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LOW TEMPERATURE LITHIUM/SULFUR SECONDARY BATTERY

Annual Progress Report, December 1, 1974—December 1, 1975

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April 1976

EIC Corporation
Newton, Massachusetts

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

Division of Electric Energy Systems

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ABSTRACT

The purpose of this program is to develop an ambient temperature Li/S secondary battery. The proposed configuration is

Li/Organic Electrolyte, Dissolved S/catalytic electrode
or
current collector

In a typical practical arrangement, this battery will have an energy density of 100 Whr/lb, including the weight of cell hardware, if a 5M S solution is discharged with 50% efficiency at 2.0V. Investigations of S solubility and electrochemistry have been undertaken in polar, aprotic nonaqueous solvents, chosen for their stability toward Li.

Highest S solubility was achieved if S were dissolved in the form of Li polysulfides, Li_2S_n. Both electrochemical and chemical techniques were surveyed as methods for preparing Li_2S_n electrolytic solutions. Of the solvents tested, highest S solubilities were achieved in dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF), where 9-10M S solutions were obtained as Li_2S_{9-10}. The solutions of highest S concentrations were most readily prepared through the direct reaction of S_8 with Li_2S in the presence of the solvent.

The discharge and charge capacities of such solutions, 1-2M in S, were measured galvanostatically (1 mA/cm^2) between preset limits of 1 and 3.7V (vs. Li) in a specially designed coulometry cell. The working electrode was C cloth. The capacities measured from the i-t curves were checked in the case of DMSO by chemical analysis of total S and S^{-2} before and after cycling. In this solvent, discharge of a 2M S solution prepared as Li_2S_{24} yielded a Li_2S_5 solution ($\sim$0.33 e$^-$/S). Two plateaus were observed, at 2.7V and at 2.2V. Discharge capacities of approximately 0.25 e$^-$/S were observed in THF and in methyl acetate (MA). Recharge generally occurred between 2.5 and 3.0V. Solutions were subjected to >10 cycles. Some loss of capacity was noted for each cycle, but much of this was inherent in the design of our coulometry cell.

The reasons for limitations of charge and discharge capacities were sought in spectroelectrochemical investigations of dilute polysulfide solutions. In DMSO, such experiments on individual polysulfides showed that S_8 or S_8^{-2} could not be reduced on C below S_4^{-2}, positive of 1.0V vs. Li^+/Li. However, S^{-2} and S_4^{-2} could be readily oxidized on C up to $S_{n>10}^{-2}$, without the formation of (insoluble) S_8. Only S_8^{-2} gave S_8 precipitation upon oxidation.

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It is therefore concluded that the cycling capacity of the dissolved Li_2S cathode has been limited so f by the reduction of $S_{n\leq4}^{-2}$ on C. During the next report period, a sea for an appropriate heterogeneous or homogeneous catalyst for this reduct will be carried out.

Work on the Li electrode in these polysulfide solutions is being undertaken on another program.[*] Preliminary results indicate that 10 $coul/cm^2$ of Li may be repeatedly cycled on a Li substrate with an 85% efficiency in THF, 5M S (as Li_2S_{10}). This efficiency is comparable to that in the S-free solvent, and indicates that rechargeability of the negative will not be a special problem.

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I. INTRODUCTION

Secondary batteries based on alkali metal/chalcogen systems have attracted a large amount of attention, both here and abroad. These systems have high theoretical energy densities (Li/S has a theoretical energy density >1300 Whr/lb, based on the thermodynamic potential of 2.45V (1,2)), and involve raw materials that are cheap, widely available and generally non-toxic. Much of the current work is directed towards batteries for electric automobiles. In this regard, it is generally agreed that a battery with an energy density of 100 Whr/lb at the 1-hour rate would permit a simple replacement of present automotive power plants, with little change in life-style. Batteries with only $\sim$30 Whr/lb at the 1-hour rate, coupled with special lightweight construction techniques, would allow extensive deployment of short-range commuter vehicles (3) and major reduction in air pollution. Electric automobiles are also likely to yield substantial increases in energy conversion efficiencies.

The major effort in development is currently concentrated on high temperature Na/S and Li/S batteries containing a solid or molten salt electrolyte. Both systems have very high rates of discharge and charge because of high working temperatures and use of liquid electrodes. However, the practical success of these batteries depends on solving very substantial materials and corrosion problems. Cell failures occur because of accumulation of resistive materials on the positive electrode, deterioration of the solid electrolyte or the seals, or more general corrosion (4,5). These problems fundamentally result from the operation at high temperature. The lower limit of operating temperature is 300-400°C, depending upon the battery type and design.

In order to mitigate these problems, we have been exploring a Li/S battery which operates at low temperature ($\leq$ 100°C), but which, because of its soluble cathode configuration, can approach the rate, energy density, and rechargeability capabilities of the high temperature systems. The aim is to develop a battery with an energy density of $\geq$100 Whr/lb at the 5-hour rate, with a cycle efficiency of $\geq$70% and a cycle life $\geq$1000 cycles. The proposed battery has the configuration

Li/Organic Electrolyte, Dissolved S/Current Collector.

It is an analogue of the high rate, soluble cathode, ambient temperature Li/SO_2 and Li/$SOCl_2$ cells. The aspects of this battery which need to be chemically optimized are:

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- Sulfur solubility

- Sulfur redox chemistry

- Lithium cycling and stability

The Li/S couple has a very favorable theoretical energy density of about 1300 Whr/lb, based on the equivalent weights of Li and S and a theoretical potential of 2.45V at unit activity of Li^+ and S^{-2} (2). In a practical cell, there are a number of factors which reduce the energy density. An obvious one is the weight associated with cell hardware. This can only be optimized in the later phases of development, i.e., after the "chemistry" has been solved. Another major weight item relates to the nature of the dissolved S cathode; some energy density will be lost due to the weight of the solvent and electrolyte. A preliminary battery design indicates that an S solubility of ~2.3M could give a battery energy density of ~100 Whr/lb if it discharged with 100% efficiency at $\geq$2V vs. Li^+/Li. Clearly, we require an electrolyte which has maximum S solubility throughout all phases of charge and discharge. In practice, we could allow some of the final charge and/or discharge product to be partially insoluble in the electrolyte, thus precipitating in the bottom of the cell or in the electrode structure. This is less satisfactory than total S solubility, both with regard to rate capability and electrode design. Our goal has been to produce solutions of $\geq$5M in S in the charged state.

Our progress through the end of the first semiannual report, which is appended, had indicated that high S solubility could be achieved in some organic electrolytes through dissolution as long chain polysulfides (S_n^{-2}) (6). These could be formed in situ through the reaction of S with Li_2S, or through the electrochemical reduction of S_8. In dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF), it appeared that >5M S was possible, although at that time our analytical methods were not well-refined. During the present report period, we have studied in more detail the S solubility limits in these solvents (Section III.1).

In the last report, we discussed the effect of dissolving S as S_n^{-2} on the theoretical energy density: In the formation of S_n^{-2}, S is already partially reduced, and thus some of the theoretical cell capacity is lost. But, as S_8 is only sparingly soluble in all the organic electrolytes investigated, this sacrifice is necessary.

A related effect on the energy density is the redox stoichiometry of the S electrode. We want to come as close as possible to 2e$^-$/S:

$$2e^- + S \rightleftarrows S^{-2} \qquad (1)$$

The use of S in the form of polysulfides offers some complications in this regard. Individual polysulfides often have different redox and

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solubility properties, and the oxidation or reduction of S_n^{-2} can lead to a distribution of these polysulfides. We have then undertaken a mechanistic investigation of S_n^{-2} electrochemistry in order to understand cell charge and discharge reactions (Sections III.2-4). In particular, we want to determine whether electrochemically unreactive species are formed in the oxidation and/or reduction sequence. If this were the case, appropriate heterogeneous or homogeneous catalysts may be required to extract maximum cell capacity.

To aid the discussion of the results, we will briefly review the literature on ambient temperature sulfur and polysulfide electrochemistry in nonaqueous media: Most of this work has been carried out in DMSO or dimethyl formamide (DMF). Sawyer and co-workers (7,8), working in DMSO, and using spectrophotometry, cyclic voltammetry, potentiostatic coulometry and chronopotentiometry, deduced a partial mechanism for the electrochemical reduction of S_8 to S_4^{-2}. These workers determined that at 2.7V vs. Li^+/Li

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

occurs, using coulometry and by comparing the spectrum of the end product with that of Na_2S_8.* A second reduction at 2.1V corresponds to

$$2e^- + S_8^{-2} \rightleftarrows S_8^{-4}, \qquad (3)$$

although the actual end products arise from subsequent chemical reactions of the metastable S_8^{-4}:

$$S_8^{-4} \rightleftarrows 2S_4^{-2} \qquad (4)$$

$$S_4^{-2} + S_8^{-2} \rightleftarrows 2S_6^{-2} \qquad (5)$$

$$S_6^{-2} \rightleftarrows 2S_3^- \qquad (6)$$

---

*This result is in some conflict with a paper of Bonnaterre and Cauquis (9), where it is stated that in DMSO and DMF $(8/3)e^-/S_8$ can be added to the solution at 2.7V. This is seen as the overall process:

$$3S_8 + 8e^- \rightleftarrows 4S_6^{-2}$$
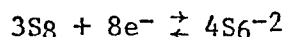
which occurs due to the dismutation:

$$4S_8^{-2} \rightleftarrows 4S_6^{-2} + S_8$$
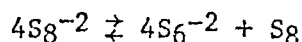
The establishment of the second equilibrium may have been quite slow, however, and hence the low-rate, final part of the S_8 reduction may have been overlooked by Sawyer.

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Thus, a reduction reaction sequence of S_8 may be written:

$$S_8 \rightarrow S_8^{-2} \rightarrow S_8^{-4} \rightarrow 2S_4^{-2} \tag{7}$$
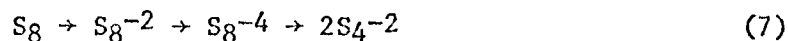
The further reduction of S_4^{-2} was not discussed. The reductions of S_6^{-2} and S_3^-, which are present as intermediates, were also not discussed, although their presence did not appear to hinder the completion of the overall reduction to S_4^{-2}.

Delamar, in some very recent work which was not reviewed in our last report, favors the assignment of the 2.1V reduction to that of S_6^{-2} (10). Hence, the following reduction sequence could be written:

$$S_8 + 2e^- \rightarrow S_8^{-2} \qquad (2.7V) \tag{8}$$

$$S_8^{-2} \rightleftharpoons S_6^{-2} + 1/4 \; S_8 \tag{9}$$

$$S_6^{-2} + 2e^- \rightarrow 2S_3^{-2} \qquad (2.1V) \tag{10}$$

$$2S_3^{-2} + S_6^{-2} \rightleftharpoons 3S_4^{-2} \tag{11}$$
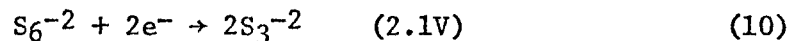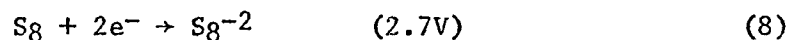
It is not clear, however, why Delamar rejects reaction (3) in his reduction sequence.

Little is known concerning polysulfide oxidation in nonaqueous electrolytes. Sawyer (8) found that the main oxidation wave at 3.1V vs. Li^+/Li was general for S_n^{-2} ($n \geq 4$), and thus assigned it to

$$(8/n) \; S_n^{-2} \rightarrow S_8 \tag{12}$$

The production of S_8 was assumed on the basis of cyclic voltammetry, but was not confirmed by more careful spectroelectrochemical investigations. Delamar and Marchon (11) found that S^{-2} in (wet) DMSO had two oxidation waves present in linear sweep voltammetry. Potentiostatic electrolysis at the first wave resulted in an oxidation of 1.6 to 1.7 e^- per S, and probably corresponds to

$$6S^{-2} \rightleftharpoons S_6^{-2} + 10e^- \tag{13}$$

as much (green) S_3^- was produced. The second wave corresponds to S_6^{-2} oxidation. This is assumed to be

$$S_6^{-2} \rightleftharpoons 3/4 \; S_8 + 2e^- \tag{14}$$

although the bulk formation of S_8 was not confirmed. Nevertheless, it appeared that S^{-2} may be oxidized almost or completely to S°.

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During the present report period, we have investigated the oxidation and reduction reactions of S_8, S_8^{-2}, S_4^{-2} and S^{-2} in DMSO and to a lesser extent in THF. These investigations have led to a clarification of some of the mechanistic features of polysulfide redox reactions, and thus of some of the factors which limit the capacity of the soluble S cathode (Sections III.3,4).

The practical energy density will also depend on the discharge potential of the battery. The published works to date, which have employed S_8 as an insoluble cathode (12,13), report open circuit potentials in DMSO or DMF-based electrolytes of ~2.7 to 2.9V, the $S_8 \rightarrow S_8^{-2}$ potential. This potential is solvent dependent: Rao (14) observed an ocp of 2.35-2.5V for a Li/S cell in propylene carbonate, 1M $LiClO_4$. On the basis of our cyclic voltammetry of S_8 in DMSO, all-soluble polysulfide cathodes should have lower open circuit and discharge potentials. Such appears to be the case for the $iPrNH_2$/dissolved S cathode claimed by Herbert (15).

Previously (6) we reported cyclic voltammetric scans of 2.5 to 5.0 mM S_8 in a variety of organic electrolytes containing 1M $LiClO_4$. We found that the $S_8 \rightarrow S_8^{-2}$ reduction, on vitreous C, Au or Pt, occurred at $E_{max} \simeq 2.7V$ in DMSO, DMF and dimethyl acetamide (DMAC), but at E_{max} 2.0V in THF, BL, sulfolane, methyl acetate, propylene carbonate and dimethyl sulfite. In the first three solvents, the second reduction (S_8^{-2}) occurred at $E_{max} \simeq 2.2V$, while in the remaining solvents it takes place at a lower potential which overlaps the first reduction. The reoxidation occurred at more similar potentials for all the solvents. It is evident, therefore, that there is a solvent effect on the discharge potential of the soluble S cathode.

At the time of the last report, some actual galvanostatic charging and discharging studies had been initiated on relatively dilute S_8^{-2} solutions (~0.1M S). Capacities in γ-butyrolactone (BL) and DMSO appeared to be ~0.25 e^-/S. These cells were run at too high a rate to obtain a reasonable estimate of charge and discharge potentials. Current-potential curves on these solutions confirmed that they could be run only at a low rate. During the present report period we have repeated these cycling studies on more concentrated solutions (1-2M S), and have obtained simultaneous measurements of capacity and discharge potential (Section III.2).

Besides maximizing the energy density, we also wish to cycle the cell many times without losing capacity from either electrode. The cycling ability of the dissolved S cathode is an unexplored area, despite some rather ambiguous patent claims (15,16). It will be important to determine and correct loss mechanisms for S activity; only a few such experiments have been carried out by us to date.

In addition, we must be able to plate and strip Li with reasonable efficiency in the presence of the electrolyte containing high concentrations

of dissolved S. Some claims have been made of bulk Li stability in such solutions (15,16), but no Li cycling experiments have been specified. We are presently carrying out a detailed study of the Li electrode in nonaqueous electrolytes on Contract NSF-RANN AER75-03779. A particular task on that program is to investigate the cycling and stability of Li in presence of dissolved S.

II. EXPERIMENTAL

Most of our procedures and instrumentation were described earlier (6). Hence, we only indicate changes and improvements. Specific experimental procedures for analysis and solvent purification are detailed in Section III.

1.   Materials

Dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) were obtained from Burdick and Jackson Laboratories. Both were determined by lot Karl Fischer analyses to contain <0.04% H_2O, and were of high purify, "distilled in glass" quality. Electrochemical characterization of these solvents indicated a higher degree of electrochemical purity than the MCB "spectroquality" reagents used previously (6). A discussion of further purification of these solvents is given in Section III.2.

"Anhydrous" $LiClO_4$ was obtained from Foote Mineral Company. To take the H_2O level below 50 ppm, the salt had to be vacuum dried at its fusion point ($\sim230°C$) (17). The dried salt was stored in vacuo. Li_2S and S (99.995%) were obtained from Ventron, and used without further purification. Na_2S_4 (96%) was also obtained from Ventron. To remove free S, the salt was washed with toluene in the Ar-filled dry box. $LiAsF_6$ (electrochemical grade) was supplied by United States Steel, Agri-Chemicals Division, Decatur, Ga., and was indicated by the manufacturer to contain <100 ppm H_2O (Karl Fischer analysis). The salt was used without further drying or other purification. Its use is discussed in detail in reference (18), and in references cited in that work.

All solutions were prepared in an Ar-filled glove box (Vacuum Atmospheres Corp.). The solutions were used as prepared, without further drying.

2.   Preparation of Electrodes

Electrodes were constructed as reported previously (6), except for the following:

● Vitreous C Electrode for Cyclic Voltammetry. A 2.7 mm diameter vitreous C rod (Atomergic Chemicals, V10 or V25 grade) was sealed in Pyrex and fabricated into an electrode according to the method of Gupta (19). The exposed C disc surface was polished to a mirror-like finish using a 0.1μ alumina dispersion.

● C Cloth Electrodes. C cloth (Union Carbide) was found to be a convenient, moderate surface area electrode (real/geometric area ≈ 3/1 (20)). The material frays quite easily, however, and is difficult to mount for electrochemical studies. Electrodes for coulometry were prepared in two ways: The first was to cut a C cloth flag, and to bind the tab to Ta wire or screen using Teflon tape. The second method was to wrap the C cloth around a strip of Ta screen and to secure the cloth at top and bottom with Teflon tape. Both methods were used for preparing electrodes for coulometry.

3.   Electrochemical Measurements

● Cyclic Voltammetry. Cyclic voltammograms were recorded using instrumentation and the cell described previously (6).

