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LOW TEMPERATURE LITHIUM/SULFUR SECONDARY BATTERY

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ABSTRACT

The objective of this program is to develop a dissolved sulfur cathode which can be repeatably charged and discharged with minimal degradation and which is compatible with a Li anode.

The redox behavior of dilute S_8, 0.1-1M $LiClO_4$ solutions in dimethyl sulfoxide (DMSO), dimethly formamide (DMF), tetrahydrofuran (THF), propylene carbonate (PC), γ-butyrolactone (BL), sulfolane (SL), methyl acetate (MA) and pyridine was investigated using cyclic voltammetry. S_8 and $S_8^=$ reductions occur at more positive potentials and the redox reactions are more reversible in DMSO and DMF than in the other solvents. Raising the temperature generally enhances reversibility and reaction rates. Some evidence exists for the precipitation of Li_2S_x species on Au and Pt working electrodes (but not on C) leading to their passivation, especially at elevated temperatures.

Solutions of Li_2S_x were prepared by (a) controlled potential electrolysis of S_8 solutions at the $S_8 \rightarrow S_8^=$ potential, (b) reaction of S_8 with Li, and (c) reaction of S_8 with Li_2S. These are all possible methods for dissolving sufficient S to achieve practical energy densities. Solutions in DMSO, DMF, and dimethyl acetamide were characteristically blue (λ_{max} = 618) while the others were red-orange (λ_{max} = 420 nm).

The electrochemical behavior of Li_2S_x solutions, prepared by method (c) above, was examined using cyclic voltammetry, slow scan voltage sweeps (i-E curves) and charge-discharge coulometry. Cyclic voltammograms of polysulfide solutions in DMSO showed generally reductions at more negative potentials and oxidations at more positive potentials than those for S_8 solutions. The polysulfide and S_8 voltammograms in THF were more comparable. Steady-state current potential curves of DMSO-Li_2S_x solutions generally revealed no sizeable reduction currents positive of $\sim$1.5 V vs. Li, considerably less favorable for a practical battery than indicated by the cyclic voltammograms.

Galvanostatic discharge of Li_2S_x solutions occurs between 1.0 and 2.0 V. Capacities are uncertain because of contributions from "background" solvent or impurity reduction. Recharge (with a 4.0 V limit) was possible in THF, BL and DMSO.

The fact that steady-state discharge in these solutions, and particularly in DMSO-Li_2S_x solutions, occurs at more negative potentials than indicated by cyclic voltammograms suggests a degradation of active species in solution following initial reduction. The solution equilibria governing

the fate of S_8^{-4}, produced by the two electron reduction of $S_8^{=}$, have been described by Sawyer et al. (8,9). The species S_3^{-}, produced by reactions of S_8^{-4} (8,9), and found here in large quantities in Li_2S_x solutions of DMSO, DMF and dimethyl acetamide (but not in THF and the other solvents investigated) may be more difficult to reduce than $S_x^{=}$. If this is the case, solvents or electrolyte additives which stabilize $S_x^{=}$ in preference to S_3^{-}, would be most favorable for use in a practical battery.

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I. INTRODUCTION AND WORK PLAN

The objective of this program is to develop an ambient temperature rechargeable Li/S battery with an organic electrolyte. Our central concept of such a battery is a solubilized S cathode, with its implications for good rechargeability and high discharge rate. A preliminary analysis shows that solutions of only ∿0.6M in S_8 (the usual solution form of S) discharged with 50% efficiency at ∿2.0 V should yield a 100 Whr/lb cell.

To achieve these goals, the following primary areas of research are required:

- Sulfur Solubility Studies. Various organic electrolytes must be surveyed with regard to their ability to dissolve S. With little or no loss of energy density, S may be dissolved as polysulfides, as S-amine complexes, or complexed by other chemical species. This solubility should preferably be maintained during all phases of charge and discharge.

- Electrochemical Activity. The reduction of S_8 or polysulfide to $S^=$ involves several intermediate steps which are governed by a number of dynamic equilibria involving $S_x^=$, S_x^- and S_x species. In the design of a cathode, one would like these multistep processes to occur at a high and relatively constant potential. Cyclic voltammetry was used to survey the best choices of solvent and electrolyte to optimize these equilibria and redox potentials. Further evaluation of these solutions can then be made by investigating their current-potential curves for discharge and recharge.

The reversibility and charge-discharge behavior of S-containing solutions can be examined using coulometric techniques. Such detailed studies should best be carried out in electrolytes which afford the best values of S solubility and S redox behavior. In the case of polysulfides, for example, $S_8^=$ is the highest commonly observed species. The theoretical energy density of a cell based upon the reaction

$$2\ Li^+ + 14\ Li + S_8^= \rightarrow 8S^= + 16\ Li^+ \qquad (1)$$

is 1175 Whr/lb, compared to 1343 Whr/lb for the corresponding $S_8 \rightarrow 8S^=$ cathode reaction. The theoretical energy density for the Li/S battery falls off very rapidly with increasing value of n for the reaction $S_8 \rightarrow (8/n)S_n^=$ or $S_8^= \rightarrow (8/n)S_n^=$. Theoretical energy densities as a function of n are plotted in Fig. 1 for S_8 and $S_8^=$ starting materials. Thus, determining the e^-/S ratio for voltage limited charge and discharge of various soluble S/organic electrolyte systems is extremely important. Useful systems must have e^-/S ratios of >1.0.

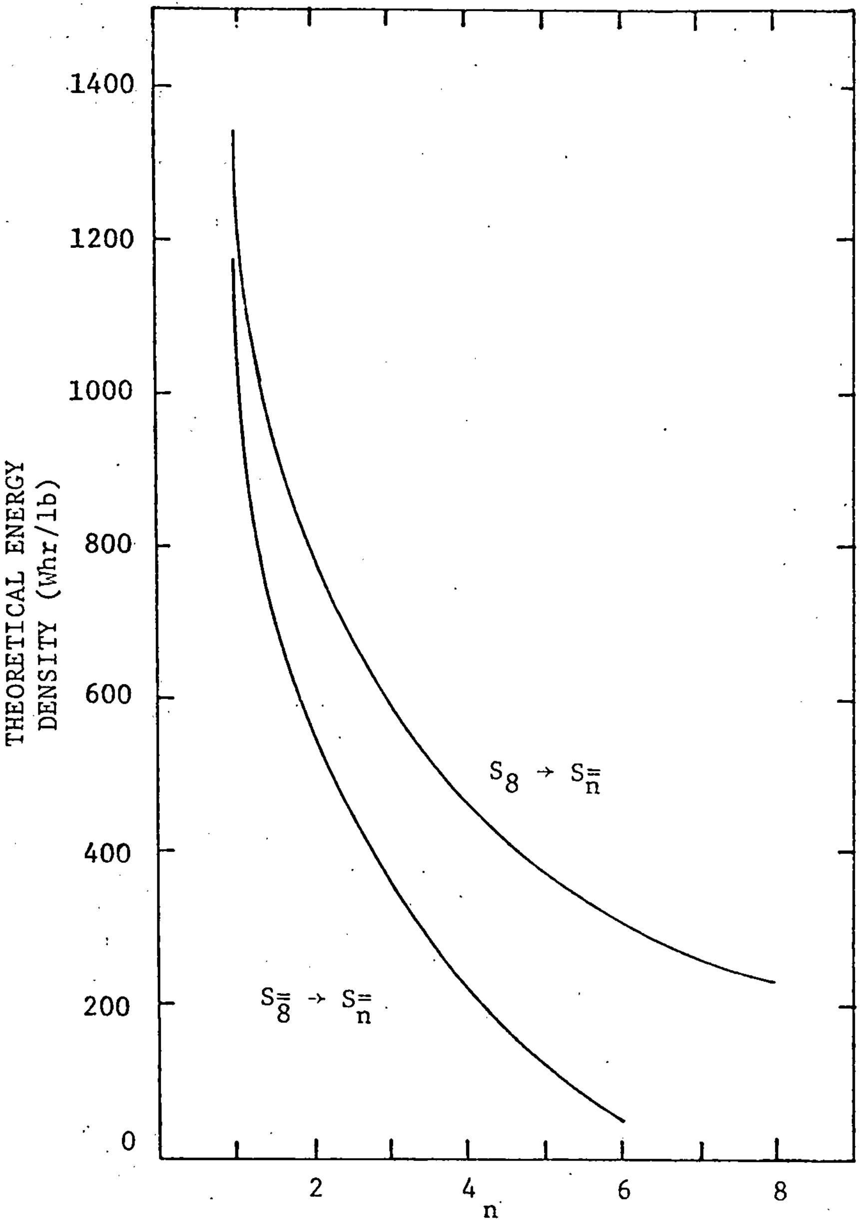

Fig. 1. Theoretical energy densities for Li/S batteries.

- Li Compatibility Studies. Determining the ability to store, charge and discharge Li in the presence of an organic electrolyte containing dissolved S is an important aspect of this study. Several approaches may be taken, including the use of Li-passivating additives to the electrolyte (1) and the use of microporous separators (2).

The specific aims of this program are thus to develop an electrolyte which will solubilize S, and in which S may be repeatedly reduced and oxidized to a stoichiometry as close to $2e^-/S$ as possible. In order to maximize the energy density, we seek to achieve high S solubility and maintain it throughout charge and discharge. The discharge potential should be as high as possible, and relatively constant, and recharge should be at as low a potential as possible. The cathode should also be utilized in a battery design compatible with the Li electrode.

Appendix I details our work plan. The various electrolyte preparations which are being tested are given first. These preparations are initially screened with regard to their redox potentials and reversibilities using cyclic voltammetry (Task I). Solutions are then examined for maximum S solubility, their charge-discharge capacities, and their compatibility with Li (Task II). Next, promising solutions are examined in detail for the influence of electrode material and changes in electrolyte composition on their charge-discharge behavior (Task III). In addition under Task III, an examination of the pertinent mechanistic details of charge and discharge will be made. Finally, construction and testing of actual cells will be carried out under Task IV.

For this, the initial 6-month period, work has been completed on the cyclic voltammetry of S_8 in a number of organic electrolytes (solutions 2(a)) which are potentially stable toward Li. This study was carried out varying both substrate and temperature. In addition, S was dissolved in these organic electrolytes as Li_2S_x by several methods, and relative solubilities have been assessed (solutions S(b) and S(c)). The current-potential behavior of several of these polysulfide solutions has been assessed using both rapid-scan (cyclic voltammetry) and steady-state techniques. Finally, the charge-discharge behavior of several polysulfide solutions has been examined as a function of such parameters as cycle number and initial $S^=/S^\circ$ ratios.

II. THE SOLUBLE SULFUR CATHODE BACKGROUND

The Li/S system is attractive as a candidate, high energy density secondary cell. Thus, both Li and S are relatively cheap, plentiful, and nontoxic. In addition, the theoretical energy density of the system is ∿1300 Whr/lb, based on the equivalent weights of Li and S and a theoretical potential of 2.45 V at unit activity of Li^+ and $S^=$ (3). Because of these advantages, the system has attracted considerable interest.

A. Prior Work

There appear to have been four attempts to develop room temperature Li/S cells. It seems that these studies were conducted without benefit of a good understanding of the state of S or its discharge products in the particular systems employed. There was specifically a lack of understanding of polysulfide equilibria in various solvents of interest. Nevertheless, published results do provide an indication of the possibilities and problems involved with the Li/S system.

Coleman and Bates (4) provide the clearest and most complete account: they attempted to utilize insoluble S and reduce it directly to $S^=$ ion. Sulfur, blended with graphite and compressed onto an Ni current collector, was employed as the cathode in an organic electrolyte battery with an Li anode. Of the electrolytes tried, dimethyl sulfoxide (DMSO)-$KClO_4$ and butyrolactone (BL)-DMSO mixtures with $KClO_4$ or KSCN proved the most successful. Utilization of up to 20% of the S (based on $S + 2e^- \rightarrow S^=$) was obtained to a cell cutoff voltage of 2.0 V. Coleman reported that "the sulfur on partial reduction forms highly colored soluble polysulfides, which diffuse into the electrolyte and escape further reduction." He found that at cell failure the carbon electrode was polarized whereas Li was not.

Rao (5) lists the preparation of several nonaqueous electrochemical cells with an insoluble S cathode and a graphite current collector. Lithium was among the anodes claimed. Suitable electrolytes were claimed to be made by dissolving salts comprising light metal or NH_4^+ cations and BF_4^-, $AlCl_4^-$, ClO_4^- or Cl^- anions in certain organic solvents, such as in PC, γ-BL, dimethyl formamide (DMF) and DMSO in 1 molar concentration. He states "... the lithium-sulfur system is rechargeable." A curve of his voltage versus current for a cell of unspecified geometry is presented. No data concerning shelf life or S utilization efficiency were reported. Rao pointedly states that whereas other solvents, particularly amines, dissolve active materials of the cell, i.e. Li, resulting in loss of capacity on standing and poor cycle life, "the solvents used in the cell of this invention are inert and do not exhibit solubilization of the active materials." Thus, Rao implies that a rechargeable Li/S cell, which presumably makes efficient use of S in an insoluble form, can be constructed.

Herbert (6) studied systems in which S was present as soluble polysulfides or gelled polysulfides, viz. of the type Li/isopropyl amine (78%), $LiClO_4$ (4%), S (18%)/C. Care was needed in preparing the electrolyte to avoid reaction of solvent with S, and to allow polysulfide to form. Once prepared, however, e.g., by mixing very slowly and ageing, the electrolyte was apparently stable. Energy densities of 136 Whr/lb of solution (at the 180 hr. rate) were claimed; there appeared to be a small performance difference between the use of Ag_2S and C current collectors. The cell was claimed to be rechargeable, and the solution was claimed to be noncorrosive with respect to Li.

Nole and Moss (7) studied systems involving both insoluble and solutionized S, with a C current collector. They used PC, ethylene carbonate (EC), dimethoxyethane (DME) and γ-BL containing Li salts as electrolytes. Formation of dissolved sulfides and polysulfides was encouraged by adding CS_2 to the electrolyte. They were found to enhance cell efficiency, i.e., to increase cathode utilization. It was suggested that these dissolved materials prevented polysulfide formation on the cathode. Based on their data, we would suggest that a major reason for better cathode utilization was dissolution of the (partially reacted) active material to form polysulfides, as has been noted also by Coleman (4) and Sawyer and co-workers (8,9). The soluble S, in our view, is more available for complete reduction than the solid. The cell was reported to be chemically reversible, but no numerical charge-discharge data were reported.

Sawyer and co-workers studied the reduction of dissolved S in Et_4NClO_4 in DMSO solutions using Au electrodes. Their earlier work (8) has been superseded by a very recent paper (9). Sulfur in solution (S_8) is reduced at -0.6 V <u>vs</u>. SCE according to

$$S_8 + 2e^- \rightarrow S_8^{=} \qquad (2)$$

Subsequently, $S_8^{=}$ reacts according to

$$S_8^{=} + 2e^- \rightarrow S_8^{4-}, \ E = -1.29 \text{ vs. SCE} \qquad (3)$$

and
$$S_8^{4-} \rightarrow 2S_4^{=} \qquad (4)$$

The resultant solution compositions were complicated by the reactions

$$2S_6^{=} \rightarrow S_4^{=} + S_8^{=}, \ K = 4 \times 10^{-2} \qquad (5)$$

and
$$S_6^{=} \rightarrow 2S_3^{-} \quad , \ K = 9 \times 10^{-3} \qquad (6)$$

The blue color of the solutions was postulated to be due to S_3^-. These conclusions were confirmed by spectroscopic investigations of Na polysulfide solutions. Reactions (2) and (3) were observed to be chemically reversible, but the reverse of reaction (2) (recharge) was ∿0.3 V more positive than the cathodic direction (discharge), probably because of the need for S_8 ring closure and opening.

Based on the literature, inferences can be drawn about four important aspects of the Li/S system:

- Li stability in presence of soluble S
- S utilization efficiency
- Rechargeability
- Rate capability

These aspects are crucial to the construction of a practical cell; they will be discussed in turn.

Li Stability. This matter is not resolved, but prospects are very hopeful. Herbert claims that Li is unreactive towards dissolved S (∿0.5M in S_8) in amine solvents. Though Rao (5) disagrees, he has not tested the system. Nole (7) presents evidence which indicates that Li is quite stable toward dissolved S: "It is also noted that when one particular cell containing the "reacted" electrolyte is permitted to set (sic) over a weekend after being depleted to 41.2% of its capacity, its open circuit voltage returns to the normal 2.55 volts and an additional 0.17 ampere hour discharge is obtained, resulting in a total discharge efficiency of 73.4%."

Coleman's (4) studies clearly indicate that polarization of the Li electrode is virtually nonexistent. "Measurements made with an auxiliary platinum electrode showed that nearly all the voltage drop observed was at the cathode, the potential at the lithium anode falling by only 5-10 mV at the beginning of discharge. The subsequent fall in cell voltage during discharge is likewise attributable to the cathode." Coleman reports that when 11.6% of the available S had been utilized in a cell, the rest of the S was absent from the cathode, i.e., dissolved. If this fraction of the S had reacted directly with the Li, we would expect worse utilization at lower current densities and better utilization at high current densities. Coleman observed the opposite effect.

Although none of these workers directly reported data on Li stability, their results suggest that it is not a major problem.

S Utilization Efficiency. Some excellent charge utilization efficiencies have been obtained, albeit at low rates.

Coleman and Bates' (4) detailed study indicates a maximum S utilization of 22%. They concluded that soluble polysulfides diffuse to the Li and react chemically with it, thereby making it unavailable for electrochemical reduction. We do not believe their data support such a conclusion. More work is needed to determine the fate of the polysulfides in this system.

Nole and Moss (7) found that S utilization is very good in their polysulfide-containing electrolyte. "The cell of the invention may be discharged (and recharged) to essentially 100% of theoretical capacity; however, because of internal resistance, the last 20-25% of capacity is normally not considered profitable." They claim 73.4% S utilization in one low rate application.

We have calculated from Herbert's data that even with his rather concentrated 0.5M S_8 ($\sim$4M in S), he obtained 50% S utilization based on $S \rightarrow S^=$, the theoretical maximum.

Rechargeability. All the battery patents on Li/S claim good rechargeability, notably that of Nole and Moss (7). No actual data are presented, but Sawyer et al.'s studies (8,9) indicate good reversibility of the overall reaction. The patent claims imply that the Li electrode can be recharged.

Rate Capability. Only Herbert (6) presents actual data (180-hr. discharge), but indications from such examples as are quoted by Nole and Moss (7) indicate relatively poor rates. Coleman and Bates (4) obtained currents in excess of 11 mA/cm^2, but with poor S utilization; however, they did not optimize for use of dissolved S. Based on published data, it is our view that rate capability is the biggest weakness of this system in its present stage of development.

B. Approaches to Improve The Sulfur Positive

The cited work suggests that the Li/S system is reasonably stable and rechargeable, and has good practical energy density. Higher energy density and higher cathode utilization are obtained when dissolution of the S is facilitated. It is likely that better rate capability is obtained under these conditions also.

The most immediate aim then is to enhance the solubility of S in common organic solvents compatible with Li. Sulfur is usually somewhat soluble in most organic solvents. It becomes very soluble in the form of polysulfides, $S_n^=$, once reduction begins. Thus, not only is S itself soluble, but its reduction product is not the almost insoluble Li_2S but the very soluble Li_2S_n.

The failure to appreciate this factor, and to try to take advantage of it, is the major reason, in our view, why the potential of the ambient temperature Li/S system is unrealized. We suggest that if the Li is stable, and if the reduction product is fairly close to $S^=$ (say $S_2^=$), a soluble cathode is preferable. One reason for this is that a soluble oxidant/soluble reductant cathode should possess excellent rechargeability, without problems arising from forming and removing insoluble insulating products, and without problems of active material shedding, etc. In the eventual development of a multicycling battery, this may be a key factor. An all soluble cathode system should also have high rate capability, especially in recharge. This, again, is partly because of absence of surface film insulators. This prediction is consistent with current experience on high-rate Li cells.*

We have proposed to take advantage of the above-mentioned solubility of polysulfides to hold S in solution. Thus, the oxidant dissolved in the cell could be, for example Li_2S_8, and the cell reaction could be, for example,

$$S_8^= + 6e^- \rightarrow 4S_2^{2-} \qquad (7)$$

With reaction (7), we lose 50% of the system's energy density, to secure the advantage, possibly, of an all-soluble system. Alternatively we may consider the general reaction

$$S_n^=(\mathrm{soln}) + (n-2)e^- \rightarrow nS^=. \qquad (8)$$

Polysulfide solubility is expected to be high in solvents of interest in a Li battery. Coleman and Bates' results (4), and Sawyer's (8,9) show that there is appreciable solubility in DMSO. Nole and Moss' data (7) indicate appreciable solubility in PC, EC, DME and γ-BL, even without addition of CS_2. Cotton and Wilkinson (14) indicate solubility of alkali polysulfides in polar solvents such as EtOH and Me_2CO. Giggenbach describes solutions of polysulfides in DMF (15). Pickering and Tobolsky (16) indicate that inorganic polysulfides are soluble in polar solvents. On general grounds, we anticipate that Li polysulfides will be soluble just as are Li salts of many big "soft" anions, such as PF_6^-, $AlCl_4^-$, etc. The $S_n^=$ ion is very soft, and its salts should be very soluble, especially as their crystal lattices should not be at all perfect. The question to be answered by experiment is just how soluble Li polysulfides are in the various solvents of interest.

Assuming that Li_2S_n ($n \geq 8$) is highly soluble in solvents of interest, we may inquire into the probable fate of this material during reduction. Sawyer's data in DMSO (9) indicate that the major reduction species in

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* The Li/$POCl_3$ (10), Li/SO_2 (11), and Li/$SOCl_2$ (12) systems have soluble cathodes and the last two, in particular, have superior rate capability over the Li/C_4F system (13), the best Li/insoluble cathode cell. This is not to imply that solid cathode systems cannot have high rates. The Pb/acid and Ni/Cd systems, for example, do. However, soluble systems seem to have higher rates in non-aqueous media.

