FEASIBILITY STUDY FOR A SECONDARY Na/S BATTERY

FINAL REPORT
for Period October 1, 1977 - September 30, 1978

by

K. M. Abraham
R. Schiff
S. B. Brummer

EIC Corporation
55 Chapel Street
Newton, Massachusetts 02158

Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Cleveland, Ohio 44135

January, 1979

CONTRACT NO NAS3-21028

NASA-Lewis Research Center
Cleveland, Ohio 44135
Joseph Singer, Project Manager
FEASIBILITY STUDY FOR A SECONDARY Na/S BATTERY

FINAL REPORT

for Period October 1, 1977 - September 30, 1978

by

K. M. Abraham
R. Schiff
S. B. Brummer

EIC Corporation
55 Chapel Street
Newton, Massachusetts 02158

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Cleveland, Ohio 44135

January, 1979

CONTRACT NO. NAS3-21028

NASA-Lewis Research Center
Cleveland, Ohio 44135
Joseph Singer, Project Manager
The feasibility of a moderate temperature Na battery having the configuration

\[
\text{Liquid Na} / \text{Solid Electrolyte} / (\beta\text{-Al}_2\text{O}_3) / \text{Dissolved Na}_2\text{S}_n \text{ or Metal Sulfide}
\]

has been studied. This battery is to operate at a temperature in the range of 100-150°C. Two kinds of cathode were investigated: (i) a soluble S cathode consisting of a solution of Na\text{2S}_n in an organic solvent and (ii) an insoluble S cathode consisting of a transition metal dichalcogenide in contact with a Na\text{+}-ion conducting electrolyte.

Four amide solvents, dimethyl acetamide, diethyl acetamide, N-methyl acetamide and acetamide, were investigated as possible solvents for the soluble S cathode. Results of stability and electrochemical studies using these solvents are presented. The dialkyl substituted amides were found to be superior.

Although the alcohol 1,3-cyclohexanediol was found to be stable in the presence of Na\text{2S}_n at 130°C, its Na\text{2S}_n solutions did not appear to have suitable electrochemical properties.