● Coulometry. On dilute solution of polysulfides, coulometry was carried out potentiostatically, with stirring, in the cyclic voltammetry cell. The working electrode for cyclic voltammetry was replaced with carbon cloth for coulometry. The current-time curve was recorded on a strip chart recorder and was integrated by summing triangular and rectangular areas or by cutout and weigh.

On concentrated solutions of polysulfides, a three-compartment Teflon coulometry cell was employed. This cell is similar to that described previously (6), except that it is scaled down approximately by a factor of 3. The center working compartment has a capacity of 1 ml when the working electrode is in place. For DMSO solutions, Celgard 2400 microporous polypropylene (Celanese) was used to separate the counter and working compartments. For THF solutions, diffusion through the Celgard was too rapid, and Goretex microporous Teflon was used instead. The latter gave excessively high cell resistances with DMSO solutions.

Galvanostatic charging and discharging between voltage limits were accomplished using either of two methods: In the first method, a specially designed cell cycling unit was employed which could repeatedly charge and discharge the cell at a preset current to preset voltage or time limits (Bromberg Engineering Co., Weston, Ma.). The second method was to attach microswitches to a Fisher Omniscribe strip chart recorder, so that a switch would be tripped by the pen when it reached either voltage limit. This activated an spdt relay in series with the constant current source, and reversed the direction of current flow.

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1. Dissolution of S

A first requirement in developing a Li/S battery with a solubilized S cathode is to achieve high S solubility in an organic electrolyte potentially compatible with Li. We have calculated that solutions of only 4.8M S discharged with 50% efficiency at 2.0V should yield a 100 Whr/lb cell (6). One way to achieve such solubility is through the use of Li polysulfides, Li_2S_n.

As Li polysulfides are not stable in the solid phase (unlike their Na or K counterparts (22)), they must be formed in solution. In the last report (6), we described three methods for doing this:

$$2Li + n/8 \ S_8 \rightarrow Li_2S_n \tag{1}$$

$$S_8 + 2e^- \rightarrow S_8^{-2} \quad (2.7V \text{ vs. Li}) \tag{2}$$

$$Li_2S + n/8 \ S_8 \rightarrow Li_2S_{n+1} \tag{3}$$
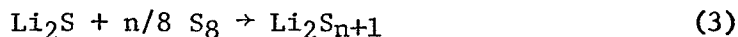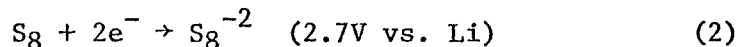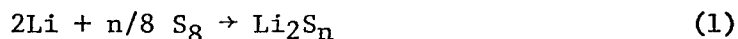
Methods (2) and (3) were generally the more successful, probably because Li metal tends to passivate in presence of S, retarding reaction (1).* Observations of S solubility were, for the most part, qualitative. The majority of the work was carried out on methods (1) and (3), because of their convenience.

Li polysulfides were most readily formed and most soluble in DMSO, dimethyl acetamide (DMAC), dimethyl formamide (DMF), and THF. Moderate solubility was noted in butyrolactone (BL) and sulfolane (SL). Propylene carbonate (PC), methyl acetate (MA), methyl formate (MF), dimethyl sulfite (DMSI), and nitromethane (NM) showed little affinity for polysulfides (formed by methods (1) or (3)). Blue polysulfide solutions (λ_{max} = 618 nm) were produced in DMSO, DMAC, DMF, BL, and SL, while the other solvents gave rise to yellow solutions. The peak at 618 nm is ascribed to S_3^-, which is formed from the reaction

$$S_6^{-2} \rightleftarrows 2S_3^- \tag{4}$$

The absorptions at 475 nm (S_6^{-2}) and 618 nm were not noted in the other solvents. Instead, maxima at 410-420 nm (S_4^{-2}) and sometimes $\sim$550 nm

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* This is, of course, desirable in the first battery as we require
  Li to be substantially stable in S or polysulfide solutions.

(unknown) were noted. No work has been published on the spectra of polysulfides in the solvents which gave yellow solutions, so assignments cannot be made in these solvents at this time.

Some exploratory work was done in DMSO and THF on the solubility of polysulfides formed by method (3) as a function of $(S^{-2})/(S^o)$. In general, lower ratios favored higher S solubility. In DMSO, the absorption spectra of S_8^{-2}, S_6^{-2} and S_4^{-2} were recorded at appropriate $(S^{-2})/(S^o)$ ratios. In THF, the spectrum was quite similar at all ratios, being dominated by the maximum at 410-420 nm.

During the last six months, we have extended considerably our investigations of Li_2S_n solubilities. A refinement of our analytical procedures has allowed a more detailed construction of the profiles of S solubility vs. $(S^{-2})/(S^o)$. In addition, we have studied in more detail electrochemical dissolution methods.

● <u>Sulfur Analysis</u>. Two methods of analysis for total S in nonaqueous solutions of polysulfides have been developed.

The first, which has been discussed in the last report (6), requires the combustion of a sample in O_2, followed by dissolution of the gaseous products (mostly SO_3) in an aqueous H_2O_2 solution, to insure complete oxidation and conversion to SO_4^{-2} (23a). Samples were prepared for combustion by evaporating a known volume of the solution on a piece of filter paper.

This method was tested on weighed-out samples of S_8 and Li_2S, as well as on polysulfide solutions of known total S concentration made up in THF, BL, DMSO, DMF, and DMAC by the reaction of Li_2S and S_8. Recoveries were 98-102% for S_8, but were variable and consistently low for Li_2S. We found that Li_2S impregnated in the filter paper was highly susceptible to hydrolysis, with a loss of S^{-2} as H_2S. Recoveries were somewhat variable for the polysulfides, too, with values of 80-100%. For DMSO solutions, it was impossible to remove all of the solvent prior to combustion, perhaps due to the formation of a complex with the solute. Results with DMSO were therefore unreasonably high, as the solvent itself contains S. These results are summarized in Table 1a.

Somewhat better results have been obtained with the oxidation of S by an aqueous solution of H_2O_2/NH_3 (23b). After the sample was added to the oxidant, the solution was heated, acidified with 6N HCl to pH 2-4.5, and titrated with $Ba(ClO_4)_2$, using a thorin indicator. Although recoveries of Li_2S were still low using this method, recoveries of S as polysulfides were 90 to 100%. Because the reagents do not oxidize organic solvents to SO_4^{-2}, this analytical method is satisfactory for determining S dissolved in DMSO and other organo-sulfur

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Table 1

A. **S Analysis in Polysulfides by the Combustion Method**

Solution	% Recovery
1. 10 mg S (solid sample)	99
2. 20 mg Li_2S (solid sample)	25
3. 15 mg Li_2S in Methanol	
a. combust immediately after impregnation of paper	57
b. let stand 10 minutes	23
c. let stand 30 minutes	15
d. impregnate in Ar-atmosphere; evaporate MeOH in vacuo; combust immediately	97
4. 1M S as Li_2S_8 in THF	94,106,102
5. 1M S as Li_2S_8 in DMSO	469,570
6. 0.2M S as Li_2S_4 in DMF	92,84
7. 0.2M S as Li_2S_4 in DMF (same procedure as 3d)	95
8. 0.2M S as Li_2S_8 in DMAC	89

B. **S Analysis in Polysulfides by Chemical Oxidation**

Solution	% Recovery
1. 1M S as Li_2S_8 in DMSO	98,98
2. 1M S as Li_2S_4 in DMSO	113
3. DMSO Blank	S Undetectable
4. 0.2M S as Li_2S_4 in DMF	94,95
5. 15 mg Li_2S (solid sample)	45

solvents. Tests of this method are summarized in Table 1b.

Sulfide S was determined by conventional iodimetry (24). Sulfide reacts with I_2 to form I^-. A known excess of I_2 is first added to the polysulfide solution, and the unreacted I_2 is titrated with standard $Na_2S_2O_3$. This method was determined accurate to within a few percent in assessing S^{-2} concentrations in DMSO and THF solutions of known polysulfide concentrations (see studies below). The original (non-aqueous) polysulfide solutions could be diluted with H_2O without significant loss of S^{-2} as H_2S if the analysis were run within a short time after the dilution.

- Electrochemical Dissolution of S. Experiments were carried out to determine the limits of solubility of Li_2S_n in DMSO, THF, butyrolactone (BL) and methyl acetate (MA), 1M $LiClO_4$, using the potentiostatic electrochemical dissolution method. A three electrode cell was used, shown in Figure 1. The working electrode was a 10 cm^2 section of C cloth. The counter electrode was doubly isolated using a second glass frit and the solution in the second counter compartment was changed frequently during the electrolysis. The working electrode compartment contained enough (insoluble) S_8 to make the final solution (15 ml volume) 5M in S. A Luggin capillary Li^+/Li reference electrode was employed.

The $S_8 \rightarrow S_8^{-2}$ reduction in DMSO occurs at 2.7V vs. Li^+/Li. S_8 was introduced into the working electrode compartment (solubility <5 mM), and the working electrode set at this potential. The average current was ~0.2 mA/cm^2. The solution turned first blue, then, as more S dissolved, dark red. After a few days, the solution had become quite viscous. The working and counter electrode solutions were combined, as considerable diffusion into the first counter electrode compartment had occurred.

A total S analysis indicated an S concentration of only 1.67M for this solution. The same solution contained only 0.07M S^{-2}. Thus, the equivalent polysulfide order is S_{24}^{-2}. Integration under the current-time curve for dissolution indicates that a charge of nearly $1e^-/S$ in solution was passed. This discrepancy further indicates that some of the dissolved S must have been reprecipitated as a low order Li sulfide during the course of the electrolysis.

The sample was diluted by a factor of 50 and a visible absorption spectrum recorded. The spectrum contained maxima at 480 nm and at 618 nm. The former peak probably represents a mixture of S_8^{-2} (492 nm) and S_6^{-2} (475 nm), while the latter peak corresponds to S_3^-. Assigning the peaks to S_6^{-2} and to S_3^-, and using Sawyer and co-workers' values of ε for these species (8), a total S^{-2} concentration of 0.052M is calculated (in fair agreement with the chemical analysis) while polysulfide S
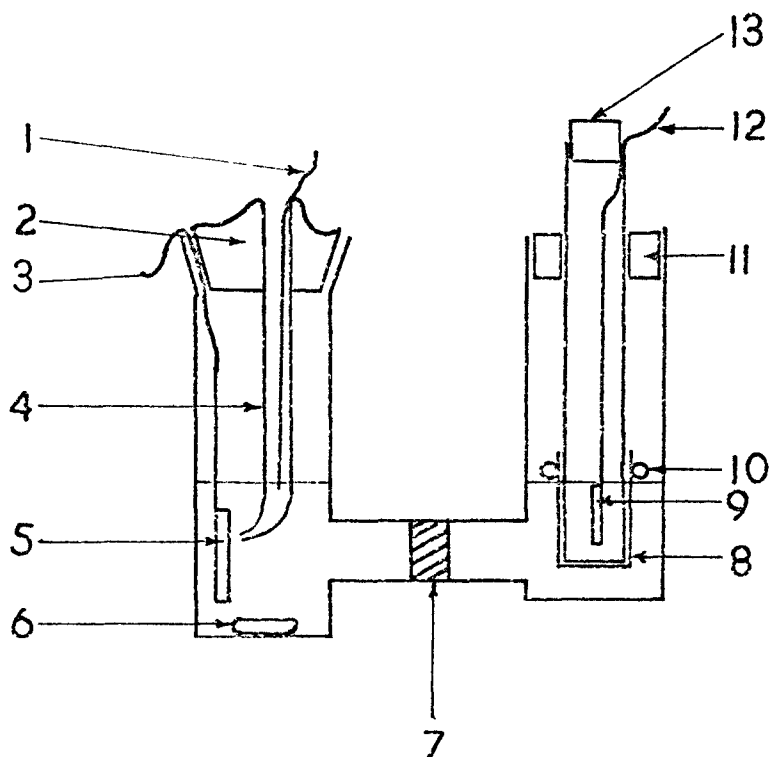
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Fig. 1: Cell for the electrochemical dissolution of sulfur.
(1) Li reference electrode lead. (2) Standard taper top.
(3) Working electrode lead. (4) Luggin capillary.
(5) C working electrode. (6) Magnetic stirring bar.
(7) Fine frit. (8) Celgard 2400 microporous polypropylene.
(9) Li counter electrode. (10) O-Ring. (11) Teflon plug.
(12) Counter electrode lead. (13) Teflon plug.

(present as S_6^{-2} and S_3^-) is about 0.3M. This analysis yields about the same result if the 480 nm peak is assigned to S_8^{-2}. We can only conclude from these considerations that the remaining (1.67M − 0.3M = 1.37M S^o) is complexed by the polysulfide. This complexed S may, like S_8, be only weakly absorbent in the visible (25).

Although the limit of S solubility was not achieved in DMSO using this method, the dissolution was too slow to render it practical. The mechanism of formation of S_{24}^{-2}, and the nature of the species in solution have not been pursued in further detail.

A similar experiment was carried out to dissolve S in THF via potentiostatic electrolysis. The cyclic voltammogram of S_8 in THF shows the onset of the $S_8 \rightarrow S_8^{-2}$ reduction at $\sim$2.2V. The first and second reductions are overlapping in THF, unlike in DMSO where they are fairly well separated (6). The electrolysis was carried out at 2.0V vs. Li^+/Li. The average current density was $\sim$0.5 mA/cm^2. The dissolution experiment was terminated after 80 hrs, the current having dropped to 0.35 mA/cm^2.

Chemical analysis indicated that the final solution was 4.3M in S. Integration of the total current showed that 0.18 e^-/S was expended in the dissolution process. Thus, polysulfides of type S_n^{-2} would have an average order greater than n = 8.

The spectrum of this solution was recorded using a 0.01 mm pathlength and is shown in Figure 2. Two maxima (418, 550 nm) are observed. The ratio A_{550}/A_{418} increased somewhat upon dilution. This may be due to equilibria

$$S_n^{-2} \rightleftharpoons 2S_{(n/2)} \qquad\qquad (5)$$
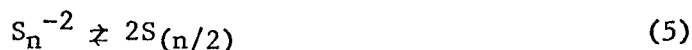
although the absence of S_3^- raises a question about the stability of anion radicals in this solvent.

Because THF is less viscous than DMSO, the electrolysis proceeded at a higher rate, making this an easy method for obtaining concentrated S solutions. However, since these experiments were completed, the solubility experiments described in the next section have proven chemical S dissolution to be a more convenient method.

Among other solvents, approximately 1M S was dissolved in MA by electrochemical reduction at 2.0V, although on standing some precipitation occurred. The solution was filtered and diluted to bring its S concentration to 0.2M (as determined by chemical analysis) for later use. This dissolution by electrochemical means occurred despite the failure to dissolve much S in MA through the reaction of Li_2S with S_8 (6).

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Fig. 2: Absorption spectrum of 4.2M S dissolved in
THF, 1M LiClO$_4$ as Li$_2$S$_{>8}$. (———) $\ell \simeq 0.01$ mm;
(———) dilution $\simeq$ 1:20, $\ell = 0.20$ mm.

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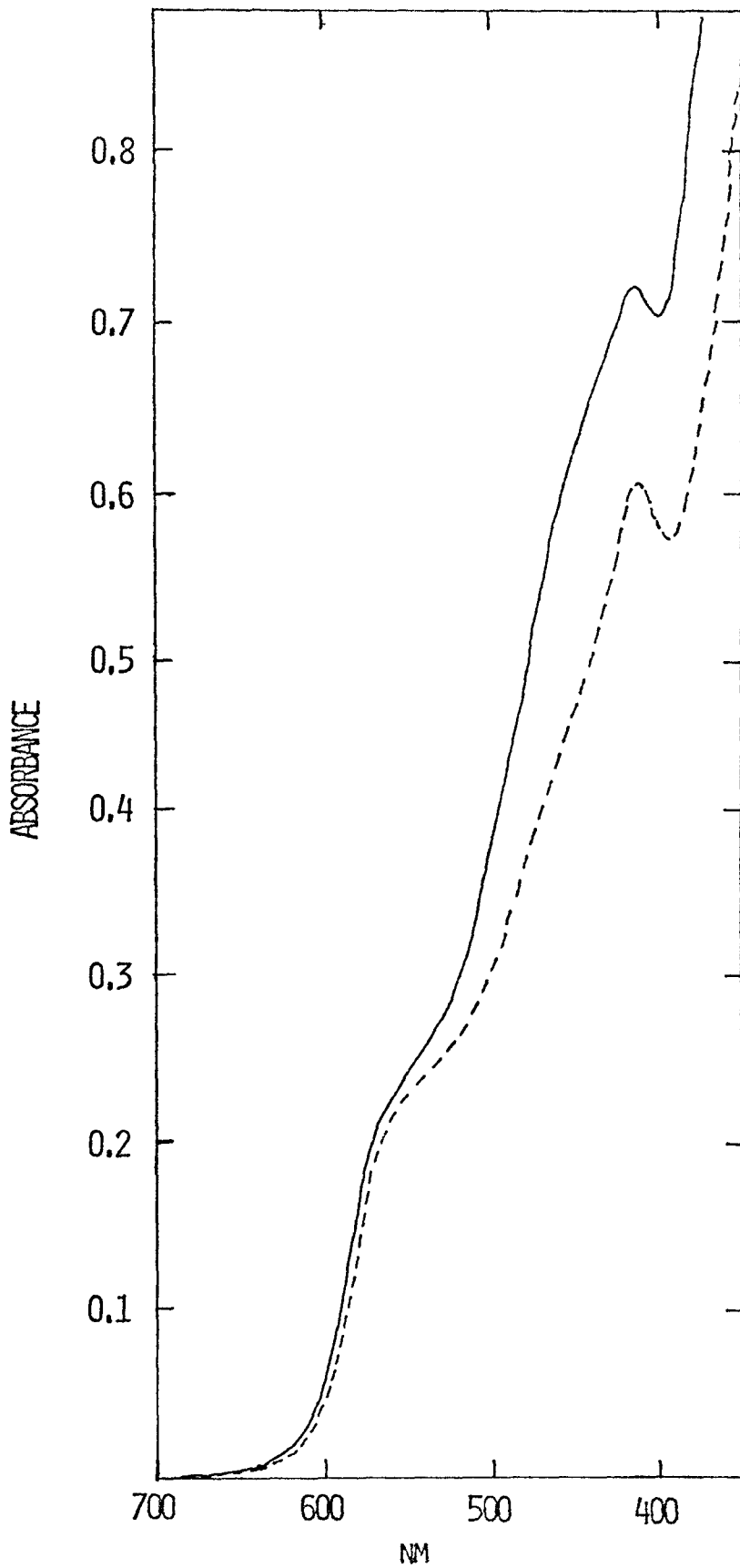γ-Butyrolactone (BL) behaved opposite to MA. Attempts to electrochemically dissolve S in BL (2.1V) resulted only in very dilute S_n^{-2} solutions. Yet moderate solubility of chemically-formed Li polysulfides has been previously noted for BL (6). As current was being passed (∿50 mA-hrs), the sulfides which were formed must have precipitated. Since the S solubility was so low in this case, further experimentation was discontinued.