TEAP electrolytes, and in presence of Na^+, is $S_4^=$. A statement of Pickering and Tobolsky (16) is appropriate here: "In both aqueous and alcoholic solutions it is found that one of the polysulfide anions shows much greater stability than the others and is present in larger amounts. Which ion is more stable depends on the counterion; for sodium the tetrasulfide anion is the most stable ..." (cf. Sawyer). They then append a table which shows that for Li^+ the most stable anion (in alcohol and aqueous solutions) is $S^=$, not $S_4^=$. There are large solvent effects; viz. compare Giggenbach (15) (DMF) and Sawyer et al. (9) (DMSO). We may note in this regard that Jellinek (17) singles out Li_2S_2 as the stable crystalline polysulfide of Li. The polysulfide chemistry of the other alkali metals, and NH_4^+ is much richer.

The substance of this discussion is that there should be a predilection for Li_2S_n to be reduced to small ions such as Li_2S_2 (contra Sawyer for Na_2S_n). Some information on what is found in practice can be seen from Herbert and Nole and Moss. Herbert saw 50% S utilization, e.g., from S to $S_2^=$. Nole and Moss found at least 75% utilization, e.g., from S to $S^=$ plus $S_2^=$. They do not say whether any Li_2S precipitates though. The ultimate form of reduced Li_2S_n is then quite close to Li_2S_2, and may be lower.

III. EXPERIMENTAL

A. Purification of Solvents

In general, solvents which were not spectroscopic grade were distilled using a Teflon spinning band (Perkin-Elmer 251 Auto Annular Still). The middle 60% was collected and stored in an argon-filled dry box (Vacuum-Atmospheres Corp.). After addition of supporting electrolyte, the solutions were treated 3X with activated Linde 5A, 600 mesh molecular sieve for at least 12 hour periods in the dry box. This procedure has been found to reduce the H_2O content in PC/1M "anhydrous" $LiClO_4$ solutions from 1200 ppm to below the Karl Fischer detection limit of 10 ppm (1). Solutions were treated with molecular sieve once after 2.5-5.0 mM S_8 were added for cyclic voltammetry studies.

The specific solvents studied, their source and purification, were the following:

- Dimethyl Sulfoxide (DMSO)

  Source: Matheson, Coleman & Bell spectroquality.
  Purification: None (18). The solvent was opened and stored in the dry box.

- Dimethyl Sulfite (DMSI)

  Source: Aldrich or Eastman
  Purification: The solvent was distilled at 80-90 torr with a pot temperature of 64-66°C and a head temperature of 55°C, and a 2:1 reflux ratio.

- N,N-Dimethyl Acetamide (DMAC)

  Source: Eastman, spectroquality
  Purification: None

- γ-Butyrolactone (BL)

  Source: Matheson, Coleman & Bell, Reagent Grade
  Purification: Distillation was at 1 torr, with the pot temperature 98°C, head temperature 52°C, and a 2:1 reflux ratio.

- Methyl Acetate (MA)

  Source: Fisher Certified Reagent
  Purification: The solvent was distilled at atmospheric pressure with a pot temperature of 55-58°C, and a head temperature of 54°C, and a 2:1 reflux ratio.

- Methyl Formate (MF)

  Source: Eastman, spectroquality
  Purification: None

- Propylene Carbonate (PC)

  Source: Aldrich
  Purification: The solvent was distilled at 1 torr, with a pot temperature of 115-124°C, a head temperature of 68°C, and a 2:1 reflux ratio.

- Pyridine

  Source: Eastman, spectroquality
  Purification: None

- Sulfolane (tetrahydrothiophene-1,1 dioxide) (SL)

  Source: Eastman, practical
  Purification: The solvent was pretreated in the dry box with P_2O_5 and Li metal, decanted, and distilled as above at 1 torr. The pot temperature was 160-162°C, the head temperature 99°C, and the reflux ratio was 2:1.

- Tetrahydrofuran (THF)

  Source: Fisher Certified Reagent
  Purification: The solvent was distilled at atmospheric pressure, with a pot temperature of 59-65°C, and a head temperature of 58°C, and a reflux ratio of 2:1.

B. Purification of Salts

- $LiClO_4$

Source: Foote Mineral Company, anhydrous

Purification: For cyclic voltammetry, the salt was weighed directly in the dry box, and the resulting solution treated 3X with molecular sieve (as above). For solubility studies of polysulfides, the salt was vacuum dried at its fusion point (∿230°C) for at least 1 hour, then left under a vacuum as it cooled for about 12 hours. The dried salt was then stored in vacuo.

- Li_2S

Source: Ventron

Purification: None

- $LiBF_4$

Source: Ventron

Purification: Solutions were dried 3X with molecular sieve.

- Tetraethyl Ammonium Perchlorate (TEAP)

Source: Eastman

Purification: Solutions were dried 3X with molecular sieve.

C. Preparation of Electrodes

- Teflon-Bonded Carbon Electrodes. The carbon black used in the manufacture of the positive electrodes was purchased from Ashland Chemical Co. (XC-6310-4). The electrode binder was TFE in dispersion form, type 30, obtained from DuPont de Nemours & Co. The electrodes were fabricated by preparing a workable paste of carbon black-water (∿5-10 cm^3 H_2O/g C) and TFE dispersion. Depending on the carbon loading desired for a particular electrode, a measured quantity of this paste was spread uniformly over a pre-weighed expanded metal screen. The expanded metal substrate was cut to provide, in addition to the electrode area, an unused area which could be used as an electrical lead.

The screen and paste were then covered with Whatman #1 filter paper to wick up the excess water. This paper was selected due to its nonlinting, yet absorbent characteristics. The electrodes were then placed between pieces of fresh filter paper and absorbent paper towels. This "package" was pressed at between 500 and 1,000 pounds for 60 seconds in a Carver hydraulic press. The package was removed, and the filter papers peeled away from the electrode. Electrodes were dried in an air oven at 65°C overnight. The electrodes were then sintered in a tube furnace at

300°C for 15-20 minutes under an inert atmosphere of Ar to provide them with a mechanically stable structure.

The Teflon content was varied between 17 and 41%. Typically heavily loaded (30 mg/cm^2) electrodes, and electrodes with low Teflon content, exhibited "mud flat" cracking after the drying step. Carbon with 26% Teflon binder yielded electrodes of good appearance.

- Lithium Electrodes. Lithium electrodes were assembled simply by mounting a strip of the 0.015" Li foil onto a 5 Ni 7 - 4/0 Exmet substrate cut to an appropriate size, and with a portion of the metal screen cut to provide an electrical lead as described for the carbon cathode. This was carried out in the dry box, by placing the Li foil over the proper Ni substrate on a 304 stainless steel plate and lightly hammering the foil into the mesh of the screen.

Individual electrode potentials were, in general, measured against an Li^+/Li reference electrode contained in a separate compartment. This compartment was separated from the main cell compartment by a porous plug to reduce electrolyte exchange. The reference compartment contained the pure base electrolyte.

- Other Test Electrodes. Nonporous electrodes of Pt, vitreous C, Ni and Au were prepared by sealing into glass. These electrodes were used in cyclic voltammetry. The electrodes had the following dimensions: Pt: 0.020" wire; C: 0.130" rod; Ni: 0.015" wire; Au: 0.020" wire.

D. Electrochemical Measurements

- Cyclic Voltammetry. A specially designed function generator provided a triangular potential input to a Wenking Type 61RS potentiostat. The current output of the potentiostat was monitored on the Y axis of a Houston, Model HR100 X-Y recorder. The X axis of the recorder monitored the output of the function generator.

The cell used in these experiments was constructed from a 3-neck, 25 ml round bottom flask. The counter electrode compartment, which was inserted in the center neck, was made from a 14 mm Pyrex tube over the end of which a piece of Celgard 2402 microporous polypropylene was stretched and secured with a Viton O-ring. The other two necks were fitted with Teflon thermometer adaptors. A Luggin capillary Li^+/Li reference electrode was inserted in one such adaptor, and a sealed-in glass Pt, Au, Ni or C working electrode in the other. The reference and working electrodes were positioned in the path of the current flow from the counter electrode.

Measurements of the iR drop between reference and working electrodes were made using the current interruption method, the potential-time profile being recorded on a Tektronix Model D10 oscilloscope, with 5A18N and 5B10N plug-ins. With the currents and solution resistances encountered in these experiments, the iR drop never exceeded 20 mV.

- Coulometry. The stoichiometry of oxidation and reduction of polysulfides was evaluated galvanostatically between preset voltage limits. For these experiments a three-compartment Teflon cell was used (Fig. 2). A central working electrode compartment was surrounded by two counter electrode compartments to insure even current distribution. The working electrode was Teflon bonded C on a Ni screen. A reference electrode and a vitreous C cyclic voltammetry probe also extended into the working electrode compartment.

Galvanostatic charging and discharging were accomplished with a specially designed cell cycling unit which would repeatedly charge and discharge the cell at a preset current to predetermined voltage or time limits.

- Current-Potential Curves. Current-potential curves were measured using the cell configurations shown in Fig. 2. A Princeton Applied Research Model 373 potentiostat/galvanostat was used in the potentiostatic mode to vary incrementally the potential of the working electrode. The current was recorded at each potential after it had reached a constant value (typically 5 min). The resulting i-E curves were corrected for iR, determined as previously described.

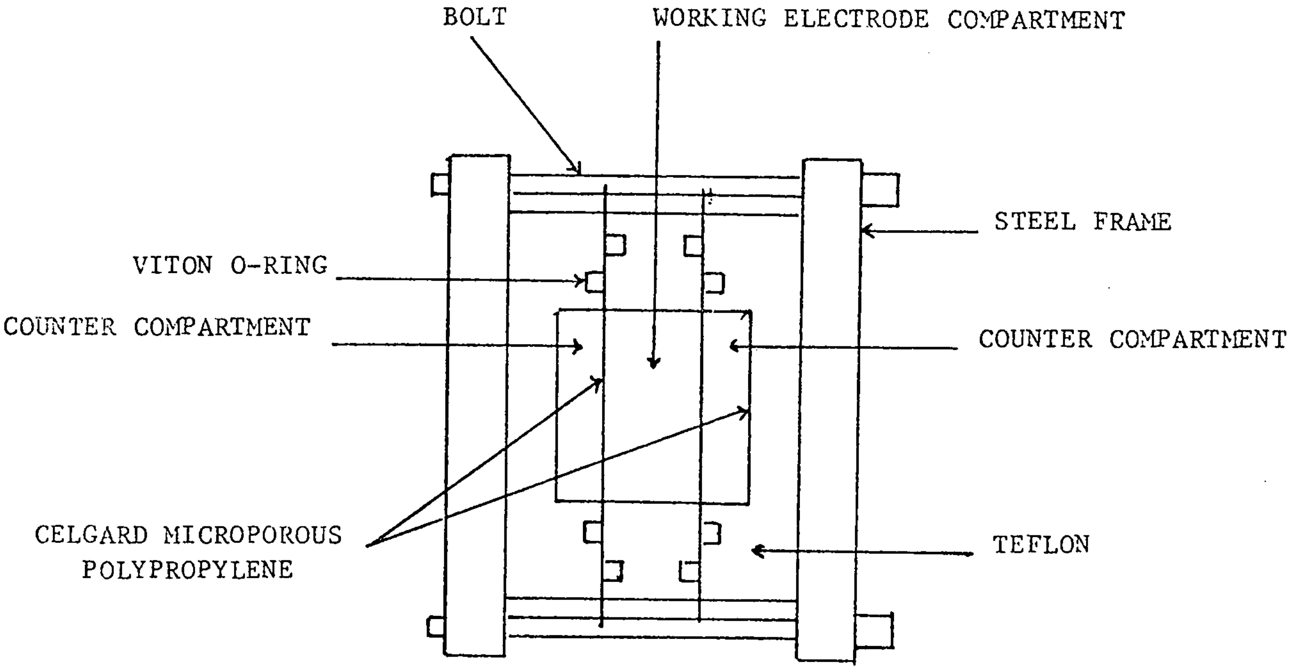


Fig. 2. Teflon coulometry cell utilizing microporous polypropylene separators. The top (not shown) contains fittings for a reference electrode and a cyclic voltammetry probe.

IV. CYCLIC VOLTAMMETRY OF DILUTE S_8 SOLUTIONS

Cyclic voltammetry is potentially a powerful tool in the design of a soluble battery. Using this technique, many electrolytes may be scanned to examine the potentials at which S_8 is reduced to polysulfides and at which these polysulfides are further reduced. The potentials at which both species are reoxidized may also be explored. Electrolytes and substrates which yield the most positive reductions and most negative oxidations have the most practical significance. In addition, many polysulfide species are apt to exist in equilibrium in solution, and these may have a variety of oxidation and reduction potentials. In a practical system, the number of species in solution and/or the variation in their redox potentials should be minimized in order to achieve non-sloping charge and discharge curves in the final battery.

The redox behavior of 2.9 mM S_8, 0.1M TEAP in DMSO has been thoroughly investigated by Sawyer et al. (8,9) using electrochemical and spectroscopic methods. The assignments of the oxidation and reduction processes observed in the cyclic voltammograms, as described in Section II, provide a point of reference for work in other electrolytes. The first task in the current work was to assess the effect of electrolyte composition, substrate and temperature upon the redox behavior of S_8. The following organic solvents were surveyed: propylene carbonate (PC), methyl acetate (MA), dimethyl sulfoxide (DMSO), butyrolactone (BL), sulfolane (SL), dimethyl formamide (DMF) and pyridine. These solvents have broad electrochemical stability, and most have promise of being stable toward Li.

A. Background

Cyclic voltammograms of the pure solvents plus 0.1M $LiClO_4$ were recorded on Pt, Au, C and Ni at ambient and one elevated temperature. Background currents due to impurity and solvent redox reactions were usually quite low on Au, Pt and C. On Ni, the background currents tended to be quite high, however, possibly due to reduction of surface oxides. Cathodization of the Ni in aqueous acid, resulting in H_2 evolution, followed by careful drying and rapid introduction into the Ar atmosphere glove box, helped to reduce the background currents, but on the whole, results on Ni were irreproducible and difficult to interpret. Pt and Au were pretreated in a similar manner, but such pretreatment did not affect the results. With the exception of Ni, measurements made on background currents comprised less than 10% of the total currents measured in solutions containing 2.5 mM S_8. Background currents did, as expected, increase with temperature, but so did the currents corresponding to the species of interest.

B. Cyclic Voltammetry of S_8 Solutions

The cyclic voltammograms of 2.5 mM S_8 in DMSO containing 0.1M $LiClO_4$, on Pt, Au and C substrates, at 25°C and 63°C are shown in Fig. 3. Correction for iR was extremely small in each case. The curves represent the first sweep in each example, beginning at the open circuit potential ($\sim$2.5 V vs. Li^+/Li) and sweeping initially in a negative direction. In most instances, there was little shifting of the peak potentials with continued cycling, but only an adjustment of the peak currents toward steady-state values.

The cyclic voltammograms on Au and C agree quite well with that reported by Sawyer et al. for 2.9 mM S_8 in DMSO, 0.1M TEAP, on Au (Table 1). Significant shifts in the peak potentials (E_p) do occur when TEAP is replaced by $LiClO_4$ as the supporting electrolyte. First, the peak potential of the two-electron reoxidation of $S_x^=$ is shifted by +0.26 V. The $S_8^{-4} \rightarrow S_8^=$ oxidation is also more difficult in the presence of Li^+ by +0.07 V. The corresponding cathodic shift of the $S_8^=$ reduction makes the $S_8^= \rightleftarrows S_8^{-4}$ redox reaction considerably less reversible in the presence of Li^+. The effect of anion is negligible: The cyclic voltammogram using $LiBF_4$ as supporting electrolyte is virtually identical to that using $LiClO_4$.

Fig. 3 also shows a major effect of the metallic substrates (Pt, Au), compared to C, using $LiClO_4$ as the supporting electrolyte. On Pt, a set of peaks at +1.32 V (reduction) and +1.81 V (oxidation) is superimposed upon the normal peaks. The oxidation peak currents corresponding to S_8^{-4} and $S_x^=$ are also smaller, on a relative scale, than on C. A new reduction peak at +1.55 V at 25°C is present on Au. These new peaks are magnified at 63°C on Pt and Au, while no new peaks appear on C at elevated temperatures.

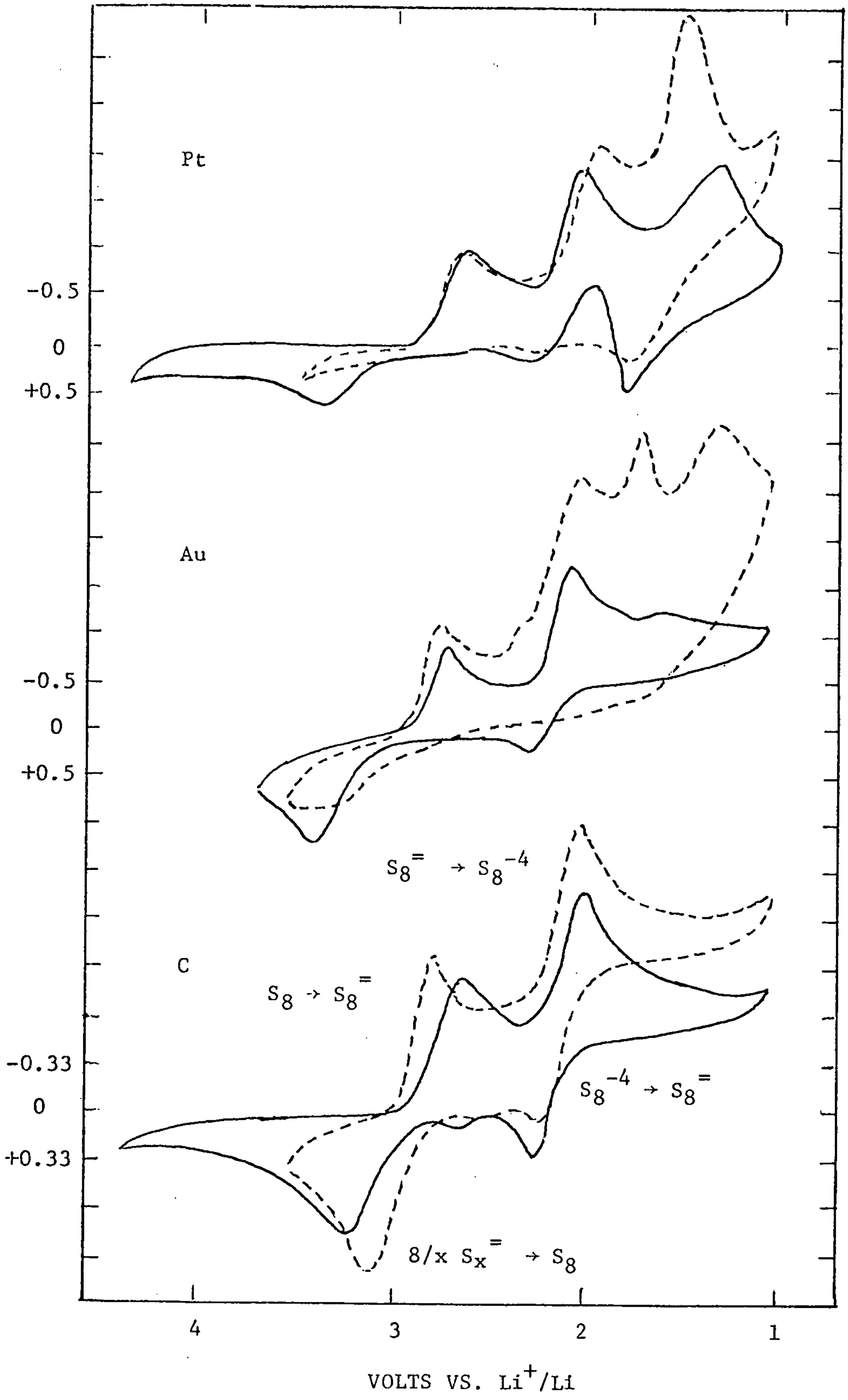
On Pt at 25°C, the sharp increase in cathodic current at 1.95 V, encountered during the positive (reverse) scan, is indicative of the removal of a (resistive, passivating) deposit on the electrode at this potential. An increase in temperature markedly increases the current carried by the new reduction peaks. The new peaks occur following the $S_8^= \rightarrow S_8^{-4}$ reduction, and probably result from further reduction of products of this reaction. The presence of this layer of reaction products also results in the formation of less of the $S_x^=$ species responsible for the oxidation at +3.5 V, or at least a passivation of the working electrode against this oxidation reaction.

The cyclic voltammogram of 5 mM S_8 in DMSO, 0.1M TEAP was also recorded on a Pt working electrode. Although there is a hint of additional structure between +1.0 and +2.0 V, the effect is very much less than in the electrolyte containing $LiClO_4$. This result probably reflects the greater solubility of tetraethyl ammonium polysulfides than Li polysulfides, resulting in less precipitation on the working electrode.

Table 1

Comparison of peak potentials on Au for the redox reactions of S_8 in DMSO as determined by cyclic voltammetry in this work and in the work of Martin, Doub, Roberts and Sawyer (9). Scan rates = 0.1 V/sec; T = ambient (∿25°C).