The limited amount of work carried out with transition metal dichalcogenides indicates that they present interesting possibilities as cathode materials in a moderate temperature Na battery.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. THE Na-DISSOLVED S BATTERY</td>
<td>5</td>
</tr>
<tr>
<td>A. Aliphatic Amides as Solvents for the Dissolved S Cathode</td>
<td>5</td>
</tr>
<tr>
<td>1. Solubilities of Na$_2$S$_n$ in Amide Solvents</td>
<td>5</td>
</tr>
<tr>
<td>2. Stabilities of Amide Solvents in the Presence of Na$_2$Sn at 130°C</td>
<td>10</td>
</tr>
<tr>
<td>3. Sodium-Sulfur Cell Studies with CH$_3$CONR$_2$/Na$_2$Sn Cathodes</td>
<td>32</td>
</tr>
<tr>
<td>B. Sodium-Sulfur Cell with a 1,3 Cyclohexanediol (CHD)/Na$_2$S$_n$ Cathode</td>
<td>40</td>
</tr>
<tr>
<td>1. Cell with CHD/Na$_2$S/0.5M NaBr Solution as the Initial Catholyte</td>
<td>40</td>
</tr>
<tr>
<td>2. Cell with CHD/Na$_2$S$_4$/0.5M NaI Solution as the Initial Catholyte</td>
<td>42</td>
</tr>
<tr>
<td>III. THE Na-TRANSITION METAL SULFIDE BATTERY</td>
<td>44</td>
</tr>
<tr>
<td>A. Preparation and Characterization of the Disulfides</td>
<td>44</td>
</tr>
<tr>
<td>1. Titanium Disulfide, TiS$_2$</td>
<td>44</td>
</tr>
<tr>
<td>2. Tantalum Disulfide, TaS$_2$</td>
<td>47</td>
</tr>
<tr>
<td>B. Stability Characteristics of Metal Sulfide/Amide Mixtures</td>
<td>47</td>
</tr>
<tr>
<td>C. Electrochemical Evaluation of Transition Metal Disulfides</td>
<td>47</td>
</tr>
<tr>
<td>1. Titanium Disulfide as the Cathode</td>
<td>47</td>
</tr>
<tr>
<td>2. Tantalum Disulfide as a Cathode</td>
<td>49</td>
</tr>
<tr>
<td>IV. SUMMARY AND CONCLUSIONS</td>
<td>56</td>
</tr>
<tr>
<td>V. REFERENCES</td>
<td>57</td>
</tr>
</tbody>
</table>
### LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figures</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Experimental set-up for determination of Na$<em>{2}$S$</em>{n}$ solubilities.</td>
</tr>
<tr>
<td>2</td>
<td>A) Sample tube for stability test; B) Manometer assembly.</td>
</tr>
<tr>
<td>3</td>
<td>Absorption spectra of DMAC or DMAC/Na$_{2}$S solutions before and after heating at 130°C</td>
</tr>
<tr>
<td>4</td>
<td>Vapor phase IR spectrum of the gases from AC/Na$_{2}$S solution after 18 days of heating</td>
</tr>
<tr>
<td>5</td>
<td>Visible spectrum of a solution of Na$<em>{2}$S$</em>{n}$ in DMAC after heating for 21 days at 130°C</td>
</tr>
<tr>
<td>6</td>
<td>A plot of the amount of gas produced vs. heating time for amide/Na$<em>{2}$S$</em>{n}$ solutions.</td>
</tr>
<tr>
<td>7</td>
<td>Vapor phase infrared spectrum of gases from DMAC/Na$<em>{2}$S$</em>{8}$ solution after 21 days of heating at 130°C</td>
</tr>
<tr>
<td>8</td>
<td>Visible spectra of solutions of Na$<em>{2}$S$</em>{8}$ in DMAC</td>
</tr>
<tr>
<td>9</td>
<td>Visible absorption spectra of the DEAC/S reaction product in solution</td>
</tr>
<tr>
<td>10</td>
<td>Visible absorption spectra of the DMAC/S reaction product in solution</td>
</tr>
<tr>
<td>11</td>
<td>Vapor phase infrared spectrum of the gases from DMAC/S solution after 21 days of heating at 130°C</td>
</tr>
<tr>
<td>12</td>
<td>Mass spectrum of the gases from DMAC/S solution after 21 days of heating at 130°C</td>
</tr>
<tr>
<td>13</td>
<td>High temperature electrolytic cell having a β-Al$<em>{2}$O$</em>{3}$ separator</td>
</tr>
<tr>
<td>14</td>
<td>Galvanostatic charge (C)/discharge (D) curves for a cell of configuration molten Na/β-Al$<em>{2}$O$</em>{3}$/Na$<em>{2}$S$</em>{4}$ (2.4M S) NaBF$_{4}$ (0.04M), DMAC/carbon felt at 130°C</td>
</tr>
<tr>
<td>Figures</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>15</td>
<td>The third discharge (3C) and fourth discharge (4D) curves for a cell, liquid Na/β-Al₂O₃/Na₂S₄ (4M S), 0.75M NaI, DMAC/Teflon-bonded C electrode at 130°C.</td>
</tr>
<tr>
<td>16</td>
<td>Galvanostatic discharge/charge curves for a cell, liquid Na/β-Al₂O₃/Na₂S₄ (2M S), 0.5M NaI, DBAC/Teflon-bonded C electrode at 130°C.</td>
</tr>
<tr>
<td>17</td>
<td>The third discharge (3D), third charge (3C) and fourth discharge (4D) curves for the cell shown in Fig. 16.</td>
</tr>
<tr>
<td>18</td>
<td>Cycles five through ten of the cell shown in Fig. 16.</td>
</tr>
<tr>
<td>19</td>
<td>Galvanostatic charge/discharge curves for a cell, liquid Na/β-Al₂O₃/Na₂S (2M S), 0.5M NaBr, CHD/Teflon-bonded C at 130°C.</td>
</tr>
<tr>
<td>20</td>
<td>Galvanostatic discharge/charge curves for the cell, liquid Na/β-Al₂O₃/CHD, 0.5M NaI, 2M S as Na₂S₄ (9 ml) Teflon-bonded C at 130°C.</td>
</tr>
<tr>
<td>21</td>
<td>The discharge/charge curves for the cell liquid Na/β-Al₂O₃/DMAC (1M NaI), TiS₂ at 130°C.</td>
</tr>
<tr>
<td>22</td>
<td>Galvanostatic discharge/charge curves for the cell, liquid Na/β-Al₂O₃/DMAC (1M NaI), TiS₂ at 130°C.</td>
</tr>
<tr>
<td>23</td>
<td>The galvanostatic discharge curve for the cell liquid Na/β-Al₂O₃/DMAC (1M NaI), TaS₂ at 130°C.</td>
</tr>
<tr>
<td>24</td>
<td>Galvanostatic discharge/charge curves A and B for the cell liquid Na/β-Al₂O₃/DMAC (1M NaI), TaS₂ at 130°C.</td>
</tr>
</tbody>
</table>
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Tables</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SOME PHYSICAL PROPERTIES OF ACETAMIDE, N-METHYL-ACETAMIDE, DIMETHYLACETAMIDE</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>SOLUBILITY DATA FOR Na$_2$S$_n$ IN AMIDE SOLVENTS AT 150°C</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>STABILITY TEST DATA FOR ACETAMIDE/Na$_2$S$_n$ MIXTURES AT 130°C</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>STABILITY TEST DATA FOR NMAC/Na$_2$S$_n$ MIXTURES AT 130°C</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>STABILITY TEST DATA FOR DIMETHYLACETAMIDE/Na$_2$S$_n$ MIXTURES AT 130°C</td>
<td>17</td>
</tr>
<tr>
<td>6</td>
<td>STABILITY TEST DATA FOR DEAC/Na$_2$S$_n$ MIXTURES AT 130°C</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>TEMPERATURE PROFILE FOR THE PREPARATION OF TiS$_2$ FROM Ti AND S</td>
<td>45</td>
</tr>
<tr>
<td>8</td>
<td>X-RAY DIFFRACTION DATA CALCULATED FOR HEXAGONAL TiS$_2$ AND OBSERVED LINES</td>
<td>46</td>
</tr>
<tr>
<td>9</td>
<td>STABILITY TEST DATA FOR AMIDE/TiS$_2$ MIXTURES AT 130°C</td>
<td>48</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