It should be noted that for BL, THF and MA, the $S_8 \rightarrow S_8^{-2}$ reduction apparently occurs at the same potential as polysulfide reductions (∿2.1V). Hence, polysulfides of lower order than 8 are probably formed in these solvents during electrolysis. Unlike DMSO, the nature of the polysulfide cannot be controlled. In the case of BL, it is very possible that insoluble, low order polysulfides are formed in a single step at the electrode.

● <u>Chemical Dissolution of S</u>. We have begun to construct detailed profiles of Li_2S_n solubility as a function of polysulfide order (n) in a number of nonaqueous solvents. In such experiments, enough Li_2S was added to the solvent to make a 1M solution, if it all dissolved. Aliquots of S were added in 1M steps. After each S addition, a sample of the solution plus suspension was withdrawn and centrifuged. The supernatant was analyzed for S^o and S^{-2}, from which the concentration and order of polysulfide were calculated. A portion of the sample was diluted, and an absorption spectrum recorded. After a 10:1 S^o/S^{-2} ratio had been achieved, a large excess of S^o was added, and the limiting S^o/S^{-2} ratio was recorded.

Results to date have been obtained for DMSO and for THF. Solubility data are reported in Tables 2 and 3. The analysis of each solution was repeated twice. The THF samples, which were analyzed using the combustion method, showed ±5% reproducibility. The DMSO samples, which were oxidized with H_2O_2, gave ±2.5% reproducibility. Errors were obviously exclusively due to sampling procedures, as the SO_4^{-2} titration had higher than 1% reproducibility, depending on sample size.

DMSO was also less susceptible to evaporation than THF. Some evaporation obviously occurred in the latter during centrifugation, moving the centrifuge tubes in and out of the glove box, and the pipetting of solutions. This led to somewhat elevated total S and S^{-2} values in THF (e.g., Sample THF-6, in which all added S^o and S^{-2} had dissolved, gave a total S concentration of 8.8M rather than 7.0M). The S^{-2}/S^o ratios were nevertheless quite reasonable.

In both cases, the limiting solubility of S^o is attained only at n < 3.5 and at n > 12. At intermediate values of n, all the S went into solution, so that [S] was maintained at greater than 5M. At least 12M S

Table 2

Solubility of Li_2S_n in DMSO and DMSO, 1M $LiClO_4$

(Analyzed Values are ±10%)

Sample		Added		Analyzed		
		$S^o(M)$	$S^{-2}(M)$	$S^o(M)$	$S^{-2}(M)$	S_n^{-2}
DMSO	1	1.0	1.0	1.1	0.4	$S_{3.7}^{-2}$
	2	2.0	1.0	1.9	0.8	$S_{3.6}^{-2}$
	3	3.0	1.0	2.9	1.0	$S_{4.0}^{-2}$
	4	4.0	1.0	3.7	1.0	$S_{4.6}^{-2}$
	5	5.0	1.0	4.6	1.1	$S_{5.2}^{-2}$
	6	6.0	1.0	5.4	1.0	$S_{6.3}^{-2}$
	7	7.0	1.0	–	1.0	–
	8	8.0	1.0	–	1.0	–
	9	9.0	1.0	8.6	1.0	$S_{10.0}^{-2}$
	10	10.0	1.0	8.8	0.5	$S_{18.2}^{-2}$
DMSO, $LiClO_4$	1	1.0	1.0	1.1	0.4	$S_{3.8}^{-2}$
	3	3.0	1.0	2.3	0.7	$S_{5.7}^{-2}$
	7	7.0	1.0	6.8	1.0	$S_{7.9}^{-2}$
	10	10.0	1.0	8.5	0.9	$S_{10.3}^{-2}$
	11	Excess	1.0	8.4	1.1	$S_{8.5}^{-2}$

Table 3

Solubility of Li_2S_n in THF – First Run

Sample		Added		Analyzed		
		$S^o(M)$	$S^{-2}(M)$	$S^o(M)$	$S^{-2}(M)$	S_n^{-2}
THF	1	1.0	1.0	1.1	0.3	–
	2	2.0	1.0	2.6	0.5	–
	3	3.0	1.0	2.9	0.8	$S_{4.5}^{-2}$
	4	4.0	1.0	3.3	1.0	$S_{4.5}^{-2}$
	5	5.0	1.0	5.6	1.2	$S_{5.8}^{-2}$
	6	6.0	1.0	7.6	1.2	$S_{7.1}^{-2}$
	7	7.0	1.0	8.8	1.2	$S_{8.4}^{-2}$
	8	8.0	1.0	9.3	1.2	$S_{8.5}^{-2}$
	9	9.0	1.0	10.5	1.2	$S_{9.9}^{-2}$
	10	10.0	1.0	11.1	1.2	$S_{10.3}^{-2}$

could be achieved at high S^o/S^{-2} ratios. Such solutions were quite viscous, which could limit their usefulness in a practical cell. Insofar as comparisons can be made, chemically and electrochemically prepared solutions of equivalent stoichiometry are the same.

2. Galvanostatic Cycling of S Solutions

In order to test the coulombic capacity of S solutions, experiments involving the repeated galvanostatic reduction and oxidation of these solutions have been devised. The cell used for cycling such concentrated solutions is described in Section II.3.

In the last semiannual progress report (6), charge-discharge curves were reported for THF, BL and DMSO polysulfide solutions. Not only were these solutions rather dilute (0.1M), but background contributions from the reduction of solvent impurities were shown to contribute to the discharge curves. This made uncertain the discharge stoichiometries. Solvent purification was therefore undertaken.

● <u>Purification of Electrolytes</u>. The contributions of background currents were determined from steady-state current-potential curves in the electrolyte on a Teflon-bonded C working electrode (as is used for the S-containing solutions). Such measurements were carried out on solutions of 1M LiClO4 (fuse dried) in MA, THF, and DMSO, which had been treated several times with activated molecular sieve. The results are summarized in Figure 3.

All background currents were essentially as reductions. Initial current potential curves generally showed an onset of ∿1.5V, and currents rose to >5 mA/cm^2 at 1.0V in MA and DMSO. Galvanostatically cycling the pure solutions between ∿1.2 and 4V showed less "background" capacity with each cycle. Little difference in background was noted when LiBF4 was substituted for LiClO4.

Further purification of DMSO was carried out by placing the solvent over KOH for several days, then distilling in a spinning band column under reduced pressure. Background currents were improved for this material (1M in LiClO4), and were better with more treatments of molecular sieve (up to 6 treatments). We find that DMSO purified in this way can be used down to a potential limit of 1V.

The effect of galvanostatic cycling in reducing "background" capacity led us to develop an electrochemical method for ridding DMSO and THF solutions of electroactive impurities. This purification should enhance the stability of these solutions toward Li, as well as allow the accurate determination of S reduction and oxidation stoichiometries between fairly wide potential limits without competition from impurity reactions.
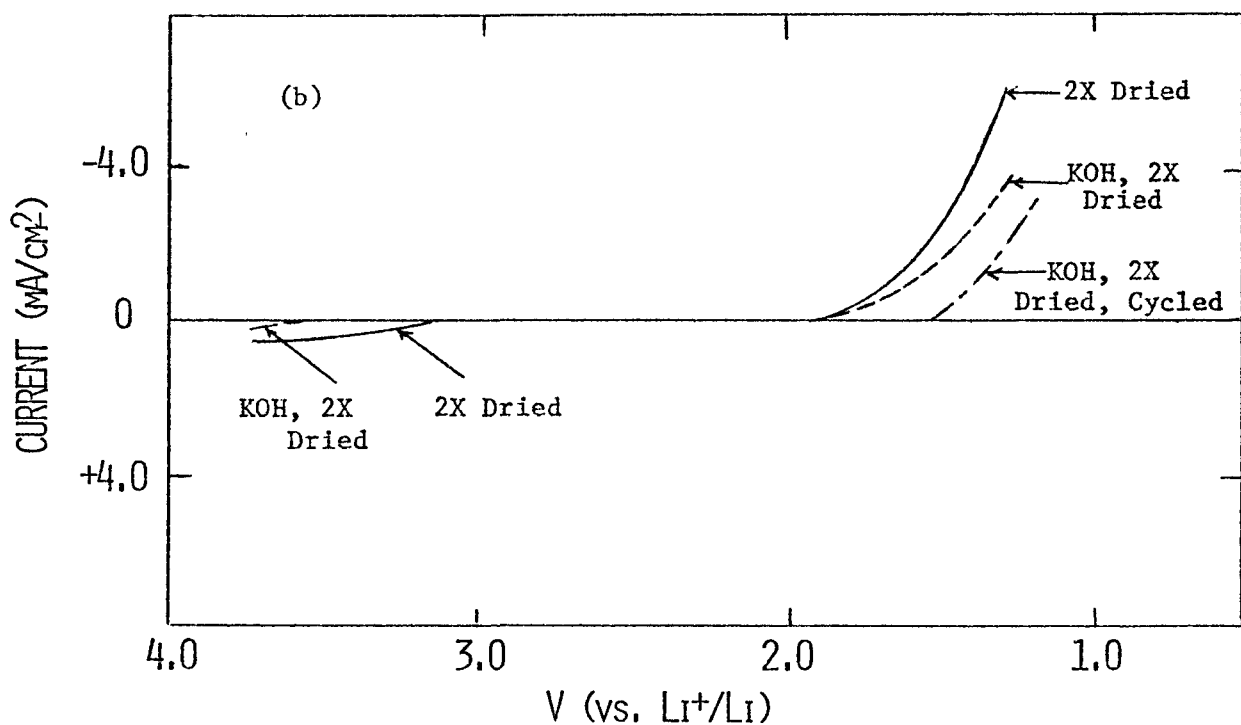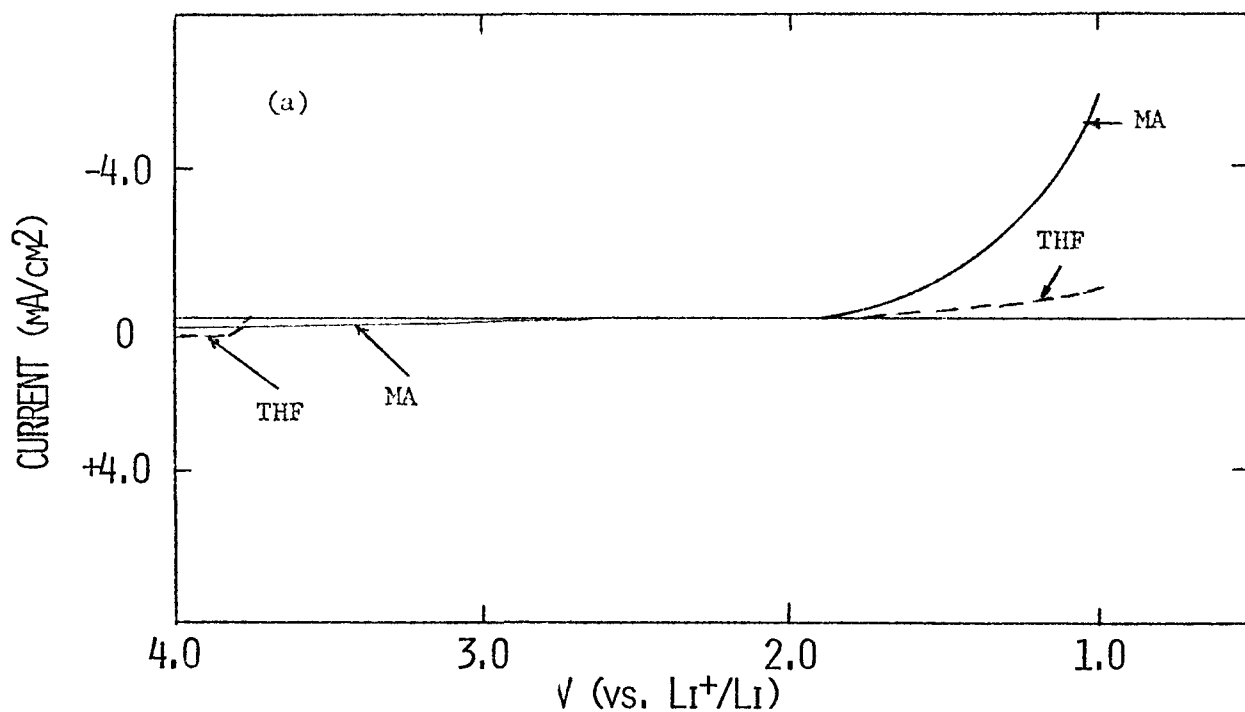
Fig. 3:   Current potential curves for various electrolytes, using a Teflon bonded
C electrode.   (a) MA, 1M LiClO4 and THF, 1M LiClO4, treated 2X with
molecular sieve.   (b) DMSO, 1M LiClO4 (———) treated 2X with molecular
sieve; (- - -) treated with KOH prior to fractional distillation, then
treated 2X with molecular sieve following addition of LiClO4; (- -—) same,
but after cycling between 1.0 and 3.8V on a Teflon-bonded C electrode.

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The following procedure was adopted: Solutions were made up 1M in LiClO$_4$ which had been fuse-dried. Cyclic voltammograms (on Pt) and steady-state current-potential curves (on C cloth) were recorded for these solutions prior to potentiostatic electrolysis. The electrolysis cell consisted of a 100 ml 3-neck round bottom flask fitted with a carbon cloth working electrode (18 cm^2/side), a capillary Li$^+$/Li reference electrode, a fine-fritted counter electrode compartment containing a Li electrode, and a magnetic stirring bar. After introduction of 75 ml of the solution to be cleaned, the working electrode was potentiostated at 0.9V vs. Li$^+$/Li and the current monitored. At periodic intervals the electrolysis was stopped and a cyclic voltammogram was taken. At the end of the electrolysis, another steady-state current-potential curve was recorded.

DMSO was obtained from two sources, MCB (spectroquality) and Burdick and Jackson (distilled in glass). The steady-state current-potential curves measured for the MCB solvent showed an onset of reductive activity at 1.5V, while the B and J material showed an onset at 1.25V (Figure 4a). Thus, the B and J solvent was chosen for further use. The cyclic voltammogram of this solution showed a major reduction peak at 1.4V, possibly due to H$_2$O. This peak was seen to diminish from 400 μA/cm^2 to 70 μA/cm^2 during the course of the potentiostatic electrolysis (Figure 5a). The change did not show up as dramatically on the steady-state current-potential curve taken at the end of the electrolysis (Figure 4a).

The THF obtained from B and J was also superior electrochemically to that obtained from MCB. This is clearly demonstrated from the steady-state current-potential curves shown in Figure 4b. The effect of potentiostatic electrolysis was not very large, although some reduction in steady-state and rapid sweep background currents was noted (Figures 4b, 5b).

Attempts to continue the electrolysis at 0.6V were fruitless for both solvents, a yellow coloration and increased oxidative background currents being developed in both DMSO and in THF. It is not known whether this decomposition reaction is inherent to the solvents or is a result of solution impurities.

In the case of DMSO, the electrochemically-cleaned solution is notably more stable toward Li. This can be seen by observing the reactions in the counter electrode compartment during the potentiostatic electrolysis. At the beginning of electrolysis, the counter solution rapidly yellowed and was changed often to avoid contamination of the purified solvent. Each time it was changed, it was replaced by some of the solution in the working electrode compartment. As the electrolysis proceeded, the yellowing became less and less significant.

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i (MA/CM²)

Fig. 4a: i-E curves of DMSO, 1M LiClO₄; C cloth electrode.

— — — MCB, spectroquality
— · — B and J, before electrolysis at 0.9V
———— B and J, after electrolysis at 0.9V

Fig. 4b: i-E curves of THF, 1M LiClO₄.

— — — MCB, spectroquality
— — — B and J, before electrolysis at 0.9V
———— B and J, after electrolysis at 0.9V

VOLTS (VS LI)

Fig. 5a: Cyclic voltammograms on Pt of DMSO, 1M LiClO4

------Before electrolysis
——After electrolysis at 0.9V vs. Li

Fig. 5b: Cyclic voltammograms on Pt of THF, 1M LiClO4.

-- --Before electrolysis
——After electrolysis at 0.9V vs. Li

i (MA/CM²)

VOLTS (VS LI)

The THF appeared stable to Li during all phases of the electrolysis. However, polymerization of uncleaned THF solutions in contact with Li has been noted in past experiments.

