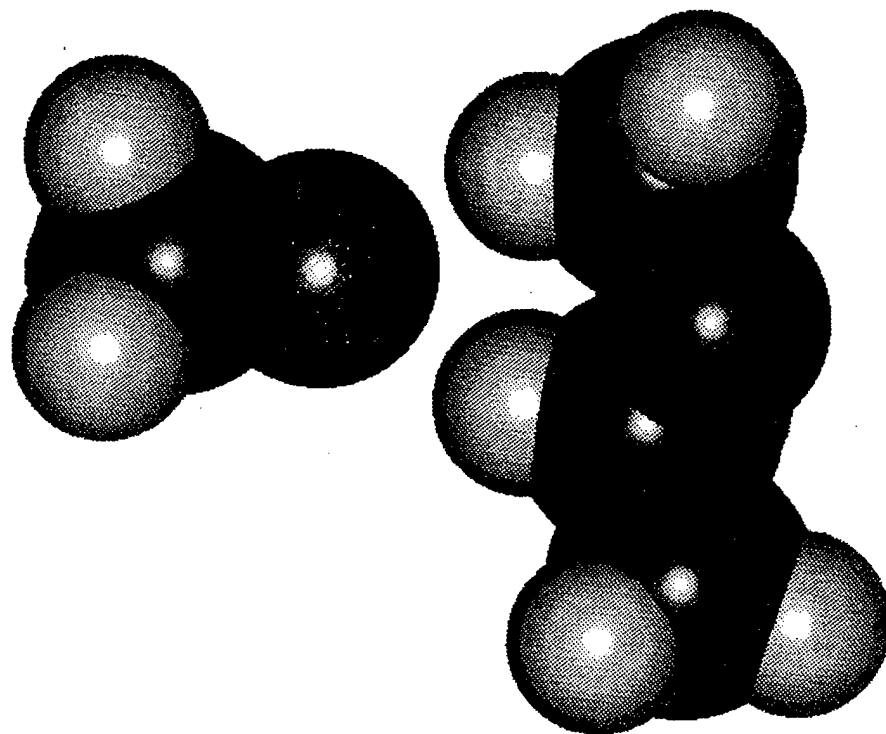
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