The aim of this research program has been to investigate the feasibility of a moderate temperature, secondary Na battery utilizing S cathodes. The S cathode is either in the dissolved form as Na sulfides, Na$_2$S$_n$, n $\geq$ 1, in a suitable organic or inorganic solvent, or in the insoluble form as a transition metal sulfide such as TiS$_2$. This system, having the cell configuration,

$$\text{Liquid Na} \quad \text{Solid Electrolyte} \quad \text{Dissolved Na}_2\text{S}_n$$

or metal sulfide

is aimed at high energy density and high power density applications and is expected to have an operating temperature in the range of 100$^\circ$C to 150$^\circ$C. The solid electrolyte is $\beta$-Al$_2$O$_3$, an ionic conductor permeable only to Na$^+$ ions.

The dissolved S cathode battery would be a modification of the much researched (1,2) system,

$$\text{Liquid Na} \quad \beta$-Al$_2$O$_3 \quad \text{Molten S}$$

The latter system was first described by Kummer and Weber (3). In this system the fully charged cathode usually consists of a conductive graphite felt matrix imbedded in a pool of nonconductive liquid S. During discharge, Na$^+$ ions migrate through the solid electrolyte to form various Na polysulfides (Na$_2$S$_n$) at the surface of the porous graphite cathode. The initial discharge reaction is believed to be

$$2\text{Na}^+ + 5\text{S} + 2e^- \rightarrow \text{Na}_2\text{S}_5 \quad (1)$$

Further discharge products would involve S$_4^{2-}$ and S$_3^{2-}$ species, coupled with chemical steps involving ion-radical species. The operation of the system, however, is temperature-limited, and further complicated by formation of various phases, as described in its phase diagram (4). Upon discharge, insoluble Na$_2$S$_3$ precipitates out when the overall composition reaches a critical value. Because of the solidification of Na$_2$S$_3$, the lower limit of the operating temperature is 300$^\circ$C. Furthermore, on charge, when the overall composition exceeds Na$_2$S$_5$, two immiscible liquid phases
(Na$_2$S$_5$, S) coexist; of these, the S phase is nonconductive. The porous graphite cathode operation is believed to be transport-limited (5), as a result of the high exchange current density, the complicated phase-relationship, and the nonconductivity of S-rich phase.

Since the discharge reaction stops at Na$_2$S$_3$, the attainable energy density of this system is considerably less than that corresponding to the theoretical reaction

$$2\text{Na} + \text{S} \rightarrow \frac{1}{2}\text{Na}_2\text{S} \ (\approx 700 \text{ Whr/lb})$$

(2)

The theoretical energy density with an end-of-discharge composition of Na$_2$S$_3$ is 345 Whr/lb. The high operating temperature (>300°C) of the molten S system has introduced severe problems in the implementation of this battery concept. The successful development of the battery is contingent upon solving severe corrosion and materials problems: Cell failures occur because of accumulation of sensitive materials on the positive electrode, deterioration of the solid electrolyte or of seals, or more general corrosion (5,1). These problems fundamentally result from operation at very high temperature.

It is evident that many of the problems encountered in the Na/molten S system could be resolved by lowering the operating temperature. One way to achieve this is to use a S cathode as Na sulfides dissolved in a solvent so that the operating temperature is just above the melting point of Na, i.e., in the range of 100 to 150°C. In this case, if the solvent dissolves appreciable amounts of Na$_2$S, it might be possible to achieve the end-of-discharge composition closer to the theoretical Na$_2$S. Also the use of a solvent which dissolves appreciable amounts of Na-polysulfides (i.e., Na$_2$S$_n$ where, n >> 5) could eliminate the undesirable phase separation problems encountered in the molten S battery.*

An alternative approach is to use an insoluble transition metal sulfide cathode in contact with a Na$^+$-ion containing electrolyte so that during discharge the cell reaction is the intercalation of Na into the sulfide lattice, as depicted in Equation 3.

$$\text{MS}_2 + \text{Na}^+ + e^- \rightarrow \text{NaMS}_2$$

(3)

*Some solution to this problem has been found (1) by the use of metal sulfide additives such as FeS to the molten S cathode.
Such a battery would be analogous to the ambient temperature Li/TiS₂ cell and should operate conveniently at a temperature in the range of 100 to 150°C.