Prior to cycling of polysulfide solutions, it has become a matter of procedure to cycle first just the solvent plus supporting electrolyte (1M LiClO4 or LiAsF6) between the preset voltage limits (usually 1.0 - 3.7V vs. Li+/Li). For THF and DMSO which had been cleaned via the above procedure, less than 0.01 mA/hr capacity ($\sim 10^{-4}$ eq/ℓ) due to solvent impurities was observed on either charge or discharge of 6 ml of electrolyte. In all cycling experiments performed on polysulfides dissolved in these purified solvents, this represented less than 0.5% of the total solution capacity.

● Galvanostatic Cycling of S in DMSO. A solution of 2M S in DMSO, 1M LiClO4 was prepared by electrochemical dissolution of S_8 at 2.5V vs. Li. In this initial experiment the solvent had not been electrochemically purified. The total S concentration was determined by the analytical procedures described above. The final composition of the solution was presumably Li_2S_8, although no spectrophotometry or sulfide analysis was carried out on these concentrated solutions. This solution was cycled galvanostatically between voltage limits of 1.0 and 3.7V vs. Li. The working electrode was Teflon-bonded C pressed onto a Ta screen. The coulometry cell was that described in the previous semiannual report (6), and not the "scaled down" model described in Section II.3. The discharge was initiated at 4 mA/cm^2, and a curve having three plateaus was obtained (2.1, 2.0, and 1.3V). The discharge was terminated at 1.3V, after achieving a capacity of $\sim$0.25 e$^-$/S. Upon lowering the discharge current to 0.8 mA/cm^2, a small amount of additional capacity was obtained at $\sim$2.0V, followed by a drop to a plateau at 1.3V. In subsequent cycles, the plateau at 1.3V virtually disappeared, and thus is ascribed to a solvent impurity which is removed electrochemically. Subsequent cycling was carried out at 0.8 mA/cm^2.

Both charge and discharges showed two plateaus: 2.7V and 2.05V on discharge, and 2.2V and 2.75V on charge. The total capacity was 0.25 - 0.33 e$^-$/S on both charge and discharge. The experiment was terminated voluntarily after 5 cycles. The results are summarized in Figure 6. The discharge potential and reversibility of the system are considerably more favorable than observed for 0.1M S in DMSO, reported on earlier (6). The rate of charge and discharge were probably too high in the previous experiment. Disassembly of the cell following a final charge cycle revealed some precipitate in the working electrode compartment. The working electrode itself appeared free of deposit. The precipitate may consist of $S_n^{\,o}$ species.
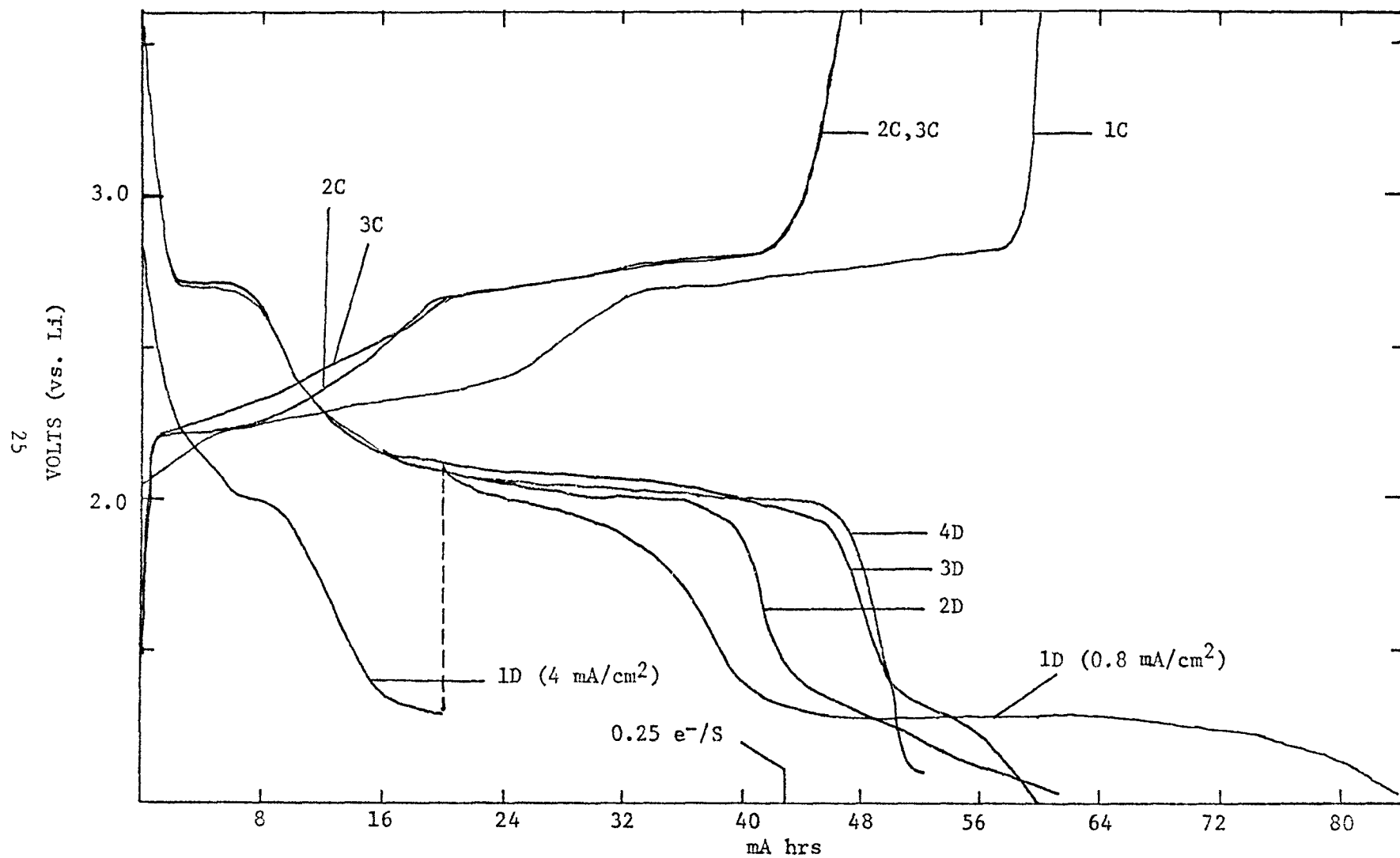
Fig. 6: Galvanostatic charge-discharge curves of 2M S dissolved in DMSO electrochemically as Li_2S_8. Working electrode is Teflon-bonded C; current = 0.8 mA/cm^2.
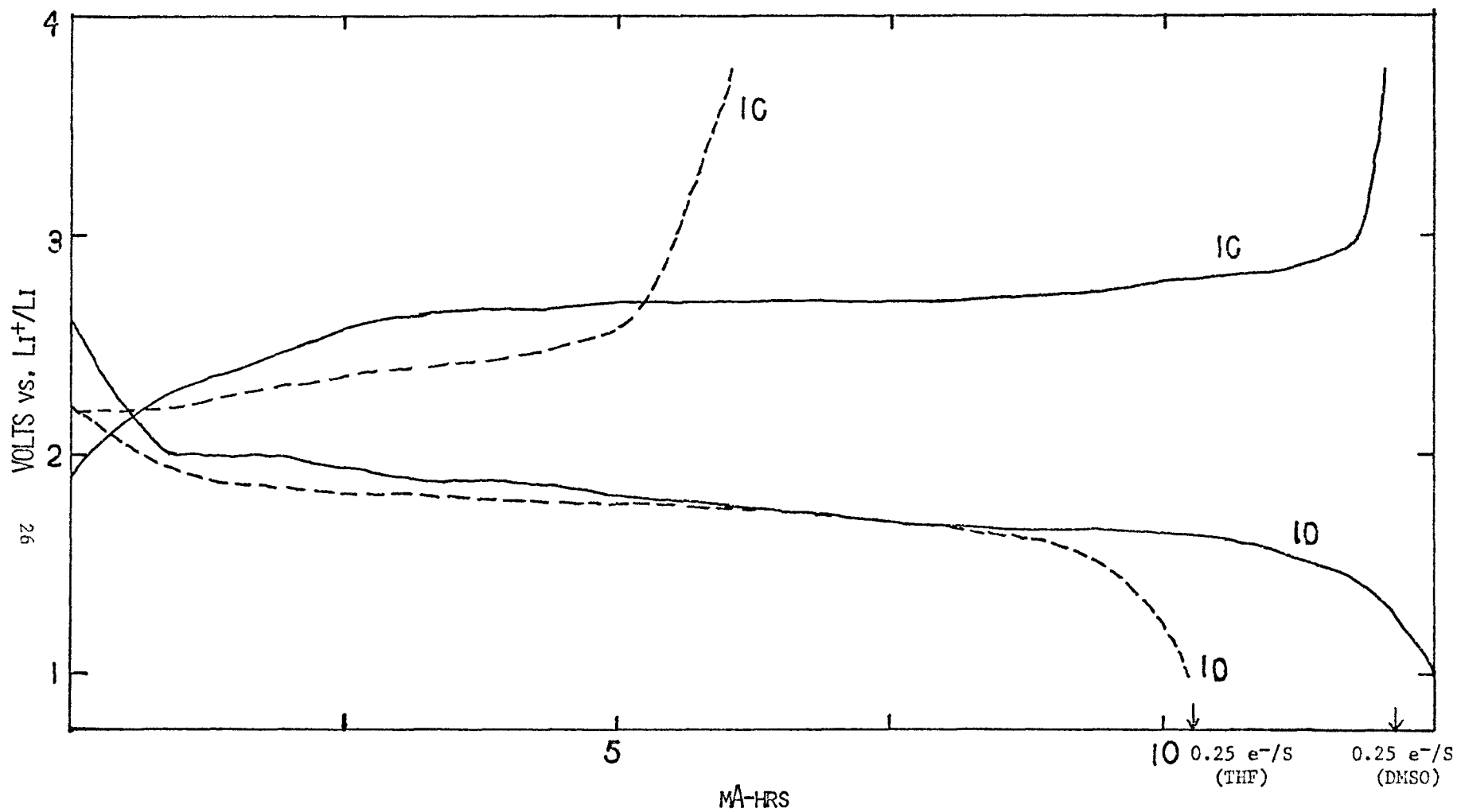
Fig. 7: Galvanostatic cycling of Li_2S_8 solutions containing 1M $LiClO_4$ on a carbon cloth working electrode.
i = 1 mA/cm^2. Voltage limits = 1.0 and 3.7V vs. Li^+/Li. (———) 1.65M S in DMSO; (———) 1.5M S in THF.
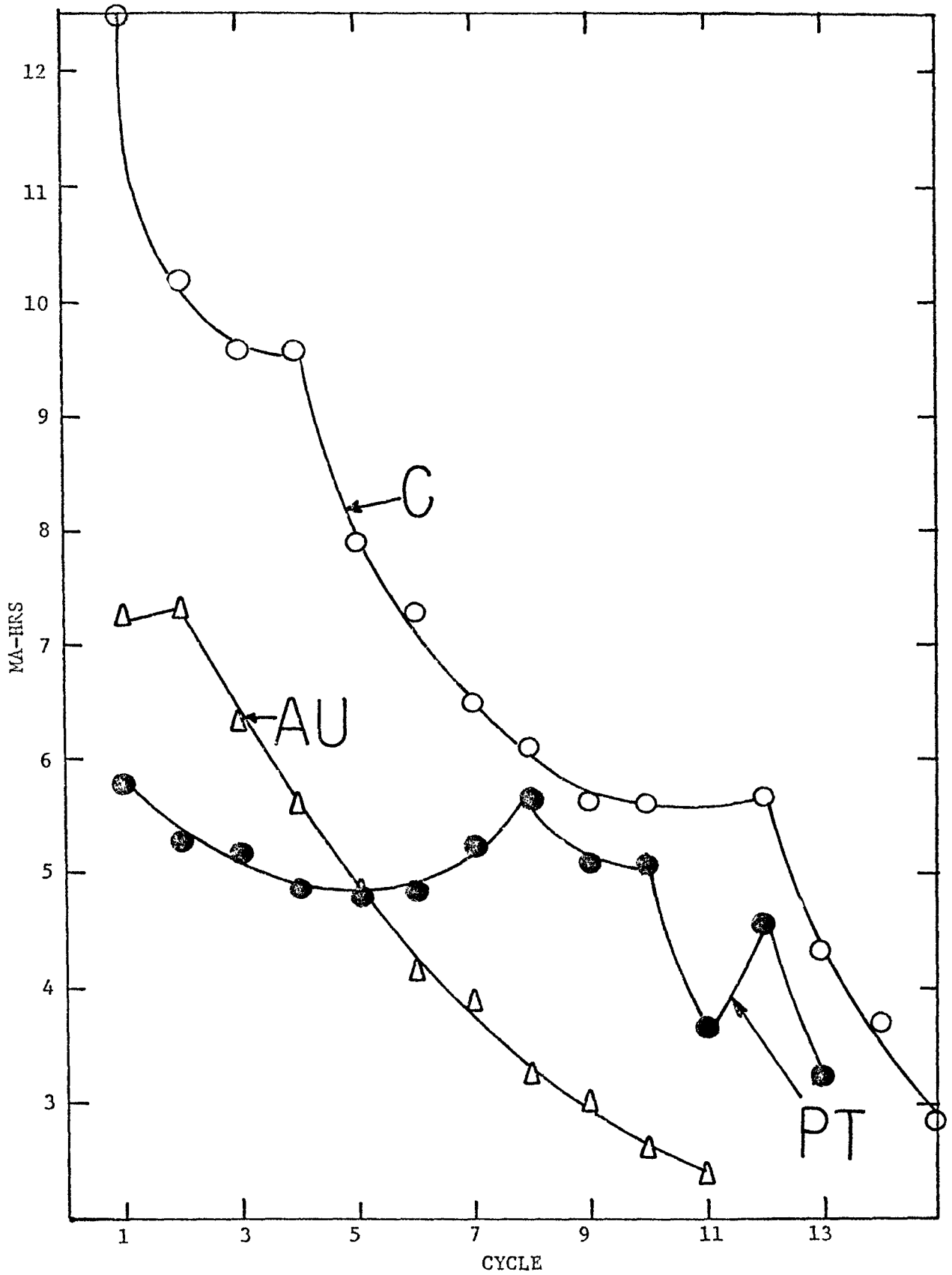
Fig. 8: Discharge capacity versus cycle of 2M S as Li_2S_8 in DMSO, 1M $LiClO_4$. Current = 1 mA/cm^2.

In this experiment, the true capacity of the solution on the
first discharge (at least) was made ambiguous by the presence of
solution impurities which reduce between 1 and 1.2V. The experiment
was thus repeated with the electrochemically purified DMSO, 1M LiClO$_4$.
This solution was made 1.67M in S, electrochemically, as described in
the previous section. The working electrode was C cloth. The cell
was cycled at 1 mA/cm^2 between limits of 1.0 and 3.7V vs. Li$^+$/Li.

The results of the first discharge and charge are shown in
Figure 7. The stoichiometry on the first discharge is slightly
greater than 0.25 e$^-$/S. The experiment was continued for 15 cycles.
Each cycle showed less capacity than the previous one. The variation
of capacity with cycle is shown in Figure 8. This is at least partially
an artifact, induced by distribution of the polysulfides into the
counter electrode compartments. But some other mechanism of capacity
loss with cycle may be operating, and this requires continued investi-
gation.

For a solution of this concentration, the rate of discharge
employed obviously gave significant concentration polarization. As
determined in the earlier experiment, slow discharge occurs at two
plateaus at $\sim$2.7 and 2.2V. This was verified in the present experiments
for one cycle, which was run at 0.3 mA/cm^2.

A sample was withdrawn from the working electrode compartment
following the first discharge. Chemical analysis showed the S^{-2}/S^0
ratio to be $\sim\frac{1}{4}$, so that the average order of discharge product was
S$_5^{-2}$. The spectrum of a 1:50 dilution of the discharge product was
similar to that of the starting solution (Figure 9) with regard to
the values of λmax. The absorbances were nevertheless higher in the
discharged solution.

The gross discharge reaction therefore appears to be

$$S_{24}^{-2} \rightarrow 4.8 \; S_5^{-2} \tag{6}$$

which would correspond to a stoichiometry of 0.33 e$^-$/S. That our
experimental stoichiometry turned out slightly lower than this is
probably a result of diffusion of polysulfide species to the counter
electrode compartment during the discharge. This loss mechanism was
confirmed by analysis for total S in the working electrode compartment
before and after discharge. A summary of the analytical results
contained in this experiment is given in Table 4.

