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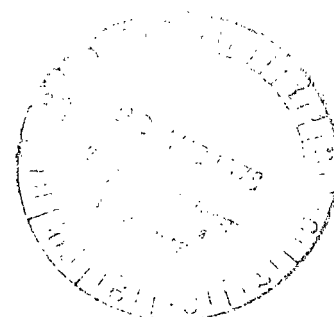
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Solubility, Stability, and Electrochemical Studies of Sulfur-Sulfide Solutions in Organic Solvents

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SOLUBILITY, STABILITY, AND ELECTROCHEMICAL STUDIES OF

SULFUR-SULFIDE SOLUTIONS IN ORGANIC SOLVENTS

by William L. Fielder and Joseph Singer

Lewis Research Center

SUMMARY

Representatives of many classes of organic solvents (as determined by functional groups) were screened qualitatively for their applicability in a low temperature (100° to 120° C) sodium-sulfur secondary battery system with a dissolved sulfur electrode. Primary screening criteria were the solubilities of Na_2S and Na_2S_2 and the stabilities of the solutions. From this screening and further quantitative studies, two classes of solvents were selected for further investigation: amides (e.g., acetamide, N,N-dimethylacetamide, and N,N-dimethylformamide) and cyclic polyalcohols (e.g., 1,3-cyclohexanediol).

Voltammetric and Na-S cell charge-discharge studies were made at 120° C with a screened in amide (e.g., N,N-dimethylformamide) as the organic solvent and either graphite or platinum as the electrode current collector. The sodium, which was used as the reference electrode for the voltammetric studies and as the negative electrode for the cell studies, was contained in a sodium beta-alumina ceramic tube. Based on the data, reactions and mechanisms are proposed for the oxidation-reduction processes occurring at the sulfur electrode. Peak voltage differences for each oxidation-reduction reaction were typically 0.3 volt and exchange current densities were 10^{-3} to 10^{-4} A/cm^2, indicating moderately poor reversibilities. Because the reduction at the sulfur electrode went to Na_2S_2, and even to Na_2S, it may be possible to achieve the maximum Na-S energy density.

INTRODUCTION

There is a need for high-energy-density secondary battery systems for space and terrestrial applications (e.g., electric vehicles). The energy-density goals for these systems are about 100 to 200 W-hr/kg and 50 to 100 W/kg.

One battery system being considered is the high-temperature molten Na-S cell, which operates at 300° to 350° C and uses a sodium beta-alumina ceramic as the sodium-ion-conducting separator (ref. 1). However, considerable materials problems are being experienced at these temperatures. Furthermore, the discharge is not allowed to go beyond Na_2S_3 because solid Na_2S_3 forms; thus the available energy density is only about one-half of the theoretical value for Na_2S.
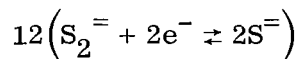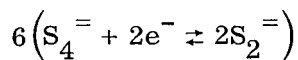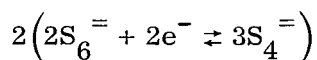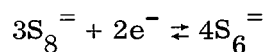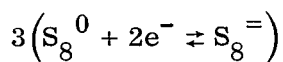
An analogous Na-S cell operating at lower temperatures may be practical because the materials problems should be less severe. This investigation was conducted to determine the feasibility of such a cell. For this cell, both electrodes may have to be in the liquid state, that is, molten or dissolved to achieve useful current densities; this sets the lower temperature at 98° C – the melting point of sodium. For the sulfur electrode, anhydrous solvents must be used because the sulfides react slowly with water to evolve H_2S and because water is detrimental to the sodium beta-alumina separator. Organic solvents are investigated in the present work.

Using an organic solvent to dissolve the sulfur reactants and products adds additional weight to the cell and thereby decreases its energy density. As a consequence, the ability to discharge this cell from elemental sulfur or a polysulfide with a high sulfur content to Na_2S (or at least to Na_2S_2) is highly desirable for obtaining the maximum energy density. High Na_2S and Na_2S_2 solubilities are also desirable for practical cell current densities.

Because very little information is available in the literature on the solubilities and stabilities of Na_2S or polysulfides in organic solvents, many classes of organic solvents (as determined by functional groups) were screened. The choice of solvents to represent each class was based primarily on their physical properties and availability. For example, 1,4-butanediol was chosen as representative of aliphatic polyalcohols because it is a liquid at 25° C, has a relatively low vapor pressure at 120° C, and is commercially available at suitable purity (≥ 99 percent). For the screening studies, approximate solubilities and stabilities of Na_2S and Na_2S_2 in these solvents were then determined at 120° C. The Na_2S and Na_2S_2 were chosen as representative sulfides because, according to preliminary investigations, they are less soluble in organic solvents than the higher polysulfides. Some of the more attractive solvents as suggested by the screening results ("screened-in" solvents) were then investigated further to obtain more quantitative measurements of the sulfide solubilities and stabilities. These studies resulted in the selection of two classes of solvents for further work: amides (e.g., acetamide, N,N-dimethylacetamide, and N,N-dimethylformamide) and cyclic polyalcohols (e.g., 1,3-cyclohexanediol).

Electrochemical studies were undertaken with solutions of elemental sulfur or various sodium sulfides in a few of the screened in solvents. In general, voltammograms for the sulfur or sulfide solutions in solvents such as N,N-dimethylformamide

suggested that five sets of oxidation-reduction reactions were occurring during the voltage scanning from 3.5 to 0.1 volt (relative to the sodium reference electrode). Peak voltage differences for each of these five reactions indicated moderately poor reversibilities on the working electrodes of high-density graphite or platinum. For any practical soluble-sulfur cell, a reasonably large exchange current density ($>10^{-3}$ A/cm^2) is desirable to minimize polarization. However, the values obtained from cell charge-discharge studies, about 10^{-3} to 10^{-4} A/cm^2, also suggest moderately poor reversibilities. Finally, some reactions and mechanisms are discussed for the five proposed reactions, which are as follows:

$$3\left(S_8{}^0 + 2e^- \rightleftarrows S_8{}^=\right)$$

$$3S_8{}^= + 2e^- \rightleftarrows 4S_6{}^=$$

$$2\left(2S_6{}^= + 2e^- \rightleftarrows 3S_4{}^=\right)$$

$$6\left(S_4{}^= + 2e^- \rightleftarrows 2S_2{}^=\right)$$

$$12\left(S_2{}^= + 2e^- \rightleftarrows 2S^=\right)$$

EXPERIMENTAL DETAILS

Preparation and Purification of Materials

Unless otherwise specified, all handling of the materials used in the present investigation (e.g., solvents, sulfides, and electrode current collectors) and all manipulations and operations were performed inside nitrogen or argon dry boxes to minimize water pickup.

Most of the organic solvents (55) were obtained from the Aldrich Chemical Co. Five solvents were obtained from the Eastman Organic Chemical Co. Most of the solvents were used without further purification, particularly for the screening studies. Commercial acetamide, which is a solid at room temperature, was purified further by drying in vacuum over P_2O_5 for 1 week and subliming in vacuum at about 100° to 120° C.

Elemental sulfur (99.9995 percent pure), Na_2S (99.3 percent pure), and Na_2S_4 (96 percent pure) were obtained from Ventron Corp. and were used without further purification. Neither Na_2S_8 nor Na_2S_2 are commercially available. The Na_2S_2 was prepared from a 1:1 mixture of Na_2S and S (ref. 2). The mixture was ground and sieved

(in nitrogen) through a 100-mesh screen. The ground sample was put into a glass ampoule and then removed from the nitrogen dry box. After it was evacuated, the ampoule was sealed and rolled to insure mixing. The mixture was reacted at 250° C (solid state) for 15 to 20 hours and then at 575° C (liquid state) for 1 hour. The ampoule, containing the final product, was then returned to the nitrogen dry box for storing and handling. X-ray diffraction indicated that the reaction product was essentially Na_2S_2 with a trace of unreacted Na_2S and presumably sulfur. No Na_2S_4 or Na_2S_5 was detected.

Commercial Na_2S_4 was used to prepare Na_2S_8 solutions. A known quantity of a 0.5 molar solution of Na_2S_4 in N, N-dimethylformamide was placed in a previously dried electrochemical cell (described later) inside an argon dry box. The solution was heated to 120° C, and the Na_2S_4 was converted to Na_2S_8 by passage of the required number of coulombs.

Commercial, high-purity $NaBF_4$, obtained from Ozark-Mahonning, was used as the supporting electrolyte. It was dried in vacuum at 115° C for about 75 hours and stored in nitrogen.

Various types of graphite were studied as electrode current collectors. High-purity, high-density, nonporous pyrolytic graphite was donated by Union Carbide. Rectangular strips (about 0.2 cm by 0.3 cm by 4 cm) were cut with a dry diamond wheel so that the largest face was parallel to the graphite plane. The density of the strips was 2.18 g/cm^3 (97 percent of theoretical). The strips were smoothed with a number-400 carborundum paper and then rinsed with acetone and absolute alcohol. After they were dried in vacuum at 450° to 500° C for 1 hour, the strips were redried in vacuum for 6 to 8 hours at 115° C just before use. Porous graphite was obtained from National Co. as spectrographic-grade rods (0.64 cm o.d.) with a density of 1.94 g/cm^3 (86 percent of theoretical). The rods were dried in vacuum at 115° C for about 6 hours just before use. Graphite felt, obtained from Hitco Corp., was rinsed with acetone and absolute alcohol and then dried as were the high-density electrodes. For a few experiments, platinum wire (0.08 cm diam) and platinum foil (1 cm by 1 cm) were used as electrode current collectors after they were dried at 115° C for 1 hour.

Sodium, contained in a sodium beta-alumina ceramic tube, was used as both the reference electrode for voltammetric studies and as the negative electrode for cell charge-discharge experiments. These tubes, obtained from British Railways, were about 0.8 centimeter in inside diameter, 1.1 centimeters in outside diameter, and 17 centimeters in length. They were dried at 900° C for 1 hour inside an argon dry box. Sodium was added to the tubes after they were cooled and then was heated to about 200° to 250° C to wet the ceramic.

Solubilities and Stabilities

For the screening experiments, Na_2S or Na_2S_2 and 10 to 15 milliliters of an organic solvent were put into a glass ampoule inside the nitrogen dry box. This quantity of sulfides was sufficient to yield a 1- to 2-molar solution if all of the solids dissolved. The stoppered ampoule was removed from the dry box and the sulfide-solvent mixture was frozen with dry ice. After the ampoule was outgassed, it was sealed under vacuum. The sample was heated to 120° C and the sulfide solubilities were estimated from the volume of the undissolved solids or from the color and appearance of the solution. Any reactions were noted by visual observation of any gas evolution or phase or color changes.

Two methods were used to determine the quantitative solubilities of the sulfides in several screened in solvents at 130° C: one method involved weighing the undissolved solid residue, and the other method involved chemically analyzing the saturated solution. Occasionally both methods were used for a particular sample. In the residue method, a known quantity of the sulfide was heated with 10 to 15 milliliters of the solvent in a tared beaker inside the nitrogen dry box. Simultaneously, a tared coarse-glass frit was preheated to 80° to 110° C to minimize sulfide precipitation during the filtration. The slurry was suction filtered and the undissolved solid residues (in the beaker and on the frit) were rinsed with three 10- to 15-milliliter rinses of absolute alcohol to remove occluded liquor. Auxiliary tests showed that less than 5 percent of the sulfide was lost in these rinses. After the system was evacuated to remove the residual rinse alcohol, the beaker and frit were reweighed to give the quantity of undissolved sulfide.

The apparatus shown in figure 1 was used to determine the sulfide solubilities by chemical analysis of the saturated solutions. Excess sulfide was added to the apparatus along with about 15 to 20 milliliters of the solvent. After the stopcock was closed, the apparatus was removed from the nitrogen dry box and the mixture was heated to 130° C. A sample of the saturated liquor was pipetted into a small, capped weighing bottle for chemical analyses. Exposure of the sample to moisture would lead to slow evolution of H_2S. Therefore, the exposure time during sampling was kept to a minimum, and the sample was then introduced directly into an aqueous hydroxide solution for analysis.