The major advantages of a moderate temperature system are:

1. Minimal problems from corrosion, seal fracture and thermal cycling.

2. Less expensive and simpler sealing procedures, e.g., the use of plastics becomes possible below 200°C.

3. Less insulation and hence less weight and cost, making smaller battery packages economical.

A preliminary battery design with a soluble S cathode indicates that for an end-of-discharge composition of Na₂S, a charged-state S solubility of 1.6M in S₈ is required to give an energy density comparable to that of a molten S battery designed for 100 Whr/lb performance. On the other hand, if the end-of-discharge product is Na₂S₂, the required S₈ concentration is ≈3.3M. We must, of course, take into account that compared with operation at 300-350°C, there will be some energy loss due to increased resistance of the β-Al₂O₃ and, possibly from polarization losses at the electrodes. The resistivity of β-Al₂O₃ at 300°C is ≈3 ohm cm and at 150°C it is 18 ohm cm. With tubes 0.8 mm thick, and discharge rates of 50 mA/cm², this involves a loss of 0.012V at 300°C and 0.072V at 150°C. Since the OCV is 2.08V, there is a corresponding additional loss from working at lower temperatures of 3%. In the high temperature cell, there is a further ohmic drop in the catholyte compartment about equal to that of β-Al₂O₃ (7). We can expect at least this additional loss at the lower temperature. Thus the overall energy loss from ohmic polarization in a soluble S battery would be of the order of 10%. Although the additional ohmic voltage drops associated with operation at lower temperature will effect the battery's ability to deliver the required energy density at the highest rates, it is not improbable that at less than the highest rates the soluble S battery (150°C) could achieve energy density comparable to the molten S battery (350°C). Rate goals of 25 mA/cm² at 1.8V seem reasonable for most applications.

The moderate temperature Na battery is analogous to the Na/SbCl₃ battery under development with EPRI support for electrical load-levelling (8). The latter battery is to operate at ~200°C with current densities up to 25 mA/cm² of β-Al₂O₃. It is projected to have power densities of ~50 mW/cm². This battery overcomes one of the major difficulties of the Na/molten S system, that of sealing. Plastic seals appear to be satisfactory (9).
A preliminary study, carried out at EIC (10), has shown the basic feasibility of the liquid Na/dissolved S battery concept. In this study, a liquid Na/β-Al₂O₃/dissolved S cell utilizing N,N-dimethyl acetamide (DMAC) as the S-solubilizing agent, exhibited, during short term cycling studies, good reversibility between voltage limits of 1.00 and 2.70V. The average cycling stoichiometry at 130°C corresponded to

\[ 5S_2^- \nrightleftharpoons S_{10}^- + 8e^- \]  

(4)

No elemental S was formed during cell charging, but only long chain, soluble polysulfides. The major system limitation was found to be the termination of discharge (sharp voltage cut-off to 1.00V) in the vicinity of a polysulfide composition of \( \sim S_2^- \). The principal reasons for this appeared to be the very low solubilities of the lower order polysulfides and the consequent choking of the carbon felt current collector by the precipitated Na sulfides.

Studies (10) of Na₂S in various aliphatic amides had shown that its solubility decreased with increasing N-alkyl substitution. Thus acetamide (AC), N-methylacetamide (NMAC) and dimethylacetamide (DIAC) dissolved Na₂S in the amounts of 1.10, 0.60 and 0.0075 M/l respectively at 150°C. The long term stability characteristics of these amides in the presence of Na₂Sn had not been determined.

In the present program a detailed investigation was carried out to determine the suitability of the amides as solvents for the dissolved S cathode. The major areas of investigation were solubility determinations of Na₂Sn in the amides at \( \sim 150°C \), long term stability characteristics of the amides in the presence of Na₂Sn at 130°C, and cell cycling studies in practical configuration utilizing β-Al₂O₃ as the solid electrolyte. We have also evaluated 1,3 cyclohexanediol (CHD) as a possible solvent for the dissolved S cathode.