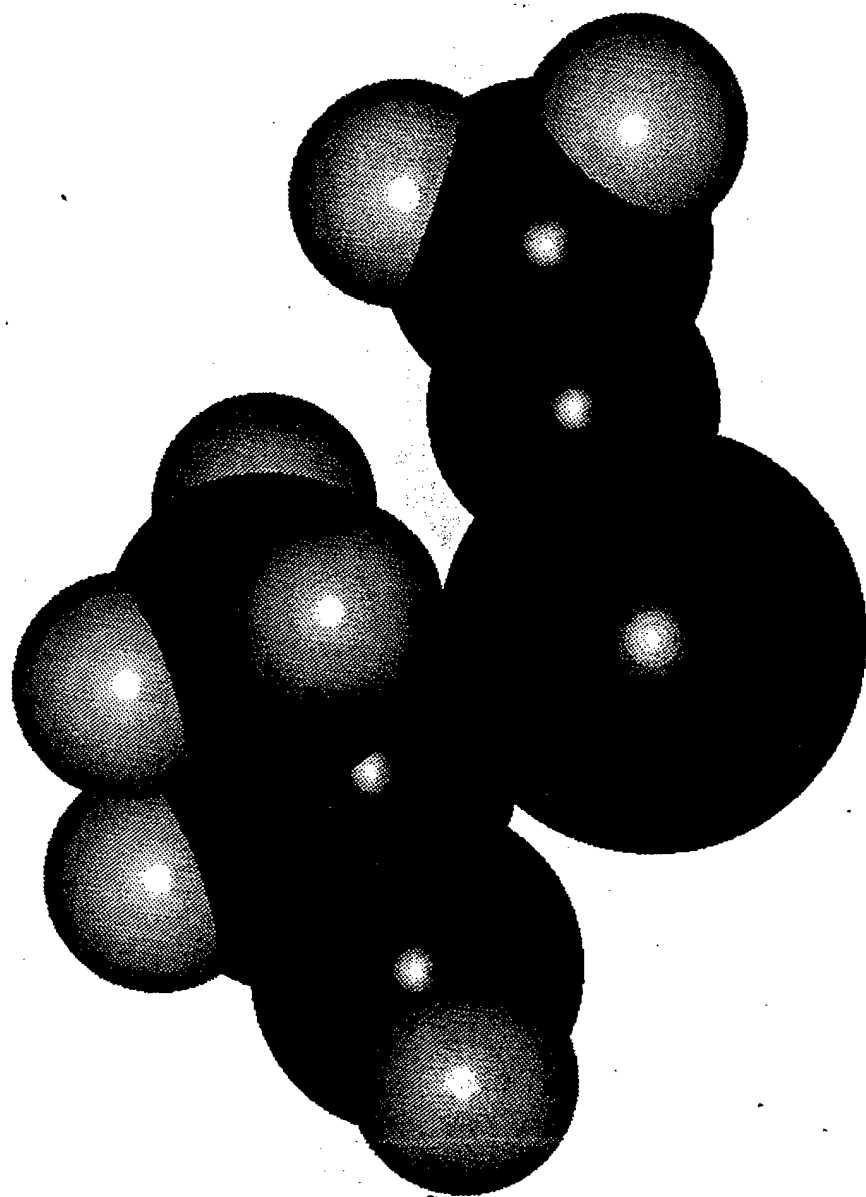
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