Before sampling, the stability of the solution was determined at 130° C in the apparatus of figure 1 by observing any gas evolution or phase or color changes. Occasionally, H_2S evolution occurred after an initiation period of 1 to 3 days. Consequently, most of the solutions were observed for at least 3 to 4 days unless gas evolution started earlier. The presence of H_2S was detected with lead acetate paper.
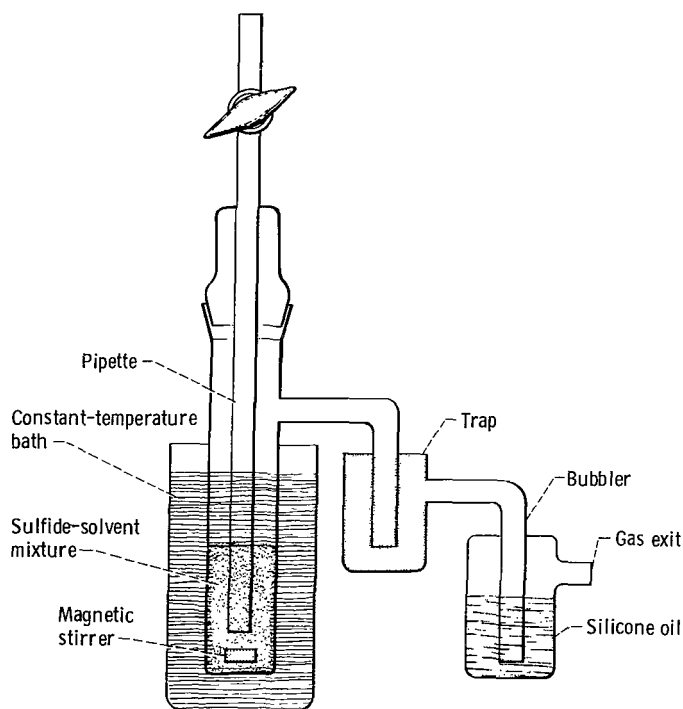
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Figure 1. - Apparatus for determining solubilities and
stabilities of sulfide-solvent mixtures.

Electrochemical Measurements

A three-electrode glass cell, shown in figure 2, was used for the voltammetry ex-
periments. The working-electrode current collectors were high-density pyrolytic
graphite, porous graphite, or platinum wire. The counter-electrode current collec-
tors were usually graphite felt and occasionally platinum foil (with the platinum wire).
A coarse-glass frit was placed between the counter- and working-electrode compart-
ments to minimize diffusion of a species from one compartment into the other. The
reference electrode was sodium contained in a sodium beta-alumina tube versus a
fixed concentration of sodium ions in the sulfide solution. The $NaBF_4$, when added to
the solution as the supporting electrolyte (0.1 M), fixed the sodium ion concentration.

The desired sulfur or sulfide solution was placed into the cell inside the argon dry
box. The brass fittings, which contained fluorocarbon (or silicone) O-rings, were
closed to preserve the argon atmosphere introduced into the cell. The cell, still in-
side the argon dry box, was then heated at 120° C for about 15 minutes. Any gas pres-
sure buildup was relieved by momentarily loosening the O-ring fitting. The cell was
then held at 120° C for about 2 hours before voltammograms were obtained.
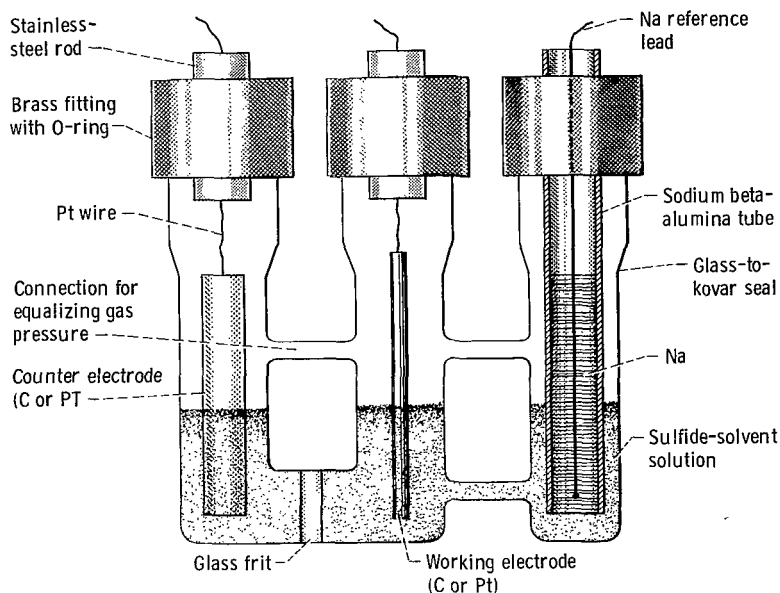
Figure 2. - Three-electrode voltammetry cell.

The three-electrode cell leads were connected to a Wenking potentiostat. The voltage sweeps were obtained by using a Tacussel triangular wave signal generator. The solution was scanned at various rates over the desired voltage ranges relative to the sodium reference electrode. The currents were measured by means of the voltage developed across a standard resistor in series with the cell. Plots of current versus voltage were obtained with an X-Y recorder.

The two-electrode cell, which is essentially two compartments of the three-electrode cell, was used for the cell charge-discharge experiments. The electrodes were high-density graphite and liquid sodium (contained in the sodium beta-alumina tube). A supporting electrolyte of $NaBF_4$ (0.1 M) was usually added to decrease the cell resistance. A known quantity of the sulfur or sulfide solution was placed into the cell (inside the argon dry box). Any gas pressure buildup was relieved and the cell was then held at 120° C for 1 to 2 hours. The open-circuit voltage of the cell was noted, and the corresponding cell voltages were measured at various current loads during cell charge or discharge. For cell charging, an opposing constant voltage (2 to 3 V) was applied from a precision direct-current power supply connected in series with the cell. About 30 to 60 seconds were usually sufficient to obtain an equilibrium cell voltage at each current load. The currents were measured by means of the voltage developed across an external standard resistor. The current densities were estimated from the currents and from the apparent electrode surface wetted by the solution. The

7

cell current-resistance (IR) polarization was usually obtained by extrapolating the straight-line portion (i.e., the higher current portion) of a current-voltage curve to zero current. Cell polarizations were estimated from the cell voltages and the cell IR polarizations.

RESULTS AND DISCUSSION

For simplicity, most of the data are presented in the appendixes. The solubilities and stabilities of sulfides in many classes of organic solvents, obtained during the screening process, are given in appendix A. The voltage peaks obtained for the five sets of sulfur-sulfide oxidation-reduction reactions by using various sulfur starting materials, solvents, and electrode current collectors are given in appendix B. The Tafel equation calculations for the various mechanisms that could be involved in the oxidation and reduction reactions are given in appendix C. Additional data are presented in the main text: Table I contains some quantitative solubility and stability mea-

TABLE I. – QUANTITATIVE SOLUBILITIES AND STABILITIES OF

Na_2S, Na_2S_2, AND Na_2S_4 AT 130° C

Solvent	Sulfide	Solubility, M	Method of determination	Remarks
Acetamide	Na_2S	1.0	Residue	-------------
	Na_2S_2	.8	Residue	-------------
	Na_2S_4	1.4	S analyses	Stable at 130° C
N, N-Dimethylacetamide	Na_2S	0.007	Na analyses	Stable at 130° C
	Na_2S_2	.03	Na, S analyses	Stable at 130° C
	Na_2S_4	1.5	Na, S analyses	Stable at 130° C
1, 3-Cyclohexanediol	Na_2S	0.3	Residue	-------------
	Na_2S_2	.9	Residue	-------------
	Na_2S_4	1.5	Residue	Stable at 130° C
N, N-Dimethylformamide	Na_2S	<0.01	Residue	-------------
	Na_2S_2	.12	Residue; Na, S, and $S_x^=$ analyses	H_2S evolved after 3 days at 130° C
	Na_2S_4	.95	Residue; S analyses	H_2S evolved after 3 days at 130° C
Formamide	Na_2S_4	------	------------------	H_2S evolved after 3 hours at 130° C

TABLE II. – OXIDATION-REDUCTION OF ELEMENTAL SULFUR AND SODIUM SULFIDES

Reactions		Mechanisms	
		Reduction	Oxidation
First	$S_8^0 + 2e^- \rightleftarrows S_8^=$	$2\left[S_8^0 + 1e^- \rightleftarrows \left(S_8^-\right)\right]$ RDS $2\left(S_8^-\right) \rightleftarrows S_8^0 + S_8^=$	$2\left[S_8^= \rightleftarrows \left(S_8^-\right) + 1e^-\right]$ RDS $2\left(S_8^-\right) \rightleftarrows S_8^0 + S_8^=$
Second	$3S_8^= + 2e^- \rightleftarrows 4S_6^=$	$S_8^= \rightleftarrows 2\left(S_4^-\right)$ $2\left[\left(S_4^-\right) + 1e^- \rightleftarrows S_4^=\right]$ RDS $2\left[S_4^= + S_8^= \rightleftarrows 2S_6^=\right]$	$2\left[2S_6^= \rightleftarrows S_8^= + S_4^=\right]$ $2\left[S_4^= \rightleftarrows \left(S_4^-\right) + 1e^-\right]$ RDS $2\left(S_4^-\right) \rightleftarrows S_8^=$
Third	$2S_6^= + 2e^- \rightleftarrows 3S_4^=$	$S_6^= \rightleftarrows 2\left(S_3^-\right)$ $2\left[\left(S_3^-\right) + 1e^- \rightleftarrows S_3^=\right]$ RDS $2S_3^= + S_6^= \rightleftarrows 3S_4^=$	$3S_4^= \rightleftarrows S_6^= + 2S_3^=$ $2\left[S_3^= \rightleftarrows \left(S_3^-\right) + 1e^-\right]$ RDS $2\left(S_3^-\right) \rightleftarrows S_6^=$
Fourth	$S_4^= + 2e^- \rightleftarrows 2S_2^=$	$S_4^= \rightleftarrows 2\left(S_2^-\right)$ $2\left[\left(S_2^-\right) + 1e^- \rightleftarrows S_2^=\right]$ RDS	$2\left[S_2^= \rightleftarrows \left(S_2^-\right) + 1e^-\right]$ RDS $2\left(S_2^-\right) \rightleftarrows S_4^=$
Fifth	$S_2^= + 2e^- \rightleftarrows 2S^=$	$S_2^= + 1e^- \rightleftarrows \left(S_2^{-3}\right)$ $\left(S_2^{-3}\right) + 1e^- \rightleftarrows S_2^{-4}$ $S_2^{-4} \rightleftarrows 2S^=$	$2S^= \rightleftarrows S_2^{-4}$ $S_2^{-4} \rightleftarrows \left(S_2^{-3}\right) + 1e^-$ $\left(S_2^{-3}\right) \rightleftarrows S_2^= + 1e^-$

surements for some of the sulfides in a few screened in solvents. Table II summarizes the five sets of proposed oxidation-reduction reactions and mechanisms.

Solubilities and Stabilities

For useful sodium-soluble-sulfur cell current densities, the discharge products should have adequate solubilities (0.5 M or greater) to minimize the formation of high-resistivity films by excessive precipitation of the sulfides on the sodium beta-alumina

ceramic or on the sulfide electrode current collector. Many classes of organic solvents were screened. All the solvents could be classified into five groups, as shown in appendix A. The solvents in group 1 gave moderately high solubilities (~0.5 to 2 M) for both Na_2S and Na_2S_2 at 120° C. Group 1 includes the following classes: alcoholamines, amides, cyclic alcohols, glycols, aliphatic polyalcohols, and cyclic polyalcohols. In subsequent tests, gas-bubble formation showed aliphatic polyalcohol and glycol solutions to be generally unstable.

Group 2, a somewhat larger group of solvents, gave poor-to-moderate solubilities for Na_2S and Na_2S_2 at 120° C. The solubilities were estimated from the solution color as well as from the quantity of remaining undissolved solids. Soluble polysulfides generally give highly colored solutions in organic solvents (ref. 3). Group 2 includes alcohol-ethers, amides (aliphatic, cyclic, and phosphorous), cyclic ketones, lactones, sulfolanes, and sulfoxides.

Group 3 contained three solvents that formed gels or slurries with Na_2S and Na_2S_2 at 120° C. Because the undissolved solids did not settle rapidly, solubility estimates were difficult to make. Additional investigations would be necessary to determine whether this gel or slurry formation is specific to that particular solvent or is representative of its class.

The majority of the organic solvents were less desirable. The group 4 solvents gave poor Na_2S or Na_2S_2 solubility. And several group 5 solvents reacted with Na_2S and Na_2S_2, usually to evolve H_2S.