The transition metal disulfides, TiS₂ and TaS₂ were investigated as possible cathode candidates. The studies included determination of their long term stabilities in the presence of DMAC or DEAC at 130°C and evaluation of their cycling behavior in NaI solutions of these amides.
II. THE Na-DISSOLVED S BATTERY

The successful development of a Na-dissolved S battery is contingent upon the selection of a high boiling solvent which shows high S solubility, intrinsic thermal stability up to 150°C, and which is unreactive towards Na2S_n. Our preliminary studies (10) had indicated that aliphatic amides were promising solvents with respect to many of these properties. Another class of solvents showing appreciable solubilities of the Na sulfides, including Na2S, was aliphatic alcohols. The present study therefore emphasized these two class of compounds.

A. Aliphatic Amides as Solvents for the Dissolved S Cathode

The suitability of aliphatic amides as solvents for the Na/S battery was evaluated by studying their ability to dissolve Na sulfides, Na2S_n, (n ≥ 1) at ~ 130°C, their long-term stability properties in the temperature range of 100-150°C, and by examining the electrochemical behavior of solutions of Na2S_n in these amides. The aliphatic amides investigated in the program were AC, NMAC, DMAC, and diethylacetamide (DEAC). Some physical properties of these solvents are shown in Table 1.

1. Solubilities of Na2S_n in Amide Solvents

The solubilities of Na2S_n (n = 1, 2, 4 or 8) in each of the amides, AC, NMAC, DMAC or DEAC at 150°C were measured. The experimental procedures and the results are given below.

* General Experimental

The experiments were carried out in the absence of air and moisture using standard techniques employed for the manipulation of air sensitive compounds (11). Whenever appropriate, the handling and transfer of reagents were also carried out in an argon-filled dry box (Vacuum-Atmospheres Corporation).

* Reagents

Commercially obtained reagents were purified as described below:

Acetamide (Fisher Scientific, Lot No. 742523) was twice-recrystallized from a mixture of methanol and diethyl ether. In this procedure, acetamide was initially dissolved in anhydrous MeOH (~1g AC/0.8 ml MeOH). It was then crystallized out by adding anhydrous diethyl ether
### TABLE 1

**SOME PHYSICAL PROPERTIES OF ACETAMIDE, N-METHYLCETAMIDE, DIMETHYLACETAMIDE AND DIETHYLACETAMIDE**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Acetamide</th>
<th>N-methylacetamide</th>
<th>N,N-dimethyl acetamide</th>
<th>N,N-diethyl acetamide</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.P., °C</td>
<td>80.5</td>
<td>29.5</td>
<td>-20</td>
<td>-</td>
</tr>
<tr>
<td>B.P., °C</td>
<td>221.5</td>
<td>206.0</td>
<td>165</td>
<td>185</td>
</tr>
<tr>
<td>Density, g/ml</td>
<td>0.967 (120°C)</td>
<td>0.9503 (30°C)</td>
<td>0.936 (25°C)</td>
<td>0.924 (25°C)</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.4274 (78°C)</td>
<td>1.4277 (30°C)</td>
<td>1.4351 (25°C)</td>
<td>-</td>
</tr>
<tr>
<td>Viscosity, CP</td>
<td>1.06 (120°C)</td>
<td>3.885 (30°C)</td>
<td>9.2 (25°C)</td>
<td>-</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>74 (25°C, extrap)</td>
<td>186 (25°C, extrap)</td>
<td>27 (25°C)</td>
<td>-</td>
</tr>
<tr>
<td>Min. Specific Conductance (Ω-1cm-1)</td>
<td>$2.6 \times 10^{-6}$ (94°C)</td>
<td>$1 \times 10^{-7}$ (40°C)</td>
<td>20 (25°C)</td>
<td>-</td>
</tr>
</tbody>
</table>
(\(\sim 10 \text{ ml Et}_2\text{O/g AC}\)), yielding long needle-like crystals. The crystals were further dried in vacuum \((\sim 10^{-3}\text{ torr})\) by continuously pumping for \(\sim 20\) hr. The melting point of the twice-recrystallized material was found to be 78-79°C, very close to the reported value (12) of 80.5°C.

High purity N-methylacetamide, obtained from Aldrich Chemical Co. (Lot No. 021777) was used after the following treatment for removal of its water content. About 100g of NMAC was dissolved in \(\sim 100\text{ ml anhydrous diethyl ether}\) and the solution was then passed through a chromatography column (1.5 cm ID and 28 cm long pyrex glass tube) packed with freshly regenerated\(^*\) Linde 4Å molecular sieves. The flow rate of the solution through the column was maintained at \(\sim 1\text{ ml/min}\). The ether from the sieved solution was removed in vacuum by collecting it in a dry ice/acetone cooled cold trap. Final drying of the amide was carried out by continuously pumping it in vacuum at room temperature for \(\sim 20\) hr. The N,N-dimethylacetamide was obtained from Burdick and Jackson Laboratories, Muskegan, Michigan. This material was of high purity, "distilled in glass" quality. The water content of the solvent was further reduced by passing over activated Linde 4Å molecular sieves. Diethylacetamide was vacuum distilled first using a spinning band column (Perkin-Elmer Corp.) and then dried over molecular sieves.