Assignment	E_p, ref. 9 vs. Li^+/Li 0.1M TEAP, $[S_8]$ = 2.92 mM	E_p, this work, vs. Li^+/Li 0.1M TEAP, $[S_8]$ = 2.6 mM	E_p, this work, vs. Li^+/Li 0.1M $LiClO_4$, $[S_8]$ = 2.5 mM
$S_8 \rightarrow S_8^{=}$	+2.68	+2.75	+2.68
$S_8^{=} \rightarrow S_8^{-4}$	+2.01	+2.03	+2.03
$S_x^{=} \rightarrow S_8$	+3.07	+3.09	+3.37
$S_8^{-4} \rightarrow S_8^{=}$	+2.15	+2.15	+2.24



. 3. Cyclic voltammograms of 2.5 mM S_8 in DMSO, 0.1M $LiClO_4$, on Pt, Au and C substrates at 25°C (——) and 63°C (– – –). Sweep speed = 0.1 V/sec. Assignments are from Sawyer et al. (8,9).

The cyclic voltammogram of S_8 (saturated) in THF, 1M $LiClO_4$, shown in Fig. 4, is quite dissimilar from that in DMSO. The first reduction peak upon scanning cathodic from the open circuit potential (∿2.3 V) occurs at less than 2.0 V. The associated oxidation peak is shifted by -0.25 to -0.50 V from its position in DMSO. Raising the temperature from 25°C to 45°C results in a decrease in the relative peak current of this oxidation, especially on Pt and Au. In THF, as in DMSO, there are indications of passivation of Pt and Au in the potential region of 1.00 to 1.75 V. The currents ascribed to these species are, as in DMSO, increased sharply by raising the temperature.

Figs. 5 and 6 show the cyclic voltammograms of the same THF solution at 0.5 V/sec and 0.02 V/sec, respectively. The voltammogram is simplified at 0.5 V/sec on all three substrates, the extra peaks being notably reduced or absent. Similarly, the generalized reoxidation peaks at about +3.0 V are much more pronounced than on the slower scans. Conversely, the scans at 0.02 V/sec show almost no reoxidation, and a very distinct area between 1.0 and 2.0 V. These data suggest the possibility that these extra peaks correspond to the reduction and oxidation of a passivating film.* They are, of course, superimposed on the diffusion limited reduction currents of species in solution.

The voltammograms of S_8 in MA, PC, BL and SL are given in Figs. 7-10. The data are presented for Pt, Au and C working electrodes at 25°C and at one elevated temperature. In addition, cyclic voltammograms, at room temperature only, were recorded for S_8 dissolved in DMF and pyridine; they are not reproduced in this report. No two solvents give completely identical voltammograms but the solvents may, nevertheless, be divided into two groups: DMSO and DMF give similar patterns, with the $S_8 \rightarrow S_8^=$ peak reduction potential occurring between +2.50 and +2.75 V, considerably anodic of the (presumed) corresponding reduction in the other solvents. The peak potentials of the $S_8 \rightarrow S_8^=$ reduction are summarized in Table 2 for all the solvents investigated. In addition, DMSO and DMF show a distinct area of reoxidation of S_8^{-4} at +2.25 and +2.10 V, respectively, which is not obvious in the other solvents.** Both of these results indicate an ability of DMSO and DMF to stabilize polysulfide species.

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*This is not an academic issue. If these peaks correspond to further reductions of polysulfides in solution, the substrates Pt and Au would be shown to influence greatly the mechanism of the multistep polysulfide reduction, compared to C, in a way which may be favorable to cell performance. If Pt and Au are passivated more easily than C, then C is a better choice for a practical catalytic electrode.

**These interpretations are most easily made by comparing the results on C, where there are no extra peaks.

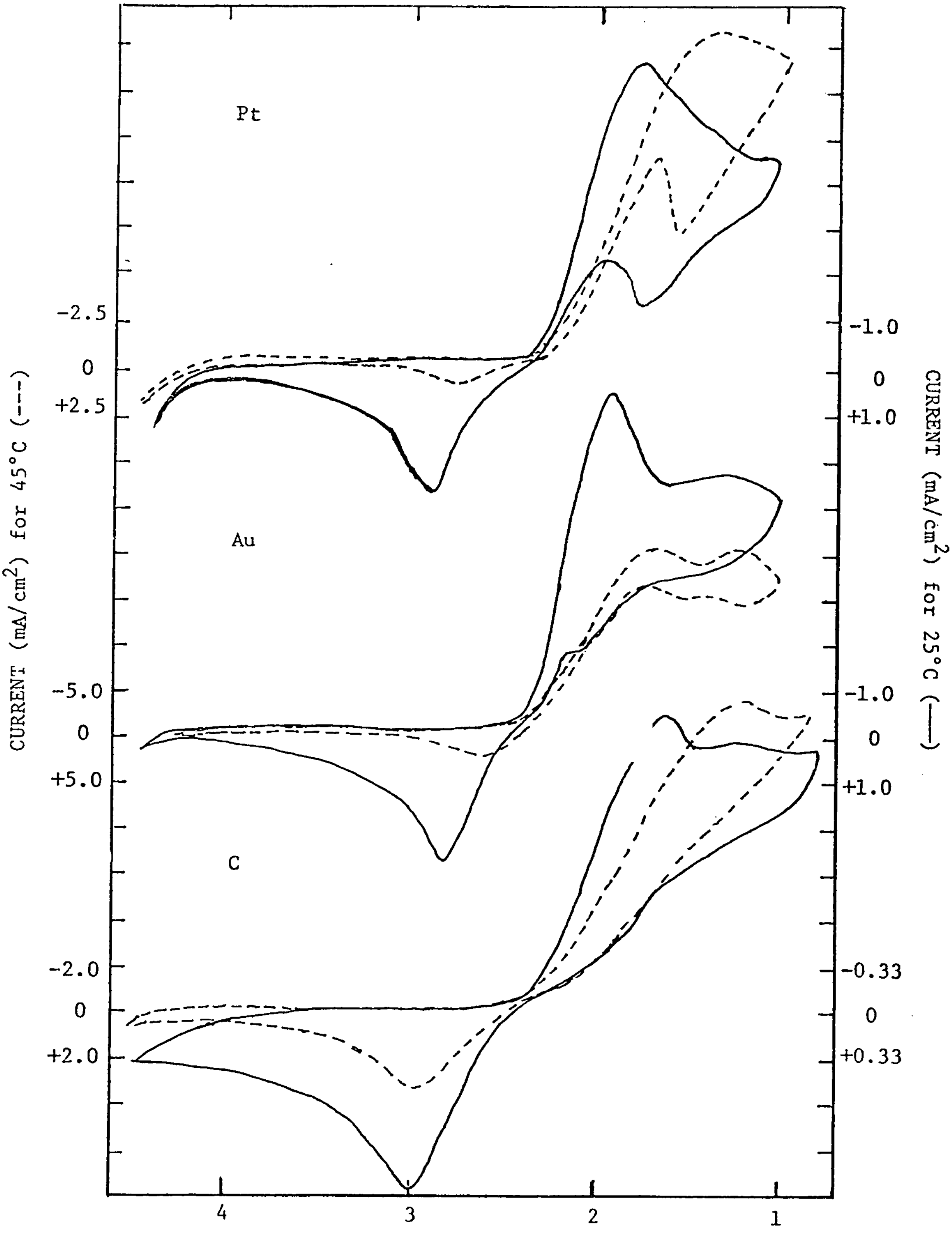

Fig. 4. Cyclic voltammograms of saturated (∿5 mM) S_8 in THF, 0.1M $LiClO_4$, on Pt, Au and C substrates at 25°C (——) and 45°C (– – –). Sweep speed = 0.1 V/sec.

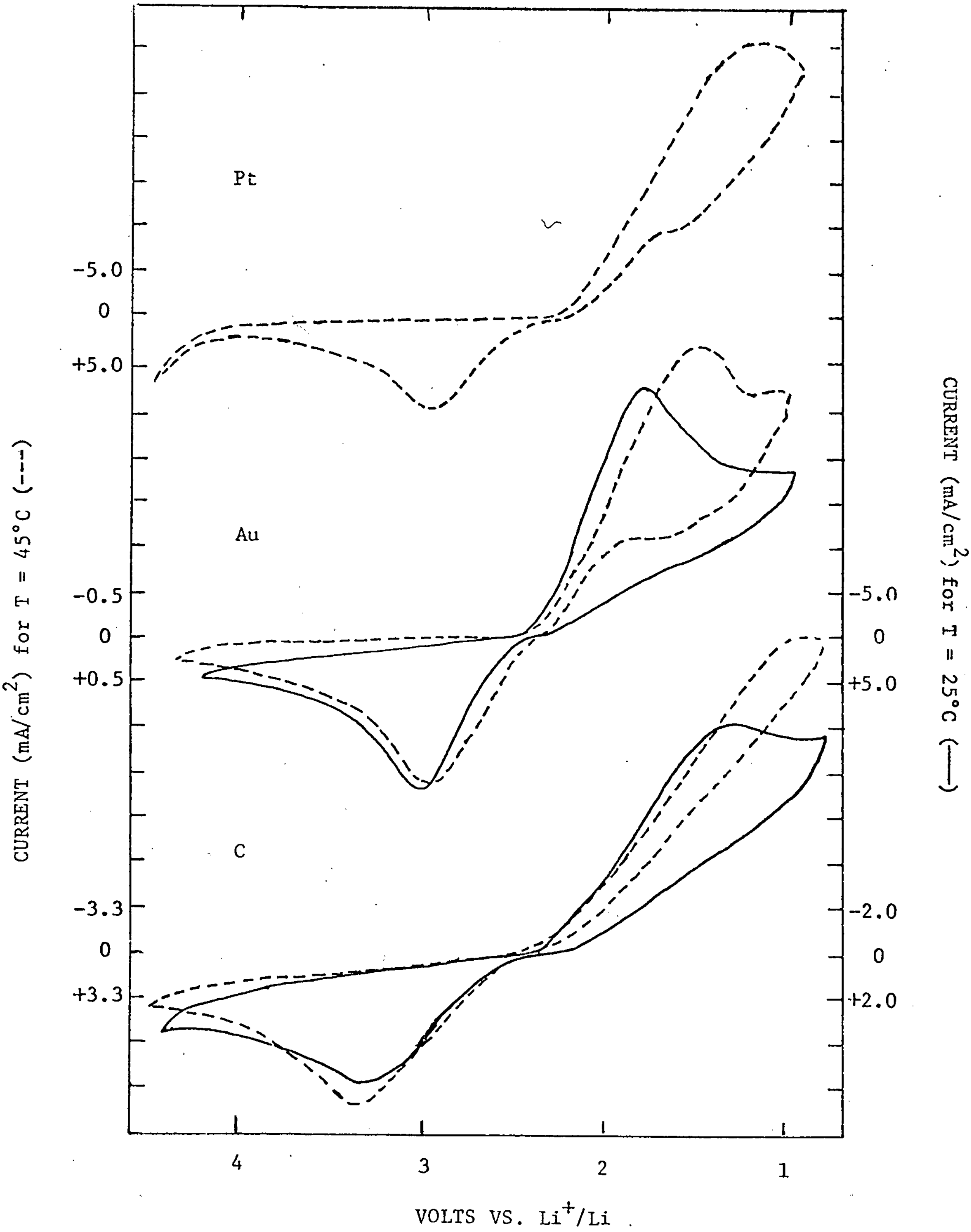

Fig. 5. Cyclic voltammograms of saturated (~5 mM) S_8 in THF, 0.1M $LiClO_4$, on Pt, Au and C substrates at 25°C (——) and 45°C (---). Sweep speed = 0.5 V/sec.

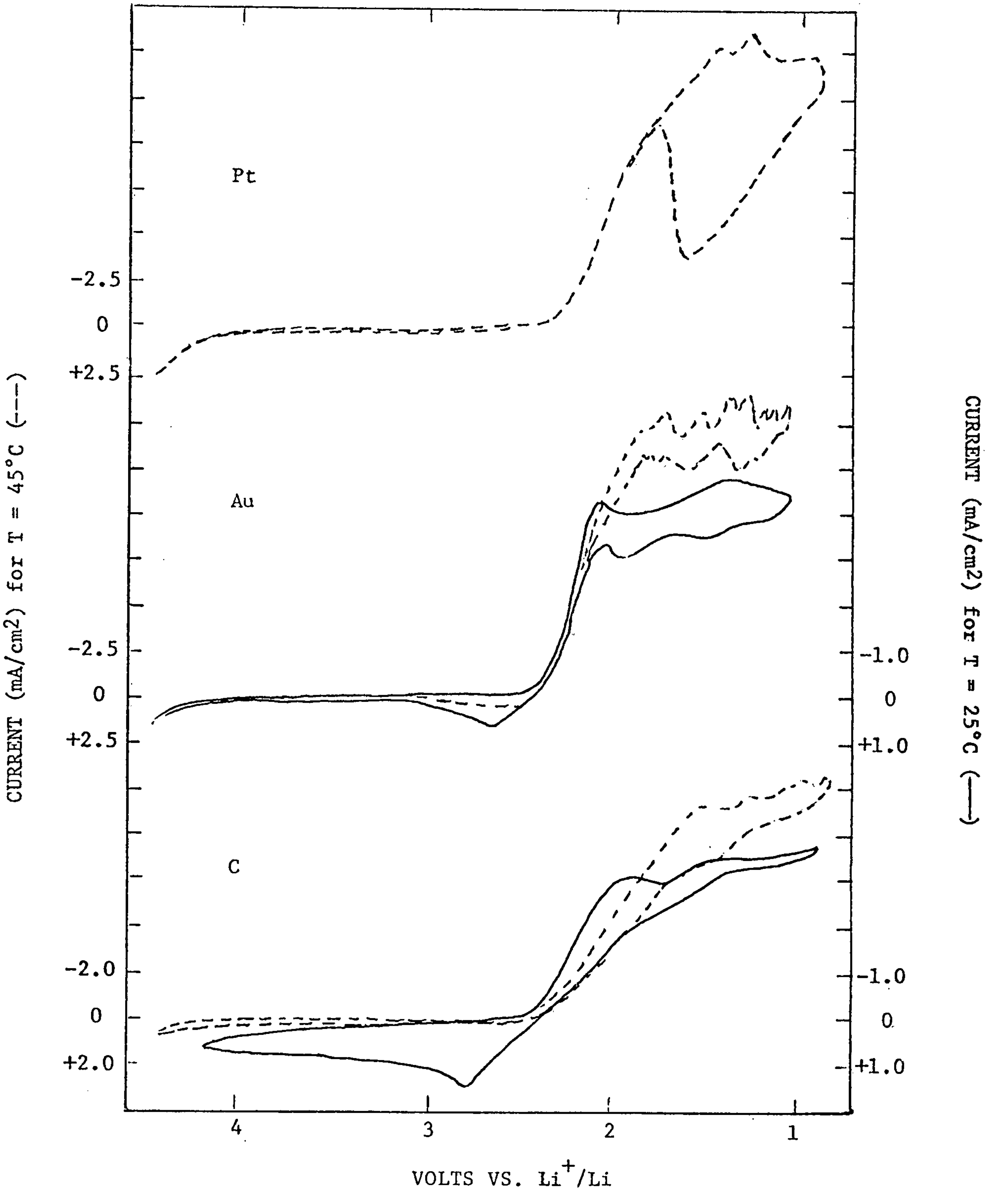

Fig. 6. Cyclic voltammograms of saturated (∼5 mM) S_8 in THF, 0.1M $LiClO_4$, on Pt, Au and C substrates at 25°C (——) and 45°C (---). Sweep speed = 0.02 V/sec.

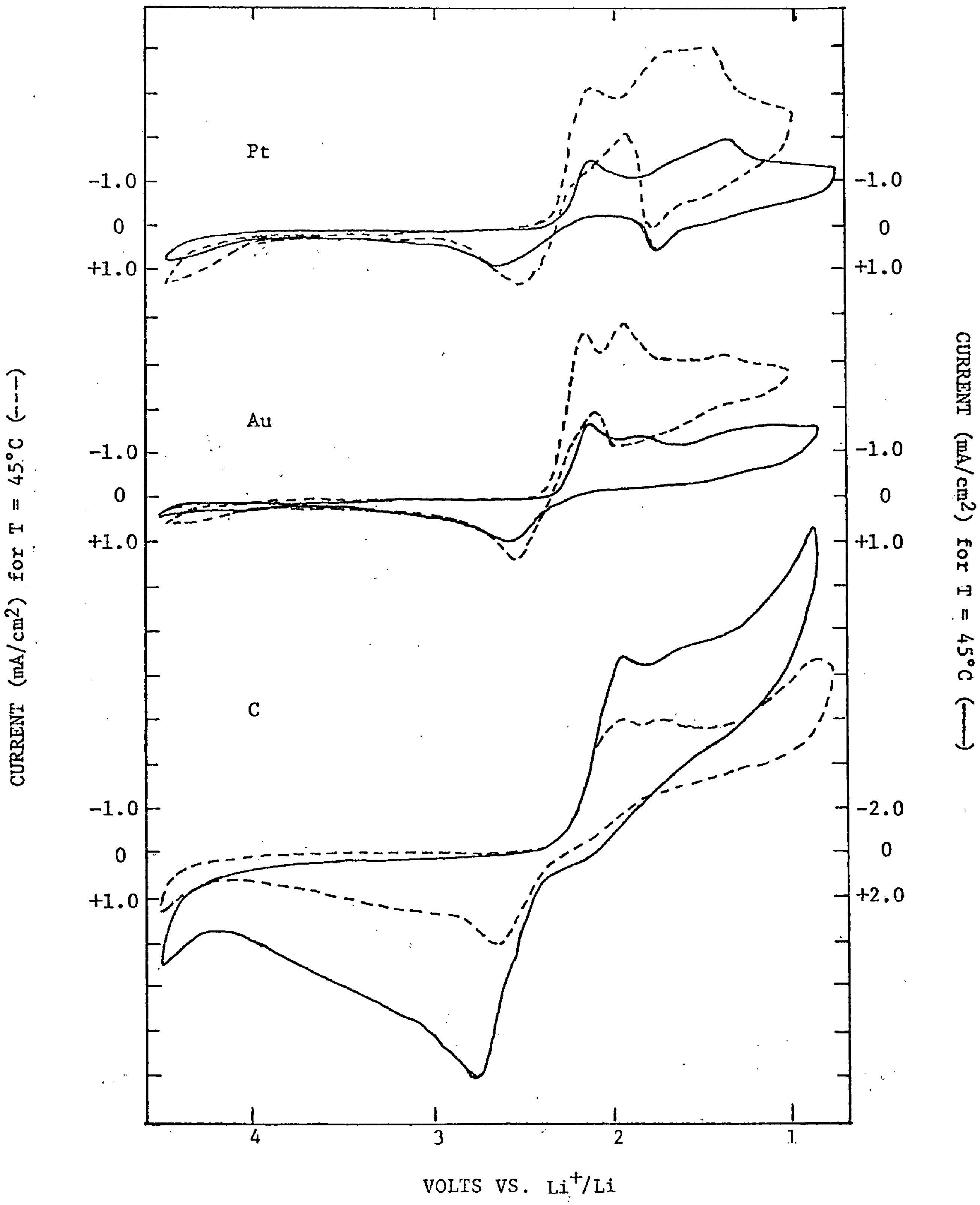

Fig. 7. Cyclic voltammograms of saturated (∿5 mM) S_8 in MA, 1M $LiClO_4$, on Pt, Au and C substrates at 25°C (——) and 45°C (– – –). Sweep speed = 0.1 V/sec.

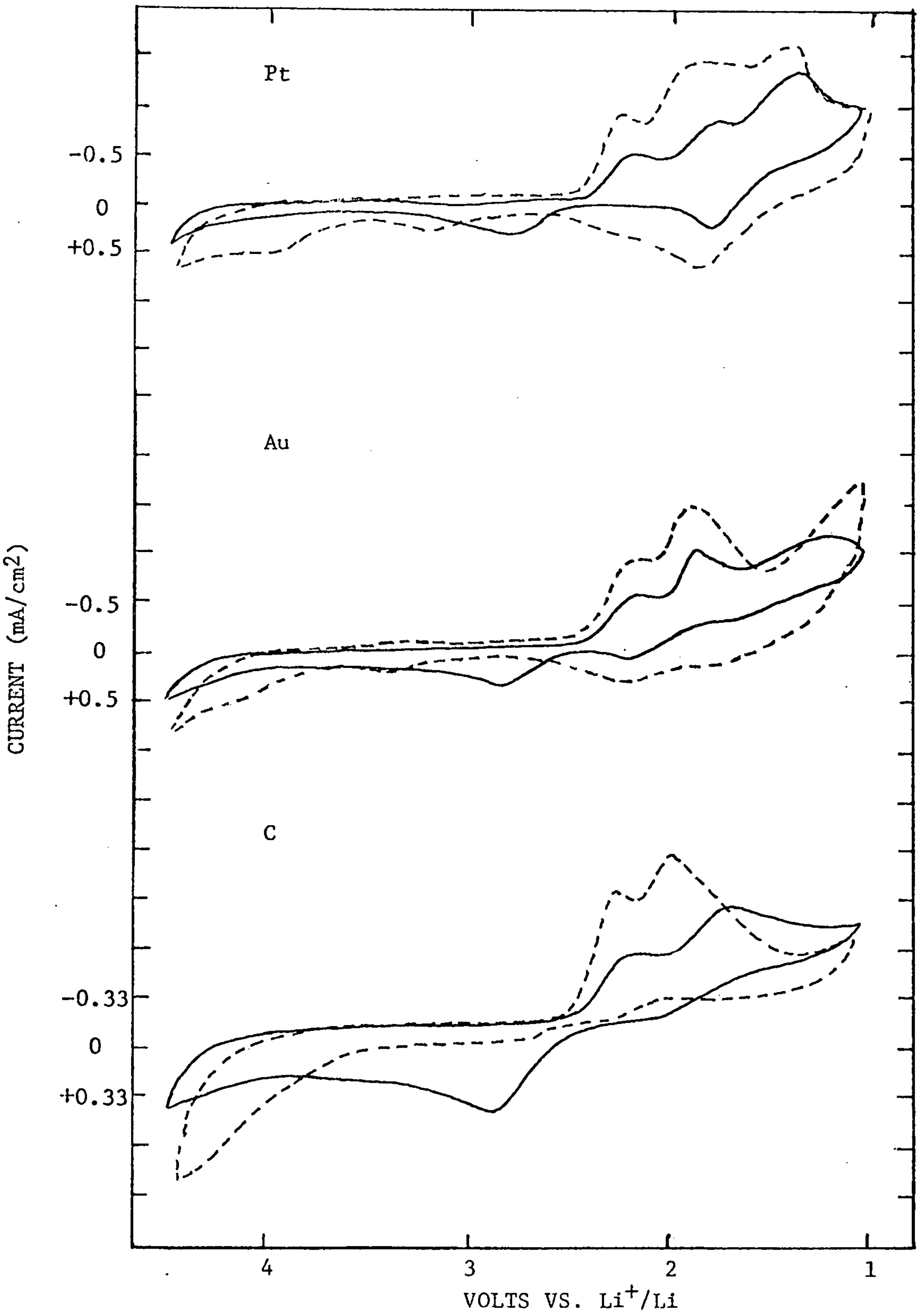

Fig. 8. Cyclic voltammograms of 2.5 mM S_8 in PC, 0.1M $LiClO_4$, on Pt, Au and C substrates at 25°C (←——) and 70°C (←– –). Sweep speed = 0.1 V/sec.