The more promising classes of solvents, as suggested by the screening experiments, were the amides and cyclodiols of group 1 and the amides, lactones, sulfolanes, and sulfoxides of group 2. Quantitative solubility and stability measurements were then made at 130° C for a few of these screened in solvents, and the results are given in table I. Two amide solutions (acetamide and N,N-dimethylacetamide) and the cyclodiol solution (1,3-cyclohexanediol) seemed to be stable. The other two amide solutions (N,N-dimethylformamide and formamide), however, were less stable and evolved H_2S after an initiation period. Only one solvent in table I (i.e., acetamide) was dried. Evolution of H_2S for two of the solvents (i.e., formamide and N,N-dimethylformamide) might have been due to traces of water contamination.

The solubilities of Na_2S and Na_2S_2 at 130° C are in fair agreement with the values obtained by Brummer at 150° C (ref. 4). He obtained Na_2S and Na_2S_4 solubilities of 1.19 and 1.59 molar, respectively, in acetamide and 0.0075 and 1.33 molar, respectively, in N,N-dimethylacetamide. The solubility of Na_2S in N,N-dimethylformamide (<0.01 M) is somewhat less than Brummer's value of 0.05 molar at 150° C. Of the five solvents studied quantitatively, acetamide and 1,3-cyclohexanediol may be more useful for low-temperature sodium-sulfur cells than for high-temperature cells because the solubility of Na_2S (usually the least soluble species) is still relatively high.

Electrochemical Results

In general, five sets of oxidation-reduction reactions occurred during the voltage scanning of solutions of elemental sulfur, $S_8{}^0$; sodium polysulfides, Na_2S_x; and Na_2S in most of the solvents studied over the voltage range of 3.8 to 0.1 volt (relative to the sodium reference electrode). For some of the solutions, however, the fourth and fifth sets of peaks were not readily observed. This is illustrated in figure 3 where three
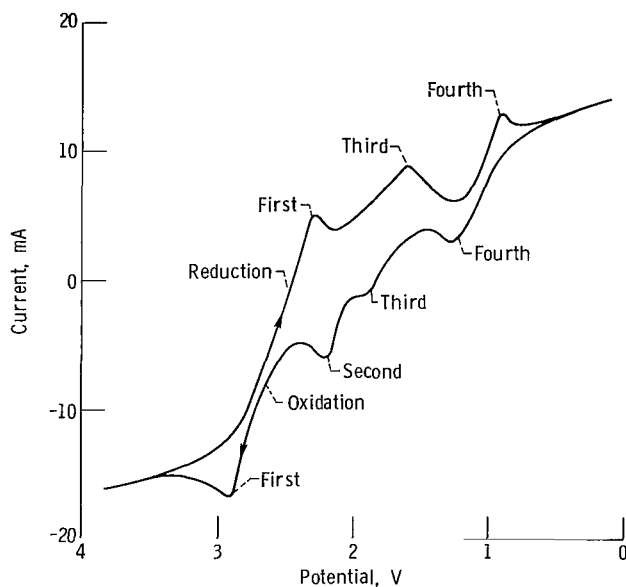

Figure 3. – Cyclic voltammogram of 0.1 molar Na_2S_4 - N, N-diethylacetamide at 120^0 C with a platinum electrode collector. Scan rate, 0.04 V/sec.

reduction and four oxidation peaks were obtained for the cyclic voltammogram of a 0.1 molar solution of Na_2S_4 in N, N-diethylacetamide at 120^0 C with 0.1 molar $NaBF_4$ as the supporting electrolyte and platinum wire as the electrode current collector. A fifth set of oxidation-reduction peaks was not observed presumably because of the low solubility of the product of the fourth reduction (i.e., Na_2S_2) in the organic solvent. Still, under the proper conditions, a fifth set of peaks was observed for some of the systems in the range of 1 to 0.6 volt.

The five sets of proposed reactions and mechanisms are summarized in table II for the oxidation-reduction of elemental sulfur and sodium sulfides in organic solvents. The reactions are discussed in this report as individual steps and are compared with reactions and mechanisms appearing in the literature.

First oxidation-reduction reactions. - The open-circuit voltage at 30° C was about 2.7 volts between the sodium reference electrode and the 0.01 molar solution of elemental sulfur $\left(S_8^0\right)$ in N, N-dimethylformamide (DMF). Starting at the open-circuit voltage, a reduction voltammogram for this solution was obtained at 30° C over the voltage range of 2.7 to 1.6 volts, as shown in figure 4(a). From the one reduction peak obtained, the first reduction of S_8^0 occurred at about 2.25 volts relative to the sodium reference electrode. This peak and its corresponding first oxidation peak are shown in figure 4(b) in the cyclic voltammogram of another S_8^0-DMF solution (0.001 M) at 120° C on a high-density graphite electrode collector. The first oxidation and reduction peaks were obtained at 2.45 and 2.30 volts, respectively. Although not shown in figure 4(b), when the voltage scan was stopped before appreciable reduction of S_8^0 could occur (e.g., scanning between 3.0 and 2.4 V), the corresponding first oxidation peak was not obtained. Therefore, the species being oxidized during the oxidation scan

(a) Reduction voltammogram of 0.01 molar S_8^0 at 30^0 C with a porous graphite electrode. Scan rate, 0.08 V/sec.

(b) Cyclic voltammogram of 0.001 molar S_8^0 at 120^0 C with a high-density graphite electrode. Scan rate, 0.02 V/sec.

(c) Cyclic voltammogram of 0.007 molar Na_2S_2 at 120^0 C with a high-density graphite electrode. Scan rate, 0.01 V/sec.
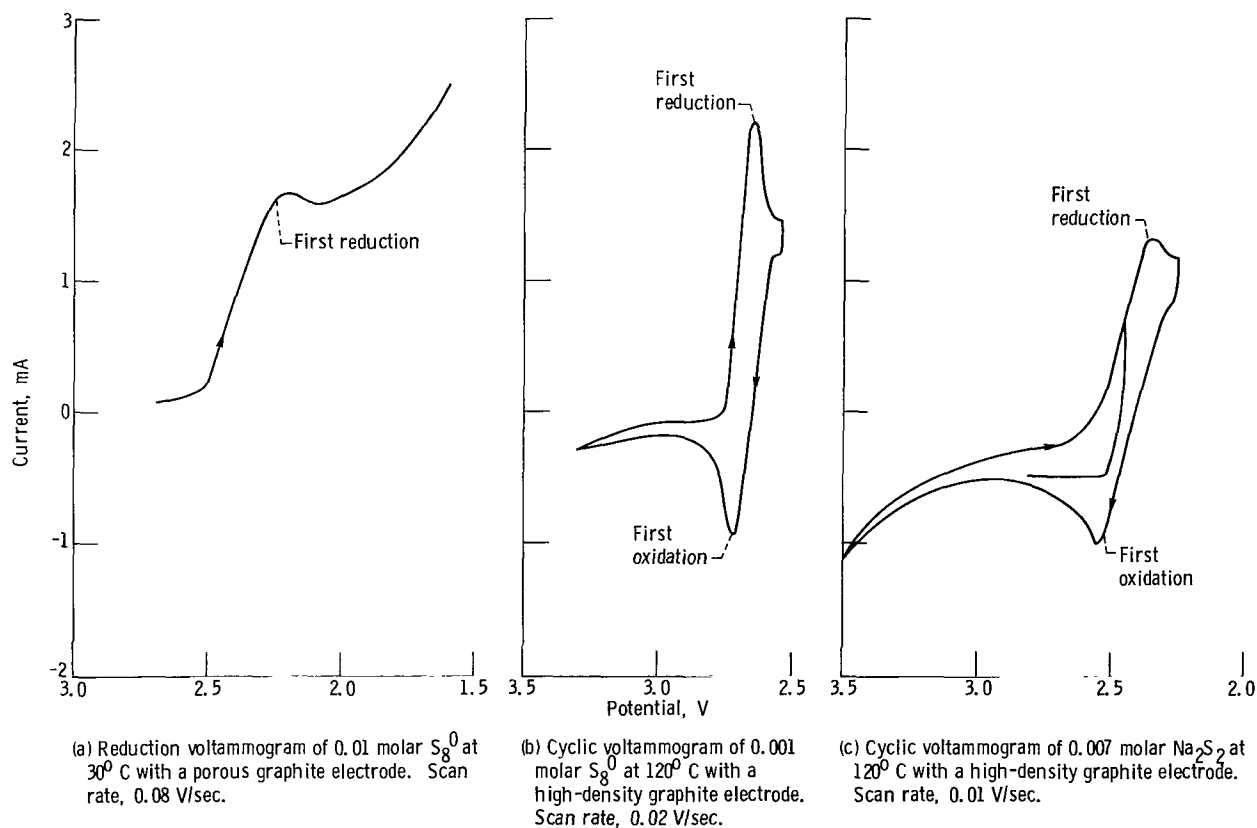
Figure 4. - Voltammograms of N, N-dimethylformamide solutions with graphite electrode collectors.

12

must have been produced during the preceding reduction scan.

These first sets of oxidation-reduction reactions can also be obtained with other polysulfide solutions as starting materials. For example, after a few cycles over the entire voltage range of 3.5 to 0.1 volts, the first oxidation-reduction peaks were readily seen upon subsequent cycling through the first oxidation-reduction range of 3.5 to 2.25 volts. This is illustrated in figure 4(c) for a dilute Na_2S_2-DMF solution, where the first oxidation-reduction peaks were obtained at 2.55 and 2.35 volts, respectively. As shown in figure 4(c), the first oxidation peak was greatly decreased if the reduction sweep was limited to 3.5 to 2.45 volts.

The peak voltages for both the oxidation and reduction reactions were related to the voltage scan rate as shown in figure 5. Essentially straight lines were obtained for a plot of these voltages versus the square root of the scan rate by using various sulfide starting materials on both porous and high-density graphite electrodes. A scan rate of about 0.01 to 0.02 V/sec was usually sufficiently slow to give peaks at about 2.6 and 2.3 volts, respectively, for the first oxidation-reduction reactions for most of the solutions. The results are shown in appendix B.

The voltage differences between the first oxidation and reduction peaks at about 0.01 to 0.02 V/sec indicate the reversibility of the process: A system is considered to be reversible if the difference in the peak voltages is approximately 0.05 volt (ref. 5).
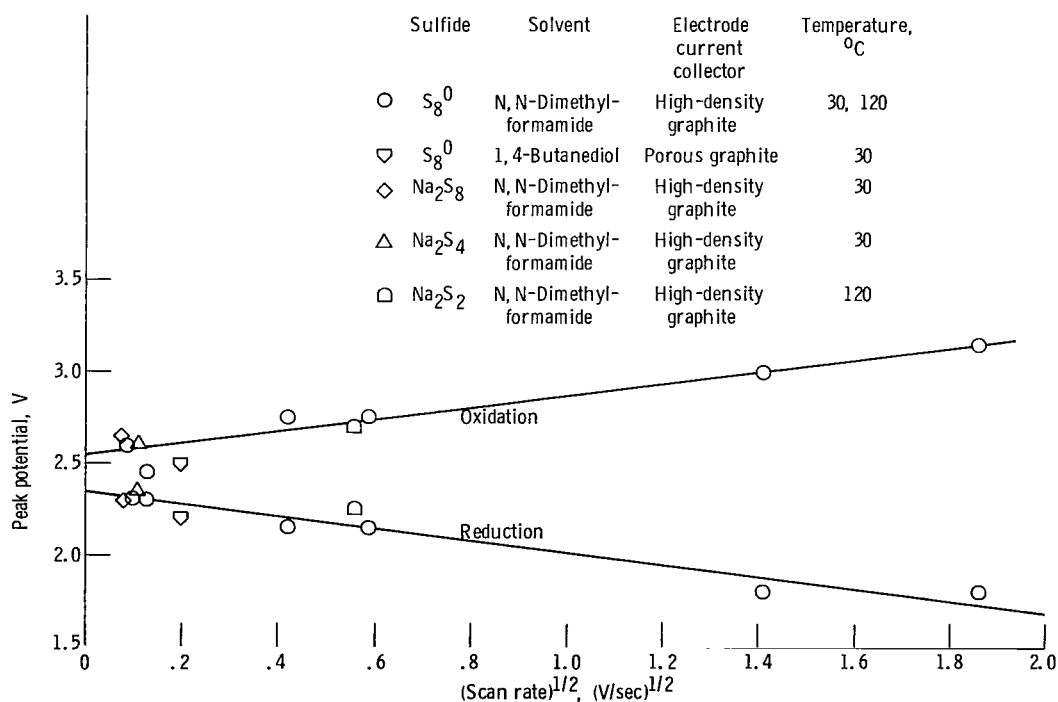

Figure 5. - Peak voltages with scan rates for oxidation-reduction reactions.