Elemental S (Ventron, random pieces), Na\(_2\)S (Ventron) and Na\(_2\)S\(_4\) (Ventron) were used as-received. The polysulfides, Na\(_2\)S\(_2\) and Na\(_2\)S\(_8\), were prepared from stoichiometric mixtures of Na\(_2\)S and Na\(_2\)S\(_4\) respectively with elemental S.

- **Solubility Determination**

  The experimental setup for solubility determination is shown in Figure 1. In a typical experiment, a mixture consisting of an excess of the sulfide (equivalent to 2-12M S) and a known amount of the solvent (10 ml) was taken in A and the system was thoroughly flushed with dry N\(_2\). The mixture was then heated with stirring to 150°C and maintained at this temperature for \(\sim 3\) hr for equilibration. After the 3 hr of heating, any undissolved sulfide was allowed to settle down. Thereafter, by maintaining a N\(_2\) flow, the joint at B was disconnected and an aliquot of the sample was withdrawn for analysis of total sulfur and S\(^{-2}\). Sampling was done by means of a pipette which had been heated to 150°C using a heating tape. Analytical procedures for sulfur determination are given below in detail.

\(^*\)Fresh molecular sieves obtained from the manufacturer were regenerated by heating at 400°C under a stream of Ar for \(\sim 16\) hr. About 0.30g of molecular sieves/ml of the solution was used. Use of molecular sieves has been suggested as the best method for removal of H\(_2\)O content of amide solvents (13).
Fig. 1: Experimental set-up for determination of $\text{Na}_2\text{S}_n$ solubilities.
• **Sulfide Analysis**

Sulfide analysis was carried out iodimetrically (14). It is based on the reactions,

\[
I_2 + S_n^{-2} \rightarrow nS^8 + 2I^-
\]  
(5)

\[
2S_2O_3^{-2} + I_2 \rightarrow S_4O_6^{-2} + 2I^-
\]  
(6)

Samples of the polysulfide solution, measuring 0.50 ml, were quickly added to an excess of standardized I₂ solution (0.05N). The solution was then titrated immediately with standard thiosulfate solution (0.05N) to a starch end point. When sulfide solution is added to I₂ solution, a white to off-white precipitate is formed at the neutral point. The precipitate is elemental S, Equation 5. In the presence of excess I₂ the solution has a yellow to pink color, showing unreacted iodine. Sodium thiosulfate neutralizes this iodine according to Equation 6. The S⁻² concentration is calculated from the amount of iodine consumed.

• **Total Sulfur Analysis**

Total S analysis was carried out by oxidation of the polysulfide to SO₄⁻², with H₂O₂ in ammoniacal medium and determination of SO₄⁻² by titration with standardized Ba(ClO₄)₂ solution (15).

\[
S_n^{-2} + (2n-2) OH^- + (2n+1) H_2O_2 \rightarrow nSO_4^{-2} + 4n H_2O
\]  
(7)

A sample of the nonaqueous polysulfide solution, 0.50 ml, was withdrawn. An excess of 50% NH₄OH, followed by excess 30% H₂O₂ were immediately added, until a colorless solution was obtained within a few minutes. The solution was then heated to boiling to destroy unreacted H₂O₂ and to insure complete oxidation of S. Heating was continued to drive off all the NH₃. The solution was then diluted to 50 ml, adjusting the pH to 2.5-4.0 with 1N HCl. (Very little or no acidification should be necessary if the NH₃ is completely removed). To a 2-5 ml aliquot, sufficient CH₃OH was added to make the solution 80%. One drop of thorin indicator solution (0.2%) was added and the solution was titrated with 0.005M standardized Ba(ClO₄)₂ to a pink end point.

The following procedures are important for obtaining accurate results:

For very dilute S solutions, a 1/5 dilution of the Ba(ClO₄)₂ should be used for titration. The end point is indicated by a change from yellow to pink. Practice is required to distinguish the intermediate orange from the final pink to within several drops (∼0.02 ml/drop in a 25 ml buret). It is helpful to have, for comparison, a sample that has been titrated beyond its end point.
Results and Discussion

The solubilities at 150°C of Na$_2$Sn, _n_ = 1, 2, 4 or 8, in AC, NMAC, DMAC and DEAC, respectively, are shown in Table 2. It can be seen that AC dissolves 1.06M Na$_2$S and NMAC dissolves 0.75M Na$_2$S. In general, the total S solubility in the two solvents is seen to increase with increasing polysulfide chain-length, reaching an upper limit when the S$_n^{-2}$ chain-length is _n_4. The solubility of Na$_2$S in AC or NMAC at 150°C is much higher than in DMAC. The observed trend of AC > NMAC > DMAC for the Na$_2$S-solubilizing properties of the three solvents is consistent with the increasing H-bonding ability in going from DMAC to AC. Thus from the standpoint of S solubility, both AC and NMAC are superior to DMAC. However, preliminary stability studies, carried out as described previously (10) along with the solubility experiments indicated that in the long run, solutions of Na$_2$Sn in AC or NMAC might be less stable than solutions of Na$_2$Sn in DMAC or DEAC.