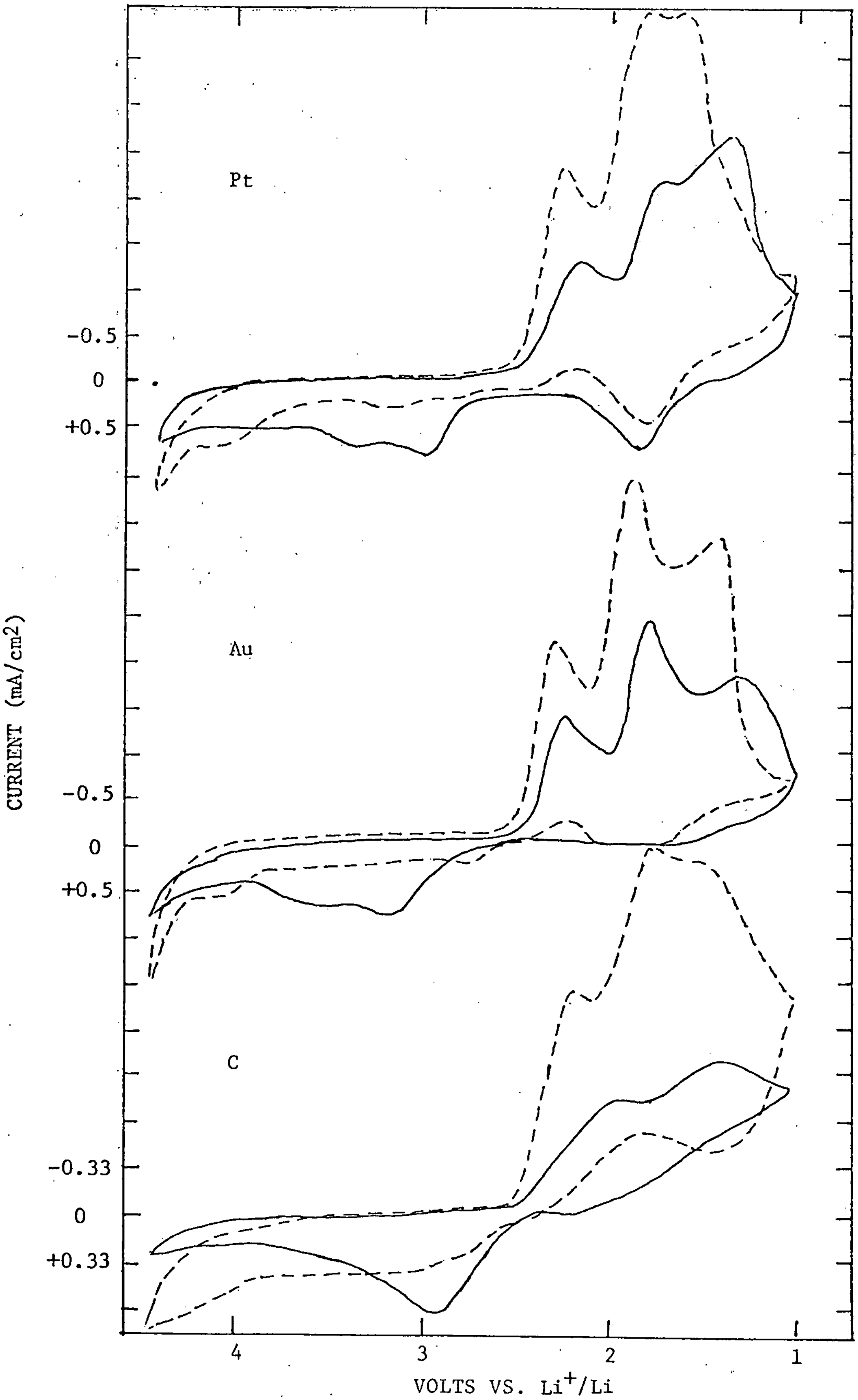

Fig. 9. Cyclic voltammograms of 2.5 mM S_8 in BL, 0.1M $LiClO_4$, on Pt, Au and C substrates at 25°C (——) and 70°C (– – –). Sweep speed = 0.1 V/sec.

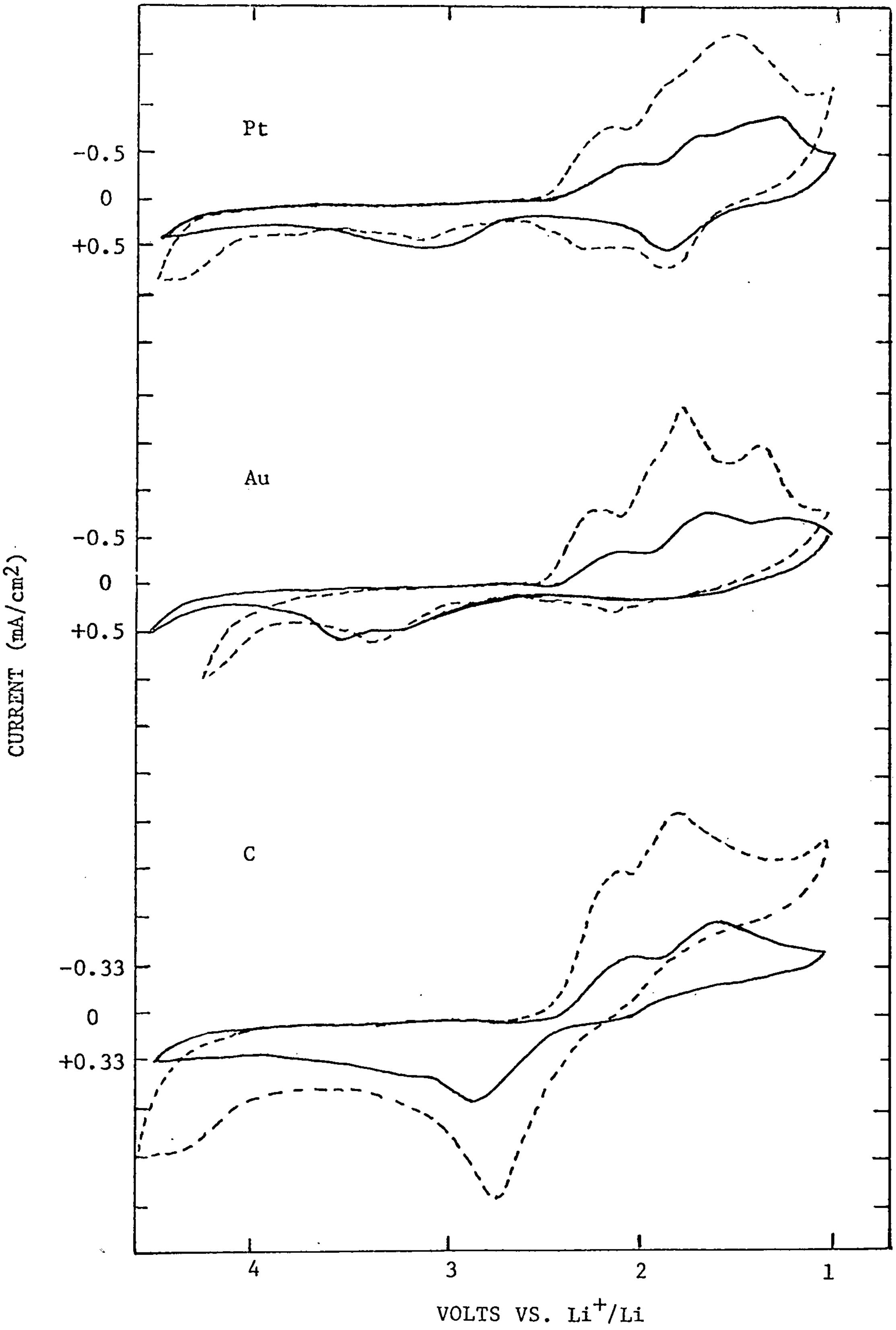

Fig. 10. Cyclic voltammograms of 2.5 mM S_8 in SL, 0.1M $LiClO_4$, on Pt, Au and C substrates at 25°C (——) and 70°C (– – –). Sweep speed = 0.1 V/sec.

Table 2

Cyclic voltammogram peak potentials (E_p) of $S_8 \rightarrow S_8^=$ reduction on Au, Pt and C in various electrolytes. Sweep rate = 0.1 V/sec; $[S_8]$ = 5 mM unless otherwise indicated. The first number is at room temperature, the second at the upper temperature (T_2) given in column 1. Potentials are all vs. Li^+/Li.

System	E_p(Au)	E_p(Pt)	E_p(C)
PC, 0.1M $LiClO_4$; T_2 = 70°C	2.14/2.15	2.17/2.25	2.18/2.23
BL, 0.1M $LiClO_4$; T_2 = 70°C	2.25/2.30	2.17/2.26	1.95/2.18
Sulfolane, 0.1M $LiClO_4$; T_2 = 70°C	2.10/2.22	2.05/2.15	2.05/2.10
DMSO, 0.1M $LiClO_4$; T_2 = 63°C	2.63/2.67	2.63/2.67	2.63/2.76
MA, 1M $LiClO_4$, sat. S_8; T_2 = 45°C	2.12/2.15	2.09/2.11	1.90/1.92
THF, 1M $LiClO_4$, sat. S_8; T_2 = 45°C	1.92/*	1.76/*	1.63/*
DMF, 1M $LiClO_4$, sat. S_8	2.53/--	-- / --	2.35/--
Pyridine, ∿0.5M $LiClO_4$, sat. S_8	2.02/--	1.83/ --	1.79/--

*Peak not discernable.
--Not measured.

The remaining solvents have peak reduction potentials of S_8 and $S_8^=$ (by inference, from the work of Sawyer et al. (8,9)) much closer together (and more negative) than DMSO and DMF. This result is probably due to the lower stability or energy of solvation of polysulfides in these solvents (see below for solubility studies). The peak potentials for $S_8^=$ reduction in the electrolytes under investigation are given in Table 3. The peak potential of this reaction is much more of a function of substrate than is the S_8 reduction. Usually $E_p(Pt) > E_p(C) > E_p(Au)$. With a few exceptions, increasing the temperature results in a small positive shift in E_p, implying faster reduction kinetics.

The reversibility of the $S_8 \rightleftarrows S_8^=$ reaction may be assessed in most cases by the difference $E_p(S_x^= \rightarrow [x/8]S_8) - E_p(S_8 \rightarrow S_8^=)$. These values are given in Table 4. In MA, THF, DMF and pyridine, best reversibility was achieved on Au, in BL on Pt, and in PC, sulfolane and DMSO on C. Raising the temperature generally improved the reversibility, except in the case of PC.

The peak current for the oxidation at $E_p(S_x^= \rightarrow [x/8]S_8)$ is very solvent, substrate and temperature dependent. The ratios

$$R = \frac{i_p(S_x^= \rightarrow x/8\ S_8)}{i_p(S_8 \rightarrow S_8^=)} \qquad (9)$$

are given in Table 5. Note that i_p values are tabulated from complete cyclic voltammograms, rather than from scans of only the pair of peaks involved. Hence, R is sometimes greater than 1 due to the oxidation of $S_x^=$ species other than $S_8^=$. Table 5 shows that in every case at 25° and higher temperatures, R is greater on C than on Pt or Au. Second, for all cases except DMSO on C, raising the temperature reduces the value of R; in some cases, the reoxidation peak disappears at elevated temperatures. THF shows the greatest effect of temperature, while DMSO shows one of the smaller effects.

For THF and DMSO, the effect of sweep speed upon R was also computed, at room temperature. In the case of THF, R was increased with increased sweep speed, and decreased with slower sweep speed. This effect was most prominent on Au and C. In DMSO, however, sweep speed had only a small effect on R.

Examination of all the cyclic voltammograms reveals in many cases areas of significant oxidation anodic of 4.0 V not ascribable to background. In addition, in many cases the oxidation reactions do not account for as much current at the reduction reactions. This leads to an extreme diminution in the reduction peaks with repeated cycling. Such a result was noted for

Table 3

Cyclic voltammogram peak potentials (E_p) of $S_8^{=} \rightarrow S_8^{-4}$ reduction on Au, Pt and C in various electrolytes, cf. Table 1.

System	E_p(Au)	E_p(Pt)	E_p(C)
PC, 0.1M $LiClO_4$; T_2 = 70°C	1.70/1.97	1.86/1.88	1.70/1.80
BL, 0.1M $LiClO_4$; T_2 = 70°C	1.40/1.50	1.80/1.88	1.74/1.80
Sulfolane, 0.1M $LiClO_4$; T_2 = 70°C	1.57/1.77	1.75/1.77	1.75/1.85
DMSO, 0.1M $LiClO_4$; T_2 = 63°C	1.97/1.98	2.03/1.97	2.05/1.95
MA, 1M $LiClO_4$, sat. S_8; T_2 = 45°C	1.60/1.70	1.83/1.93	1.7 /1.8
THF, 1M $LiClO_4$, sat. S_8; T_2 = 45°C	1.25/(1.25)	*	*
DMF, 1M $LiClO_4$, sat. S_8	1.87/ --	1.93/ --	∿1.7 / --
Pyridine, ∿0.5M $LiClO_4$, sat. S_8	1.74/ --	1.57/ --	1.45/ --

*Peak not discernable.
--Not measured.

Table 4

$/E_p(ox)-E_p(red)/$ for $S_8 \rightleftarrows S_8^=$ on Au, Pt and C in various electrolytes, cf. Table 1.

System	Au	Pt	C
PC, 0.1M $LiClO_4$; T_2 = 70°C	0.7 /1.26	0.67/0.95	0.67/*
BL, 0.1M $LiClO_4$; T_2 = 70°C	0.95/*	0.83/*	0.98/*
Sulfolane, 0.1M $LiClO_4$; T2 = 70°C	1.3 /1.16	1.05/1.00	0.78/0.63
DMSO, 0.1M $LiClO_4$; T_2 = 63°C	0.74/0.68	0.75/*	0.59/0.33
MA, 1M $LiClO_4$; T_2 = 45°C	0.43/0.37	0.51/0.44	0.72/0.82
THF, 1M $LiClO_4$, sat. S_8; T_2 = 45°C	0.91/*	1.14/*	1.37/*
DMF, 1M $LiClO_4$, sat. S_8	0.30/ --	--	0.50/--
Pyridine, ∿0.5M $LiClO_4$, sat. S_8	0.48/ --	0.81/ --	0.93/--

*Peak not discernable.
--Not measured.

Table 5

R = $i_p(S_x^{=} \rightarrow [x/8]S_8)/i_p(S_8 \rightarrow S_8^{=})$, calculated from cyclic voltammograms of S_8 in various solvents at 25°C and one elevated temperature (cf. Table 1). Sweep speed = 0.1 V/sec, unless otherwise indicated.

System	R(Au)	R(Pt)	R(C)
PC, 0.1M $LiClO_4$; T_2 = 70°C	0.58/0.20	0.55/0.26	0.21/0.08
BL, 0.1M $LiClO_4$; T_2 = 70°C	0.57/0.11	0.62/0.13	0.84/0.24
SL, 0.1M $LiClO_4$; T_2 = 70°C	1.0 /0.81	1.25/0.5	0.63/1.3
DMSO, 0.1M $LiClO_4$; T_2 = 63°C	1.33/0.77	0.65/*	0.93/1.0
Repeat, 0.02 V/sec	--	0.55/ --	0.90/ --
Repeat, 0.5 V/sec	--	0.88/ --	1.2 / --
MA, 1M $LiClO_4$, sat. S_8; T_2 = 45°C	0.59/0.42	0.53/0.42	1.15/0.67
THF, 1M $LiClO_4$, sat. S_8; T_2 = 45°C	0.38/0.08	0.44/0.06	0.52/0.27
Repeat, 0.02 V/sec	0.16/0.03	-- /0.02	0.47/0.02
Repeat, 0.5 V/sec	0.62/0.50	-- /0.33	0.6 /0.43

*Peak not discernable.
--Not measured.

all solvents except DMSO and DMAC, but was most evident on Pt and Au. The important point to be noted in the foregoing discussion is that, under many circumstances, the oxidation peak at 2.5-3.5 V is much attenuated, or missing. Once again, there is no hard evidence to indicate whether this is due to electrode passivation or to differences in solution polysulfide equilibria and substrate catalysis. In a practical battery, for example, Table 5 implies that for many solvents at elevated temperatures, much of the recharge would necessarily be at a potential positive of 4.0-4.5 V.

Several factors contribute to the value of R and to the general current-potential behavior in the region of oxidation. First, the substrate can affect the distribution of products formed during the reduction part of the cycle. In addition, changing the temperature will alter the distribution of polysulfide species through shifts in the solution equilibria. Thus, it is possible that on the metallic (Au, Pt) substrates, and at elevated temperatures, in some electrolytes, polysulfide species which are oxidized at potentials positive of 4.0 V are favored over those which oxidize between 2.7 and 3.5 V.

Alternatively, materials which are adsorbed onto the substrate may simply passivate the electrode at potentials negative of 4.0 V, and in most electrolytes this effect is magnified at higher temperatures, and on Au or Pt. It is difficult to separate out the contribution of adsorption reactions in all the voltammograms presented without more detailed investigations. In BL, PC and SL, the reduction peaks which had become severely attenuated on repeated sweeping between 1.0 and 3.5 V could be regenerated by wiping the electrode, but not just by stirring the solution. If the positive sweep limit were extended out to 4.5 V or beyond, depending on the point of solvent oxidation, the attenuation of the reduction peaks with repeated cycling was not nearly as noticeable. Yet, the integrated amount of oxidized material in extending the sweep limit from 3.5 to 4.5 V was not sufficient to account for this (steady-state) difference in reducible material. These facts support the removal or partial removal of a film from the electrolyte during the additional positive sweep.

The preliminary conclusions which can be drawn from the studies of cyclic voltammetry of these dilute S_8 solutions are the following:

1. The most positive reduction potentials were observed for DMSO and DMF. The worst solvent in this regard was THF. In several instances, reductions on vitreous C occurred at considerably more negative potentials than on Pt or Au.

2. Highest reversibilities were achieved on Au or C, depending upon the electrolyte. Best solvents in this regard were MA or DMF.

3. The supporting electrolyte can have an effect on the oxidation and reduction potentials of S_8. In DMSO, the potential of $S_x^= \rightarrow S_8$ was shifted positive by 260 mV by substituting 0.1M $LiClO_4$ for 0.1M TEAP (on C). The other redox reactions were affected to a lesser degree.

4. Raising the temperature generally enhances reversibility and reaction rates, but, in some cases, seems to lead to greater precipitation of reaction products on the working electrode, leading to partial passivation. Passivation is more common on Pt and Au than on C.

On the basis of these results, DMSO, DMF or MA are the best choices for solvents in a practical cell. Particularly relevant is the ease of reduction of S_8 and $S_8^=$, and the reverse of these reactions. It must be noted, however, that reduction can extend below 1.0 V, and that the reduction potentials of all the likely polysulfide species remain undetermined. Empirically, we must measure current-potential curves (i.e., very slow scan linear voltage sweeps) to assess steady-state currents as a function of potential after cell charge and discharge. Several such studies are reported below for polysulfide solutions.

Also on the basis of these results, Pt and Au are apparently susceptible to "poisoning" reactions during polysulfide reduction, especially at elevated temperature. Although this effect may be alleviated somewhat by substitution of TEAP for $LiClO_4$ in DMSO, high area C would appear to be the best electrode choice for this system in which the presence of Li^+ ions is unavoidable.

V. SOLUBILITY, VOLTAMMETRY AND CURRENT-POTENTIAL STUDIES OF LI POLYSULFIDES IN NONAQUEOUS ELECTROLYTES

A. Formation of Li_2S_x

Although a series of sodium and potassium polysulfides have been synthesized and characterized in the crystalline state, the only Li polysulfide known is Li_2S_2 (17). However, nonaqueous solutions of Li polysulfides may be produced either chemically or electrochemically. Three such methods have been investigated in this work. The first is the direct reaction of elemental S with Li metal:

$$2\ Li + x/8\ S_8 \rightarrow Li_2S_x \qquad (10)$$

Here, elemental S was first added to the electrolyte (0.6M/1), only a small fraction of which dissolved. An excess of Li metal dispersion (70μ) was then added. The solutions became somewhat colored immediately, the degree of such reactions varying with solvent. The qualitative observation for several organic solvents are shown in Table 6. In general, the reaction proceeded slowly, with extensive reactions taking place only in DMSO, BL, THF and DMSI. In the first three solvents, highly colored polysulfide species were formed, while in DMSI, Li plus S reacted to form a colorless solution. DMSO and SL were blue-green when the polysulfide concentration was low. As more polysulfide formed in DMSO, the solution became dark red. In THF and BL, the blue color was not produced at high dilution.