For these first oxidation-reduction reactions, the difference of about 0.3 volt obtained for the two peaks for both solvents and for both graphite electrodes suggests that the reversibility was moderately poor at 120° C.

The reduction of elemental sulfur, the first reduction reaction, was investigated at 120° C in Na-S cells. One cell had N,N-dimethylformamide as the solvent and high-density graphite (HDG) as the electrode current collector, as follows:

$$\text{Na}(\ell)\,|\,\text{sodium beta-alumina}\,|\,0.004\text{ M S}_8{}^0 - \text{DMF}(0.1\text{ M NaBF}_4) - (\text{HDG})$$
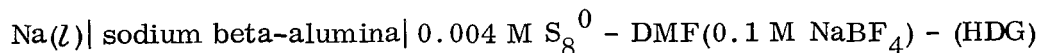
The current-voltage plot for discharging the cell is shown in figure 6. The cell resistance was estimated from an extrapolation of the straight-line portion of the curve
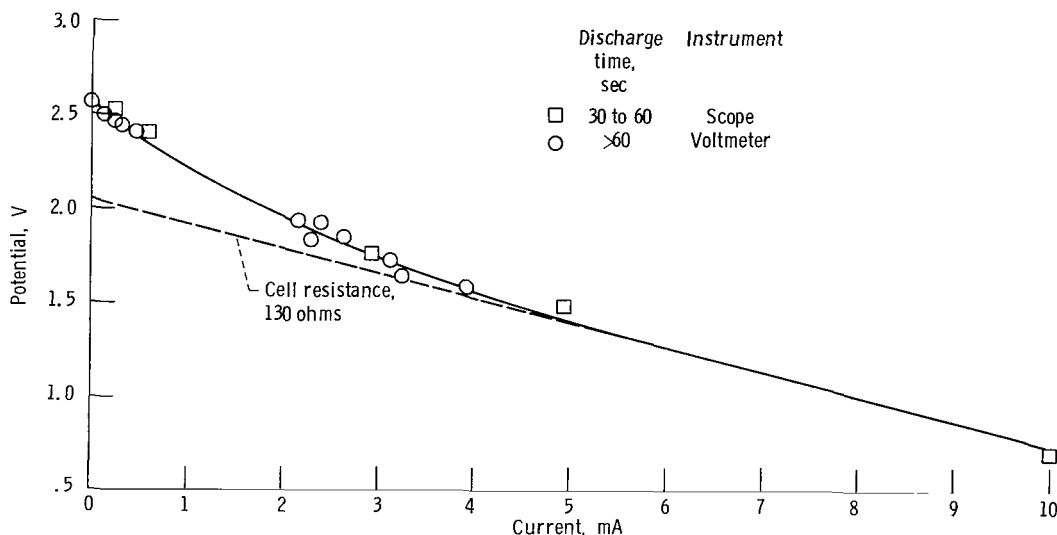

Figure 6. – Discharging of a Na(ℓ)/sodium beta-alumina/0.004 molar $S_8{}^0$ – N,N-dimethylformamide cell (0.1 M NaBF$_4$) at 120° C with a high-density graphite electrode collector (2.5 cm^2). Open-circuit voltage, 2.561 V.

(i.e., the higher current portion). Although the resistance for this cell was about 130 ohms, the resistances for most of the cells were 20 to 30 ohms. Because the liquid-sodium electrode should be reversible at 120° C, the calculated cell polarization (after accounting for the IR polarization) was assumed to represent the activation polarization of the sulfur electrode. This polarization was then plotted against the cell current density (Tafel plot) as shown in figure 7, giving a slope of 0.36 volt per decade. Extrapolating the straight-line portion of the data to zero polarization gives an apparent exchange current density of about 10^{-4} A/cm^2. Keeping in mind our cyclic voltammogram result, we interpret this relatively low exchange current density to be indicative of a moderately poor reversibility for the first reduction reaction of sulfur on high-
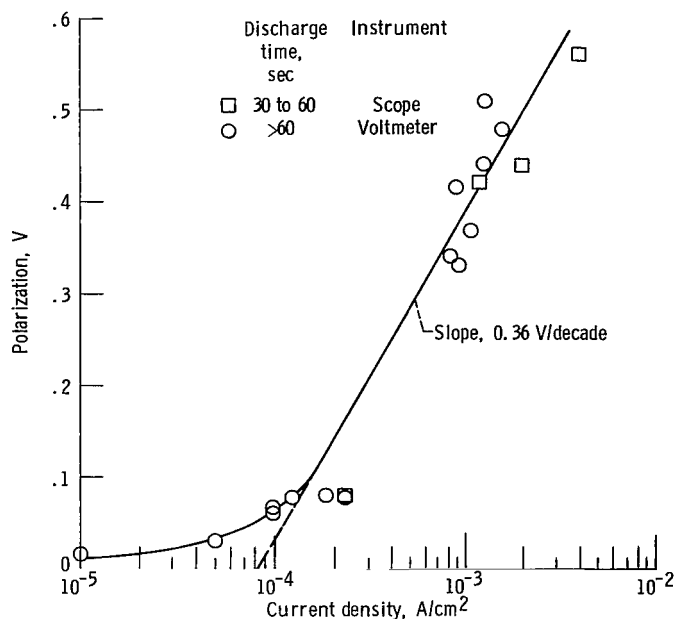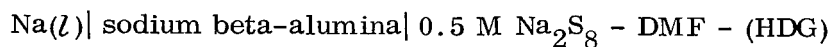
Figure 7. – Tafel plot of discharging of a Na(ℓ)/sodium beta-alumina/ 0.004 molar S_8^0 - N, N-dimethylformamide cell at 120° C with a high-density graphite electrode collector.

density graphite. (More reversible systems, such as the evolution of hydrogen on platinum, have exchange current densities $>10^{-3}$ A/cm^2 (ref. 6).) Furthermore, this low current density (10^{-4} A/cm^2) may lead to excessive polarization losses for any practical soluble sulfur cell operating at acceptable currents. For example, at currents of 25 to 50 mA/cm^2, an exchange current density of greater than 10^{-3} A/cm^2 may be required to limit polarization to less than 0.2 volt.

Two additional cells containing elemental sulfur were discharged at 120° C: One cell contained 1,4-butanediol as the solvent with platinum wire as the electrode current collector; the other cell contained N,N-dimethylformamide as the solvent with porous graphite as the electrode current collector. Averaging the slopes for all three S_8^0 cells gave a value of 0.39 for the first reduction reaction of S_8^0.

A solution of Na$_2$S$_8$ in DMF was used to study the first oxidation reaction. Because Na$_2$S$_8$ was not available commercially, it was prepared in situ by oxidation electrolysis of a 0.5-molar solution of Na$_2$S$_4$ at 120° C (using high-density graphite) in the following cell:

$$\text{Na}(\ell)|\text{ sodium beta-alumina}| 0.5 \text{ M Na}_2\text{S}_8 - \text{DMF} - \text{(HDG)}$$

The current-voltage curve data gave a cell resistance of 28 ohms. The Tafel plot is shown in figure 8. A slope of 0.18 volt per decade and an exchange current density of
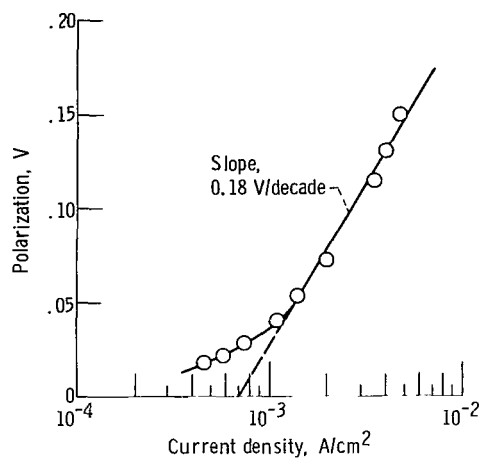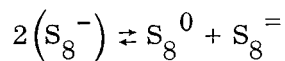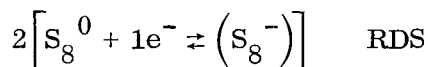
15

Figure 8. – Tafel plot of charging of a Na(l)/ sodium beta-alumina/0.5 molar Na$_2$S$_8$ – N, N-dimethylformamide cell at 120^0 C with a high-density graphite electrode collector.

10^{-3} A/cm^2 were obtained for this first oxidation reaction.

The overall reaction for the initial reduction of elemental sulfur (i.e., the first reduction reaction) is the reduction to S$_8^=$ as follows:

$$S_8^{\,0} + 2e^- \rightleftarrows S_8^{\,=}$$
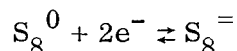
By using the method reported by Fraser (ref. 7) and Del Duca (ref. 8), Tafel slopes (obtained from the Tafel plots) were used to calculate the electron transfer coefficients β. For example, the average Tafel slope, obtained from discharging cells containing S$_8^{\,0}$, was 0.39 volt per decade. This slope was used to calculate β for various possible mechanisms (appendix C). Mechanisms giving β closest to 0.5, the theoretical value, were then assumed to be more likely for the first reduction mechanism of S$_8^{\,0}$. Among those mechanisms considered, we believe the following one-electron transfer and disproportionation steps are more likely because they gave a calculated β of 0.8:

$$2\left[S_8^{\,0} + 1e^- \rightleftarrows \left(S_8^{\,-}\right)\right] \quad \text{RDS}$$

$$2\left(S_8^{\,-}\right) \rightleftarrows S_8^{\,0} + S_8^{\,=}$$

This mechanism is given in appendix C as equations (1) and (2); equation (1) is the rate-determining step (RDS). The step involving the addition of one electron to the

16

$S_8{}^0$ species for the rate-determining step seems intuitively more plausible because it involves the breaking of a $S_8{}^0$ ring. The radical $\left(S_8{}^-\right)$ species may then dispropor-tionate to form $S_8{}^0$ and $S_8{}^=$.
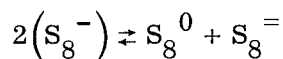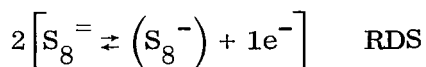
Two alternative reduction mechanisms also gave β of 0.8 and cannot be rejected categorically. However, we believe that these mechanisms are more difficult and less likely. One mechanism (eqs. (3) and (4) in appendix C) involves two consecutive one-electron transfer steps. The other mechanism (eqs. (5) and (6)) may require an appreciable concentration of the final product, $S_8{}^=$, before reduction of the radical $S_8{}^-$ can occur to produce $S_8{}^=$.

A similar reaction is proposed for the corresponding first oxidation reaction:

$$S_8{}^= \rightleftharpoons S_8{}^0 + 2e^-$$
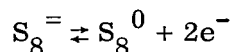
The Tafel slope of 0.18 volt per decade, obtained from the charging of a Na_2S_8 cell, was used to calculate β for various oxidation mechanisms (table in appendix C). Among those mechanisms, we believe the following (eqs. (8) and (9)) are more likely for the first oxidation reaction because they gave a calculated β of 0.4.

$$2\left[S_8{}^= \rightleftharpoons \left(S_8{}^-\right) + 1e^-\right] \quad \text{RDS}$$

$$2\left(S_8{}^-\right) \rightleftharpoons S_8{}^0 + S_8{}^=$$

Two other mechanisms also gave β of 0.4 but are considered to be less likely for reasons similar to those given for the first reduction process. One of these mecha-nisms (eqs. (10) and (11)) may require an appreciable concentration of the final product, $S_8{}^0$, before oxidation of the radical $\left(S_8{}^-\right)$ can occur. The other oxidation mechanism (eqs. (12) and (13)) involves two consecutive one-electron transfer steps.