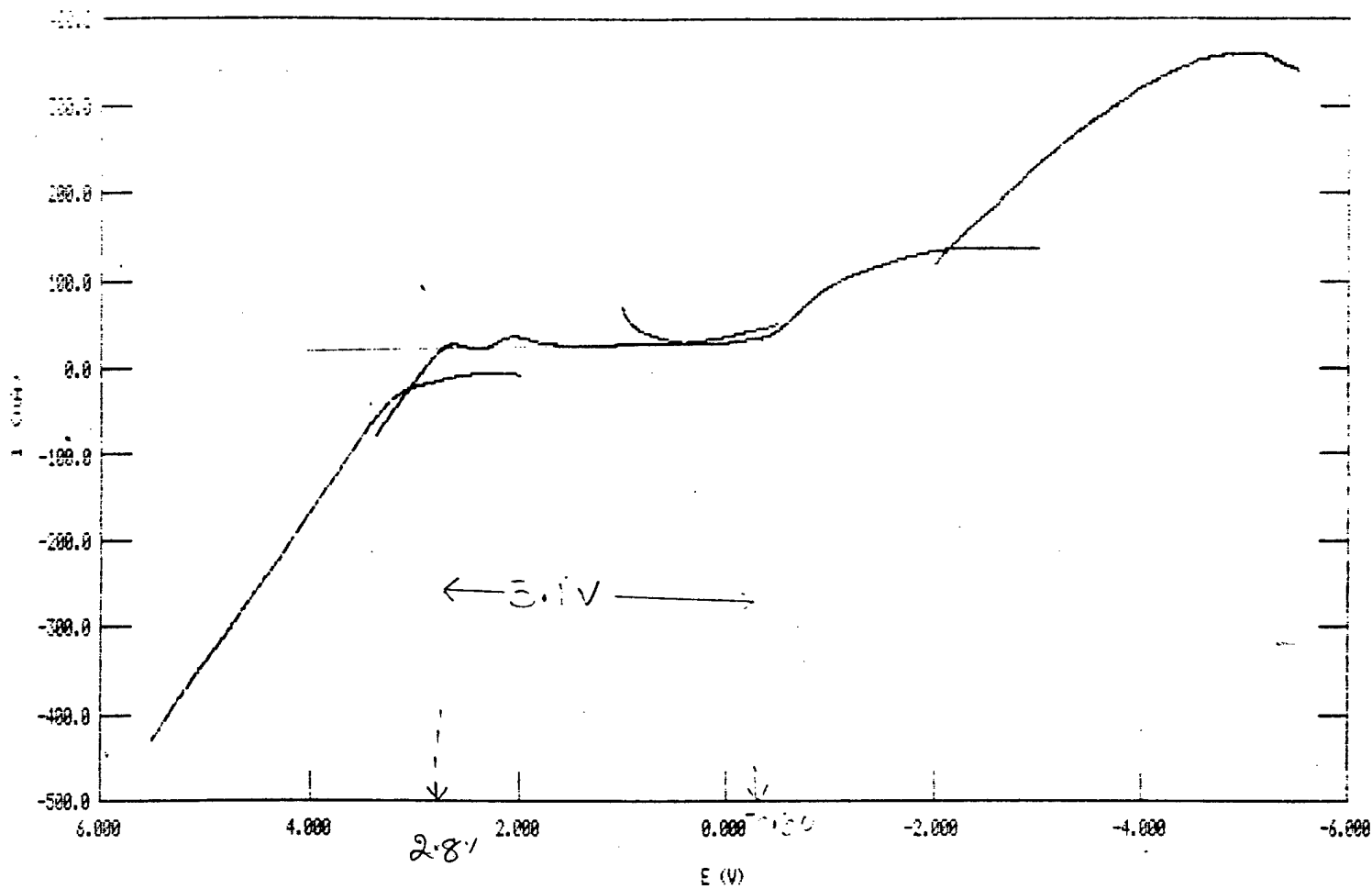