The second method of Li polysulfide formation was to potentiostatically reduce S_8 in the organic electrolyte on a catalytic (e.g., C) electrode. In previous work in this laboratory (19), we have shown that S may be dissolved in DMSO to a level of at least 0.6M S_8 via constant potential electrolysis at 2.38 V on Teflon bonded C. The stoichiometry of this reduction was 0.3 e^-/S instead of 0.25 e^-/S, as would be expected for $S_8 \rightarrow S_8^=$. Some overlap of the $S_8^= \rightarrow S_8^{-4}$ reduction probably occurs at this potential.

Although the reaction of Li + S was not very successful in MA, the polysulfides were readily formed and dissolved through electrolysis. In a preliminary experiment, electrolysis was conducted with a stirring on a C cloth working electrode at a constant potential of 1.7 V vs. Li^+/Li. The cell had a working and counter electrode compartment separated by a fine glass frit. 0.25M S_8 was dissolved in MA, 1M $LiClO_4$, with an approximate stoichiometry of $2e^-/S_8$. Further electrolysis resulted in a white precipitate in the working electrode compartment, probably Li_2S.

Table 6

Observations of polysulfide formation through the reaction of S_8 with Li metal dispersion in various organic electrolytes. The amount of S initially present is 0.6M/l, with Li metal in excess.

Solvent	Observations
PC	Yellow solution; little S actually dissolved.
BL	Dark red-brown solution; about 75% S dissolution.
SL	Light green solution; little S actually dissolved.
DMSO	Dark brown solution becomes blue upon dilution;* most S dissolved.
MA	Yellow solution; little S actually dissolved.
THF	Dark red solution; most S dissolved.
DMSI	Colorless solution; most S dissolved.

*Spectrophotometry reveals large 618 nm peak, corresponding to S_3^- (9).

The stoichiometry could not be assessed in this experiment due to extensive diffusion of polysulfide species into the counter electrode compartment.

The dissolution of S_8 via electrolysis was monitored using cyclic voltammetry. The principal change during reduction was in the magnitude of the oxidation peak. Before electrolysis, scanning the saturated S_8 solution initially anodic from open circuit led to no oxidation on the first sweep as expected. As S_8 became reduced to polysulfide and dissolved, an oxidation peak at 3.2 V developed. After some dissolution, this peak was always present on the first (anodic) sweep. This method of dissolving S is currently being pursued in greater detail.

By far, the most work on Li polysulfide done during this report period was carried out on polysulfide formation via the reaction

$$Li_2S + (x-1)/8\ S_8 \rightarrow Li_2S_x. \qquad (11)$$

This method of dissolution is faster and more easily controlled than the previous two methods. A survey was first carried out to determine the relative extent of reaction (11) and the polysulfide solubility in several organic electrolytes. Solutions were made up by adding 0.06g Li_2S + 0.12g S to 10 ml of solvent in the argon-filled dry box. This would give a 0.5M S solution with an $S^{=}/S^{\circ}$ ratio of 1/3 if all the S dissolved. The qualitative observations are listed in Table 7. Complete dissolution was noted only for DMSO and DMAC. Dissolution was nearly complete in pyridine, but a chemical reaction appeared to occur, leading to gel formation. Solutions usually started out blue, but became red with time or with more dissolution. DMSO and DMAC, however, remained blue to purpose even after total dissolution.

The solutions summarized in Table 7 were filtered and their visible absorption spectra recorded. Composite visible absorption spectra of solutions in DMSO, DMAC, THF, BL and SL are shown in Fig. 11. The first three solutions were diluted 1:25, in order to record the spectrum using the thinnest cell available to us (0.5 mm).

A major peak at 618 nm is evident in DMSO, DMAC and SL (i.e., blue solutions), which has been assigned by various authors to a polysulfide anion radical, evidentally S_3^-. The peak at 420 nm (BL, THF) has been assigned by Sawyer et al. (9) to $S_4^{=}$ in DMSO. The polysulfide solutions in DMSO itself, along with SL and BL, give rise to a broad absorption at about 440 nm, which may correspond to an overlap between $S_4^{=}$ and $S_6^{=}$ (475 nm). Peaks at 360 nm in THF and SL, and at 560 nm in BL and THF, are as yet unidentified. It is quite clear, nevertheless, that the BL and THF (orange-yellow) solutions are dominated by the peak at 420 nm ($S_4^{=}$), while the DMSO and DMAC solutions are dominated by the 618 nm peak (S_3^-). This result probably reflects differences in the equilibria

Table 7

Observations of polysulfide formation through the reaction of Li_2S with S_8 in various organic electrolytes. If all the S dissolved, (S) = 0.5 m/l and $S^=/S^\circ = 1/3$.

Solvent	Observations
PC	Solution is initially blue, but after several days becomes pale yellow; little total dissolution.
BL	Solution is initially blue, then becomes dark red, opaque after several days. Most material dissolves initially, but ∿25% precipitates after several days.
SL	Solution is initially blue-green. After several days at 35°C, solution becomes dark red-brown, ∿50-75% dissolution.
DMSO	Solution is blue-green. Virtually complete dissolution.
MA	Solution is initially yellow, becoming red-orange after several days. Only partial dissolution, with some additional precipitation on standing.
MF	Solution is initially pale yellow; very little dissolution, even after several days.
THF	Solution is initially yellow-orange, becoming deep red-brown after several days. About 75% dissolution.
DMSI	Little or no dissolution after several days.
DMAC	Solution immediately dark blue, turning purple with complete dissolution after one hour.
Pyridine	Solution initially blue, but turned red-brown as material dissolved. After several hours, most material had dissolved, but solution had gelled.
Nitromethane	Little or no dissolution after several days.

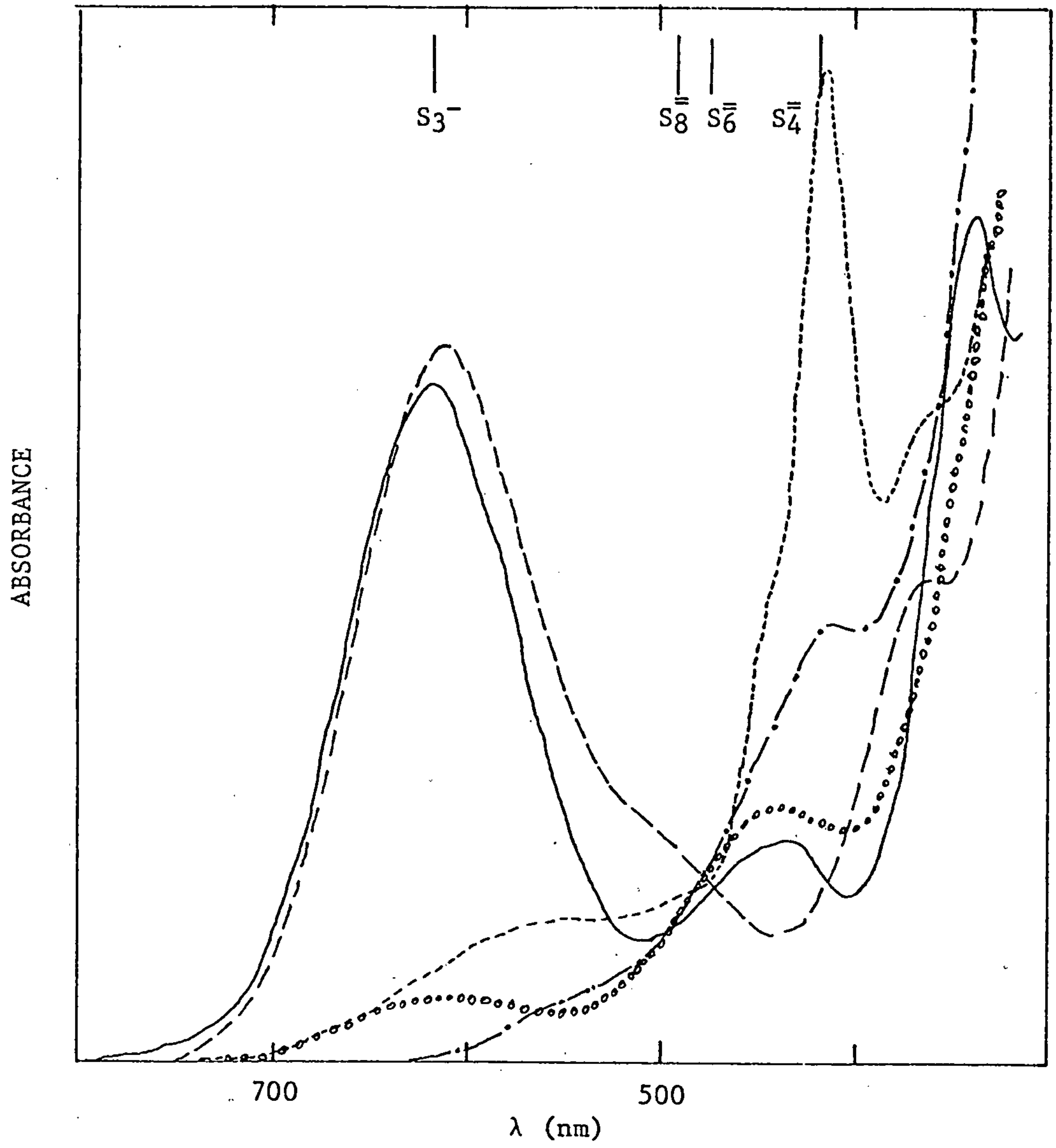

Fig. 11. Visible absorption spectra of solutions containing 1:3 $S^=/S^o$ in (——) DMSO, (– – –) DMAC, (·——·) THF, (----) BL and (oooo) SL. Absorbance scale is in relative units. DMSO, DMAC and THF solutions were diluted 1:25.

$$2S_4^{=} \rightleftarrows 2S_3^{-} + S_2^{=} \tag{12}$$

and

$$S_6^{=} \rightleftarrows 2S_3^{-} \tag{13}$$

for the different solvents (9): DMSO and DMAC seem to stabilize free radical species such as S_3^{-}, and this stability seems to be accompanied by high polysulfide solubility.

On completion of this survey of polysulfide solubility, an attempt was made to determine polysulfide solubility in DMSO, THF and BL as a function of $S^{=}/S^{\circ}$, added as Li_2S and S_8. For each solvent, three solutions were made up: $S^{=}/S^{\circ} = 1/1$, $S^{=}/S^{\circ} = 1/3$ and $S^{=}/S^{\circ} = 1/7$. Each solution had a total S concentration of 1M; the Li^+ concentration was adjusted to 1M using anhydrous $LiClO_4$. Solutions were made up by weighing out the solid materials into a volumetric flask, then adding the purified solvent. After approximately 24 hrs of stirring, the solutions were filtered. The absorption spectra were recorded, and analyses of the solutions for total S were attempted (see below).

For THF, the higher solubilization was noted for $S^{=}/S^{\circ}$ ratios of 1/7 and 1/3. All three solutions were red-orange. The solutions were diluted 1/25 so that visible absorption spectra could be recorded. The diluted solutions were still red-orange. The absorption spectra from 300-800 nm are similar for all three solutions (Fig. 12), with the primary visible maximum at 410 nm, tailing out to 550 nm. Absorption increases below 380 nm, and peaks at 322 nm. Thus, the primary species appears to be $S_4^{=}$, even in the 1:7 $S^{=}/S^{\circ}$ solution. Peaks associated with $S_6^{=}$ and $S_4^{=}$ could easily be buried in the tail below 500 nm. The peak at 322 nm cannot be identified.

In the case of BL, the solubility was lower than for THF. The 1:1 $S^{=}/S^{\circ}$ solution was green-brown. Its absorption spectrum shows maxima at 418 nm, 420 nm and 350 nm. In the 1:3 and 1:7 solutions, the peak at 618 nm is absent, but peak are present at 420 nm. Again, the order of solubility was 7:1 > 3:1 > 1:1.

For DMSO, the apparent order of solubility was also 7:1 > 3:1 > 1:1. All solutions started out blue, but on standing, the 3:1 and 1:1 solutions became yellow-red. Dissolution was virtually complete for the 7:1 and 3:1 solutions. Visible spectra were recorded on the 1:25 dilutions of each solution (Fig. 13). On dilution, all solutions became distinctly blue. The diluted 1:1 and 3:1 solutions have their absorption maxima at 618 nm, 440 nm and 335 nm. The first two maxima probably correspond to S_3^{-} and to a mixture of $S_4^{=}$ and $S_6^{=}$. For the diluted 1:7 solution, absorption maxima at 618 nm and 495 nm are evident, corresponding to S_3^{-} and to $S_8^{=}$.

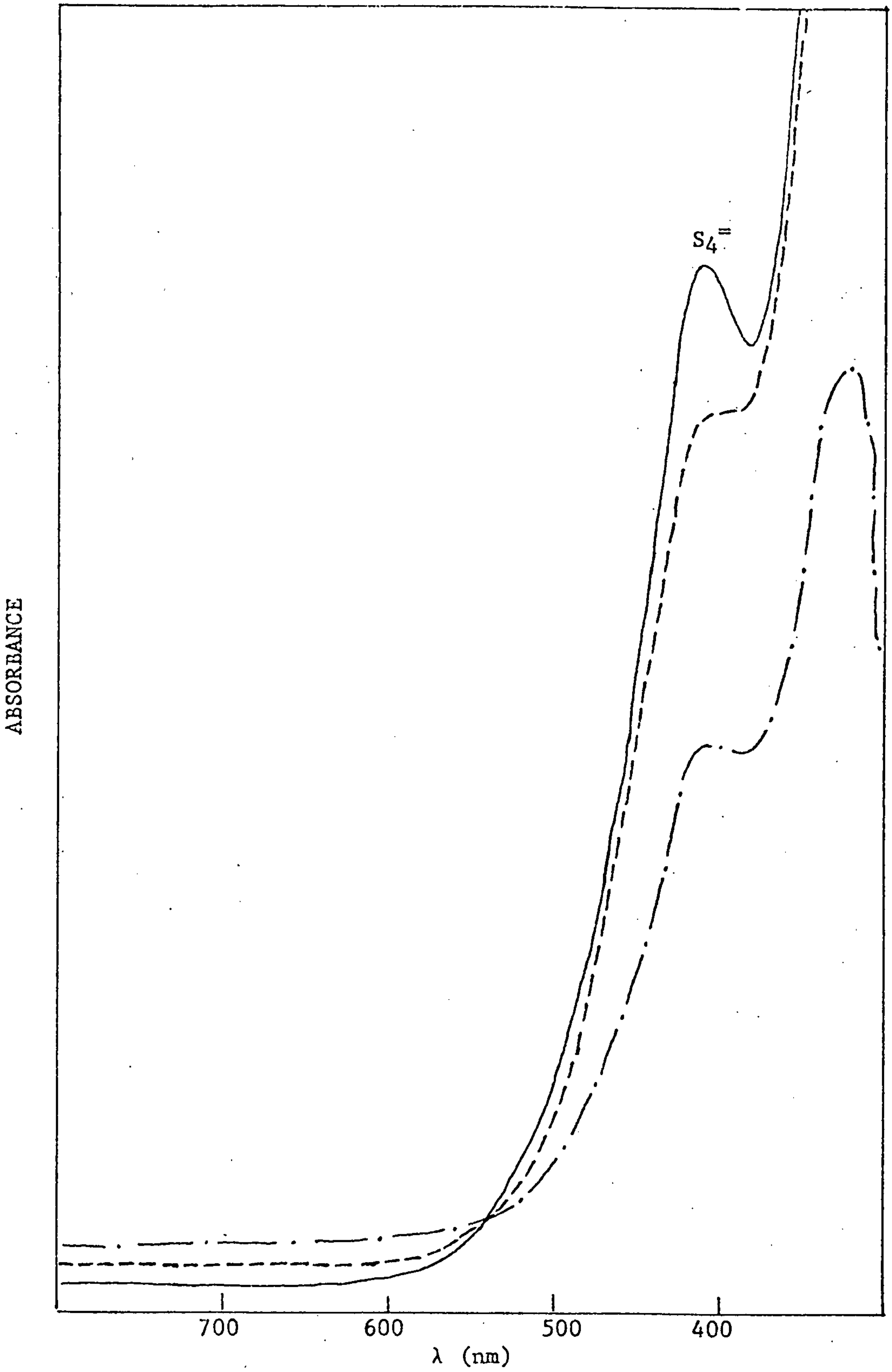

Fig. 12. Visible absorption spectra of Li polysulfide solutions in THF of composition 1:1 $S^{-2}/S°$ (—·—), 1:3 $S^{-2}/S°$ (– – –) and 1:7 $S^{-2}/S°$ (——).

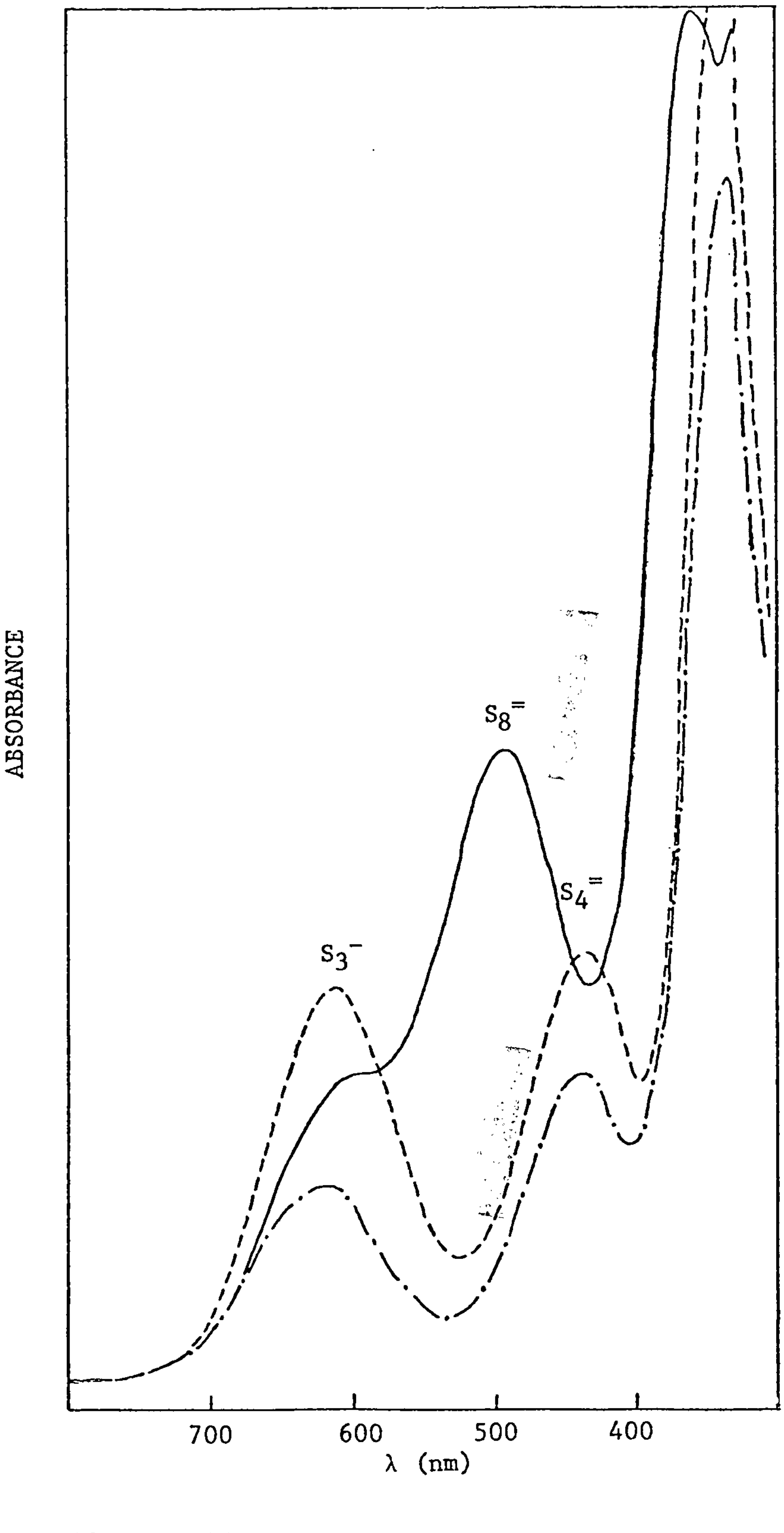

Fig. 13. Visible absorption spectra of Li polysulfide solutions in DMSO of composition 1:1 $S^=/S°$ (—·—), 1:3 $S^=/S°$ (– – –) and 1:7 $S^=/S°$ (——).

B. Sulfur Analysis

Procedures for analyzing the total S content of nonaqueous polysulfide solutions are currently being developed, in order to determine quantitatively the solubility of polysulfides in various solvents. The methods tried so far involve the total oxidation of S to $SO_4^=$. Initially, a method involving the H_2O_2 oxidation of $S_x^=$ followed by an acid base titration of the OH^- consumed during the reaction (20) was attempted. Poor results were obtained, due to incompleteness of the oxidation. As an alternative, the Schöninger combustion method (21) was used. Here, 0.1 ml of the solution is used to soak a piece of filter paper, and the solvent subsequently evaporated. The paper, impregnated with the S species, is then combusted in a closed container containing an O_2 atmosphere. At the bottom of the vessel is an aqueous H_2O_2 solution, to insure the complete oxidation of S to $SO_4^=$. The sulfate is then titrated with Ba^{+2}, and a Ba^{+2} complexing indicator (thorin) is used to judge the end point (22). Although the end point is quite subtle, practice gives reproducibility of about 1% for weighed-out samples of S_8.

For THF, the analytical procedure showed total dissolution of the 1M S for $S^=/S°$ ratios of 1/7 and 1/3. The 1/1 solution showed 70% dissolution. DMSO gives results which are consistently too high. This appears due to difficulties in removing all of the (S-containing) solvent from the filter paper prior to combustion. Analysis of other S solutions is currently in progress.