    ● Galvanostatic Cycling of S in THF. A solution 1.5M in S
was prepared electrochemically in THF, 1M LiClO$_4$. The cycling conditions
were the same as for DMSO. The first discharge occurred at about

Table 4

Results of S Analysis Before and After Discharge of

Li_2S_n in DMSO, 1M $LiClO_4$

	$[S]_{tot}$ Before	$[S]_{tot}$ After	$[S^{-2}]$ Before	$[S^{-2}]$ After	$[S_n^{-2}]$ Before	$[S_n^{-2}]$ After
Chemical Analysis	1.67M	1.0M*	0.07M	0.21M	$S_{23.8}^{-2}$	$S_{4.8}^{-2}$
Visible Absorption Spectrum	0.3M	0.87M	0.052M	0.16M	–	–

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* Probably low because of diffusion of some of the polysulfides into the counter electrode compartment.
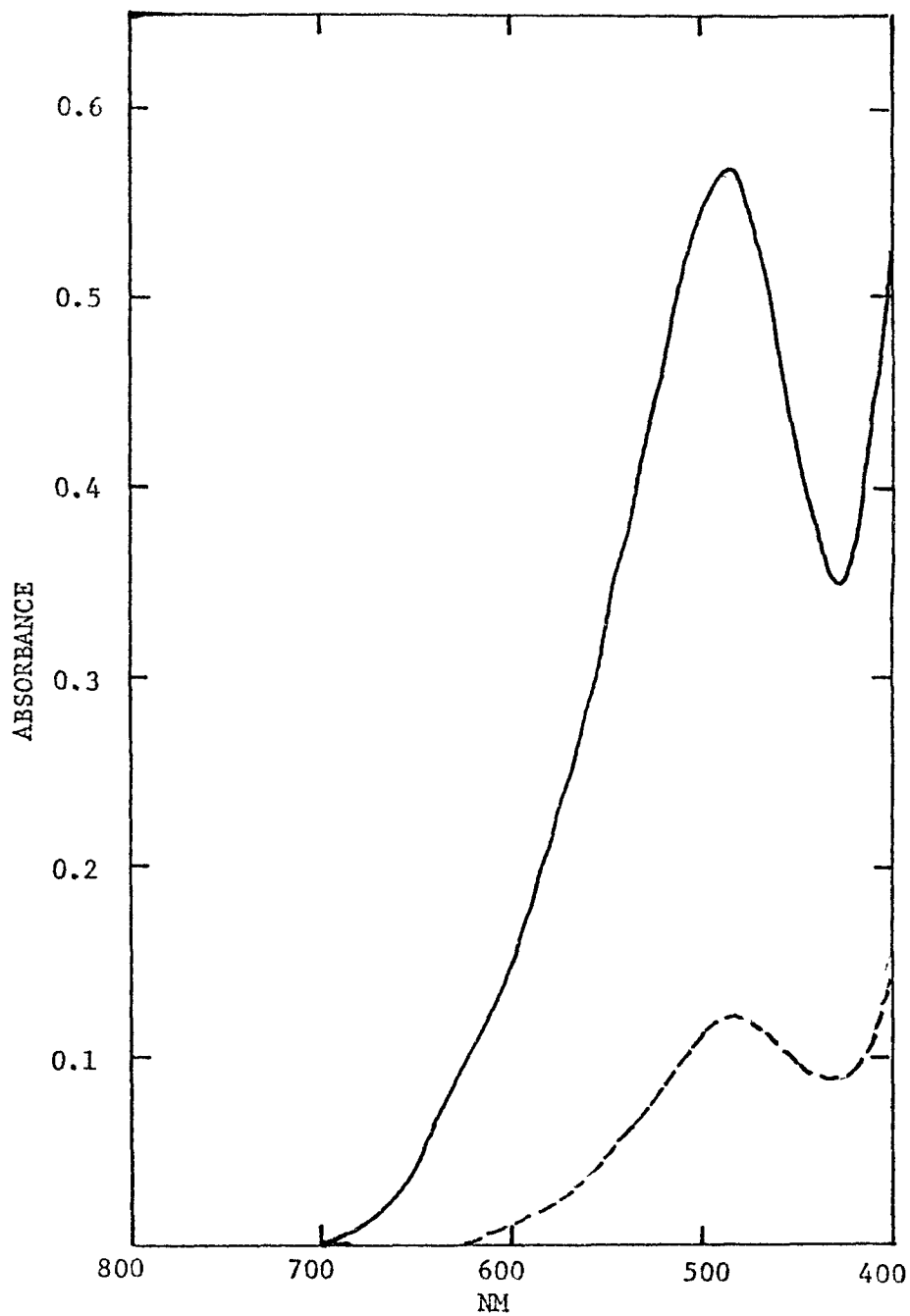
Fig. 9: Visible absorption spectra of Li_2Sn in DMSO, 1M $LiClO_4$
(----) before discharge and (——) after discharge (see
Table 4). Solutions were diluted 1/50 before recording
spectra in a 0.1 cm cell.

1.75V, and the capacity approached 0.25 e⁻/S (Figure 7). Charging occurred at 2.25 – 2.5V, and was only about 60% of the first discharge in capacity. The cell was operated for 73 cycles. The capacity decreased with each cycle until, by the 73rd cycle, the capacity had dropped over 90%. It was later discovered that THF could wet the walls of the Teflon coulometry cell, and that much active material was lost during cycling by seepage out the top. In addition, diffusion through microporous Teflon or Celgard separator is much more rapid for THF than for DMSO. Both effects contribute to the loss of capacity with cycle, so, as with DMSO, this loss is probably not a chemical problem.*

 • Galvanostatic Cycling of S in MA. A solution of 0.2M S in MA, 1M LiClO₄ was continuously cycled between 1.2 and 3.7V. Between these limits, an average discharge capacity of 0.25 e⁻/S was obtained over 5 cycles at 4 mA/cm². The average charging potential was 3.7V, and the discharge potential was about 1.5V. Current-potential curves of the solution in its initial and discharged state showed that, following discharge, little or no material reducible positive of 1.2V was present (Figure 10).

The cycling studies described above indicate that low order polysulfides are difficult to reduce. This, of course, limits the capacity of a practical battery. More detailed studies of the mechanism of polysulfide reduction, described in the next section, can lead us to methods for reducing these species.

3.   Redox Processes of Polysulfides in DMSO

The apparent limitation of cycling capacity of polysulfide solutions to 0.25 – 0.33 e⁻/S, demonstrated in the previous section, must be overcome if the soluble S cathode is to become practical. Since the last semiannual report, detailed mechanistic investigations of the redox reactions of polysulfides in DMSO have been undertaken. In particular, we have sought to understand the redox reactions of individual polysulfides between the limits of 1.0 and 4.0V vs. Li⁺/Li, in order to find which species lead to insoluble or electrochemically unreactive products.

The main techniques for studying the gross redox reaction mechanisms were potentiostatic coulometry, cyclic voltammetry and visible spectroscopy. Typically, dilute polysulfide solutions were

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* We are currently trying to ameliorate this problem by using less porous separators, by using the polysulfide solution to be tested in all three compartments of the coulometry cell, and/or by increasing the rate of cycling.
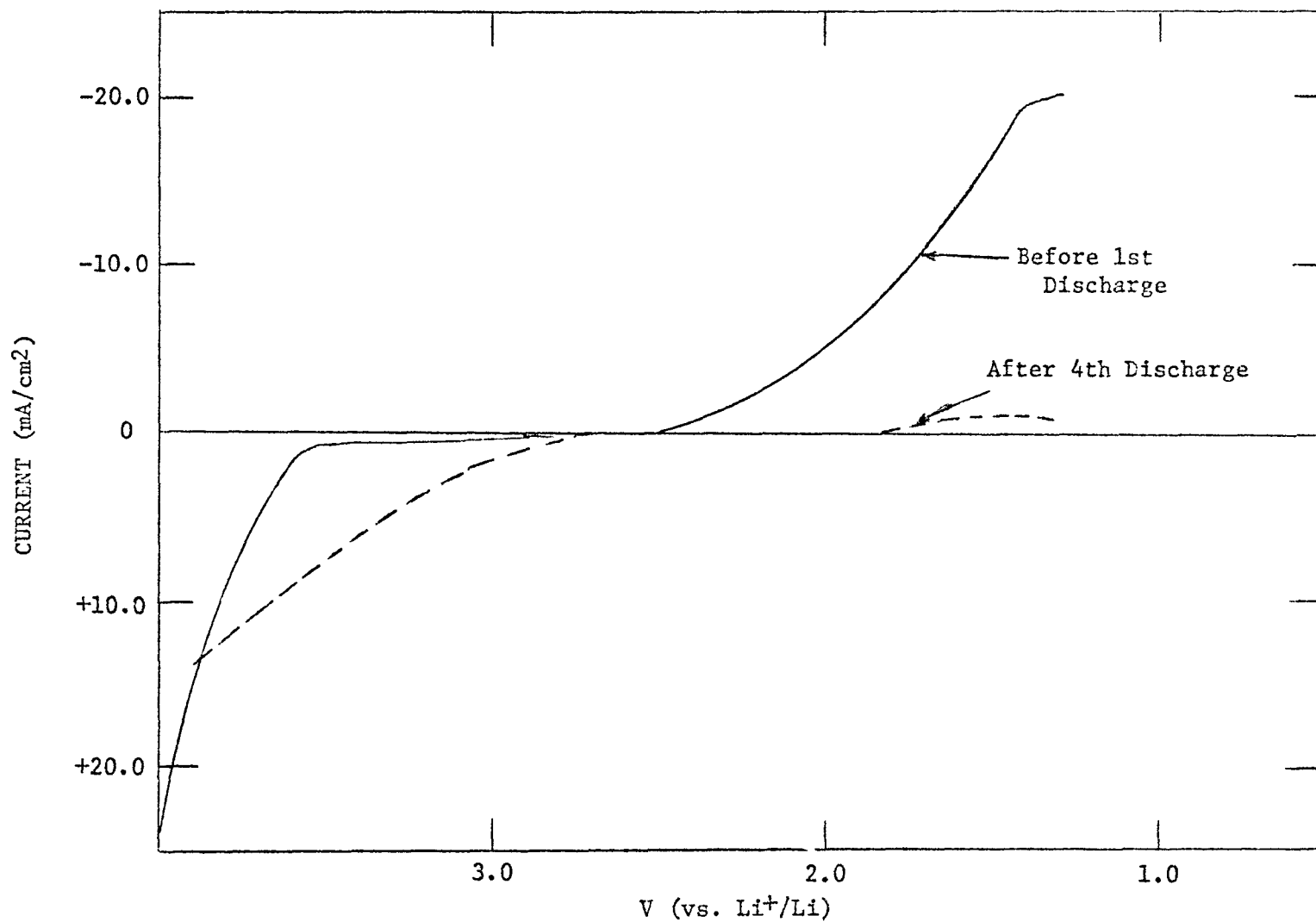
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Fig. 10: Current-potential curves of MA, 1M LiClO4, 0.2M S (electrochemically dissolved as $S_8^=$), on a Teflon bonded C working electrode. Minor corrections have been made for solvent background currents.

used so that spectra and cyclic voltammograms could be recorded during the course of a potentiostatic oxidation or reduction without the necessity of prior dilution.

● <u>Electrochemistry of S_8</u>. The redox reactions of S_8 in DMSO have been studied by Sawyer and co-workers (7,8) and very recently by Delamar (10,11). The cyclic voltammogram and probable assignments of redox peaks of 5 mM S in DMSO, 1M $LiClO_4$ is shown in Figure 11. As described earlier (6), a substrate effect resulting from adsorption of products onto the electrode occurs for Pt and Au, but not for C. Therefore, to eliminate these complications, vitreous C was chosen for the cyclic voltammetry working electrode for all of these studies.

S_8 is only sparingly soluble in DMSO. It shows no oxidation reactions out to 4.0V vs. Li^+/Li. The most facile reduction is $S_8 \rightarrow S_8^{-2}$, which occurs at $E_{max} = 2.7V$. This is associated with an oxidation wave ($E_{max} = 3.1V$), corresponding evidently to $S_8^{-2} \rightarrow S_8$. Although Sawyer indicates that this peak corresponds to. a general oxidation

$$S_n^{-2} \rightarrow n/8 \ S_8 + 2e^-, \tag{7}$$

the reaction as written seems rather improbable: S_8 has an octagonal structure, while S_n^{-2} species are linear chains. Chronopotentiometric experiments have shown this oxidation to involve two electrons (7). It is more likely that the S^o species which is produced at this electrode would subsequently react with a polysulfide ion, i.e.,

$$S_n^{-2} \rightarrow S_n^{\ o} + 2e^- \tag{8}$$

$$S_n^{\ o} + S_m^{-2} \rightarrow S_{n+m}^{-2} \tag{9}$$

This reaction sequence will be discussed in more detail below.

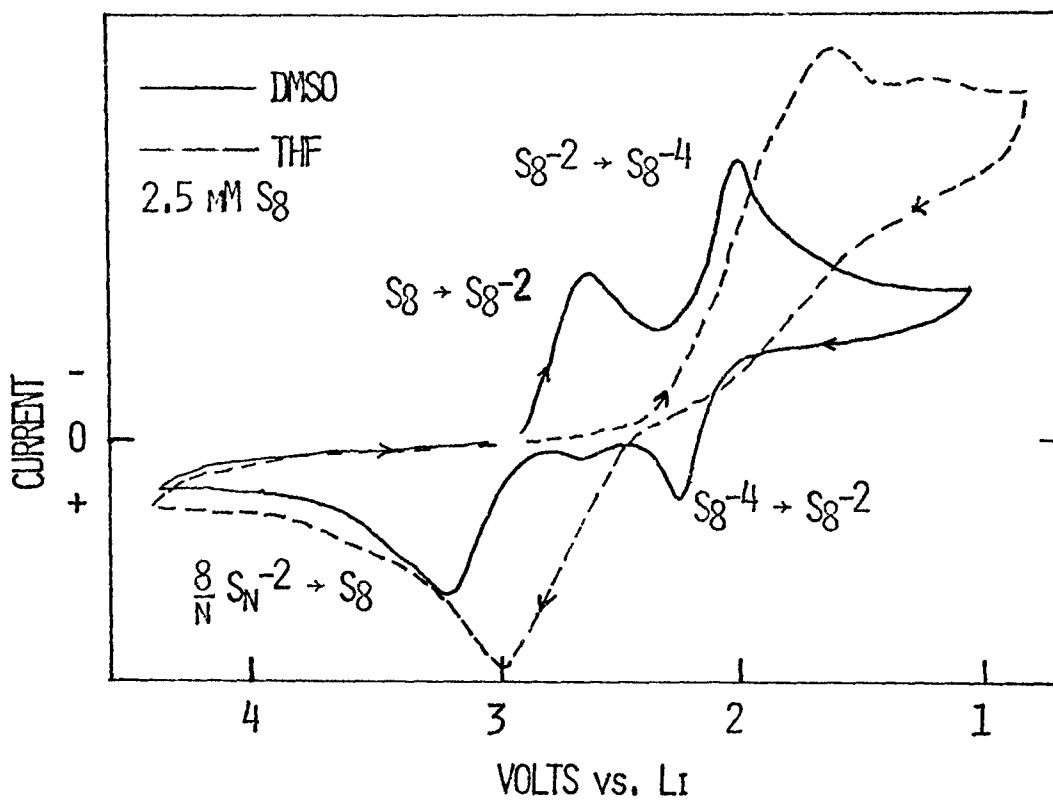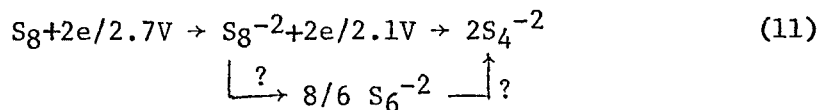The second reduction peak in S_8 solutions in DMSO occurs at $E_{max} = 2.1V$. It has been assigned to

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Fig. 11: Cyclic voltammograms of S_8 in DMSO and THF, 1M $LiClO_4$. Assignments are according to Sawyer and co-workers (8).

$$2e^- + S_8^{-2} \rightarrow S_8^{-4} \tag{10}$$

S_8^{-4} is unstable, so that the reoxidation peak at 2.3V is considerably smaller than the reduction peak. S_8^{-4} breaks down to S_4^{-2}. S_4^{-2} in turn reacts with S_8^{-2} to form S_6^{-2}. In dilute solutions, S_6^{-2} is in equilibrium with substantial S_3^-. S_3^- has a characteristic absorption at $\lambda_{max} = 618$ nm, and its presence is easily identified.

A quantitative reduction of the 5 mM S_8 solution was carried out. The DMSO solution was first reduced at 2.5V (vs. Li), the $S_8 \rightarrow S_8^{-2}$ potential. The solution was blue throughout this initial reduction, and the spectrum revealed the existence of both S_8^{-2} and S_3^- species. After the passage of 0.8 e^-/S_8, the current had dropped to 0.1 mA/cm^2. To increase the rate, the electrolysis was continued at 2.0V ($S_8^{-2} \rightarrow S_8^{-4}$). After an initial drop in the S_3^- absorption, S_3^- regained a nearly constant concentration during the passage of an additional 3 e^-/S_8. The peak at 490 nm (S_8^{-2}) gradually moved to 420 nm (S_4^{-2}) during the course of this reduction. Toward the end of this reduction, a new peak at 340 nm appeared (S_2^{-2}?). The reduction was continued to 4.2 e^-/S_8 at 1.7V, at which point the current had dropped essentially to zero. By this time, as the spectrum shows, the solution had become pale yellow. The absorption spectra are shown in Figure 12.