Similar reactions have been obtained by other investigators for these first oxidation-reduction reactions. For example, Merritt (ref. 9) and Martin (ref. 10) studied the cyclic voltammetry (using a calomel electrode as the reference) and elec-trolysis of a solution of elemental sulfur in methyl sulfoxide on gold at room tempera-ture. They obtained peaks for the first oxidation-reduction reactions at -0.3 and -0.6 volt, relative to the calomel electrode. These values correspond to about 2.6 and 2.3 volts, relative to the sodium reference electrode, which is in good agreement with the present investigation. They also found that two electrons were passed for each $S_8{}^0$ reacted, which suggested that $S_8{}^0$ was reduced to $S_8{}^=$. A similar reaction was ob-served by Kennedy (ref. 11) for a solution of elemental sulfur in fused LiCl-KCl at 420^0 C. Controlled reduction electrolysis at his first reduction voltage gave 0.265

electron for each sulfur atom (two electrons per S_8^0).

Other investigators have suggested that this first reduction mechanism is bielectronic (i.e., a two-electron transfer step) (ref. 9). This mechanism is shown in appendix C as equation (7). However, this two-electron transfer mechanism is probably less likely than the proposed one-electron transfer mechanism. First, a two-electron mechanism for this first reduction is not expected intuitively: A one-electron transfer would seem more reasonable. Furthermore, although Merritt (ref. 9) presented a two-electron step for the reduction of S_8^0 to $S_8^=$, his data led to an n (i.e., the number of electrons transferred) considerably less than 2. For example, n = ~1.4 if 0.5 is assumed for the electron transfer coefficient. Finally, this two-electron mechanism for the first reduction reaction seems less likely because its calculated β of 0.9 is somewhat larger than the β calculated for the one-electron transfer mechanism.

The corresponding first oxidation mechanism suggested by previous investigators is less clear. Essentially, they have suggested that the reverse of the first reduction reaction occurs by a two-electron mechanism. However, such a two-electron transfer mechanism (appendix C, eq. (14)) is probably less likely because its calculated β of 0.2 is considerably smaller than the β obtained for the proposed one-electron transfer mechanism.

Second and third oxidation-reduction reactions. - The species obtained during the first reduction reaction can be reduced further by extending the voltage sweeps to less than 2.3 volts relative to the sodium reference electrode. This is illustrated in figure 9(a) for a cyclic voltammogram of a dilute solution of elemental sulfur, S_8^0, in N, N-dimethylformamide where the voltage was cycled between 3.6 and 1.3 volts. As expected, the first oxidation-reduction peaks were observed at about 2.6 and 2.3 volts, respectively. Three additional peaks were obtained for this solution: a reduction peak at 1.55 volts, labeled the third reduction peak; and two oxidation peaks, a small peak at 2.1 volts and a larger one at 1.75 volts. These oxidation peaks have been labeled the second and third oxidation peaks, respectively. The corresponding second reduction peak was not observed, presumably because it is overshadowed by the nearby larger first or third reduction peaks. Straight lines were obtained for a plot of peak voltages for the third oxidation-reduction reactions as a function of (scan rate)$^{1/2}$. Most polysulfide solutions (after only a few initial cycles between 3.5 and 0.1 V) also gave similar peaks for these second oxidation and third oxidation-reduction reactions. For example, as shown in appendix B, the S_8^0 and polysulfide solutions gave the second oxidation peak at about 2.2 volts and the third oxidation-reduction peaks at about 1.9 and 1.6 volts, respectively, relative to the sodium reference electrode. This peak difference of 0.3 volt for the third oxidation-reduction peaks suggests that the reversibility of these reactions was moderately poor at 120° C.

18

(a) 0.002 Molar S_8^0 in N, N-dimethylformamide; high-density graphite electrode collector.

(b) 0.1 Molar Na_2S_4 in N, N-diethylacetamide; platinum electrode collector.
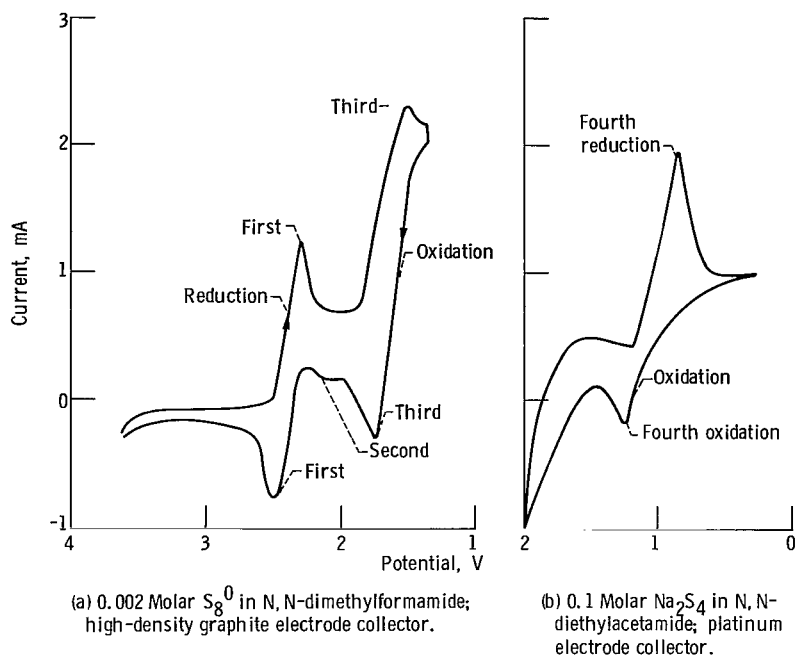
Figure 9. - Cyclic voltammograms for amide solutions at 120° C. Scan rate, 0.02 V/sec.

The second reduction mechanism was then investigated at 120° C with a high-density graphite electrode by discharging a cell containing a 0.5 molar solution of Na_2S_8 in N, N-dimethylformamide:

$$Na(\ell)| \text{ sodium beta-alumina}| 0.5 \text{ M } Na_2S_8 - DMF - (HDG)$$
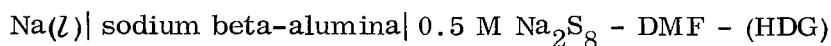
The Tafel plot for this cell gave a slope of 0.29 volt per decade and an exchange current density of about 2×10^{-3} A/cm^2.

The third oxidation reaction was studied by charging cells containing solutions of Na_2S_4 at 120° C. For the first cell, HDG and DMF were used; and for the second cell, porous graphite (PG) and N, N-diethylacetamide (DEA) were used. The cells were as follows:

$$Na(\ell)| \text{ sodium beta-alumina}| 0.9 \text{ M } Na_2S_4 - DMF - (HDG)$$

$$Na(\ell)| \text{ sodium beta-alumina}| 0.1 \text{ M } Na_2S_4 - DEA - (PG)$$
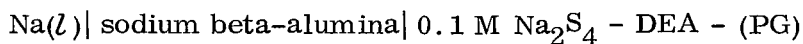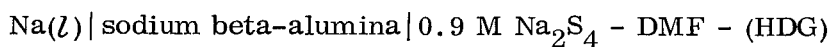
Tafel plots for the first and second cells gave slopes of 0.16 and 0.13 volt per decade, respectively. An exchange current density of about 3×10^{-4} A/cm^2 was obtained for the first cell. This relatively low exchange current is probably indicative of moderately

19

poor reversibility of the third oxidation-reduction reaction, as supported by the cyclic voltammetry results.

We propose the following overall reaction for the second reduction:

$$3S_8^= + 2e^- \rightleftarrows 4S_6^=$$
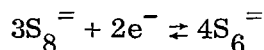
The Tafel slope of 0.29 was used to calculate the electron transfer coefficient β by assuming various mechanisms for the second reduction reaction (appendix C). Three mechanisms, involving one-electron transfer steps, gave a calculated β of 0.7. The following mechanism (eqs. (15) to (17)) is favored because it is simpler:
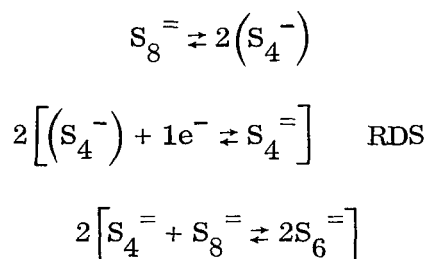
$$S_8^= \rightleftarrows 2\left(S_4^-\right)$$

$$2\left[\left(S_4^-\right) + 1e^- \rightleftarrows S_4^=\right] \quad \text{RDS}$$

$$2\left[S_4^= + S_8^= \rightleftarrows 2S_6^=\right]$$

This mechanism is supported by the fact that certain divalent polysulfides dissociate to form radical species (ref. 3). Consequently, an equilibrium between $S_8^=$ and the radical $\left(S_4^-\right)$ species might be expected. And the subsequent equilibrium between $S_6^=$ and the two species of $S_4^=$ and $S_8^=$ is supported by an observation of Martin (ref. 10). He found that the spectrum for an $S_6^=$ solution was similar to that obtained for a mixture of $S_8^=$ and $S_4^=$ solutions. The other one-electron transfer mechanisms are probably less likely: One mechanism (eqs. (18) to (21) in appendix C) requires a combination of the $\left(S_4^-\right)$ radical with the $S_8^=$ before the rate-determining step (eq. (20)) can occur; the other mechanism (eqs. (22) to (25)) requires the reduction of the S_2^0 species in preference to its combining to form S_8^0.

We made no attempt to follow the corresponding second oxidation reaction by charging a cell containing Na_2S_6. However, it seems reasonable to propose that this second oxidation mechanism is the reverse of the corresponding second reduction process.

$$2\left[2S_6^= \rightleftarrows S_8^= + S_4^=\right]$$

$$2\left[S_4^= \rightleftarrows \left(S_4^-\right) + 1e^-\right] \quad \text{RDS}$$

$$2\left(S_4^-\right) \rightleftarrows S_8^=$$

20
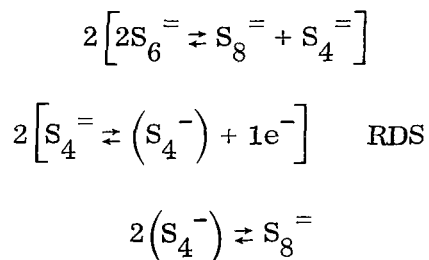
For the third reduction reaction, the $S_6^=$ species (produced during the second reduction reaction) is subsequently reduced to $S_4^=$. And the corresponding third oxidation reaction is assumed to be the reverse, as follows:

$$3S_4^= \rightleftarrows 2S_6^= + 2e^-$$
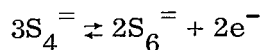
The Tafel slope of 0.15 volt per decade, obtained as an average value from the charging of two Na_2S_4 cells, was used to calculate an electron transfer coefficient β for various assumed third oxidation mechanisms. Four mechanisms gave a calculated β of 0.5. The following one-electron transfer mechanism (eqs. (26) to (28) in appendix C) is favored:

$$3S_4^= \rightleftarrows S_6^= + 2S_3^=$$

$$2\left[S_3^= \rightleftarrows \left(S_3^-\right) + 1e^-\right] \qquad \text{RDS}$$

$$2\left(S_3^-\right) \rightleftarrows S_6^=$$
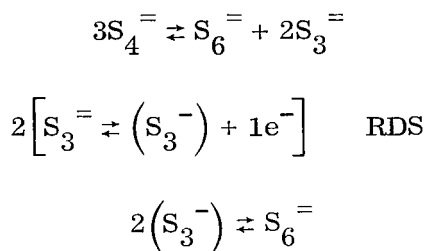
This disproportionation of the $S_4^=$ species seems analogous to that occurring for $S_6^=$. Furthermore, the equilibrium between the $\left(S_3^-\right)$ radical and $S_6^=$ is well known (ref. 12). Thus any $\left(S_3^-\right)$ produced by the oxidation of $S_3^=$ can form the final product of $S_6^=$. Two of the one-electron mechanisms seem unlikely: One (eqs. (32) to (35)) requires the formation of an S_{12}^{-6} species before oxidation can occur; the other mechanism (eqs. (36) to (38)) requires a preferential reaction of any S_2^0 species to form $S_6^=$ rather than combining to form S_8^0.