C. Cyclic Voltammetry of Polysulfide Solutions

Cyclic voltammograms of the 1:1, 1:3 and 1:7 $S^=/S°$ solutions, made up to 1M total S, were measured in THF, BL and DMSO. The 1:7 solutions showed high resistance between the counter and working electrodes (>5K, measured on an AC conductivity bridge). Addition of 1M $LiClO_4$ lowered the cell resistance to below 100Ω. Apparently the Li_2S_x species are highly associated in solution. Because of this problem with internal cell resistance, all solutions were made 1M in $LiClO_4$ for cyclic voltammetry. Cyclic voltammograms were recorded on the 1M S solutions, and the same solutions diluted 1:25. The working electrode was vitreous C.

Not surprisingly, the open circuit potential (OCP) of the working electrode vs. Li^+/Li increased with decreasing $S^=/S°$. The OCP's for the solutions under investigation are summarized in Table 8. Sweeps were initiated in a positive direction, starting at the OCP. In all cases, oxidizable material was present on the first sweep. In the THF voltammograms illustrated in Fig. 14, the sweep of the high concentration solution showed little diffusional limitation at current densities in excess of 30 mA/cm^2. The 1:25 diluted solutions give voltammograms not the same as to that of THF/saturated S_8 (Fig. 4). The primary differences are

Table 8

Open circuit potentials vs. Li^+/Li for polysulfide solutions 1M in S, 1M in $LiClO_4$, on a vitreous C working electrode.

Solvent	$S^{=}/S^{\circ}$	OCP (volts)
THF	1:7	2.32
	1:3	2.28
	1:1	2.20
BL	1:7	2.58
	1:3	2.48
	1:1	2.28
DMSO	1:7	2.72
	1:3	2.30
	1:1	2.26

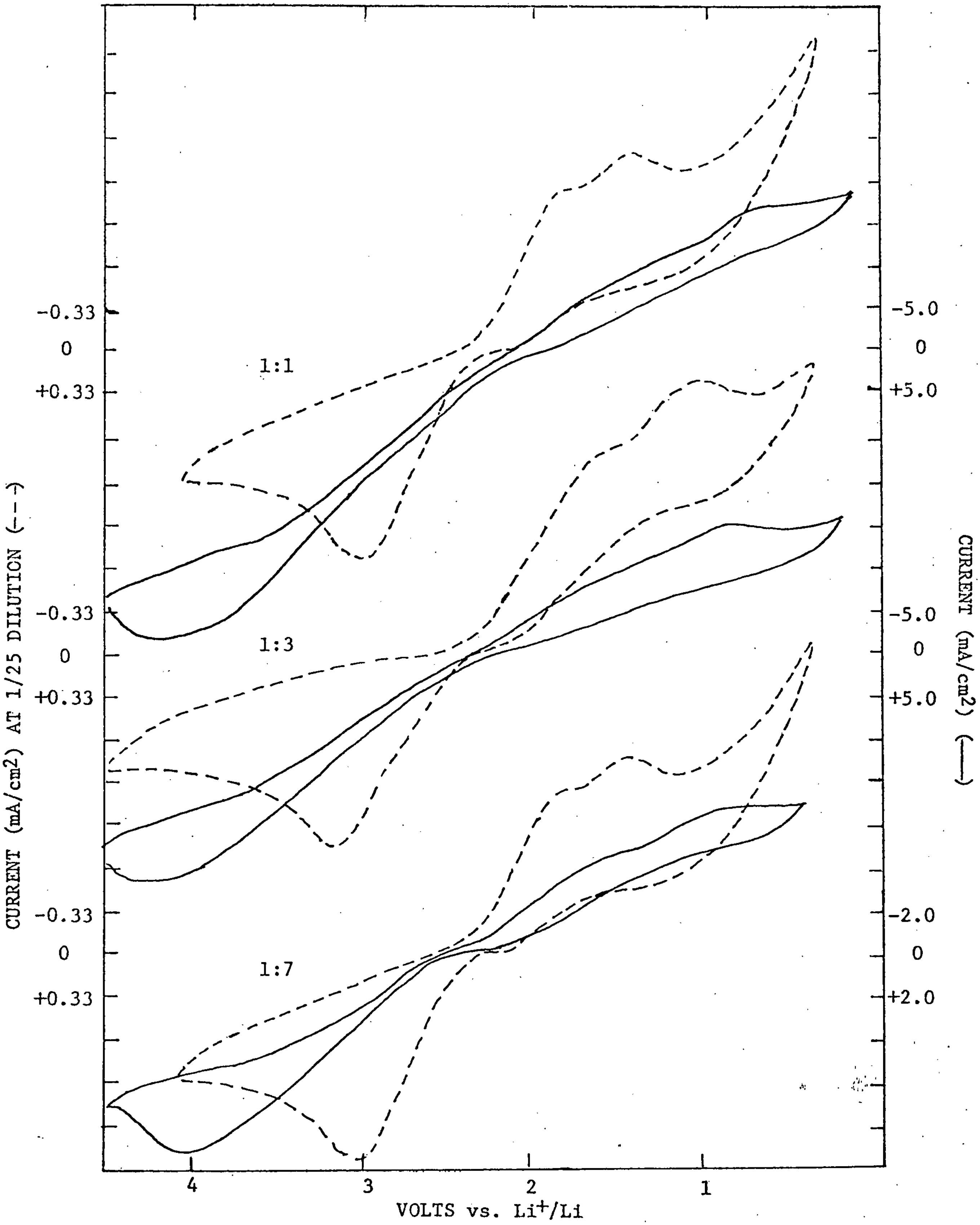

Fig. 14. Cyclic voltammograms of 1:7, 1:3 and 1:1 $S^=/S°$ polysulfide solutions in THF, 1M $LiClO_4$, on a vitreous C substrate at 25°C; (——) 1M S, (- - -) 1/25 dilution. Sweep speed = 0.1 V/sec.

that the reduction maxima are shifted 100-300 mV in the positive direction for the polysulfide solutions compared to the S_8 solutions. Such a result is favorable for the design of a practical battery, in which concentrated polysulfide solutions are used for the cathode material. Compared to S_8 solutions, polysulfide solutions in THF should discharge at a more positive potential, and should be more reversible with regard to charge and discharge potentials.

For the BL-polysulfide solutions (Fig. 15), the similarity to the S_8 voltammograms is quite high (Fig. 9). The position of the oxidation maximum shifts in a positive direction with increasing $S^{=}/S^{\circ}$, indicating that lower order polysulfides are harder to reoxidize.

The voltammograms of the polysulfide/DMSO solutions, shown in Fig. 16, are quite different from those recorded for S_8 solutions. In the concentrated solutions, the reduction peak associated with S_8 is very much attenuated. In the 1:7 $S^{=}/S^{\circ}$ solution, the $S_8^{=}$ reduction peak at ∿2.0 V is quite prominent. The visible absorption spectrum of this solution diluted 1:25 also showed a maximum corresponding to $S_8^{=}$. Also present in all three polysulfide solutions is a reduction process at 1.5-1.7 V which is not present for C electrodes in the S_8 solutions. This may correspond to the reduction of S_3^{-}, which the absorption spectra show is present in all three solutions at rather high concentrations. These species cannot be assigned with certainty, however, without more detailed study.

The results presented in this section indicate that cyclic voltammograms of S_8 solutions are not always readily interpretable in terms of a practical polysulfide battery. The various equilibria for polysulfides in DMSO, outlined by Sawyer and co-workers (8,9), indicate that the species in a concentrated battery electrolyte, or those formed by chemical reaction between Li_2S and S_8, may be quite different from those formed in sweeping the potential of an electrode in an S_8 solution. Indeed the Li polysulfide solutions in DMSO, whose cyclic voltammograms are shown in Fig. 16, show more negative reductions and more positive oxidations than the S_8 solutions. Conversely, polysulfides in THF appear to be more suitable for a practical cell than the S_8 voltammograms would indicate.

D. Cycling and Current-Potential Behavior of Polysulfide Solutions

"Rapid" voltage scan techniques such as cyclic voltammetry can provide mechanistic information and a relatively facile comparison of the effect of environment on S and polysulfide redox behavior. However, in terms of practical battery design, steady-state current-potential curves are more relevant, in that they reflect the steady-state composition of oxidizable or reducible material present during charge or discharge.

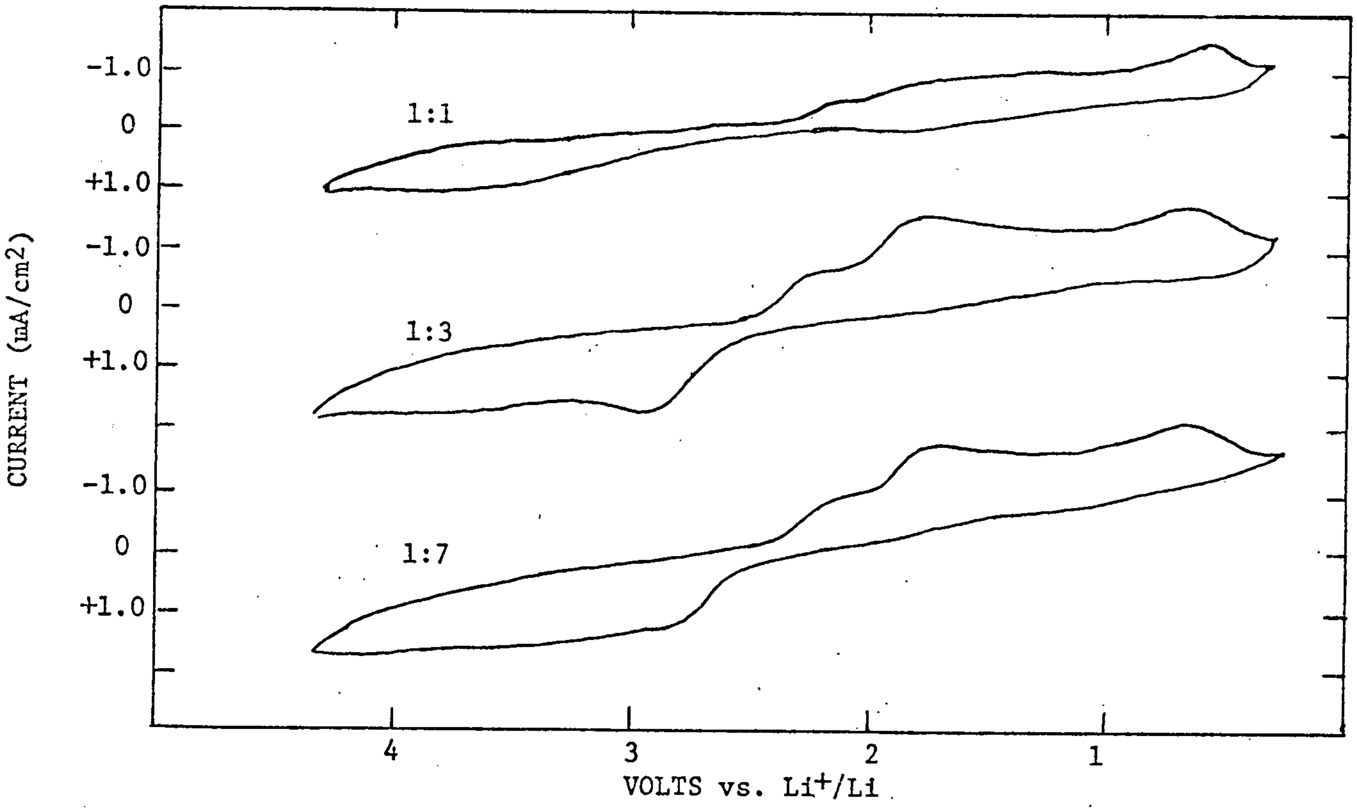

Fig. 15. Cyclic voltammograms of 1:7, 1:3 and 1:1 $S^=/S^\circ$ Li polysulfide solutions in BL, 1M $LiClO_4$, on a vitreous C substrate at 25°C; saturated solution (>0.1M S). Sweep speed = 0.1 V/sec.

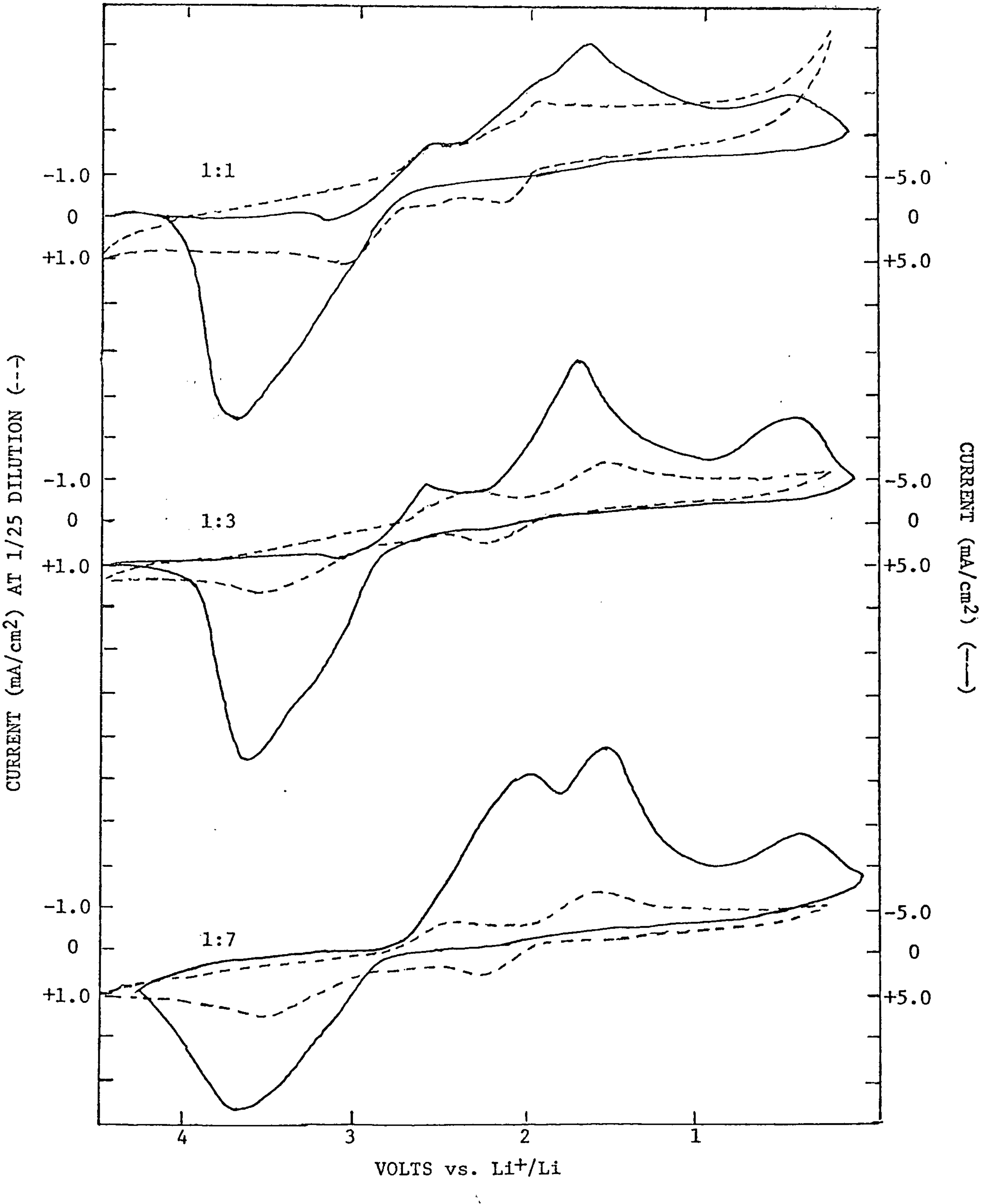

Fig. 16. Cyclic voltammograms of 1:7, 1:3 and 1:1 $S^{=}/S^{\circ}$ Li polysulfide solutions in DMSO, 1M $LiClO_4$, on a vitreous C substrate at 25°C; (——) 1M S, (---) 1/25 dilution. Sweep speed = 0.1 V/sec.

Experiments were carried out in a three-compartment Teflon cell which had been designed to have a low volume for the exhaustive electrolysis of concentrated polysulfide solutions. The center (working) compartment had a capacity of 7 ml (Fig. 2). The two outside (counter) compartments were separated from the working compartment using Celgard 2402 microporous polypropylene, which provided minimal mixing with a low internal resistance. A 10 cm^2 Teflon bonded C working electrode (5 cm^2/side) was used for exhaustive electrolytes, and filled much of the compartment. The exhaustive electrolyses were thus carried out without stirring. Stirring the working solution after electrolysis did not lead to additional capacity. The reference electrode was Li^+/Li inside a Luggin capillary which extended into the central compartment.

For convenience in recording the current-potential curves, a 1 cm^2 Teflon bonded carbon electrode was used. Beginning at the open circuit potential, the potential was stepped in 100 mV increments, and the current measured when it no longer charged rapidly (usually about 5 minutes). If a current-potential curve were being measured when the system was fully discharged, the region negative of OCP would be scanned first. If the solution was fully charged, the region positive of OCP would be scanned first. This was done to minimize changes in the solutions composition during the experiment.

Initial studies were carried out on solutions 0.1M in S, dissolved as Li_2S_x, and 1M in $LiClO_4$ (fuse dried in vacuo). For 7 ml of such a solution in the working electrode compartment, 140 coul of charge (39 mAhrs) is equivalent to 2 e^-/S, i.e., reduction of $S°$ to $S^=$. Experiments were carried out on polysulfide solutions made up at $S^=/S°$ ratios of 1:7, 1:4 and 1:3. Solvents employed so far have been THF, BL and DMSO.

Results were first recorded for a solution of composition 1:7 $S^=/S°$ in BL. The current-potential behavior of this solution was also monitored in its charged and discharged state. Typical charge-discharge curves, and i-E curves for both charged and discharged electrolyte are shown in Figs. 17 and 18. The charge and discharge current density in this experiment was 0.5 mA/cm^2. Initially, the cell discharge approached 12 mAhrs (cathodic limit = 0.5 V vs. Li^+/Li), while the charge was approximately 6 mAhrs. At this current density, a charge plateau at 3.55 V comprised most of the charging curve, while discharge was sloped between 1.5 and 0.5 V. The electrolyte tended to lose capacity during cycling - some material was being reduced during discharge to a species which could be reoxidized only with difficulty (i.e., beyond 4.0 V). This behavior was also indicated in the cyclic voltammograms of S_8 and polysulfide solutions already reported. By the 7th cycle, discharge capacity was down to 5-6 mAhrs, and was dropping more slowly. This level is, however, less than 0.25 e^-/S.

The current-potential curves in Fig. 18 show, for the initial solution, a general area of reduction beginning at 2.0 V vs. Li^+/Li and

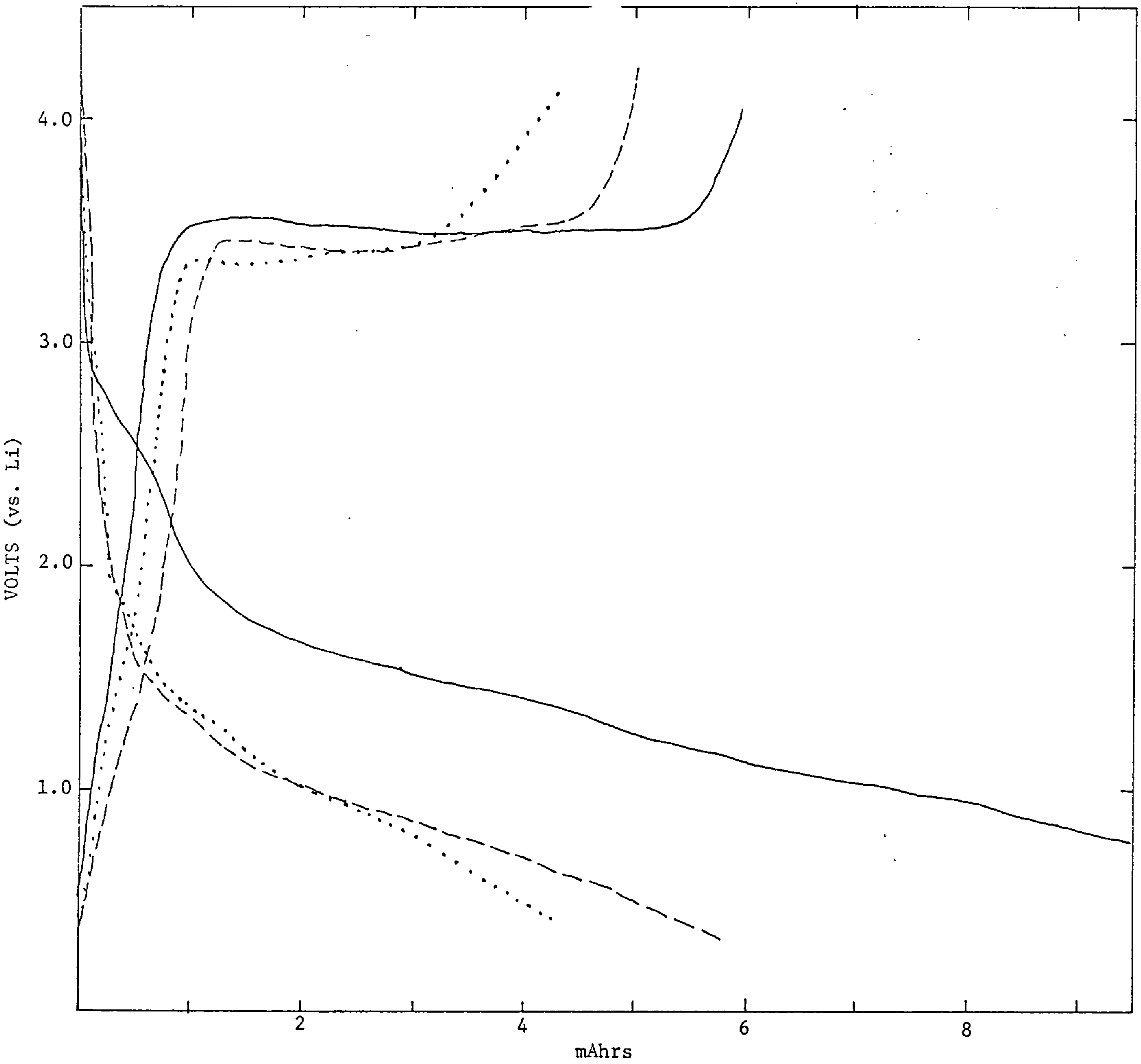

Fig. 17. Charge-discharge curves of 0.1M S as Li_2S_x in BL, 1.0M $LiClO_4$. $i = 0.4$ mA/cm^2 on Teflon bonded C. (——) C1, D1; (- - -) C7, D7; (• • •) C12, D12.