The reduction of S_8 in DMSO proceeded according to the mechanism already published in the literature (7,8):

$$S_8 + 2e/2.7V \rightarrow S_8^{-2} + 2e/2.1V \rightarrow 2S_4^{-2} \tag{11}$$
$$\llcorner \overset{?}{\longrightarrow} 8/6\ S_6^{-2} \longrightarrow \urcorner?$$

Although S_6^{-2} can be identified spectrally during the course of the reduction ($\lambda_{max} = 475$ nm), the route leading to its formation is not certain. Sawyer (8) assumes the equilibrium
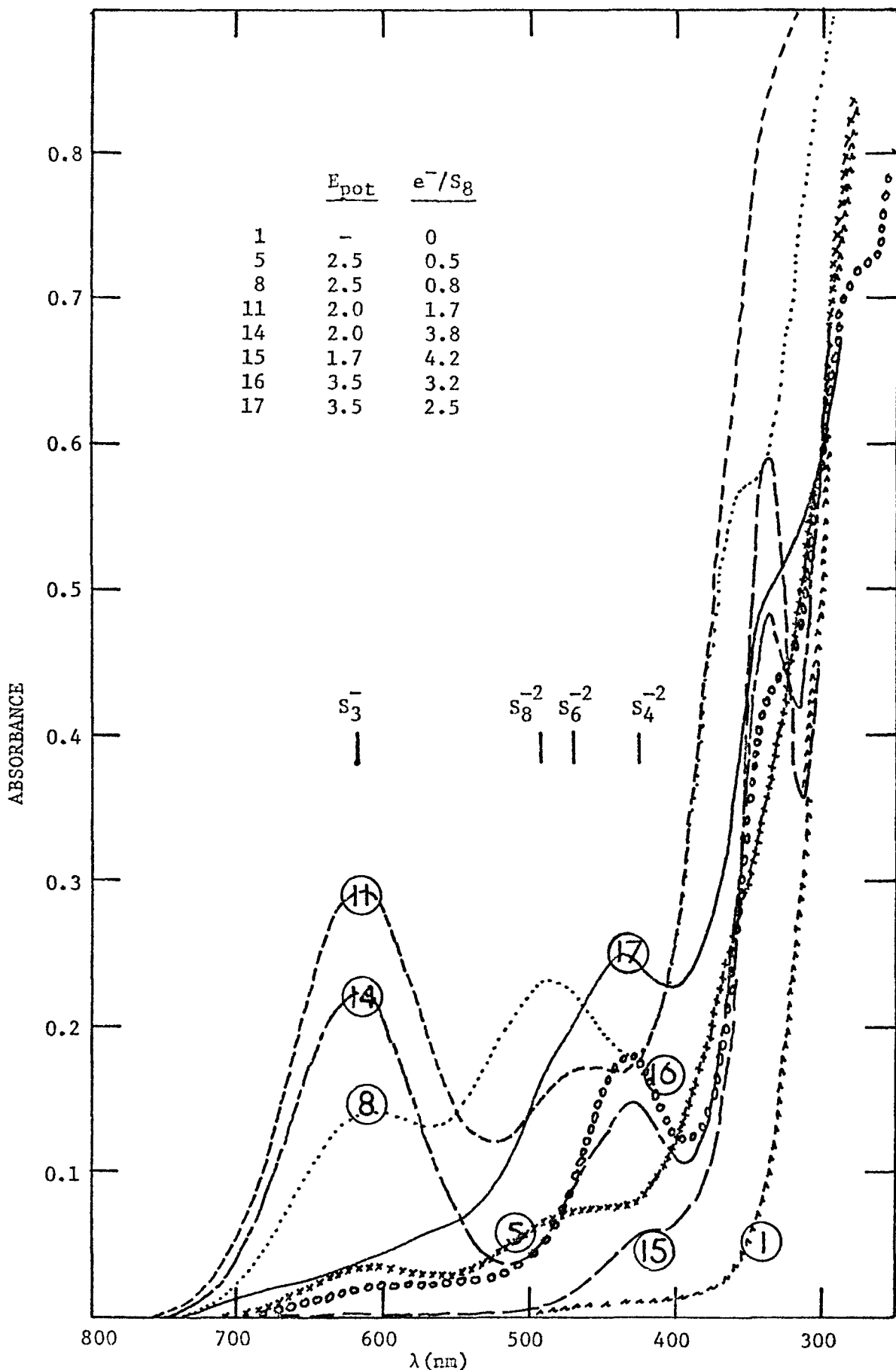
$$S_8^{-2} + S_4^{-2} \rightleftharpoons S_6^{-2} \tag{12}$$

Fig. 12: Spectra of potentiostatic reduction products of 0.01M S as S_8 in DMSO, 1M $LiClO_4$ on a C electrode.

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on the basis of visible spectroscopic studies of mixtures of Na_2S_4 and Na_2S_8.

We were unable to determine directly from these experiments the reduction potentials of S_6^{-2} and S_3^{-2}. The intermediacy of the S_6^{-2} species (determined spectroscopically) did not appear to prevent the reaction from proceeding to the S_4^{-2} level, at 2.1V $(S_8^{-2} \rightarrow S_8^{-4})$ so it would be a safe assumption that at least S_6^{-2} also reduces at around 2.1V. This will be verified in a later experiment.

• Electrochemistry of S_8^{-2}. The cyclic voltammogram of S_8^{-2} is very similar to that of S_8 with the exception of the $S_8 \rightarrow S_8^{-2}$ reduction at 2.7V. In S_8^{-2} solutions in DMSO, only a very small area of reduction is present at this potential on the first cathodic sweep, presumably arising from the equilibrium

$$4S_8^{-2} \; \rightleftharpoons \; 4S_6^{-2} + S_8 \qquad (13)$$

A typical cyclic voltammogram is shown in Fig. 15.

In order to determine the effect of concentration on the S_8^{-2} spectrum and redox behavior, the following experiment was carried out:

Solutions of Li_2S_8 with total S concentrations of 1.0, 0.5, 0.2, 0.1, 0.05 and 0.02M were prepared from the reaction of Li_2S and S. Their spectra were recorded before and after addition of 1M $LiClO_4$ as a supporting electrolyte. The cyclic voltammograms of the solutions containing 1M $LiClO_4$ were then recorded using a finely polished vitreous C working electrode. Finally, the 0.05M solution was quantitatively reduced on a carbon cloth electrode at 2.1V vs. Li^+/Li, and the absorption spectrum and cyclic voltammogram monitored during the course of the reduction. The visible spectrum of Li_2S_8 shows only one peak when [S] $\geq 0.1M$, that at 492 nm, corresponding to S_8^{-2}. At lower concentrations, the 618 nm absorption due to S_3^- grows in. This is presumably due to the equilibria

$$4S_8^{-2} \; \rightleftharpoons \; 4S_6^{-2} \; \rightleftharpoons \; 8S_3^- \qquad (14)$$

These absorption spectra are summarized in Fig. 13. Spectra of solutions of Li_2S_8 containing >2M S also showed only S_8^{-2} absorption. The cyclic voltammograms exhibited no significant changes upon dilution, giving the familiar S redox pattern (as in Fig. 15). Cathodic shifts in peak potentials for the 0.5 and 1.0M S solutions were ascribed to iR drop and diffusional complications arising in very concentrated solutions. Thus, the reduction or oxidation of S_3^- within these voltage limits is not evident.

The reduction of the Li_2S_8 solution containing 0.05M S was carried out at 2.2V vs. Li. The peak at 2.2V corresponding to S_8^{-2} reduction,
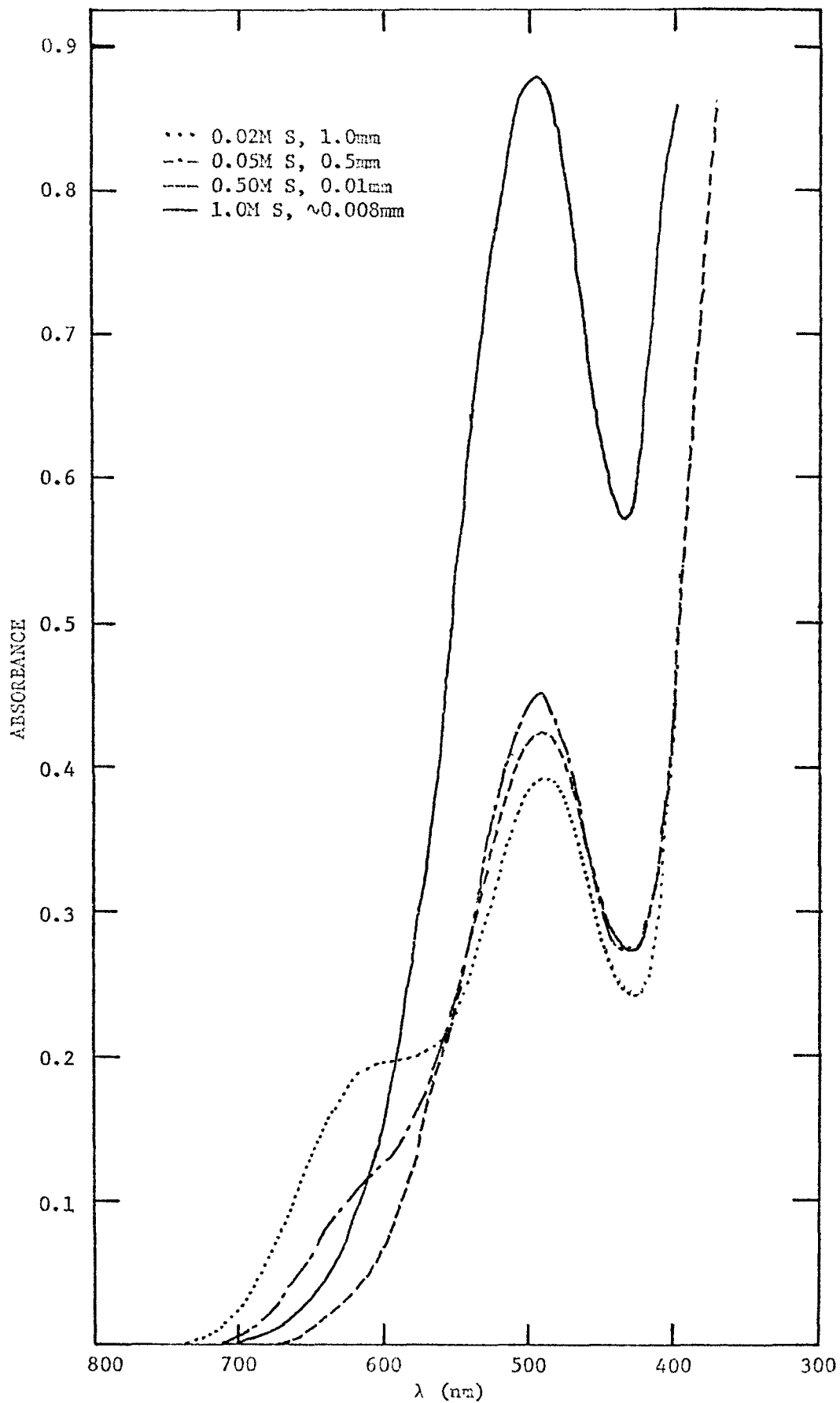
Fig. 13: Spectra of Li₂S₈ in DMSO as a function of concentration.

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seen by sweeping negative from the open circuit potential, is depleted at a stoichiometry of 0.25 e^-/S. The spectrum at this point shows that the solution is about 95% S_4^{-2} and 5% S_3^- (λ_{max} = 430, 620 nm) (Fig. 14). The reduction of neither specie is evident between 1 and 4V vs. Li, although the oxidation wave is relatively unchanged from the original solution.

A low current, possibly due to solvent background impurities, can be maintained at 2.2V. If this current is allowed to pass, then, after an apparent 0.53 e^-/S, the solution has become dark red-brown and the characteristic 420 nm and 618 nm peaks have disappeared, in favor of a structureless tail extending out to beyond 400 nm (Fig. 14). The form of the oxidation wave, observed in the cyclic voltammogram (Fig. 15) changes, and the typical S redox pattern cannot be regenerated, even on subsequent oxidation at 3.1V. We have not determined the exact source of this irreversibility, but it may relate to the reduction of polysulfides with dissolved O_2 and with O_2 present at low levels in the glove box (see below).

A second experiment was carried out to determine the products of S_8^{-2} oxidation. A solution of total S concentration 0.063M was made up at a 1/7 $S^{-2}/S°$ ratio. The major absorption of this solution was at 492 nm, with a shoulder at 618 nm. Potentiostatic oxidation was carried out at E_{max} = 3.1V, as determined by cyclic voltammetry.

There were, however, several serious ambiguities in this experiment which became evident in later analysis of the data. First, assigning the absorption at 492 to S_8^{-2}, and the absorption at 618 nm to S_3^-, the total S concentration calculates to be only 0.011M. Chemical analysis, however, gives 0.063M S. Thus, a portion of the S seems to be complexed as non-absorbing species in the visible.

The cyclic voltammogram of this solution shows about four times as much $S_8 \rightarrow S_8^{-2}$ reduction as $S_8^{-2} \rightarrow S_8$ oxidation. Evidently, the unaccounted for S_8 was complexed with the S_8^{-2}, while some of the Li_2S remained undissolved. This solution, therefore, appeared more S° rich than that used for reduction. Unfortunately, the S^{-2} analysis was not carried out on the solution before electrolysis.

Potentiostatic oxidation of S_8^{-2} + S_8 solution resulted in a change in color to light yellow and the precipitation of sulfur. The absorption spectrum of this oxidized solution had only a tail out to 500 nm (Fig. 16). The cyclic voltammogram of this final solution was similar to that of an S_8 solution (Fig. 17). The total oxidation stoichiometry was only 0.04 e^-/S, based on 0.063M S. Based on 0.01M S as S_8^{-2}, as calculated from the spectrum, this is precisely equivalent to 2.0 e^-/S_8^{-2}.

From this experiment, it appears that the reaction

$$S_8^{-2} \rightarrow S_8 + 2e^- \qquad\qquad (15)$$

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Fig. 14: Spectra of Li_2S_8 (0.05M S) in DMSO, 1M $LiClO_4$, during reduction of 2.1V vs. Li^+/Li

1. Before reduction
2. 0.24 e^-/S°
3. 0.53 e^-/S° (apparent)

40

Fig. 15: Cyclic voltammograms of Li_2S_8 (0.05M S) in DMSO, 1M $LiClO_4$ on vitreous C, 0.1 V/sec, cathodic sweep first. (— —) before reduction; (—·—) after passing 0.24 e^-/S at 2.1V; (— —) after 0.53 e^-/S at 2.1V.

i (MA/CM2)

VOLTS (VS LI)

Fig. 16: Absorption spectra of S_8^{-2} in DMSO, 1M $LiClO_4$ before (——) and after (—–) oxidation at 3.2V vs. Li. Charge passed $\approx 2e^-/S_8^{-2}$. [S] $\approx$ 0.06M.

ABSORBANCE

NM

42

Fig. 17: Cyclic voltammograms of Li_2S_8 in DMSO, 1M $LiClO_4$ before (——) and after (---) oxidation at 3.2V.

Sweep 1

Sweep 2

CURRENT

VOLTS vs. Li^+/Li

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probably occurs, even though the real species undergoing oxidation may be $nS^\circ\cdots S_8^{-2}$. We intend to reinvestigate this reaction using solutions of certain S_8^{-2} stoichiometry, as determined by chemical analysis.

● Electrochemistry of S_4^{-2}. The spectrum of Na_2S_4 (0.0$_{}$M S) in DMSO, 1M $LiClO_4$ shows peaks at 410 nm (S_4^{-2}) and at 618 nm (S_3^-). The cyclic voltammogram of the same solution (Fig. 18) has only a small reduction peak at 2.1V, assumed to be due to higher order polysulfides present as impurities in the Na_2S_4. It is obvious that very little reduction could be carried out on this solution positive of 1V.

The solution was then oxidized quantitatively at 3.1V, using a C cloth electrode. The cyclic voltammograms recorded during the oxidation showed an increase in the reduction peak at 2.2V with increased oxidation of S_n^{-2}. This is the region of reduction of S_n^{-2}, n>4. Little or no reduction at 2.7V was noted on the first cathodic sweep, indicating the formation of negligible (stable) S_8 or other S° species during the oxidation. That these species are observed only during the cyclic voltammetric sweeps indicates that they are present for short times, and are probably dissipated through reaction with solution polysulfide species:

$$S_n^\circ + S_m^{-2} \rightarrow S_{(n+m)}^{-2} \tag{16}$$

The oxidation was continued to the level of S_{16}^{-2}, at which point the cyclic voltammogram indicated that approximately 90% of the oxidizable material had been consumed. It is interesting to note that even at this stage, little material reducing at 2.7V was present on the first cathodic sweep. This indicates that only high order soluble polysulfides are formed. The spectrum of this oxidized solution showed peaks at 460 and 405 nm, and nothing at 618 nm. This pattern is probably characteristic of such high order polysulfides.

Reversal of the current by potentiostating at 2.1V resulted in the reappearance of polysulfides absorbing at 618 nm and 460-470 nm. Thus, the high order polysulfides can successfully be broken down electrochemically into S_n^{-2}, n≤8 and S_3^-. We may conclude from this experiment that S_4^{-2} is oxidizable beyond the S_8^{-2} level. Elemental S is not formed during oxidation, but rather S_n^{-2} >8 species. Thus, in a practical cell, we might hope to oxidize beyond the S_8^{-2} level without precipitating S.