We assume that the third reduction mechanism (i.e., the reduction of $S_6^=$ to $S_4^=$) is the reverse of the third oxidation mechanism and propose the following:

$$S_6^= \rightleftarrows 2\left(S_3^-\right)$$

$$2\left[\left(S_3^-\right) + 1e^- \rightleftarrows S_3^=\right] \qquad \text{RDS}$$

$$2S_3^= + S_6^= \rightleftarrows 3S_4^=$$
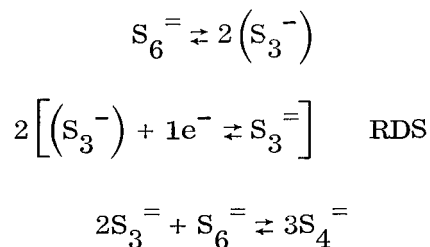
Widely differing reactions and mechanisms have been suggested by other investigators for the second and third oxidation-reduction reactions. For example, Martin (ref. 10) obtained a small oxidation peak (at -0.7 V, relative to the calomel electrode) between the first and third set of peaks but attributed this peak to the oxidation of a protonated species. This value of -0.7 volt is in reasonable agreement with the present

investigation and corresponds to about 2.1 volts relative to the sodium reference electrode. Martin's third oxidation-reduction peaks were also in reasonable agreement with the present investigation and correspond to about 1.7 and 1.6 volts, respectively, relative to the sodium reference electrode. Martin labeled these peaks as the second waves. He showed that $S_4^=$ was the product of this third reduction reaction and proposed a two-electron transfer mechanism for this reduction step. Bonneterre also studied the reduction of elemental sulfur, S_8^0, in methyl sulfoxide (ref. 12). Unlike Martin, he did not obtain the second oxidation-reduction peaks but did observe the presence of $S_6^=$. He suggested that the $S_8^=$ species, produced during the first reduction of S_8^0, disproportionated as follows:

$$S_8^= \rightleftarrows S_6^= + S_2^0$$

$$S_2^0 \rightleftarrows \frac{1}{4} S_8^0$$
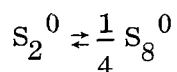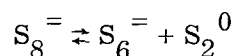
We suggest that our proposed second reduction reaction can explain the presence of $S_6^=$ more readily than Bonneterre's disproportionation reaction. In support of this, $S_6^=$ was produced electrochemically. For example, Martin indicated that current continued to flow even after the S_8^0 had been reduced by two electrons. After 2.7 electrons (or eight electrons per $3S_8^0$) had been passed, the spectrum of the solution was similar to that obtained for a solution of Na_2S_6, implying an end product of $S_6^=$.

Bonneterre observed the visible spectrum of S_8^0 near his first reduction voltage. If $S_8^=$ was disproportionating to $S_6^=$, some $S_6^=$ should have been present as soon as $S_8^=$ was being produced electrochemically in the first reduction reaction. However, Bonneterre found that only the $S_8^=$ species was present until two electrons had been passed per S_8^0. No $S_6^=$ was produced during this time. Continued electrolysis led to a decrease in the formation of $S_8^=$ with a corresponding increase in the formation of $S_6^=$. Finally, after 2.7 electrons had been passed per S_8^0, the $S_8^=$ species was no longer present and the $S_6^=$ species had increased to its maximum.

Badoz-Lambling also studied the reduction of S_8^0 in methyl sulfoxide (ref. 13). In agreement with the present investigation, he suggested that the third reduction reaction was involved in the continued reduction of $S_6^=$ to $S_4^=$. He implied that the mechanisms for both the third oxidation and reduction reactions involved a two-electron transfer step. However, we suggest that this two-electron mechanism is less likely than our proposed one-electron mechanism. In support of this, the calculated β for the two-electron mechanism (eqs. (42) and (43) in appendix C) is about 0.3, but the β for our proposed one-electron transfer mechanism for this third oxidation step is about 0.5.

Fourth oxidation-reduction reactions. – Reduction of the $S_4^=$ species to $S_2^=$ occurred in a 0.1-molar solution of Na_2S_4 in N, N-dimethylacetamide on porous graphite. Starting at its open-circuit voltage, the voltage was swept to about 0.1 volt relative to the sodium reference electrode. A broad reduction peak was obtained, with its maximum at about 0.8 volt. Since the $S_4^=$ should be the primary species in the solution, it is assumed that this fourth reduction process involves the reduction of $S_4^=$ to $S_2^=$. The fourth set of peaks were also seen in the cyclic voltammograms at 120° C for a 0.1-molar solution of Na_2S_4 in N, N-diethylacetamide with platinum as the electrode current collector. As shown in figure 9(b), sweeping between 2 and 0.2 volts gave the fourth oxidation-reduction peaks at 1.25 and 0.85 volts, respectively. Other sulfide solutions gave similar peaks. However, the peaks often were small and difficult to see because Na_2S_2 and Na_2S have smaller solubilities in most of the solvents studied. Some of the data for these fourth peaks are given in appendix B. The various solutions gave the fourth oxidation-reduction peaks at about 1.3 and 0.9 volts, respectively. This peak difference of about 0.4 volt suggests that the reversibility for these oxidation-reduction reactions was rather poor on either platinum or graphite at 120° C.

Although other investigators have had difficulty in observing these fourth (or fifth) oxidation-reduction peaks in aprotic solvents, the reduction of sulfides to $S_2^=$ was observed in polysulfide melts and in solutions of sulfides in fused salts (refs. 11, 14, and 15).

In the present investigation, the fourth reduction reaction was then followed by discharging at 120° C a cell containing a 0.9-molar solution of Na_2S_4 in N, N-dimethylformamide on high-density graphite:

$$Na(\mathit{l})|\text{ sodium beta-alumina}|\text{ 0.9 M } Na_2S_4 \text{ - DMF - (HDG)}$$
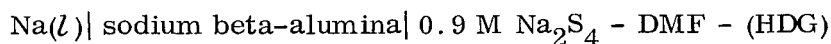
The Tafel plot for this cell gave a slope of 0.16 volt per decade and an exchange current density of about 5×10^{-4} A/cm^2. A similar cell of 0.1 molar Na_2S_4 in N, N-diethylacetamide (on platinum) gave a slope of about 0.22 volt per decade. The average for the two cells was 0.19 volt per decade.

The overall fourth oxidation-reduction reaction is assumed to be

$$S_4^= + 2e^- \rightleftarrows 2S_2^=$$
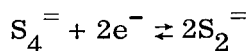
The electron transfer coefficients β were then calculated (appendix C) for various fourth reduction mechanisms. Three mechanisms gave a β of 0.6. The following mechanism (eqs. (44) and (45)) is favored because it is simpler:

$$S_4^= \rightleftarrows 2\left(S_2^-\right)$$

$$2\left[\left(S_2^-\right) + 1e^- \rightleftarrows S_2^=\right] \quad \text{RDS}$$
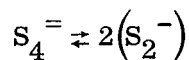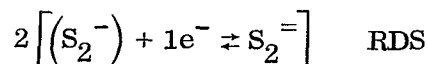
The two additional one-electron transfer mechanisms giving β of 0.6 are thought to be less likely: One mechanism (eqs. (46) to (48)) requires two consecutive one-electron transfer steps; the other mechanism (eqs. (49) to (51)) requires the reduction of S_2^0 in preference to its combining to form S_8^0. The two-electron mechanism (eqs. (52) and (53)) seems less likely because it gave a larger β of about 0.8.

We assume that the fourth oxidation mechanism (i.e., $S_2^=$ to $S_4^=$) is the reverse of the fourth reduction mechanism:

$$2\left[S_2^= \rightleftarrows \left(S_2^-\right) + 1e^-\right] \quad \text{RDS}$$

$$2\left(S_2^-\right) \rightleftarrows S_4^=$$

Fifth oxidation-reduction reactions. – As mentioned previously, no fifth oxidation-reduction peaks have been observed in aprotic solvents by other investigators. However, in the present investigation, the fifth peaks, though often difficult to see, were observed in a few cases. As shown in figure 10, a small fifth reduction peak was obtained at about 0.5 volt during the reduction sweep of a solution of Na_2S_8 in N, N-dimethylformamide at 120° C on a high-density graphite current collector. Other sulfide solutions gave similar peaks, some of which are given in appendix B. The fifth oxidation-reduction peaks were at about 1.0 and 0.6 volt, respectively. This peak difference of 0.4 volt suggests that the reversibility of the fifth oxidation-reduction reactions was rather poor.
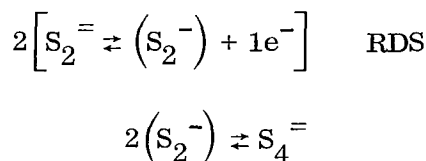
The overall fifth oxidation-reduction reaction is assumed to be as follows:

$$S_2^= + 2e^- \rightleftarrows 2S^=$$
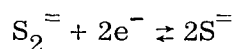
No cell studies were made for this reaction. However, we suggest the following as a possible mechanism for the fifth reduction reactions:

$$S_2^= + 1e^- \rightleftarrows \left(S_2^{-3}\right)$$

$$\left(S_2^{-3}\right) + 1e^- \rightleftarrows S_2^{-4}$$

$$S_2^{-4} \rightleftarrows 2S^=$$
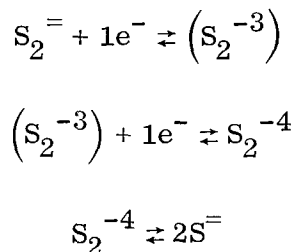
A mechanism analogous to those proposed for the reduction of the higher polysulfides
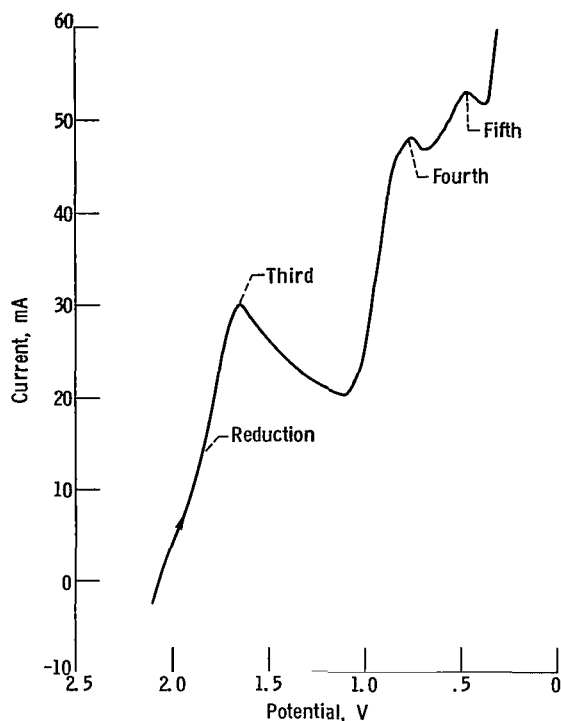
Figure 10. - Voltammogram for 0.05 molar Na_2S_8 in N,N-dimethylformamide (0.1 M $NaBF_4$) at 120° C with a high-density graphite electrode collector. Scan rate, 0.02 V/sec.

involving the dissociation of the $S_2^=$ species to a radical (S^-) species cannot be rejected categorically. However, this mechanism seems less likely. For example, although the existence of radical species such as S_3^- or S_2^- has been suggested by other investigators, no radical (S^-) species is known. Furthermore, disproportionation reactions involving the $S_2^=$ species seem less likely.

CONCLUSIONS

Solubility, stability, and electrochemical results for a soluble sulfur electrode were sufficiently encouraging to suggest that Na/sodium beta-alumina/Na_2S_x - organic solvent cells may be feasible for low temperature (100° to 120° C), high-density secondary battery systems. Some amides and a cyclic polyalcohol are promising for the sulfur electrode. Cyclic voltammograms for the sulfur-sulfide systems in amide solvents such as N,N-dimethylformamide suggest that the reversibilities on graphite at 120° C are moderately poor. In addition, cell charge-discharge experiments gave

exchange current densities (10^{-3} to 10^{-4} A/cm^2) that were somewhat smaller than desired for a practical cell (>10^{-3} A/cm^2). However, practical cell currents may still be attained for these systems: (1) by using a more effective electrode current collector to increase their reversibilities; or (2) by developing a collector with increased surface.

Reactions and mechanisms are suggested for the various sulfur-sulfide oxidation-reduction reactions and are compared with those processes suggested by other investigators.

Lewis Research Center,
  National Aeronautics and Space Administration,
    Cleveland, Ohio, April 13, 1978,
      506-23.