2. Stabilities of Amide Solvents in the Presence of Na$_2$Sn at 130°C

The ultimate usefulness of the amides as solvents for the S cathode in the Na/S battery is dependent upon their long term stabilities. The stability properties should include both intrinsic thermal stability and chemical compatibility with Na$_2$Sn at temperatures <130°C. A thorough investigation of the long term stability characteristics of AC, NMAC, DMAC or DEAC in the presence of Na$_2$Sn at 130°C has been carried out. The procedure employed for this consisted of incubating amide solutions containing Na-sulfides at 130°C in sealed, evacuated glass tubes equipped with breakseals. The tubes were opened after known intervals of time (days) and the gas pressure in each tube was measured with a manometer. The solution and gas products were analyzed spectrometrically.

Reagents

All the reagents used in these tests were carefully dried according to procedures outlined below.

N-methylacetamide, dimethylacetamide and diethylacetamide were dried and/or purified as described earlier (Section IIA.1). Acetamide was also purified by the recrystallization procedure, described in Section IIA.1. However, before recrystallization with Et$_2$O, the methanolic solution was dried by passing twice through a chromatography column containing molecular sieves.

Sodium monosulfide, Na$_2$S (Ventron), was dried by heating in vacuum at 510°C with continuous pumping for 16 hr. After the heating, some shrinking of the volume, coupled with a slight darkening of the sulfide, was observed.
### TABLE 2
SOLUBILITY DATA FOR Na₂Sn in AMIDE SOLVENTS AT 150°C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Na₂S (MS⁻²/l)</th>
<th>Na₂S₂ (MS⁰/l)</th>
<th>Na₂S₄ (MS⁰/l)</th>
<th>Na₂S₈ (MS⁰/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetamide</td>
<td>1.06</td>
<td>2.4</td>
<td>7.6</td>
<td>7.4</td>
</tr>
<tr>
<td>N-methylacetamide</td>
<td>0.75</td>
<td>1.8</td>
<td>6.2</td>
<td>7.0</td>
</tr>
<tr>
<td>Dimethylacetamide</td>
<td>0.0075</td>
<td>-</td>
<td>4.27</td>
<td>6.6</td>
</tr>
<tr>
<td>Diethylacetamide</td>
<td>†</td>
<td>-</td>
<td>3.2</td>
<td>6.9</td>
</tr>
</tbody>
</table>

†Apparently none dissolved.
-Not done.
Sodium tetrasulfide, Na₂S₄ (Ventron), was also dried in vacuum at ~215°C with continuous pumping for ~16 hr. Elemental S (Ventron, random pieces) was also dried in vacuum at ~110°C for ~24 hr. At the end of the heating, all the sulfur had sublimed off and condensed onto the cooler parts of the flask in which it was heated.

**Experimental Procedure**

The test vessels consisted of pyrex tubes (~30 ml capacity) equipped with break-seals as shown in Figure 2A. Each tube was also provided with ground glass joints, A and B, for attachment to the vacuum system. The accurate volume of each tube was obtained by measuring the amount of water it required to fill the tube. In a typical experiment, weighed amounts of the sulfide or S and the amide were charged into the reaction tube inside a dry box. The tube was then evacuated at ~10⁻³ torr and sealed off at C. The hermetically sealed tube was heated at 130°C in a constant temperature oven (Tenney Environmental Chamber) for a known period of time. Three sample tubes were used for each solution to be tested so that the tubes could be opened after different periods of heating. Before the tube was opened for measuring the gas pressure, a breaker, consisting of an iron rod sealed inside a glass tube was held above the break-seal on the sidearm of the sample tube using a pair of magnets wrapped in a piece of electrical tape. After attachment of the sample tube to the manometer assembly (Figure 2B) and evacuation, the break-seal was opened by dropping the breaker, and the gas pressure was measured. Since the volumes of the manometer assembly and the sample tube are known, the amount of gas (mmoles) could be calculated using the ideal gas equation,

\[ PV = nRT \]

where \( P = \) pressure (atmosphere)
\( V = \) volume (liter)
\( T = \) temperature, °K
\( R = \) gas constant, 0.082 liter, atmosphere/mole/0°C

After the pressure measurements, the gases were analyzed by vapor phase IR and mass spectrometric methods. The solutions were also analyzed spectroscopically using IR, NMR and mass spectra.