Several experiments on S_4^{-2} were attempted using Li_2S_4 in DMSO, 1M $LiClO_4$ or $LiAsF_6$. Such solutions were so easily oxidized, especially during preparation (Li_2S + S), that the results of these experiments still contain some uncertainties. As these experiments were carried out on dilute solutions, small amounts of dissolved O_2 or O_2 in the Ar atmosphere could cause very great error.*

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*Some S-containing organic solvents are known to deactivate the O_2 gettering agent in the dry train of the glove box.
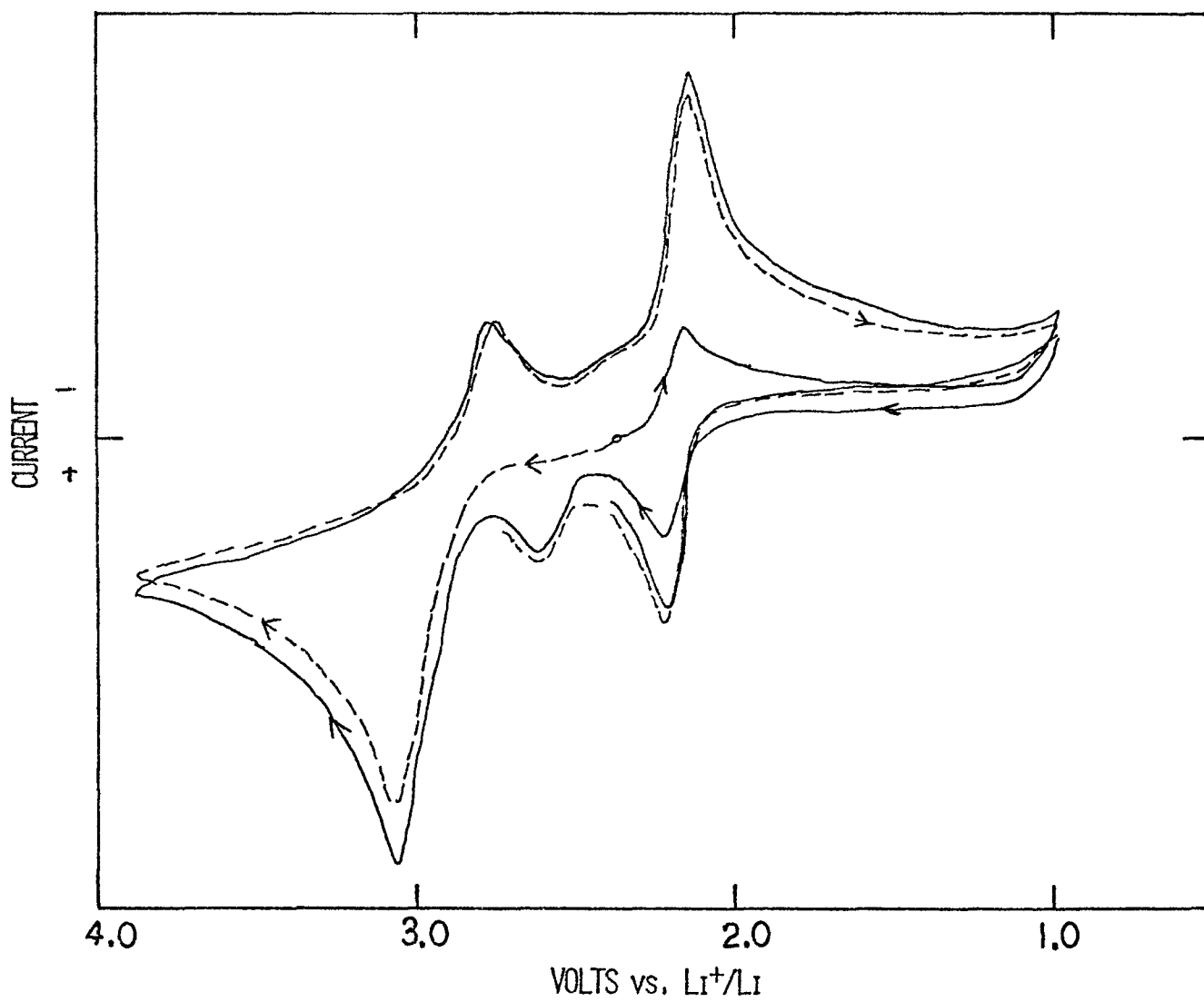
Fig. 18: Cyclic voltammogram of Na_2S_n with n ≈ 4 (0.05M S) in DMSO, 1M LiClO₄. Working electrode = vitreous C; sweep speed = 0.1 V/sec. (———) cathodic sweep first; (– – –) anodic sweep first.

In two experiments in which S_4^{-2} (0.05M S) was to be prepared by adding DMSO to a weighed ratio of $S^{-2}/S°$, the spectrum of the final product indicated a mixture of S_8^{-2}, S_6^{-2} and S_3^-. The combined S calculated from the spectrum was considerably less than that found by chemical analysis. For example, the first solution (Solution #1) made in this way showed a peak at 492 nm instead of 420 nm, and a total (spectral) S concentration, based on S_8^{-2}, of 0.03M. The total chemically analyzed S concentration was 0.060M. A second solution (Solution #2) was made under similar conditions except that Ar was bubbled through the solvent before and during the dissolution process. This solution had maxima at 462 nm and 618 nm. The spectrally analyzed S was 0.07M, while chemical analysis revealed the true S concentration to be 0.079M.

A third solution of S_4^{-2} was made up 0.5M in S. The maxima for this solution were at 438 nm and 618 nm, determined using a 0.1 cm cell. The positions of the maxima were unchanged on 1/10 and 1/50 dilution. On the solution which was diluted by 1/50, the maximum moved to 460 nm after the cuvette had been opened to the atmosphere for 10 minutes.

A more controlled observation of the reaction of polysulfides with O_2 was undertaken. The spectrum of Na_2S_4 was monitored in an open cuvette as a function of time. The peak which is originally at 410 nm moves gradually to 480 nm. Then, the solution eventually loses all color, and yields no visible absorption. The 618 nm peak moves through 470 nm $(S_6^{-2} \rightleftharpoons 2S_3^-)$. Using the values of ε for S_4^{-2} and S_6^{-2}, in about 1 hour the total (visibly-absorbing) polysulfide S concentration had dropped from 0.031M to 0.016M. Most of this must have been lost by oxidation of S^{-2} fragments to SO_n^{-2}. This increased the polysulfide order while decreasing the total S concentration.
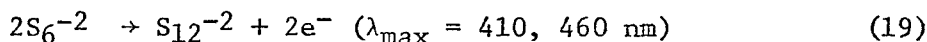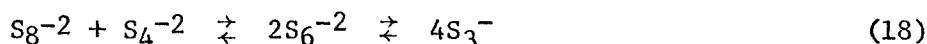
Because the problems of these side reactions have not been solved to our satisfaction, we will just summarize qualitative results of the oxidation and reduction of Solutions #1 and #2. Stoichiometries were generally irreproducible.

Solution #1 (λ_{max} = 492) was completely reduced at 2.1V. The cyclic voltammogram of the reduced solution showed no reduction positive of 1.0V. The stoichiometry was about 0.25 e$^-$/S, based upon the total S analysis. Reoxidation of this solution (3.1V) resulted first in a shift of the major absorption from 430 nm to 478 nm, then into a change of the visible spectrum to two peaks at 410 and 460 nm (no 618 nm). The latter spectrum is the same as that noted for the oxidation products of Na_2S_4 (see above). The final $S^{-2}/S°$ ratio, determined by chemical analysis, was ∿1/11.

Solution #2 (λ_{max} = 462) required only 0.1 e$^-$/S for complete reduction at 2.1V. Reoxidation of this solution again yielded the

two-peaked spectrum (410, 460 nm). Reduction of this solution at 2.1V was carried out, resulting to a product absorbing at 460 nm and 618 nm.

To summarize, it is difficult to reduce S_4^{-2} at a potential positive of 1V vs. Li^+/Li. S_4^{-2} is easily oxidized however, first to S_6^{-2}, then to S_n^{-2}. Whether S_8^{-2} was also formed was not determined; in the samples taken, the longest wavelength S_n^{-2} absorbance was 479 nm before the two-peaked spectrum (410, 460 nm) appeared. The following oxidation sequence seems consistent with the (qualitative) data:

$$2S_4^{-2} \rightarrow S_8^{-2} + 2e^- \quad (3.1V) \tag{17}$$

$$S_8^{-2} + S_4^{-2} \; \rightleftharpoons \; 2S_6^{-2} \; \rightleftharpoons \; 4S_3^- \tag{18}$$

$$2S_6^{-2} \rightarrow S_{12}^{-2} + 2e^- \quad (\lambda_{max} = 410, \; 460 \; nm) \tag{19}$$

Spectroelectrochemical results on the oxidation of chemically prepared S_6^{-2} solutions are not yet complete.*

- **Electrochemistry of S^{-2}.** Experiments have been carried out to determine what species are produced when S^{-2} is oxidized, and to measure the electron stoichiometry of the oxidation reaction. Sawyer and co-workers (7,8) claim that all polysulfide species are oxidized up to S_8 by a reaction of overall stoichiometry

$$nS_{8/n}^{-2} \rightarrow S_8 + 2e^- \tag{20}$$

on the basis of cyclic voltammetry and chronopotentiometry of S solutions in DMSO. As mentioned above, we feel that for lower order polysulfides a reaction sequence

$$S_n^{-2} \; \underset{\rightarrow}{-2e^-} \; (S_n^\circ) \; \underset{\rightarrow}{S_m^{-2}} \; S_{n+m}^{-2} \tag{21}$$
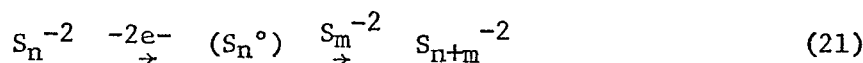
seems more likely than reaction 20.

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*It should be noted that Kovacova and Zezula (26) have reported the reduction of S_4^{-2} as well as S_2^{-2} on Hg at ∿2.5V on the Li scale. In their opinion, the reaction is catalyzed at the electrode surface, through the intermediacy of an Hg – S complex:

$$S_n^{-2} + Hg \; \rightleftharpoons \; S_{n-1}^{-2} + Hg - S$$

$$2e^- + Hg - S \rightarrow Hg + S^{-2}$$
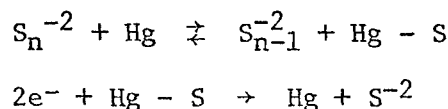
Thus, reduction of S_4^{-2} in nonaqueous solvents may be contingent on finding proper catalytic electrode.

A solution of DMSO, 1M $LiClO_4$ was made 0.05M in Li_2S, only a portion of which dissolved. The cyclic voltammogram of such a solution is shown in Fig. 19. No reduction activity can be discerned on scanning negative from open circuit, and a large area of oxidation ($E_{max} = 3.5V$) is evident on scanning in the opposite direction. On sweeping through the area of oxidation, the solution around the vitreous C working electrode turns green, probably indicating the formation of S_3^-.

The solution was next oxidized potentiostatically at 3.1V using a C cloth working electrode. Absorption spectra and cyclic voltammograms were recorded during the oxidation.

The solution around the working electrode turned immediately green when the oxidation began. At <0.5 e^-/S° taken from the solution, some S^{-2} still remained undissolved. The spectrum (Fig. 20) showed maxima at 420 nm and ~ 600 nm. Interestingly, the spectrum of K_2S_2 (27) also shows only these two peaks, so the 420 nm peak could correspond to S_2^{-2} as well as to S_4^{-2}. At 0.8 e^-/S, the spectrum had changed to $\lambda_{max} = 460$ nm and 618 nm, and all of the S had gone into solution. Up to 1.0 e^-/S, the 460 nm peak shifted slightly to longer wavelengths, and the 618 nm peak decreased. Above 1 e^-/S, the 460 nm peak decreased, and a new peak at 405 nm appeared (no 618 nm). The oxidation was terminated at 1.5 e^-/S, at which point the current had dropped to a very low value. The cyclic voltammogram showed that oxidizable material was at least 80% depleted at this point.

Based on reaction 21, logical first steps of the oxidation sequence would be

$$S^{-2} \xrightarrow{-2e^-} S^\circ \xrightarrow[\text{very fast}]{S^{-2}} S_2^{-2} \to S_2^\circ \xrightarrow{S^{-2}} S_3^{-2} \qquad (22)$$
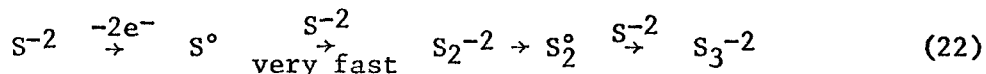
No S_4^{-2} is seen to accumulate in solution, but rather indications are that S_6^{-2} forms rather readily. A plausible explanation for this is the extreme stability of S_3^- in DMSO. This may favor the one-electron oxidation of S_3^{-2}.

$$S_3^{-2} \xrightarrow{-1e^-} S_3^- \rightleftarrows 1/2 \; S_6^{-2} \qquad (23)$$
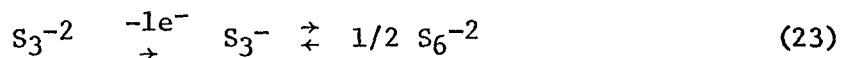
The final oxidation product contained no S_3^-; it is therefore unlikely that it contains any S_4^{-2}. It is very possible that competing (chemical) oxidations of polysulfides rendered our oxidation stoichiometries too low in this experiment. This would leave open the possibility that the end product is a long chain polysulfide, similar to that formed by the oxidation of S_4^{-2}. Since S and S^{-2} analyses were not performed during this experiment, we have no way of estimating the loss of S by such chemical pathways.

We see, though, that the oxidation of S^{-2} occurs much more smoothly than reduction of low order (S_4^{-2}) polysulfides to S^{-2}. This is an
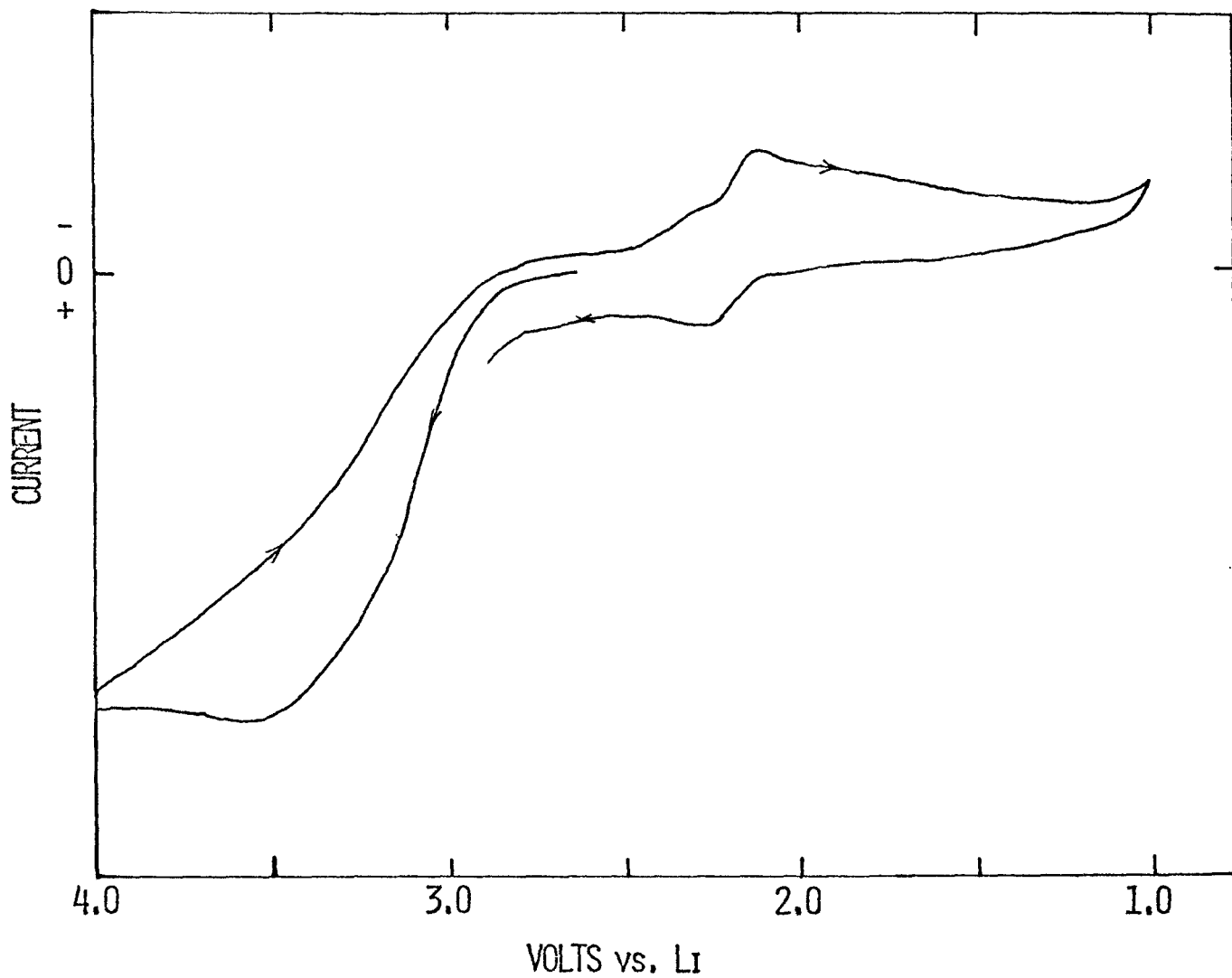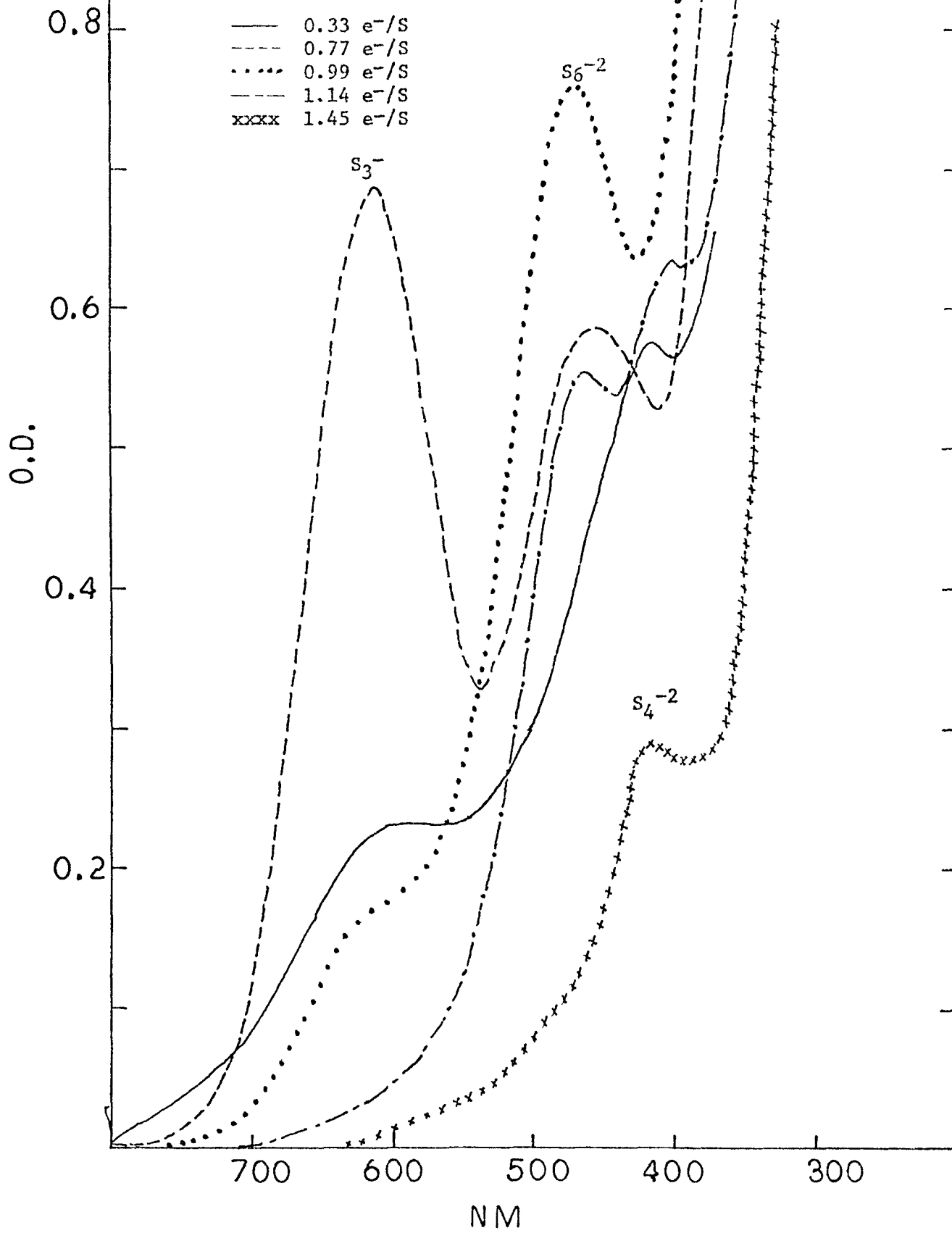
Fig. 19: Cyclic voltammogram of saturated Li_2S in DMSO, 1M $LiClO_4$. Vitreous C working electrode; Sweep speed = 0.1 V/sec; T = ambient.