APPENDIX A

SCREENING OF ORGANIC SOLVENTS AT 120° C

Group 1 – Solvents Giving Moderately High Na_2S and Na_2S_2 Solubilities

Solvent class	Solvent	Sulfide	Remarks
Alcohol–amine	Ethanolamine	Na_2S	Some solubility
		Na_2S_2	>2 Molar[a]
Amide	Acetamide	Na_2S	~1 Molar[b]
		Na_2S_2	~1 Molar[b]
Cyclic alcohol	Cyclohexanol	Na_2S	Some solubility
		Na_2S_2	~0.5 Molar[a]
Glycol	Diethylene glycol	Na_2S	~1.5 Molar[a]
		Na_2S_2	>2 Molar[a]
	Triethylene glycol	Na_2S	~1.5 Molar[a]
		Na_2S_2	>2 Molar[a]
	Tetraethylene glycol	Na_2S	~0.5 Molar[a]
		Na_2S_2	~1.5 Molar[a]
Aliphatic polyalcohol	1,4-Butanediol	Na_2S	~2 Molar[a]
		Na_2S_2	>2 Molar[a]
	1,2,6-Trihydroxyhexane	Na_2S	Some solubility
		Na_2S_2	>2 Molar[a]
	Glycerol	Na_2S	Some solubility
		Na_2S_2	>2 Molar[a]
Cyclic polyalcohol	1,3-Cyclohexanediol	Na_2S	~0.3 Molar[b]

[a]Red-brown liquor.
[b]Light-yellow liquor.

Group 2 – Solvents Giving Poor-to-Moderate Na_2S and Na_2S_2 Solubilities

Solvent class	Solvent	Sulfide	Remarks
Alochol-ether	Carbitol	Na_2S	Red-brown liquor
		Na_2S_2	Red-brown liquor
	Cellosolve[c]	Na_2S	Red-brown liquor
		Na_2S_2	Red-brown liquor
Amide (aliphatic)	N, N-Diethylacetamide	Na_2S	Red-brown liquor
		Na_2S_2	Blue liquor
Amide (cyclic)	1-Methyl-2-pyrollidinone[c]	Na_2S	Blue liquor
		Na_2S_2	Green liquor
Amide (phosphorous)	Hexamethylphosphoramide	Na_2S	Blue liquor
		Na_2S_2	Blue liquor
Cyclic ketone	Cyclohexanone	Na_2S	Colorless liquor
		Na_2S_2	Green liquor
Lactone	γ-Butyrolactone	Na_2S	Light-yellow liquor
		Na_2S_2	Red-brown liquor
	γ-Valerolactone	Na_2S	Light-yellow liquor
		Na_2S_2	Blue liquor
Sulfolane	Sulfolane	Na_2S	Red-brown liquor
		Na_2S_2	Green liquor
	2, 4-Dimethylsulfolane	Na_2S	Light-yellow liquor
		Na_2S_2	Green liquor
Sulfoxide	Methyl sulfoxide[c]	Na_2S	Green liquor
		Na_2S_2	Blue-green liquor
	Tetramethylene sulfoxide	Na_2S	Red-brown liquor
		Na_2S_2	Red-brown liquor

[c]Dried through molecular sieve.

Group 3 – Solvents Giving a Gel or Slurry with Na_2S or Na_2S_2

Solvent class	Solvent	Sulfide	Remarks
Acetal	Phenylacetaldehyde dimethyl acetal	Na_2S	White gel
		Na_2S_2	White gel
Carbonate (cyclic)	Propylene carbonate	Na_2S	Light-yellow liquor
		Na_2S_2	Yellow slurry
Ester	Methyl trimethylacetate	Na_2S	White gel
		Na_2S_2	Yellow slurry

Group 4 – Solvents Giving Poor Na_2S or Na_2S_2 Solubilities

Solvent class	Solvent	Solvent class	Solvent
Acyl halide	Octanoyl chloride	Hydrofuran	2, 5-Dimethyltetrahydrofuran
Alcohol	1-Heptanol	Halogen	1, 2-Dibromoethane
Amine	MN-Diethylaniline		Chlorobenzene[c]
	Pyridine	Nitrile	n-Butyronitrile
	Quinoline	Phthalate	Dibutyl phthalate
Aromatic	o-Xylene[c]	Sulfide	s-Butyl disulfide
Borate	Tributyl borate		Diphenyl sulfide
Carbonate	Diethyl carbonate[c]	Thiol	1, 4-Butanedithiol
Ester	n-Butyl acetate[c]	Thiophene	3-Methylthiophene
Ether	Anisole		
	Phenyl ether		

[c]Dried through molecular sieve.

Group 5 – Solvents Giving Reactions with Na_2S or Na_2S

Solvent class	Solvent	Sulfide	Remarks
Acid	Propionic acid	Na_2S	H_2S evolved at 30° C
		Na_2S_2	Solid formed at 30° C
Aldehyde	Octyl aldehyde	Na_2S	Solid formed at 30° C
		Na_2S_2	Solid formed at 30° C
Anhydride	Acetic anhydride	Na_2S	Red solid formed at 30° C
		Na_2S_2	Red solid formed at 120° C
Keto–ester	Ethyl acetoacetate[c]	Na_2S	Yellow solid formed at 30° C
		Na_2S_2	H_2S evolved at 30° C
Ketone	Acetophenone	Na_2S	Yellow solid formed at 30° C
	2, 4–Pentanedione[c]	Na_2S	H_2S evolved at 30° C
Phosphate	Tributyl phosphate	Na_2S	H_2S evolved at 30° C
		Na_2S_2	Solid formed at 120° C
Phosphite	Dimethyl phosphite	Na_2S	H_2S evolved at 30° C
Sulfate	Diethyl sulfate	Na_2S	Vigorous reaction at 30° C
		Na_2S_2	Brown solid formed at 120° C
Sulfite	Dimethyl sulfite	Na_2S	H_2S evolved at 120° C

[c]Dried through molecular sieve.

APPENDIX B

OXIDATION-REDUCTION PEAKS RELATIVE TO THE SODIUM

REFERENCE ELECTRODE

First Oxidation-Reduction Reaction

Temperature, °C	Sulfide	Solvent (a)	Electrode current collector (b)	Oxidation peak, V (c)	Reduction peak, V (c)	Peak difference V
30	S_8^0	DMF	HDG	2.60	2.30	0.30
30		DMF	PG	2.70	2.20	.50
30		BD	PG	2.50	2.20	.30
120		DMF	HDG	2.45	2.30	.15
30	Na_2S_8			2.60	2.30	.30
120	Na_2S_8			2.65	2.30	.35
30	Na_2S_4			2.60	2.35	.25
120	Na_2S_2			2.55	2.35	.20
			Average	2.6	2.3	0.3

[a]DMF denotes N, N-dimethylformamide; BD denotes 1,4-butanediol.
[b]HDG denotes high-density graphite; PG denotes porous graphite.
[c]Scan rate, 0.01 to 0.02 V/sec.

Second and Third Oxidation–Reduction Reactions

Temper- ature, ^{o}C	Sulfide	Solvent (d)	Electrode current collector (c)	Second oxidation peak, V	Third oxidation peak, V	Third reduction peak, V	Third peak difference, V
25	S_8^{0}	DMF	HDG	2.2	1.80	1.60	0.20
25	S_8^{0}		PG	---	2.00	1.45	.55
120	S_8^{0}		HDG	2.1	1.75	1.55	.20
25	Na_2S_8			2.2	1.90	1.60	.30
120	Na_2S_8			---	1.85	1.60	.25
25	Na_2S_4			---	2.00	1.65	.35
120	Na_2S_4			2.3	2.00	1.65	.35
25	Na_2S_2			---	2.05	1.70	.35
25	Na_2S_2			2.2	1.90	1.75	.15
			Average	2.2	1.9	1.6	0.3

[c]Scan rate, 0.01 to 0.02 V/sec.
[d]DMF denotes N,N-dimethylformamide.

Fourth Oxidation–Reduction Reaction

Temper-ature, °C	Sulfide	Solvent (e)	Electrode current collector (b)	Oxidation peak, V	Reduction peak, V	Peak difference, V
120	S_8^0	DMF	HDG	---	1.0	---
25	Na_2S_8	DMF	HDG	---	.8	---
120	Na_2S_8	DMF	HDG	1.2	---	---
25	Na_2S_4	DMA	PG	1.5	1.1	0.4
120		DMA	PG	---	.8	---
25		DEA	Pt	---	1.0	---
120		DEA	Pt	1.3	.9	.4
			Average	1.3	0.9	0.4

[b]HDG denotes high-density graphite; PG denotes porous graphite.

[e]DMF denotes N,N-dimethylformamide; DMA denotes N,N-dimethylacetamide; DEA denotes N,N-diethylacetamide.

Fifth Oxidation–Reduction Reaction

Temper-ature, °C	Sulfide	Solvent (f)	Electrode current collector (b)	Oxidation peak, V	Reduction peak, V
120	S_8^0	DMF	HDG	0.9	0.7
25	Na_2S_8	DMF	HDG	---	.5
25	Na_2S_4	DMA	PG	1.0	---
			Average	1.0	0.6

[f]DMF denotes N,N-dimethylformamide; DMA denotes N,N-dimethylacetamide.

APPENDIX C

TAFEL EQUATION CALCULATIONS ASSUMING VARIOUS POSSIBLE MECHANISMS

First Reduction Reaction

The first reduction reaction (a cathodic process) is assumed to be

$$S_8^0 + 2e^- \rightleftarrows S_8^= \qquad (C1)$$

The discharging of three cells containing S_8^0 at 120° C gave an average Tafel slope of -0.39 (i.e., -0.36, -0.31, -0.49). Calculations are made by assuming various successive chemical and electrochemical reactions (i.e., a one- or two-electron transfer step). Assuming a one-electron transfer step resulted in

$$2\left[S_8^0 + 1e^- \rightleftarrows \left(S_8^-\right)\right] \qquad (1)$$

$$2\left(S_8^-\right) \rightleftarrows S_8^= + S_8^0 \qquad (2)$$

The cathodic Tafel slope equations (refs. 7 and 8) for equations (1) and (2), with equation (1) assumed to be the rate-determining step (RDS), are

$$b_c = \left(\frac{-2.3\ RT}{F}\right)\left[K + (1-\beta)(M)\right]^{-1} \qquad (C2)$$

$$\beta = 1 - \left[\frac{\left(\dfrac{-2.3\ RT}{b_c F}\right) - K}{M}\right] \qquad (C3)$$

where R, T, and F are the gas constant, temperature, and Faraday constant, respectively; K is the number of electrons that must be removed so that the products of the RDS can be transferred to the final product; β is the electron transfer coefficient; and M is the number of electrons involved in the rate-determining step. For equations (1) and (2) (with eq. (1) as the RDS), M = 1; K = 0; -2.3 RT/F at 120° C = -0.078; $b_c = -0.39$; and

$$\beta = 1 - \left[\frac{\left(\frac{-0.078}{-0.39}\right) - 0}{1}\right] = 0.8 \qquad \text{(C4)}$$

First Oxidation Reaction

The first oxidation reaction is assumed to be

$$S_8^{=} \rightleftarrows S_8^{0} + 2e^{-} \qquad \text{(C5)}$$

The charging of a cell containing Na_2S_8 at 120° C gave a Tafel slope of 0.18. Assuming a one-electron transfer step resulted in

$$2\left[S_8^{=} \rightleftarrows \left(S_8^{-}\right) + 1e^{-}\right] \qquad \text{(8)}$$

$$2\left(S_8^{-}\right) \rightleftarrows S_8^{0} + S_8^{=} \qquad \text{(9)}$$

The anodic Tafel slope equations for equations (8) and (9), with equation (8) assumed to be the RDS, are

$$b_a = \left(\frac{2.3\ RT}{F}\right)[\beta M - L]^{-1} \qquad \text{(C6)}$$

and

$$\beta = \left[\frac{\left(\frac{2.3\ RT}{b_aF}\right) + L}{M}\right] \qquad \text{(C7)}$$

where L is the number of electrons removed to permit the RDS to occur once. For equations (8) and (9) (with eq. (8) as the RDS), $M = 1$; $L = 0$; $b_a = 0.18$; and

$$\beta = \left[\frac{\left(\dfrac{0.078}{0.18}\right) + 0}{1} \right] = 0.4 \qquad (C8)$$

Tafel Equation Calculations Assuming Various Mechanisms

The Tafel equation calculations are summarized in the following table, along with those for the proposed oxidation-reduction mechanisms.