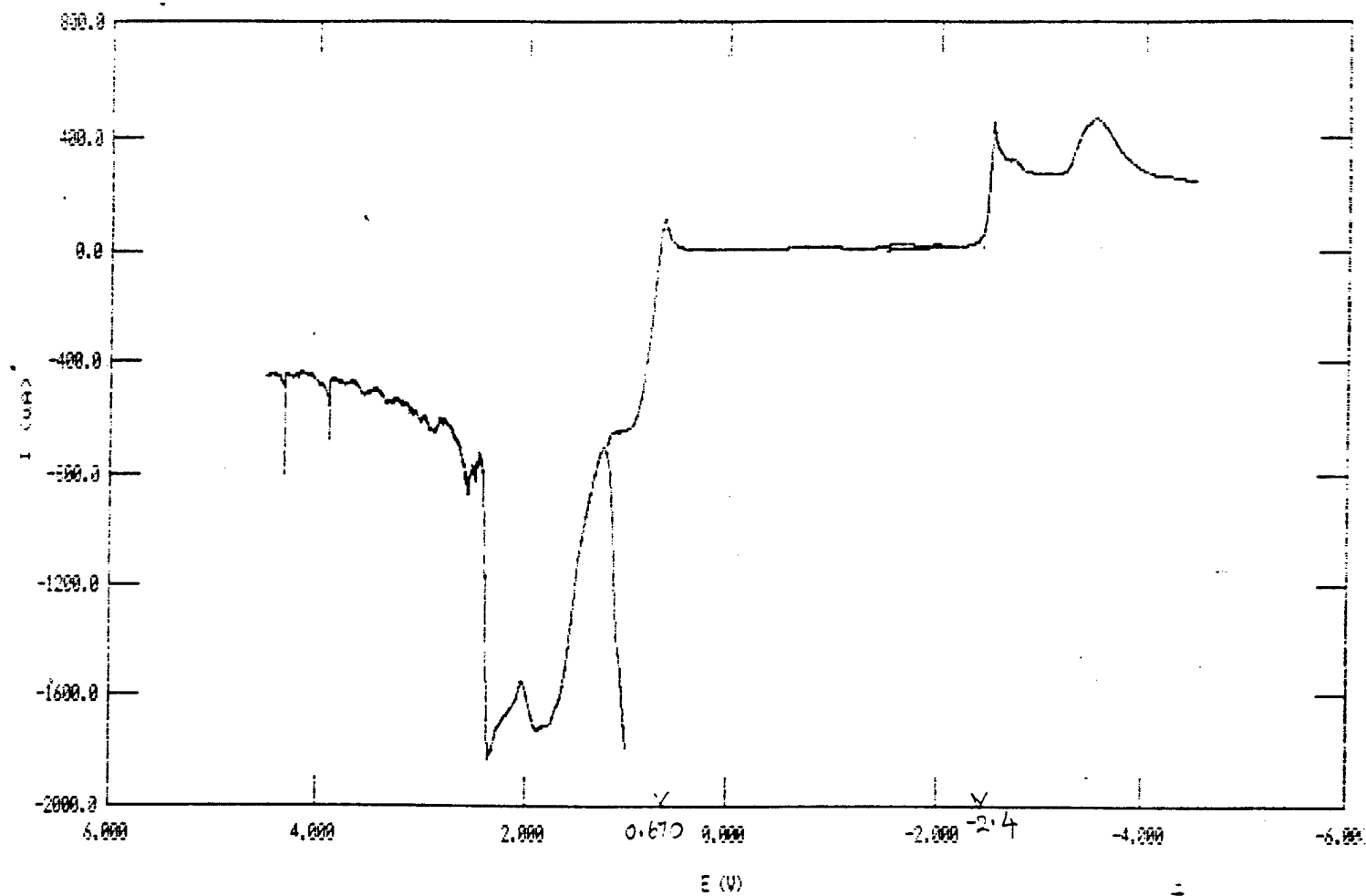
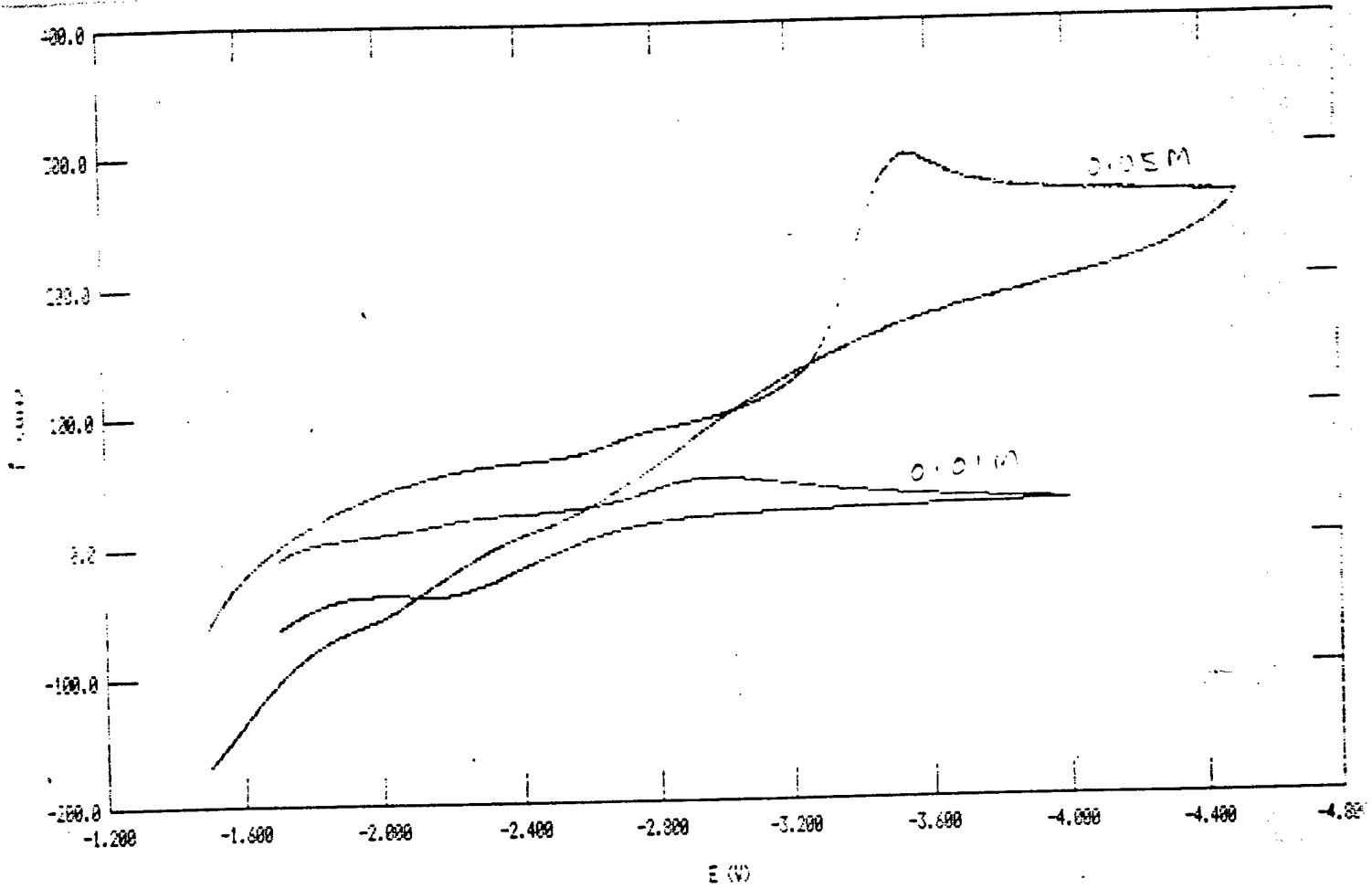