Fig. 20: Spectra of 0.05M Li_2S in DMSO, 1M $LiClO_4$, during oxidation at 3.1V vs. Li^+/Li.

——— 0.33 e^-/S
– – – 0.77 e^-/S
· · · · 0.99 e^-/S
– · – 1.14 e^-/S
xxxx 1.45 e^-/S

S_3^-
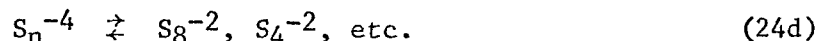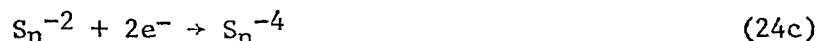
S_6^{-2}

S_4^{-2}

O.D.

NM

important conclusion, as it narrows the problem of constructing a workable cathode to the reduction of S_4^{-2}.

4.   Redox Processes of Polysulfides in THF

The spectra and redox behavior of polysulfides in THF are quite different from those in DMSO. To date, only a qualitative experiment on the reduction of S_8 in THF has been carried out. As the first reduction peak is at 2.0V in this solvent, the entire reduction was carried out at this potential. This potential also impinges upon the second reduction process. Unlike DMSO, the solution turns yellow during the reduction. Little or no S_3^- is produced, as this species is apparently destabilized in THF.

During the reduction, a spectrum was produced very similar to that of high order polysulfides in THF presented above (Fig. 2): The 550 nm peak is replaced by a tail out to 650 nm, but the shoulder at 410 nm is still present. Distinct peaks for S_6^{-2} and S_8^{-2} were not observed. The solution turned cloudy during the course of the reduction.

It is likely from the results of the previously-recorded solubility studies that long-chain polysulfides are especially favored in THF. Therefore, a likely reduction sequence in THF is

$$2e^- + S_8 \rightarrow S_8^{-2} \tag{24a}$$

$$S_8^{-2} + S_8 \rightleftharpoons S_{16}^{-2} \tag{24b}$$

$$S_n^{-2} + 2e^- \rightarrow S_n^{-4} \tag{24c}$$

$$S_n^{-4} \rightleftharpoons S_8^{-2}, S_4^{-2}, \text{ etc.} \tag{24d}$$

This sequence is, of course, conjectural. However, Na_2S_4 has low solubility in THF, and gives rise to a light yellow solution. This solution eventually deteriorates, giving a white precipitate and a darker yellow solution, probably

$$nS_4^{-2} \rightleftharpoons 4S^{-2}\downarrow + S_n^{-2} \tag{25}$$

The cloudy solution could be caused by Na_2S or Na_2S_4 precipitating.

IV. SUMMARY AND CONCLUSIONS

Research has been carried out with the objectives of finding a suitable soluble S electrolyte and understanding polysulfide redox reactions in these electrolytes. In addition, some studies of the Li electrode have been undertaken on a separate program.

Sulfur Solubility. In this report period we have studied Li_2S_n formation and solubility in nonaqueous solvents. Polysulfide synthesis was accomplished in situ both electrochemically and by the reaction of Li_2S with $S°$. Using the latter technique we have demonstrated that concentrated solutions of polysulfides of order >8 can be formed in THF and in DMSO. As limiting values, 9.6M S was obtained in DMSO as $\sim Li_2S_{10}$, and 12.25M S was dissolved in THF as $\sim Li_2S_{12}$. Using electrochemical dissolution, $\sim 2M$ S as Li_2S_{24} was created in DMSO. The spectra of these solutions are characteristic of mixtures of S_6^{-2} and S_8^{-2}, and it is postulated that these anions complex (nonabsorbing) S_8 species.

These solutions are quite viscous and may present mass transfer problems when used in a practical battery. Nevertheless, these high concentrations and levels of oxidation are very encouraging with respect to energy density, approaching $S°$ in the charged state.

Sulfur Electrode Capacity. Solutions of 1-2M Li_2S_n in DMSO and THF have been repeatedly reduced and oxidized on a C electrode at constant current between the limits of 1.0 and 4.0V vs. Li^+/Li. Background capacity due to impurities in the electrolyte has been eliminated by cleaning the electrolyte electrochemically before introducing the Li_2S_n. Stoichiometries of 0.25-0.33 e^-/S were obtained on the first discharge in both solvents. In DMSO at <1 mA/cm^2, about 0.05 e^-/S was obtained, on discharge, at 2.7V, the potential of $S_8 \to S_8^{-2}$. The remainder of the discharge in DMSO, and the entire discharge in THF, occurred at $\sim 2.2V$.

In DMSO, the total S and S^{-2} concentrations were assessed by chemical analysis before and after the aforementioned solution of 2M S as Li_2S_{24} was discharged. The precise stoichiometry turned out to be

$$S_{24}^{-2} \to 4.8\ S_5^{-2} \tag{1}$$

From this experiment and from the previously measured solution capacities, it can be concluded that reduction of S_n^{-2} of n<5 is a difficult step which potentially limits cathode capacity. As S_4^{-2} is reducible on Hg in basic aqueous solution at $\sim 2.5V$ (26), the lower order polysulfides may be reducible using an appropriate heterogeneous or homogeneous catalyst. A study of the effects of electrode material and polysulfide complexing
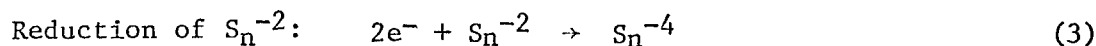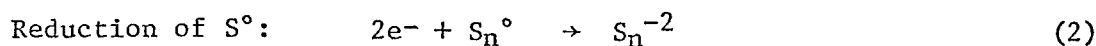
additive on the capacity of the dissolved S positive is projected for the next report period.

Evaluation of the cycle life of the dissolved Li_2S_n electrode has been somewhat hindered by the design of our coulometry cell. It appears that in THF and in DMSO the electrode loses some capacity with each cycle, but this may be due to diffusion of active material into the counter electrode compartments. These experiments are quite lengthy, and some such migration is difficult to avoid.
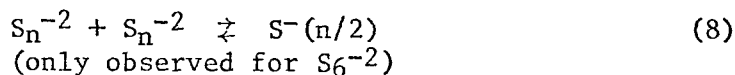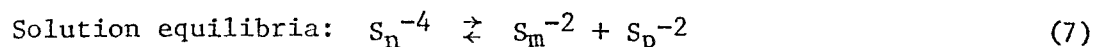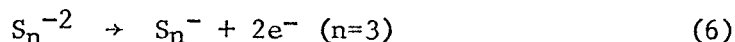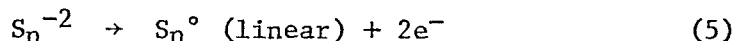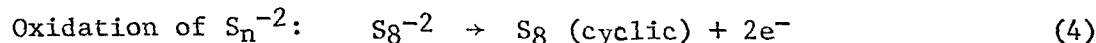
Mechanisms of Polysulfide Redox Reactions. We have investigated the oxidation and/or reduction reactions of S_8, S_8^{-2}, S_4^{-2} and S^{-2} in DMSO. Dilute solutions were used so that spectra and cyclic voltammograms could be recorded during the experiment without further dilution, and so that coulometric experiments were relatively short in duration. S_8 and S_8^{-2} are reducible only as far as S_4^{-2} (at least positive of 1.0V). S_8^{-2}, S_6^{-2} and S_3^- were monitored using visible spectroscopy. They appear as intermediates during the course of the reduction of S_8. Cyclic voltammetry of Na_2S_4 solutions confirms the difficult reduction of the S_4^{-2} species.
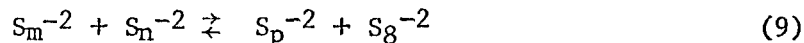
Oxidation of S_8^{-2} led to the precipitation of $S°$, probably as S_8. However, oxidation of S_4^{-2} and S^{-2} led first to S_6^{-2}, probably via S_3^-, then to a soluble long chain polysulfide. It is likely, therefore, that long chains will be favored during charging of a practical cell, and that high solubility will be maintained.

The polysulfide oxidations and reductions in DMSO all appear to be of $2e^-$ stoichiometry (7,8) except perhaps the oxidation of S_3^{-2}. In addition, S^{-2} attacks S-S bonds. Similarly, various S_n^{-2} species are in equilibrium, as can be seen from their solution spectra. Hence, the redox reaction and chemical equilibria of polysulfides may be generalized as follows:

Reduction of $S°$:	$2e^- + S_n° \rightarrow S_n^{-2}$	(2)
Reduction of S_n^{-2}:	$2e^- + S_n^{-2} \rightarrow S_n^{-4}$	(3)
Oxidation of $S°$:	Does not appear under normal conditions	
Oxidation of S_n^{-2}:	$S_8^{-2} \rightarrow S_8$ (cyclic) + $2e^-$	(4)
	$S_n^{-2} \rightarrow S_n°$ (linear) + $2e^-$	(5)
	$S_n^{-2} \rightarrow S_n^- + 2e^-$ (n=3)	(6)
Solution equilibria:	$S_n^{-4} \rightleftarrows S_m^{-2} + S_p^{-2}$	(7)
	$S_n^{-2} + S_n^{-2} \rightleftarrows S^-(n/2)$ (only observed for S_6^{-2})	(8)

$$S_m^{-2} + S_n^{-2} \rightleftarrows S_p^{-2} + S_8^{-2} \qquad (9)$$

$$S_m^{-2} + S_n^{\circ} \rightleftarrows S_{n+m}^{-2} \qquad (10)$$

$$S_n^{\circ} + S_m^{\circ} \rightleftarrows S_{n+m}^{\circ} \qquad (11)$$

From the results to date on the Li/dissolved S battery, we are able to specify the requirements for its optimization: First, we must find a catalyst which will allow reduction (3) to occur at a relatively high and constant potential for all values of n. At present, the low order polysulfides are difficult to reduce, but the results of Kovacova and Zezula (26) on the reduction S_4^{-2} in aqueous base on Hg are encouraging. Next, we prefer to maintain S solubility through all phases of charge and discharge. On charging the Li_2S_n electrode, we have found that soluble long chain S_n^{-2} species are formed rather than S° species which would precipitate. On discharge, we are less sure of solubility of low-order polysulfides. Our solubility studies indicate that appropriate high polysulfide solubility is not achieved until n>4. If we can catalyze S_4^{-2} reduction, we shall take up the suitable handling of the reduction product, i.e., Li_2S. It may be necessary to try to solubilize this product or to incorporate it in the positive electrode structure, as is done in the Li/SO_2 and $Li/SOCl_2$ batteries.

Optimization of the Li electrode will require a detailed study of the parameters influencing Li cycling efficiency and capacity loss in solutions containing S. Work has begun on another contract on the cycling of Li in the presence of polysulfides.* Special cells have been fabricated for the cycling of Li on a Li substrate. A known charge of Li (10 coul/cm²) is repeatedly plated and stripped on a Li electrode of known capacity (∿80 coul/cm²). As these cycles are not 100% efficient, a portion of the substrate is removed on each stripping cycle. The average efficiency/cycle can be calculated from the number of cycles required to remove all of the substrate Li.

Cells were run containing THF, 1M LiClO4 and DMSO, 1M LiClO4, both with and without Li_2S_n. The pertinent results are summarized in Table 5. To date, we have had less success with DMSO solutions than with TFE. In both cases, the presence of Li_2S_n <u>enhances</u> the Li cycling efficiency. In THF, a solution approximately 5M in S (as ∿Li_2S_{10}) yielded an 85.1% average cycling efficiency of Li on a Li substrate. This experiment is currently being repeated, but these initial results are very promising.

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*NSF–RANN Contract No. AER75-03779.

Table 5

Efficiency of Repeatedly Cycling Li on Li
in Electrolytes Containing Li_2S_n

Electrolyte Composition	$\dfrac{Coul/cm^2}{Cycle}$	Cycles Completed	Average Cycle Efficiency (%)
DMSO, 1M LiClO$_4$	11.4	<5	Electrolyte decomposition
~5M S as ~Li$_2$S$_{10}$ in DMSO, 1M LiClO$_4$	11.4	12	33.1
THF, 1M LiClO$_4$	10.1	26	65.1
0.1M S as ~Li$_2$S$_{10}$ in THF, 1M LiClO$_4$	11.4	24	66.5
~5M S as ~Li$_2$S$_{10}$ in THF, 1M LiClO$_4$	11.4	54	85.1

REFERENCES

1. Energy density calculations are based on potentials in "Oxidation Potentials," by W. H. Latimer (Prentice Hall, Englewood Cliffs, N.J., 1952), or, in some cases, on those in Pourbaix (Ref. 2).

2. M. Pourbaix, "Atlas of Electrochemical Equilibria," (Pergamon Press, Oxford, England, 1966).

3. J. H. B. George, L. J. Stratton and R. G. Acton (A. D. Little Co.), Final Report on Contract PH 86-67-108, May 1968.

4. H. P. Silverman, E. T. Seo, R. R. Sayano, A. Toy and N. A. Richardson, Proc. 7th I.E.C.E.C. Meeting, (1972).

5. C. Levine, Proc. 10th I.E.C.E.C., p. 621 (1975).

6. S. B. Brummer, R. D. Rauh, J. M. Marston, and F. S. Shuker, Semiannual Progress Report, Contract No. E(11-1)-2520 (July, 1975).

7. M. V. Merritt and D. T. Sawyer, Inorg. Chem., 9, 211 (1970).

8. R. P. Martin, W. H. Doub, Jr., J. L. Roberts, Jr., and D. T. Sawyer, Inorg. Chem., 12, 1921 (1973).

9. R. Bonnaterre and G. Cauquis, J. Chem. Soc. Chem. Comm., 293 (1972).

10. M. Delamar, J. Electroanal. Chem., 63, 339 (1975).

11. M. Delamar and J. Marchon, J. Electroanal. Chem., 63, 351 (1975).

12. J. R. Coleman and M. W. Bates, "Power Sources 2," Ed. D. H. Collins, (Pergamon Press, 1969), p. 289.

13. H. R. Knapp, Technical Report ECOM-2632, October, 1965.

14. M. L. B. Rao, U.S. Patent 3,413,154 (1968).

15. D. Herbert, U.S. Patent 3,248,245 (1966).

16. D. A. Nole and V. Moss, U.S. Patent 3,532,543 (1970).

17. R. Jasinski, Adv. Electrochem. and Electrochem. Eng., Vol. 8, John Wiley and Sons, New York, 1971.

18. J. B. Doe, et al., Final Report, Contract AFAPL-TR-74-63 (December, 1974).

REFERENCES
(Continued)

19. N. Gupta, Rev. Sci. Inst., $\underline{42}$, 1368 (1971).

20. R. Hand, A. Carpenter, C. O'Brien and R. Nelson, J. Electrochem. Soc., $\underline{119}$, 74 (1972).

21. A. Senning, ed., Sulfur in Organic and Inorganic Chemistry, Vol. 3, Marcel Dekker, Inc., New York, 1972, p. 27.

22. W. Schöninger, Mikrochim. Acta [Wien] $\underline{1963}$, 52.

23. G. Schwarzenbach and A. Fischer, Helv. Chim. Acta., $\underline{43}$, 1365 (1960).

24. W. Blaedel and V. Meloche, Elementary Quantitative Analysis, 2nd Ed., Harper and Row, 1963, p. 463.

25. N. G. Heatley and E. J. Page, Anal. Chem., $\underline{24}$, 1854 (1952).

26. Z. Kovacova and I. Zezula, Coll. Czech. Chem. Comm., $\underline{39}$, 722 (1974).

27. H. Lux, S. Benninger and E. Bohm, Chem. Ber., $\underline{101}$, 2485 (1968).