Reaction	Assumed mechanism	Assumed rate-determining step (RDS)	Equation	Slope	Number of electrons in RDS, M	Number of electrons removed, K	Number of electrons removed, L	Calculated electron transfer coefficient, β
First reduction (eq. (C3))	$2\left[S_8^{0} + 1e^- \rightleftarrows \left(S_8^{-}\right)\right]$	$S_8^{0} + 1e^- \rightleftarrows \left(S_8^{-}\right)$	(1)	-0.39	1	0	--	0.8
	$2\left(S_8^{-}\right) \rightleftarrows S_8^{0} + S_8^{=}$	$2\left(S_8^{-}\right) \rightleftarrows S_8^{0} + S_8^{=}$	(2)	-0.39	0	1	--	(a)
	$S_8^{0} + 1e^- \rightleftarrows \left(S_8^{-}\right)$	$S_8^{0} + 1e^- \rightleftarrows \left(S_8^{-}\right)$	(3)	-0.39	1	0	--	0.8
	$\left(S_8^{-}\right) + 1e^- \rightleftarrows S_8^{=}$	$\left(S_8^{-}\right) + 1e^- \rightleftarrows S_8^{=}$	(4)	-0.39	1	1	--	1.8
	$S_8^{0} + S_8^{=} \rightleftarrows 2\left(S_8^{-}\right)$	$S_8^{0} + S_8^{=} \rightleftarrows 2\left(S_8^{-}\right)$	(5)	-0.39	0	0	--	(a)
	$2\left[\left(S_8^{-}\right) + 1e^- \rightleftarrows S_8^{=}\right]$	$\left(S_8^{-}\right) + 1e^- \rightleftarrows S_8^{=}$	(6)	-0.39	1	0	--	0.8
	$S_8^{0} + 2e^- \rightleftarrows S_8^{=}$	$S_8^{0} + 2e^- \rightleftarrows S_8^{=}$	(7)	-0.39	2	0	--	0.9
First oxidation (eq. (C7))	$2\left[S_8^{=} \rightleftarrows \left(S_8^{-}\right) + 1e^-\right]$	$S_8^{=} \rightleftarrows \left(S_8^{-}\right) + 1e^-$	(8)	0.18	1	--	0	0.4
	$2\left(S_8^{-}\right) \rightleftarrows S_8^{0} + S_8^{=}$	$2\left(S_8^{-}\right) \rightleftarrows S_8^{0} + S_8^{=}$	(9)	0.18	0	--	-2	(a)
	$S_8^{=} + S_8^{0} \rightleftarrows 2\left(S_8^{-}\right)$	$S_8^{=} + S_8^{0} \rightleftarrows 2\left(S_8^{-}\right)$	(10)	0.18	0	--	0	(a)
	$2\left[\left(S_8^{-}\right) \rightleftarrows S_8^{0} + 1e^-\right]$	$\left(S_8^{-}\right) \rightleftarrows S_8^{0} + 1e^-$	(11)	0.18	1	--	0	0.4
	$S_8^{=} \rightleftarrows \left(S_8^{-}\right) + 1e^-$	$S_8^{=} \rightleftarrows \left(S_8^{-}\right) + 1e^-$	(12)	0.18	1	--	0	0.4
	$\left(S_8^{-}\right) \rightleftarrows S_8^{0} + 1e^-$	$\left(S_8^{-}\right) \rightleftarrows S_8^{0} + 1e^-$	(13)	0.18	1	--	-1	-0.6
	$S_8^{=} \rightleftarrows S_8^{0} + 2e^-$	$S_8^{=} \rightleftarrows S_8^{0} + 2e^-$	(14)	0.18	2	--	0	0.2

Reaction	Assumed mechanism	Assumed rate-determining step (RDS)	Equation	Slope	Number of electrons in RDS, M	Number of electrons removed, K	Number of electrons removed, L	Calculated electron transfer coefficient, β
Second reduction (eq. (C3))	$S_8^= \rightleftarrows 2(S_4^-)$	$S_8^= \rightleftarrows 2(S_4^-)$	(15)	-0.29	0	0	--	(a)
	$2[(S_4^-) + 1e^- \rightleftarrows S_4^=]$	$(S_4^-) + 1e^- \rightleftarrows S_4^=$	(16)	-0.29	1	0	--	0.7
	$2[S_4^= + S_8^= \rightleftarrows 2S_6^=]$	$S_4^= + S_8^= \rightleftarrows 2S_6^=$	(17)	-0.29	0	2	--	(a)
	$S_8^= \rightleftarrows 2(S_4^-)$	$S_8^= \rightleftarrows 2(S_4^-)$	(18)	-0.29	0	0	--	(a)
	$2[(S_4^-) + S_8^= \rightleftarrows (S_{12}^{-3})]$	$(S_4^-) + S_8^= \rightleftarrows (S_{12}^{-3})$	(19)	-0.29	0	0	--	(a)
	$2[(S_{12}^{-3}) + 1e^- \rightleftarrows S_{12}^{-4}]$	$(S_{12}^{-3}) + 1e^- \rightleftarrows S_{12}^{-4}$	(20)	-0.29	1	0	--	0.7
	$2[S_{12}^{-4} \rightleftarrows 2S_6^=]$	$S_{12}^{-4} \rightleftarrows 2S_6^=$	(21)	-0.29	0	2	--	(a)
	$2[S_8^= \rightleftarrows S_6^= + S_2^0]$	$S_8^= \rightleftarrows S_6^= + S_2^0$	(22)	-0.29	0	0	--	(a)
	$2[S_2^0 + 1e^- \rightleftarrows (S_2^-)]$	$S_2^0 + 1e^- \rightleftarrows (S_2^-)$	(23)	-0.29	1	0	--	0.7
	$2(S_2^-) \rightleftarrows S_4^=$	$2(S_2^-) \rightleftarrows S_4^=$	(24)	-0.29	0	2	--	(a)
	$S_4^= + S_8^= \rightleftarrows 2S_6^=$	$S_4^= + S_8^= \rightleftarrows 2S_6^=$	(25)	-0.29	0	2	--	(a)
Third oxidation (eq. (C7))	$3S_4^= \rightleftarrows S_6^= + 2S_3^=$	$3S_4^= \rightleftarrows S_6^= + 2S_3^=$	(26)	0.15	0	--	0	(a)
	$2[S_3^= \rightleftarrows (S_3^-) + 1e^-]$	$S_3^= \rightleftarrows (S_3^-) + 1e^-$	(27)	0.15	1	--	0	0.5
	$2(S_3^-) \rightleftarrows S_6^=$	$2(S_3^-) \rightleftarrows S_6^=$	(28)	0.15	0	--	-2	(a)
	$2[S_4^= \rightleftarrows (S_4^-) + 1e^-]$	$S_4^= \rightleftarrows (S_4^-) + 1e^-$	(29)	0.15	1	--	0	0.5
	$2(S_4^-) \rightleftarrows S_8^=$	$2(S_4^-) \rightleftarrows S_8^=$	(30)	0.15	0	--	-2	(a)
	$S_8^= + S_4^= \rightleftarrows 2S_6^=$	$S_8^= + S_4^= \rightleftarrows 2S_6^=$	(31)	0.15	0	--	-2	(a)
	$3S_4^= \rightleftarrows S_{12}^{-6}$	$3S_4^= \rightleftarrows S_{12}^{-6}$	(32)	0.15	0	--	0	(a)
	$S_{12}^{-6} \rightleftarrows (S_{12}^{-5}) + 1e^-$	$S_{12}^{-6} \rightleftarrows (S_{12}^{-5}) + 1e^-$	(33)	0.15	1	--	0	0.5
	$(S_{12}^{-5}) \rightleftarrows S_{12}^{-4} + 1e^-$	$(S_{12}^{-5}) \rightleftarrows S_{12}^{-4} + 1e^-$	(34)	0.15	1	--	-1	-0.5
	$S_{12}^{-4} \rightleftarrows 2S_6^=$	$S_{12}^{-4} \rightleftarrows 2S_6^=$	(35)	0.15	0	--	-2	(a)

[a] Indeterminate.

Reaction	Assumed mechanism	Assumed rate-determining step (RDS)	Equation	Slope	Number of electrons in RDS, M	Number of electrons removed, K	Number of electrons removed, L	Calculated electron transfer coefficient, β
Third oxidation (eq. (C7)) continued	$S_4^= \rightleftharpoons 2\left(S_2^-\right)$	$S_4^= \rightleftharpoons 2\left(S_2^-\right)$	(36)	0.15	0	--	0	(a)
	$2\left[\left(S_2^-\right) \rightleftharpoons S_2^0 + 1e^-\right]$	$\left(S_2^-\right) \rightleftharpoons S_2^0 + 1e^-$	(37)	0.15	1	--	0	0.5
	$2\left[S_2^0 + S_4^= \rightleftharpoons S_6^=\right]$	$S_2^0 + S_4^= \rightleftharpoons S_6^=$	(38)	0.15	0	--	-1	(a)
	$3S_4^= \rightleftharpoons S_{12}^{-6}$	$3S_4^= \rightleftharpoons S_{12}^{-6}$	(39)	0.15	0	--	0	(a)
	$S_{12}^{-6} \rightleftharpoons S_{12}^{-4} + 2e^-$	$S_{12}^{-6} \rightleftharpoons S_{12}^{-4} + 2e^-$	(40)	0.15	2	--	0	0.3
	$S_{12}^{-4} \rightleftharpoons 2S_6^=$	$S_{12}^{-4} \rightleftharpoons 2S_6^=$	(41)	0.15	0	--	-2	(a)
	$3S_4^= \rightleftharpoons S_6^= + 2S_3^=$	$3S_4^= \rightleftharpoons S_6^= + 2S_3^=$	(42)	0.15	0	--	0	(a)
	$2S_3^= \rightleftharpoons S_6^= + 2e^-$	$2S_3^= \rightleftharpoons S_6^= + 2e^-$	(43)	0.15	2	--	0	0.3
Fourth reduction (eq. (C3))	$S_4^= \rightleftharpoons 2\left(S_2^-\right)$	$S_4^= \rightleftharpoons 2\left(S_2^-\right)$	(44)	-0.19	0	0	--	(a)
	$2\left[\left(S_2^-\right) + 1e^- \rightleftharpoons S_2^=\right]$	$\left(S_2^-\right) + 1e^- \rightleftharpoons S_2^=$	(45)	-0.19	1	0	--	0.6
	$S_4^= + 1e^- \rightleftharpoons \left(S_4^{-3}\right)$	$S_4^= + 1e^- \rightleftharpoons \left(S_4^{-3}\right)$	(46)	-0.19	1	0	--	0.6
	$\left(S_4^{-3}\right) + 1e^- \rightleftharpoons S_4^{-4}$	$\left(S_4^{-3}\right) + 1e^- \rightleftharpoons S_4^{-4}$	(47)	-0.19	1	1	--	1.6
	$S_4^{-4} \rightleftharpoons 2S_2^=$	$S_4^{-4} \rightleftharpoons 2S_2^=$	(48)	-0.19	0	2	--	(a)
	$S_4^= \rightleftharpoons S_2^= + S_2^0$	$S_4^= \rightleftharpoons S_2^= + S_2^0$	(49)	-0.19	0	0	--	(a)
	$S_2^0 + 1e^- \rightleftharpoons \left(S_2^-\right)$	$S_2^0 + 1e^- \rightleftharpoons \left(S_2^-\right)$	(50)	-0.19	1	0	--	0.6
	$\left(S_2^-\right) + 1e^- \rightleftharpoons S_2^=$	$\left(S_2^-\right) + 1e^- \rightleftharpoons S_2^=$	(51)	-0.19	1	1	--	1.6
	$S_4^= + 2e^- \rightleftharpoons S_4^{-4}$	$S_4^= + 2e^- \rightleftharpoons S_4^{-4}$	(52)	-0.19	2	0	--	0.8
	$S_4^{-4} \rightleftharpoons 2S_2^=$	$S_4^{-4} \rightleftharpoons 2S_2^=$	(53)	-0.19	0	2	--	(a)

[a]Indeterminate.

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16. Abstract

A preliminary study of the sulfur electrode in organic solvents suggests that the system warrants further investigation for use in a low-temperature (100° to 120° C) Na-S secondary battery. A qualitative screening was undertaken at 120° C to determine the solubilities and stabilities of Na_2S and Na_2S_2 in representatives of many classes of organic solvents. From this screening and further quantitative studies, two classes of solvents were selected for further work: amides and cyclic polyalcohols. Voltammetric and Na-S cell charge-discharge studies of sulfide solutions in organic solvents (e.g., N,N-dimethylformamide) at 120° C suggested that the reversibilities of the reactions on Pt or high-density graphite were moderately poor. However, the sulfur electrode was indeed reducible (and oxidizable) through the range of elemental sulfur to Na_2S. Reactions and mechanisms are proposed for the oxidation-reduction processes occurring at the sulfur electrode.

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