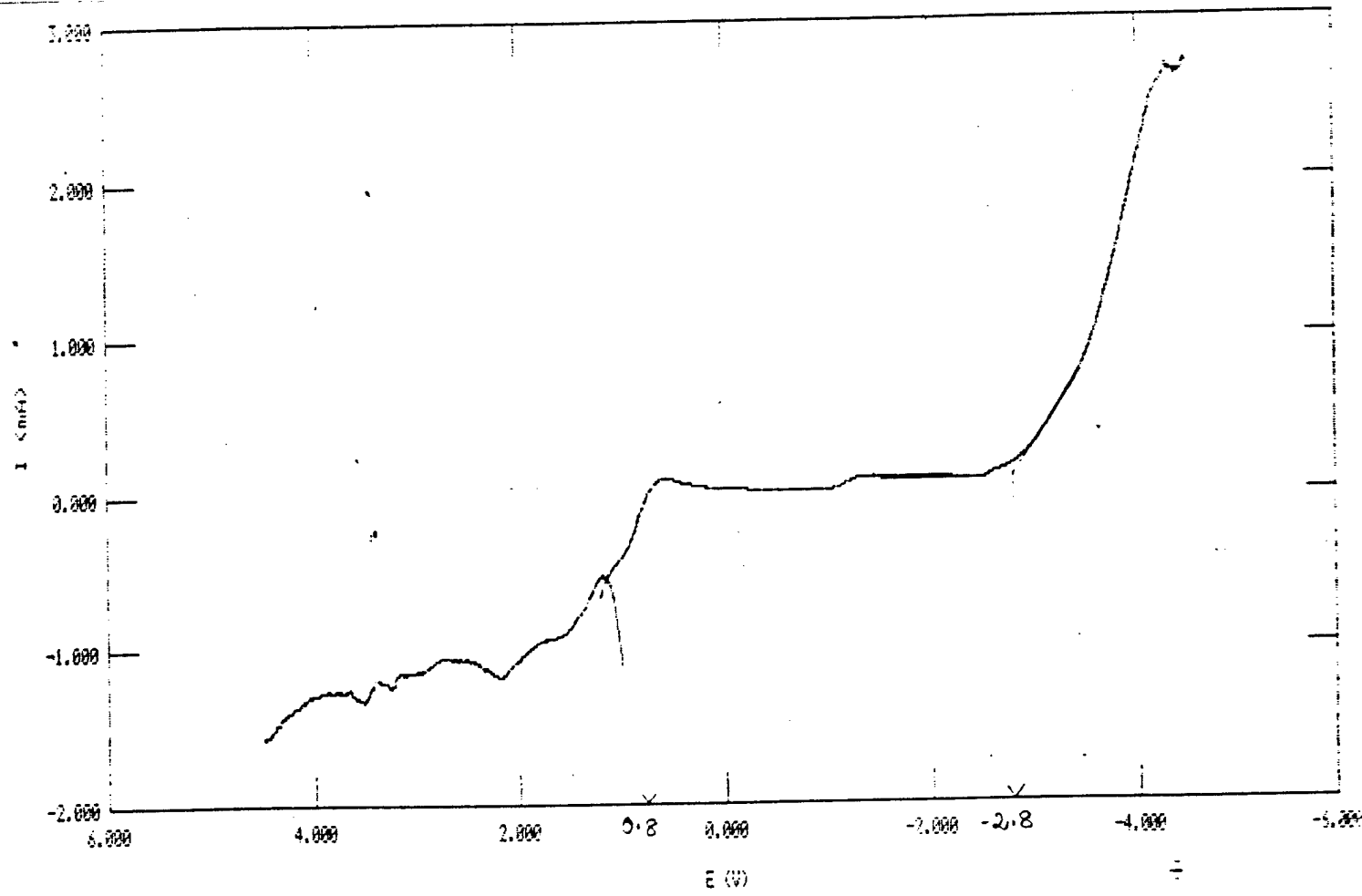llauge9.ls   - - - llauge4.ls llauge8.ls