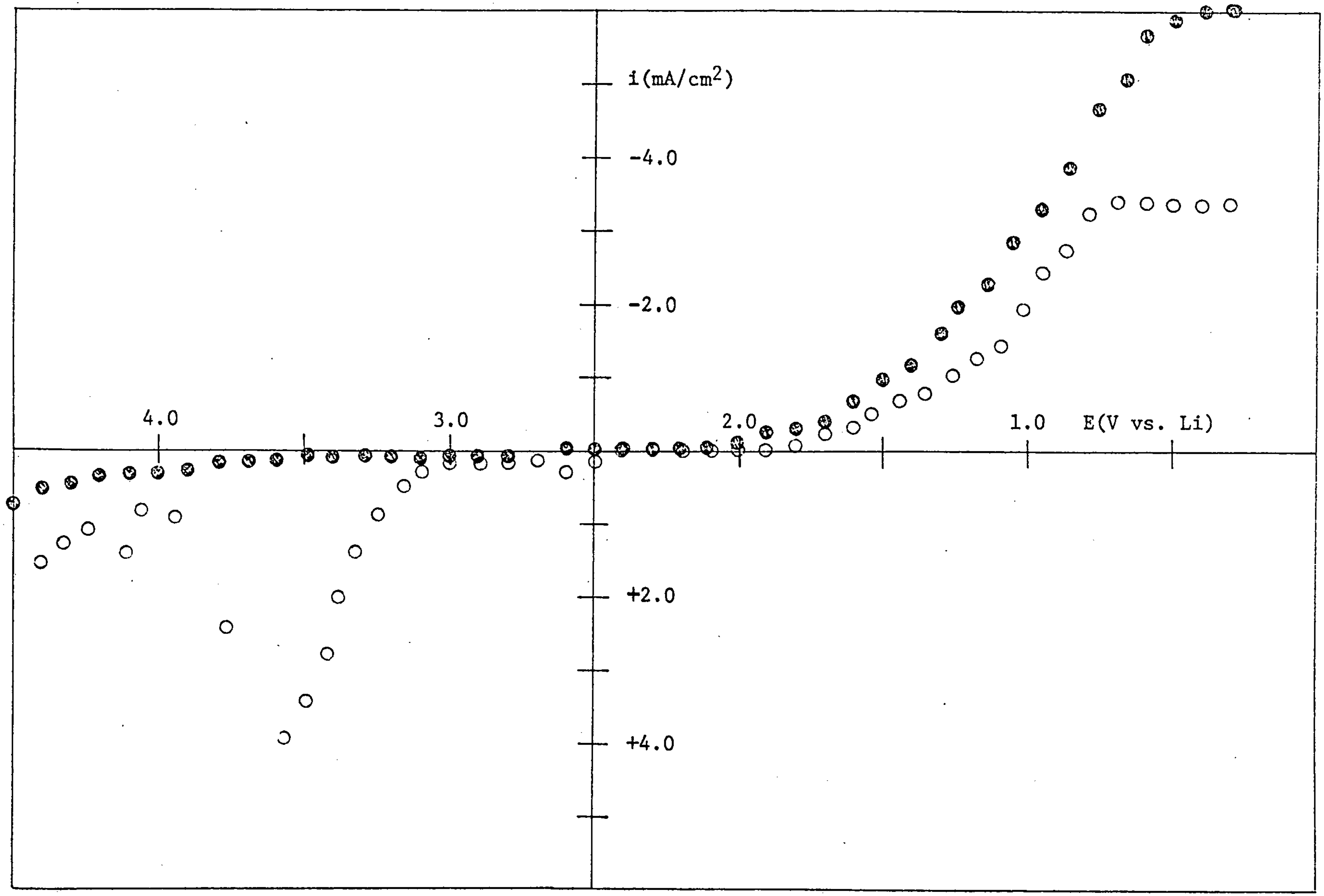

Fig. 18. Current-potential curve of Li_2S_x solutions containing 0.1M total S, 1M $LiClO_4$ in BL; (O) after 7th (partial) discharge; (●) after 12th discharge.

extending out to the chosen cathodic limit of 0.3 V. This gives rise to the sloping discharge curve of Fig. 17. On discharging the cell, a characteristic area of oxidation, peaking at 3.6 V, emerges in the i-E curve.* This relatively sharply defined area of oxidation results in the very flat charging curve for the system, also shown in Fig. 17. Thus, we may characterize the BL/0.1M Li_2S_x, $LiClO_4$ system as being quite irreversible from a potential viewpoint, yielding a sloping discharge curve, and having a capacity of ∿0.3 e^-/S between the cycling limits of 4.5 and 0.3 V (vs. Li^+/Li) at ambient temperature.

A similar experiment for THF showed a charging potential of ∿3.5 V. The cell could be charged for 2 hours at 10 mA (4 mA/cm^2) without exceeding a positive voltage limit of 4.2 V. Thus, the cell was repeatedly charged for 2 hours and discharged to a voltage limit of 0.7 V. The entire cell thus showed much greater capacity between the voltage limits than that based upon BL. The discharge capacities were measured for a constant 20 mAhr charge. As the discharge in the first several cycles exceeds 2 e^-/S, it is evident that part of the discharge was comprised of solvent or solvent impurity reduction. This is also suggested by the fact that by the 12th cycle, the solution had begun to polymerize, raising the cell resistance to a point where further cycling was impossible. Typical charge-discharge curves are shown in Fig. 19.

Similar problems were associated with cycling DMSO solutions. If the anodic and cathodic cycling limits were too extreme, severe solvent decomposition became apparent. Thus, for DMSO, a "background" current-potential curve was first recorded for the electrolyte not containing S, and is reproduced in Fig. 20. This background reduction begins to rise negative of 1.75 V to about 1.75 mA/cm^2 at 1.0 V. The background at potentials positive of 1.75 V is less than 0.1 mA/cm^2 out to 3.8 V. Cycling limits were thus chosen to be 1.0 V and 3.8 V for this solvent.** Cycling between these limits in the pure solvent showed a discharge capacity of ∿0.3 mAhrs and a charge capacity of 0 mAhrs which could be attributed to solvent background.

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*That this area has a definite peak, rather than a (diffusionally limited) plateau, suggests a passivation phenomenon occurring on recharge between 3.8 and 4.0 V: S may be precipitating on the electrode under these conditions.

**The reasons for the cathodic limitation are probably impurities in the solvent. Cyclic voltammograms of DMSO/$LiClO_4$ solutions measured in this laboratory show lower currents from 0 to 4.5 V vs. Li^+/Li if (a) molecular sieve is not in contact with the electrolyte following distillation, and (b) if the DMSO is distilled in vacuo from solid KOH. These procedures are currently being used to try to lower the background currents for the DMSO electrolyte.

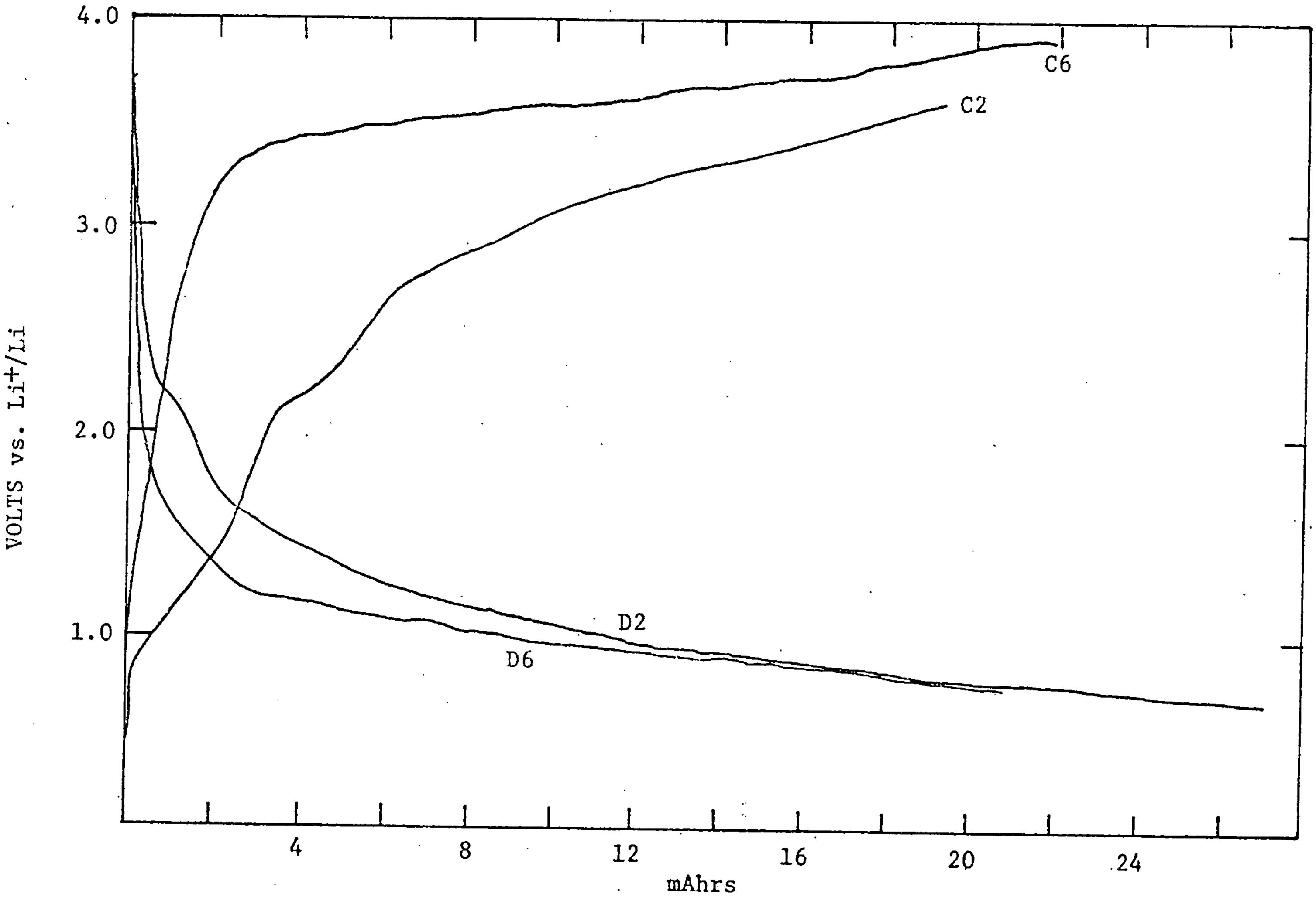

Fig. 19. Galvanostatic charge-discharge curves for 0.1M S dissolved as 1:7 $S^{=}/S^{\circ}$ Li polysulfide in THF, 1M $LiClO_4$ on a Teflon bonded C working electrode. $i = 4.0$ mA/cm^2.

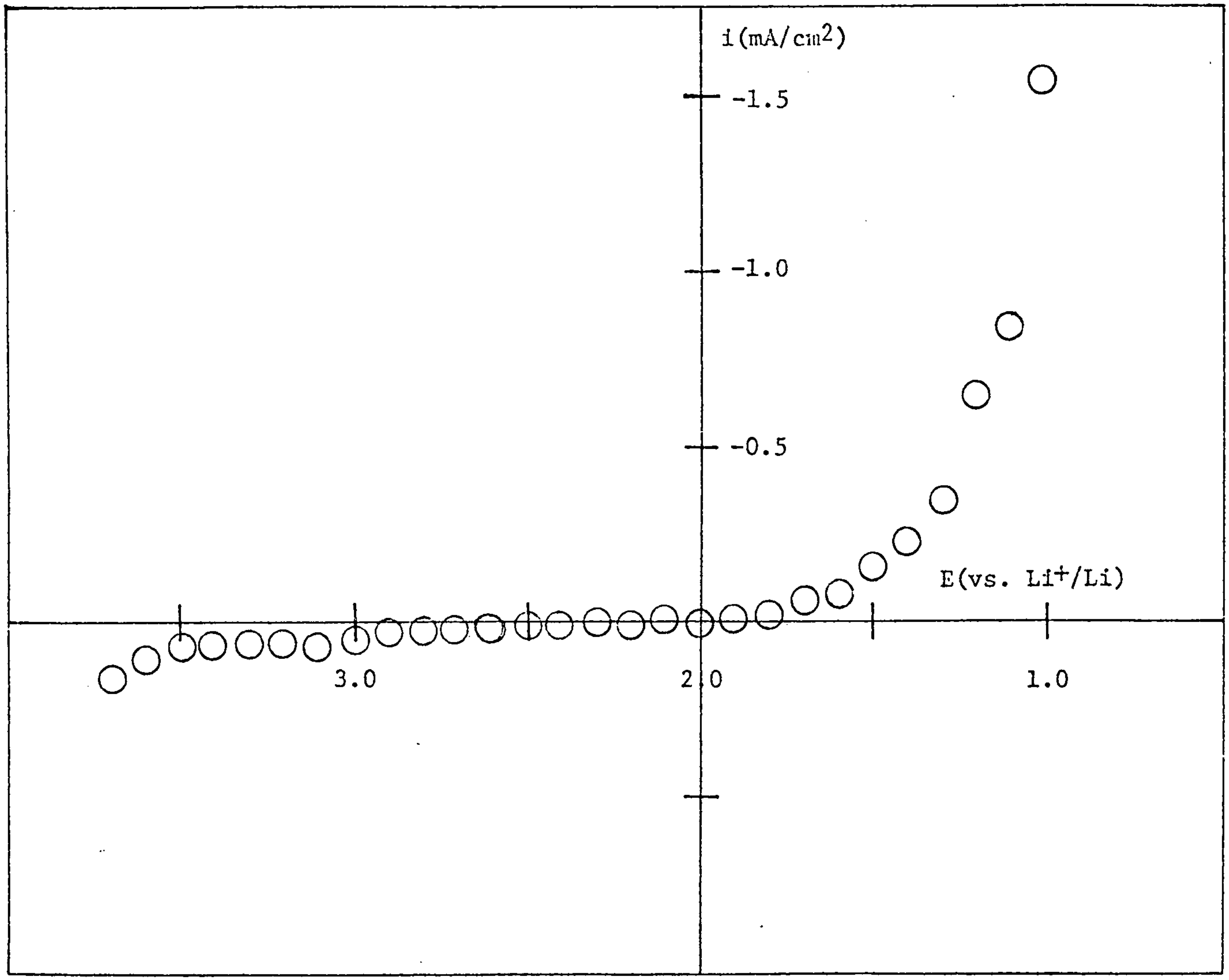

Fig. 20. "Background" current-potential curve for DMSO, 1M $LiClO_4$ on Teflon bonded C.

Cycling and current-potential studies were carried out on DMSO solutions 0.1M in S, with initial $S^=/S°$ ratios of 1:3 and 1:7. Problems of solvent decomposition were not as severe within the imposed voltage limits, although some yellowing of the solutions in the counter electrode compartments was noted after several cycles. For both the 1:3 and 1:7 $S^=/S°$ solutions, the initial charge and discharge cycles were of relatively low capacity: discharges were ∿12.5 mAhrs for the 1:3 solution and ∿2.5 mAhrs for the 1:7 solution. These capacities increased markedly with cycle. In the 1:3 solution, the third discharge was 45 mAhrs. As this result shows a reduction stoichiometry of >2 e^-/S, the experiment was terminated because of probable solvent decomposition. The 1:7 solution discharge capacity had increased to 29 mAhrs for the 4th charge and 22.5 mAhrs for the 4th discharge. Typical charge and discharge curves are shown in Fig. 21.

The current-potential behavior of the 1:7 and 1:3 $S^=/S°$ DMSO solutions are illustrated in Figs. 22 and 23. It is evident that background solvent or impurity reduction contributes significantly to the current-potential curve. In addition, it cannot be ruled out that DMSO electrochemical reduction becomes autocatalytic in the presence of polysulfides. This result would mean that it would be difficult to correct charge-discharge curves for background in this solvent. The current-potential curves have no areas of reduction or oxidation which are sharply defined as the oxidation region in BL, but rather both areas are sloped. Hence, charge and discharge curves are similarly sloped. Polysulfides dissolved in DMSO do appear to have higher charge-discharge capacity than in BL, but this conclusion is somewhat uncertain because the effect of solvent decomposition in DMSO is not very clear.

In all cases, the i-E curves show reductions which have no clear plateaus. This result could not be prediced from the cyclic voltammograms of S_8 or polysulfide solutions presented in previous sections. In addition, the i-E curves show very little reduction activity positive of 1.5 V. The reduction portion of the i-E curves, and hence the cell discharge curves, are also complicated by solvent background (which, at this stage, appears likely to be due to dissolved impurities).

The practical implications of these results are that, in the polysulfide solutions studied so far, the discharge potentials are too cathodic and the charge-discharge reversibility is unacceptable for battery use. Furthermore, solvent decomposition would be a problem in batteries based upon DMSO and THF, at the level of purification currently employed. Conceivably, the use of very highly concentrated polysulfide solutions, as is required, will improve discharge potentials and reversibilities. In addition, other means of dissolution of polysulfides are being tried, which may result in more readily reduced species and requisite solubility. Finally, other solvents and solvent purification methods are being explored in order to decrease "background" currents and extend charge-discharge ranges.

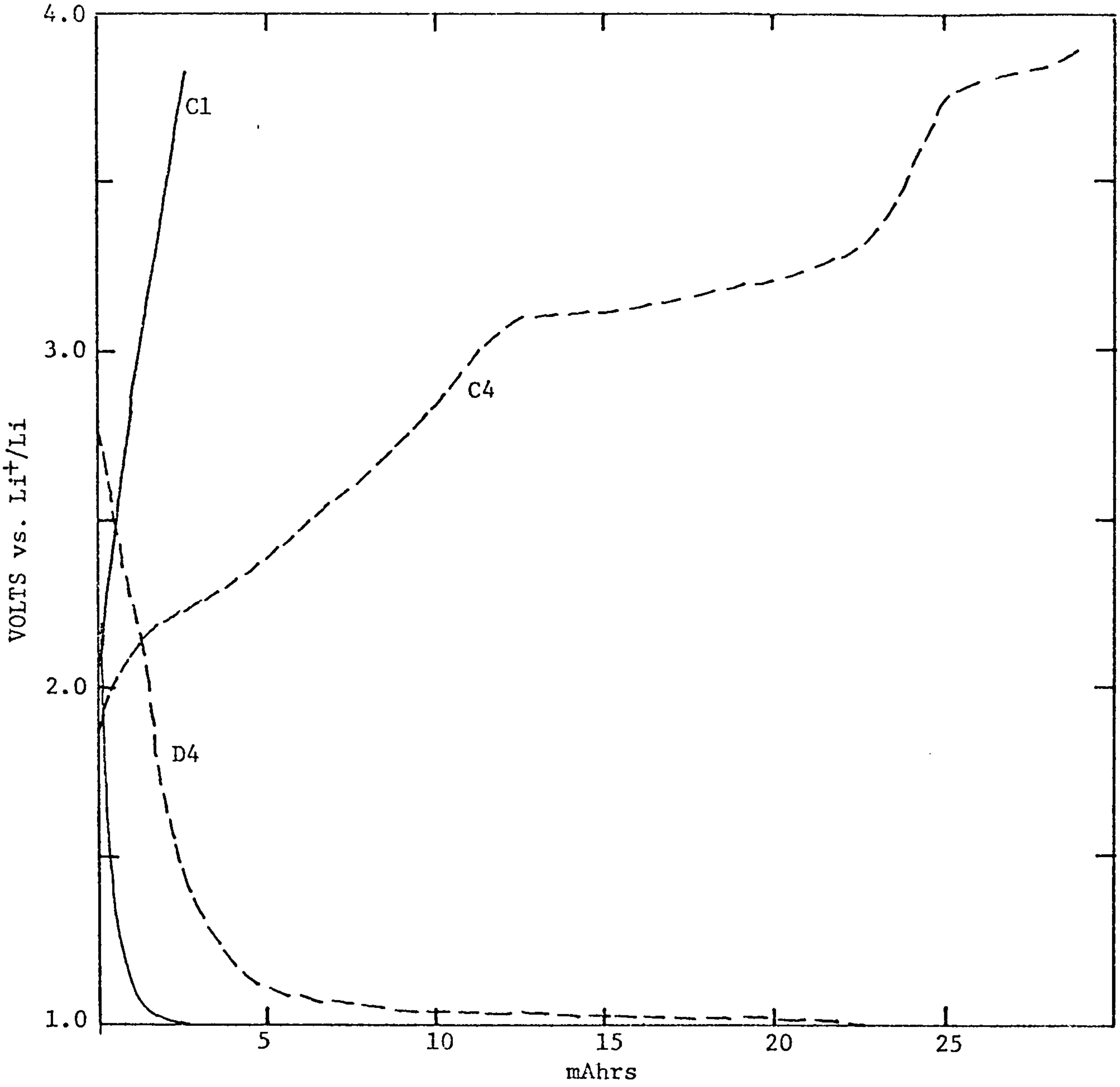

Fig. 21. Galvanostatic charge-discharge curves for 0.1M S dissolved as 1:7 $S^{=}/S^{\circ}$ Li polysulfide in DMSO, 1M $LiClO_4$, on a Teflon bonded C working electrode. i(1) = 1 mA/cm^2, i(4) = 0.5 mA/cm^2.