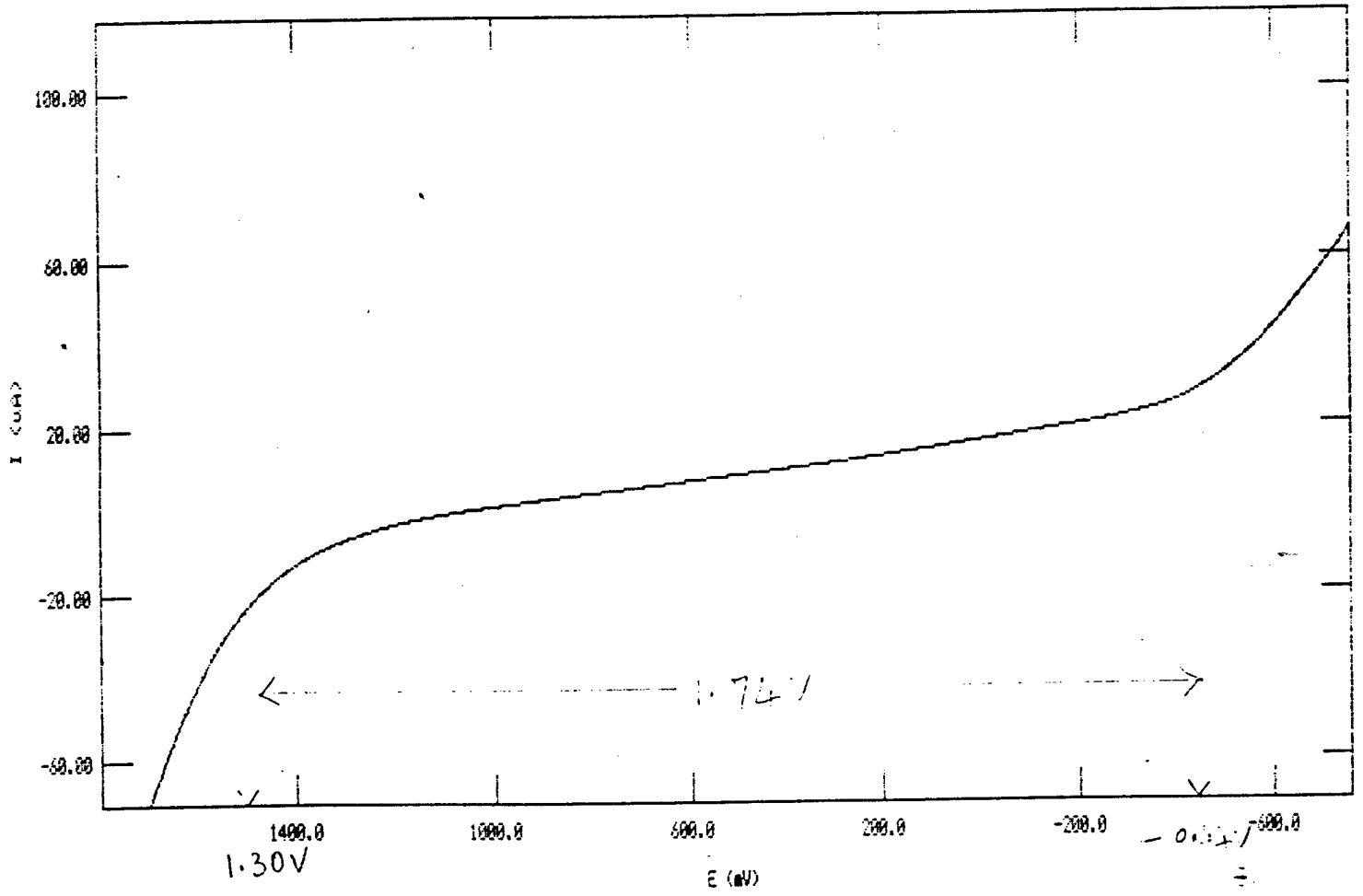
Figure 4(a)

Figure 4(b)

Figure 5(a)

Figure 6

Figure 5(b)