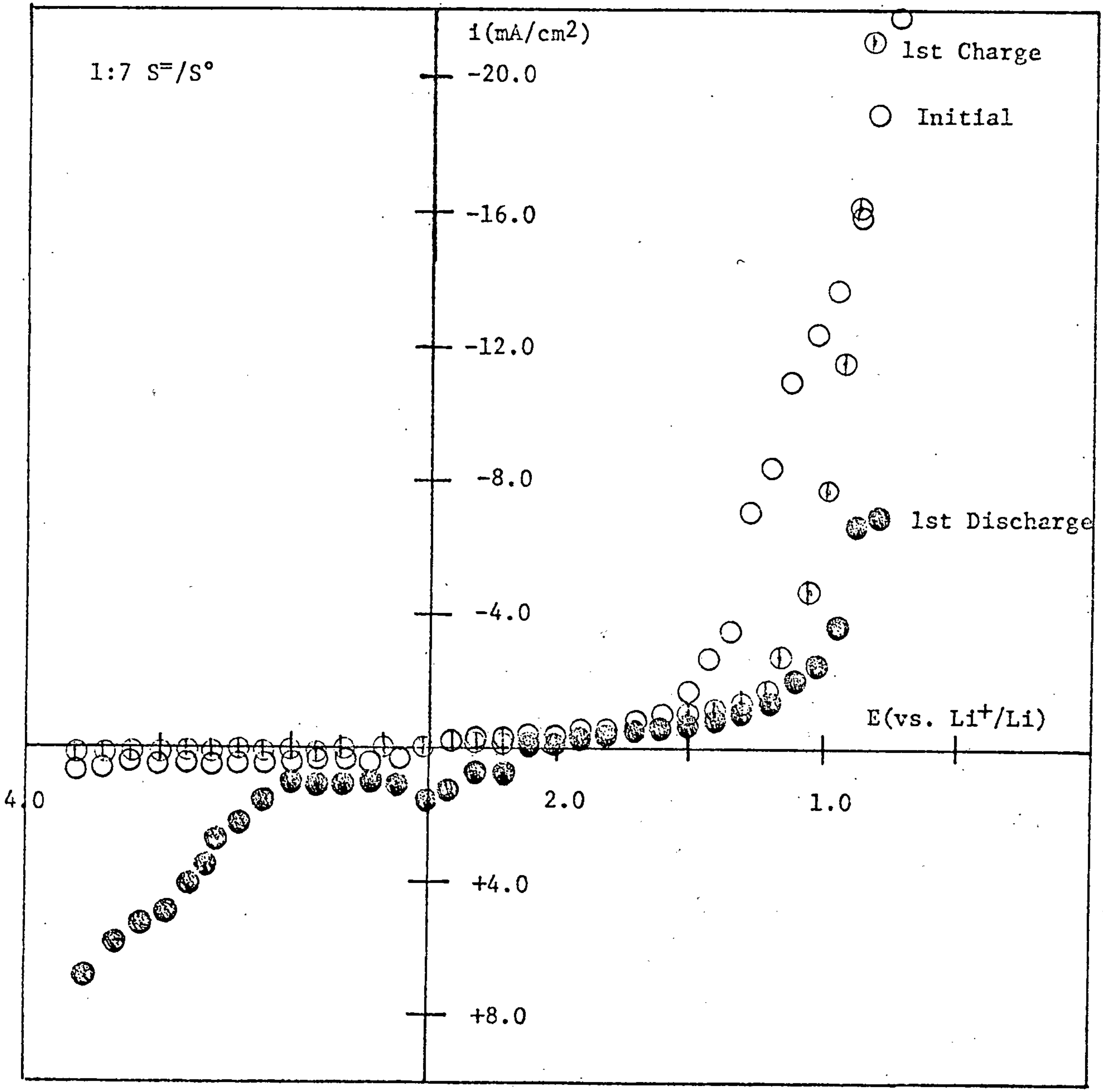

Fig. 22. Current-potential curves of 0.1M S dissolved as 1:7 $S^{=}S^{\circ}$ Li polysulfide in DMSO, 1M $LiClO_4$, on Teflon bonded C, initially, after 1st charge, and after 1st discharge.

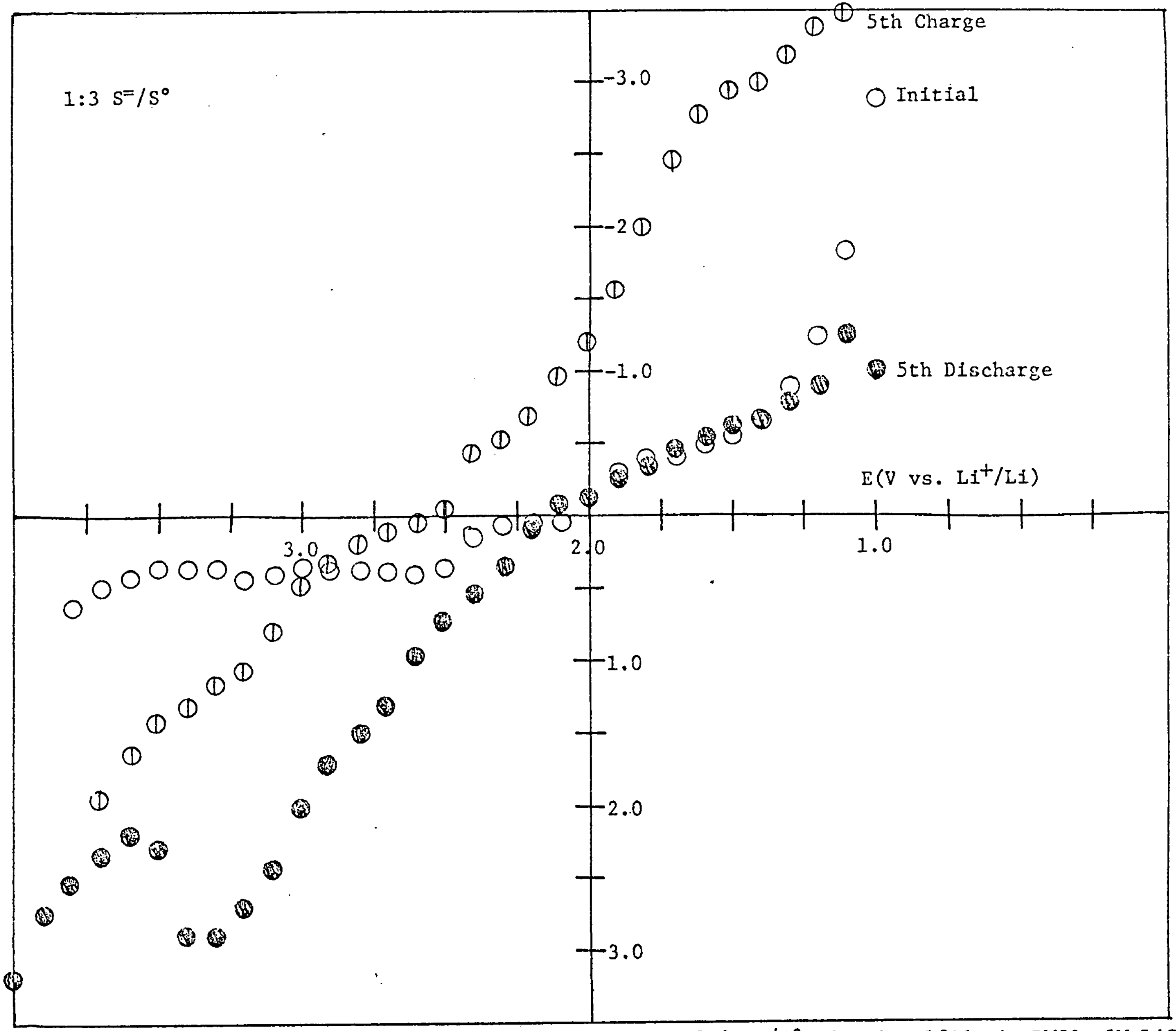

Fig. 23. Current-potential curves of 0.1M S dissolved as 1:3 $S^=/S°$ Li polysulfide in DMSO, 1M $LiClO_4$ on Teflon bonded C, initially, after 5th charge, and after 5th discharge.

VI. SUMMARY AND CONCLUSIONS

The redox behavior of dilute solutions of S_8 has been studied in a variety of electrolytes using the technique of cyclic voltammetry. The results were interpreted relative to the S_8/DMSO system, which has been thoroughly investigated (8,9). DMSO and DMF constitute one class of electrolytes: the two-electron reductions of S_8 and $S_8^=$ occur at >2.5 V and >1.9 V respectively. A peak corresponding to reoxidation of S_8^{-4} is prominent in both solvents, and a general two-electron reoxidation peak of $S_x^=$ is present at 3.0-3.5 V. The other solvents (BL, MA, PC, etc., cf. Table 2) have the S_8 reduction nearer to 2.0 V, $S_8^=$ reduction generally at 1.6-1.8 V, little or no S_8^{-4} reoxidation, and in some cases very little oxidation negative of 4.0 V. The effect of raising the temperature was generally to enhance currents and reversibilities. A substrate effect was also noted: Pt and Au often give rise to extra reduction peaks between 1.0 and 2.0 V, compared to vitreous C, especially at elevated temperature. Some evidence exists that this is due to precipitation of reduction products on Pt and Au, a phenomenon which may prevent the oxidation of $S_x^=$ at 2.5-3.5 V. If this interpretation is correct, C is a better choice than Au or Pt for a battery electrode.

Experiments were also carried out on more concentrated S solutions, the S being dissolved as Li polysulfides by chemical and electrochemical techniques. DMSO, DMF and DMAC all showed high polysulfide solubility, and yielded blue solutions. Polysulfides were less soluble in the other solvents investigated, and the solutions were generally red to orange. Visible absorption spectra of the blue solutions revealed a large peak at 618 nm, indicating the presence of S_3^- anion radical. The red-orange solutions were dominated by a peak at 420 nm, indicating $S_4^=$.

Therefore, the solvents which give S_8 cyclic voltammograms like DMSO also stabilize S_3^-, which seems to relate to high Li polysulfide solubility. These results indicate that DMSO, DMF, and, included in the polysulfide study, DMAC should be prime candidates for battery electrolytes, but subsequent results do not entirely support this conclusion.

The possible usefulness of Li polysulfide solutions as rechargeable cathodes was assessed from their cyclic voltammograms, from their slow scan current-potential curves, and from their charge-discharge capacities. The cyclic voltammograms of polysulfides were, for the most part, not totally analogous to S_8 voltammograms in the same electrolyte: reductions of polysulfide species in solutions prepared by the reaction between Li_2S and S_8 actually occurred at similar potentials on C for DMSO, THF and BL, even though the S_8 voltammograms in these solvents are quite dissimilar.

Reoxidations in polysulfide solutions are most negative in THF, followed by BL and DMSO. Evidently, the reduction potentials of S_8 and $S_8^=$, which are evident in the cyclic voltammograms of S_8, are not totally indicative of the reduction potentials of the wide variety of polysulfides formed by chemical dissolution. The distribution of species being oxidized is also clearly different in the two cells.

Slow-scan current-potential curves, measuring the steady-state redox behavior of Li polysulfide solutions, were recorded for BL and DMSO electrolytes using a Teflon-bonded C working electrode. Neither gave rise to significant reduction activity positive of 1.5 V, a result which would yield low cell discharge potentials. This situation is somewhat more pessimistic than indicated by (fast scan) cyclic voltammograms. Oxidation commenced at 2.5-3.0 V, sloping out beyond 4.0 V in DMSO, without levelling off, and peaking at 3.5 V in BL, in what appears to be a passivation phenomenon.

Charge-discharge curves were measured for the THF, BL and DMSO polysulfide solutions. Background contributions from solvent reduction were shown to contribute to the discharge curves in THF and DMSO, making uncertain the discharge stoichiometries. Discharges in all three solvents occurred below 1.5 V at current densities of 0.5 to 2.5 mA/cm^2. In future experiments of this type, efforts will be made to eliminate these background currents.

In view of these results, we will investigate the following specific problem areas in the coming months.

1. Why are the positive reduction potentials seen in the cyclic voltammetry of Li_2S_x solutions in DMSO not reflected in the steady-state reduction behavior? One probable reason for this is the somewhat slow equilibration of polysulfide species, following their initial electrochemical reduction, leading to products which are difficult to reduce. In the case of DMSO, one such species may be S_3^-. From the work of Sawyer and co-workers (8,9), it is evident that the reduction $S_8^= \rightarrow S_4^{-4}$ leads to a sizeable fraction of the sulfur in the form S_3^-, through solution reactions of S_8^{-4}. Our spectra of these polysulfide solutions also show large amounts of S_3^-. One way of studying this phenomenon is exhaustively to reduce at the $S_8^= \rightarrow S_8^{-4}$ potential a solution of 1:7 $S^=/S^\circ$ composition. The cyclic voltammograms and electrolyte spectra will be monitored to see the rate of degradation of electrochemical activity, and to try to determine the species involved in this degradation.

2. What are the differences in the (multistep) mechanism for the reduction $S \rightarrow S^=$, with S dissolved as polysulfide, between the two classes of solvents (DMSO, etc. vs. THF, etc.)? THF appears not to stabilize S_3^-, a fact which should drastically affect a battery charge-discharge mechanism.

If S_3^- is more difficult to reduce than $S_x^=$ species, the solvents like THF should give the higher discharge potentials. Thus, it is important to repeat experiments outlined for DMSO in (1) for THF, noting the relative rates of loss of solution electrochemical activity with potentiostatic electrolysis.

If certain species are more favorable than others for cell discharge, we will explore the possibility of trying to stabilize them through cation complexation or by use of mixed solvents.

3. Under what conditions can we achieve the objective of 0.6M S_8 solubility? The reaction of Li_2S with S_8 does not work well with solvents of the THF class (but is best for THF itself). Dissolution of S_8 by electrolyzing at the $S_8 \rightarrow S_8^=$ potential has shown some promise for some solvents (e.g., MA) where $Li_2S + S_8$ is not very effective. In addition, we can explore mixed solvent systems, complexation of S with amines, and other catalytic means for S dissolution. The S charge-discharge mechanism is also likely to be different with different S-complexation schemes, and these must be determined for promising cases. In this regard, reproducible analytical procedures are being worked out for solubility assessment.

4. Can Li be charged and discharged from concentrated polysulfide solutions? Reactions of $S_x^=$, S_x^- or S_x with Li may give rise to passivation of the metal against further attack, while still allowing Li^+ to discharge and charge. Lithium recharge will be examined in promising solutions.

5. To what extent can the S charge-discharge mechanism and potentials be influenced by changing the substrate? Differences in S_8 redox behavior were noted for Pt, Au and C, but it must still be answered whether these are true mechanistic differences, or whether they reflect electrode passivation phenomena. The best (i.e., cheapest) positive electrode collector is carbon. Where the reduction kinetics on carbon are not adequate, other high surface area substrates will be explored.

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APPENDIX

WORK PLAN FOR Li/S PROGRAM

SOLUTIONS FOR SCANNING (S)

(a) 2.5-5.0 mM S_8

(b) Li + S; stir with various stoichiometries

(c) Li_2S + S; stir with various stoichiometries

Initial solvents for S(a)-S(c): DMSO, BL(THF), MA, DMSI, PC, BL, SL

(d) Various battery literature recipes, viz. Nole and Moss, Herbert

(e) Other non-Li-polysulfide possibilities, viz. Me_2NH, CS_2, etc.

(f) Other solvents for Li polysulfide examination; to be selected

- with dissolved S_8
- with dissolved Li_2S_n if appropriate

I. PRELIMINARY SCANNING OF ELECTROCHEMICAL ACTIVITY

Object: To select solutions for further study.

Procedure: Do cyclic voltammetry on C, Pt, Au at room temperature and higher temperature (e.g., 70°C?).

(a) With solutions S(a) and S(d)

(b) With solutions S(e)

(c) With solutions S(f)

II. PRELIMINARY SCANNING OF SULFUR SOLUBILITY

Object: To determine polysulfide solubility and/or to assess potential of solution for practical battery use.

Procedure:

(i) Cyclic voltammetry as under I

(ii) Non-exhaustive chronopotentiometry, probably at one temperature

(iii) Examine stability of solid Li in solutions; cycle Li on Li; stability of plated Li

(iv) Exhaustive electrolysis

TASKS II(a). Solutions S(b) and/or S(c), made ∿0.5M in S_8 if possible

II(b). Solutions S(d)

II(c). Solutions S(e)

II(d). Solutions S(f)

III. DETAILED EXAMINATION OF PROMISING SYSTEMS

Object: To see if promising solutions from I and II can be developed for battery application.

Procedure:

(i) Determine S solubility as f(Li/S) and t(25 and 70°C).

(ii) Non-exhaustive chronopotentiometry and/or cyclic voltammetry at 25° (70°C?) with Pt, C (Au?, sulfide catalysts?), to assess overall catalyst selectivity. Study as f(Li/S) and concentration.

(iii) Exhaustive coulometry at various concentrations, Li/S ratios, temperatures, on high area electrode chosen as under (ii).

(iv) Examine stability of solid Li in solutions as f(Li/S), concentration, solution oxidation state. Look also at Li cycling.

(v) Consider adding other solvents, catalysts, precursors to alter activity; stability.

(vi) Examine spectra of solutions at 25°C, as f(Li/S) and concentration, to help identify species, as appropriate.

TASKS III(a). Choose solutions from Tasks II(a)/II(b), i.e., from S(b), S(c), S(d)

III(b). Choose solutions from II(c), i.e., from S(e)

III(c). Choose solutions from II(d), i.e., from S(f)

IV. BATTERY CYCLING

Aim: To determine feasibility of battery from solutions of Task III.

Procedure: Build complete, small cells (e.g., D-cells or C-cells), laboratory-sealed. Cycle till failure.

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SCHEDULE

TASK I. PRELIMINARY SCAN ELECTROCHEMICAL ACTIVITY

(a) Cyclic voltammetry with S_8 in solvents of first choice for Li polysulfide approach room temperature and 70°C on Pt, Au, C.

(b) Cyclic voltammetry under same conditions for non-Li-polysulfide approaches, viz. in Me_2NH, CS_2, etc.

(c) Similar to (a) for S_8 in less obvious solvents for Li polysulfide approach

TASK II. PRELIMINARY SCAN SULFUR SOLUBILITY

(a),(b) Scanning of solutions of I(a).

(c) Scanning of solutions of I(b).

(d) Scanning of solutions of I(c).

TASK III. DETAILED EXAMINATION OF PROMISING SYSTEMS

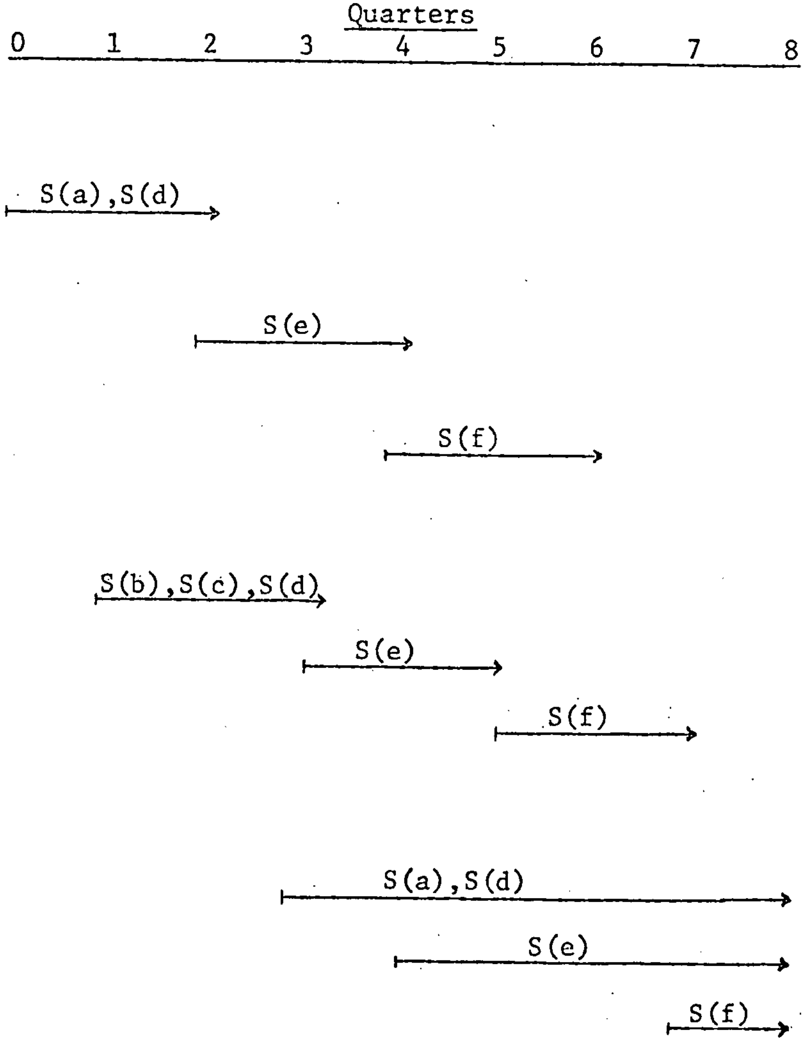
(a) Solutions from II(a),(b).

(b) Solutions from II(c).

(c) Solutions from II(d).

TASK IV. BATTERY CYCLING

On any appropriate solution



ASAP