**Results and Discussion**

**Thermal Stabilities of Aliphatic Amides.** Gas pressure measurements and spectroscopic data indicated that the aliphatic amides are thermally stable for at least 21 days at 130°C.
Fig. 2A: Sample tube for stability test.

Fig. 2B: Manometer Assembly
Thus no gases were formed from any of these amides. The IR and UV visible spectra of these solvents after the heat treatment did not show any noticeable changes. The results suggest that the overall thermal stabilities of the amides in the operating temperature range of the battery are satisfactory.

Stabilities of Amide/Na$_2$S Solutions. The test mixtures used for the evaluation are shown in Tables 3, 4, 5 and 6 respectively for the amides AC, NMAC, DMAC and DEAC. The monosulfide is only sparingly soluble in DMAC or DEAC. However, the results of tests, performed with an excess of undissolved Na$_2$S, indicated that these two amides are stable in the presence of Na$_2$S for at least 21 days at 130°C. No gases were produced from either the DMAC/Na$_2$S or the DEAC/Na$_2$S mixture. The solution maintained its colorless nature during the 21 days of heating. The visible-UV absorption spectra of DMAC or DMAC/Na$_2$S solutions recorded before and after heating are shown in Figure 3. The solutions heated for ≥ 6 days showed two absorption peaks at 285 nm and at 345 nm in addition to the peak at 265 nm due to DMAC. The peak at 285 nm is due to S$_2^-$, as evidenced by the spectrum of a freshly prepared solution* of Na$_2$S in DMAC. A similar absorption pattern at ~280 nm is exhibited by a solution of Na$_2$S in DMF (16). The absorption peak at 345 nm is due to a reaction product. However, the intensity of the peak at 345 did not increase with increasing heating time, and the relative concentration of the material exhibiting this absorption was very small. Similar experiments with DEAC/Na$_2$S mixtures indicated that its stability was similar to that of the DMAC/Na$_2$S mixture.

The monosulfide was moderately soluble in the amides NMAC or AC at 130°C (see Table 3). The stability characteristics of the AC/Na$_2$S solution was investigated in detail. A mixture containing 0.33 g (4.2 mmoles) Na$_2$S in 2.05 g AC produced 1.01 mmoles of gases in 18 days at 130°C. Vapor phase IR spectrometry (Fig. 4) indicated the gases to be mostly NH$_3$. However, it contained small amounts of H$_2$S also. The formation of these products may be explained by the following general reactions in a solution of Na$_2$Sn in acetamide:

\[
\text{CH}_3\text{CONH}_2 + S_n^- \rightarrow \text{CH}_3\text{CONH}^- + HS_n^- \quad (8)
\]

\[
\text{CH}_3\text{CONH}_2 + HS_n^- \rightarrow \text{CH}_3\text{CONH}^- + H_2S_n \quad (9)
\]

\[
H_2S_n \rightarrow H_2S + (n-1) S^- \quad (10)
\]

\[
2HS_n^- \rightarrow H_2S + S_{2n-1}^- \quad (11)
\]

\[
\text{CH}_3\text{CONH}_2 + HS_n^- \rightarrow \text{CH}_3\text{COS}_n^- + \text{NH}_3 \quad (12)
\]

*The solution was obtained by heating an excess of Na$_2$S in DMAC for ~15 min at 80°C and subsequently cooling the solution to room temperature.
<table>
<thead>
<tr>
<th>Tube No.</th>
<th>Reactants</th>
<th>No. of Days Heated at 130°C</th>
<th>mmoles of Gas</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3A</td>
<td>2.02g AC, 0.21g Na$_2$S$_9$ (5.8 mmol S)</td>
<td>5.5</td>
<td>2.75</td>
<td>Strong H$_2$S odor for gas. Strong onion odor for residue. New peak in the IR spectrum of solid at 2050 cm$^{-1}$. Vapor phase IR showed that the gas contained COS as a product.</td>
</tr>
<tr>
<td>3B</td>
<td>1.96g AC, 0.2228g Na$_2$S$_8$ (5.9 mmol S)</td>
<td>12.0</td>
<td>3.50</td>
<td>Same as above.</td>
</tr>
<tr>
<td>3C</td>
<td>1.98g AC, 0.251g Na$<em>2$S$</em>{9.5}$</td>
<td>20.0</td>
<td>4.19</td>
<td>Same as above.</td>
</tr>
<tr>
<td>2A</td>
<td>2.01g AC, 0.239g Na$_2$S$_4$ (5.5 mmol S)</td>
<td>5.5</td>
<td>0.22</td>
<td>Slight onion odor for residue. Strong H$_2$S odor for gas. COS as the major product in the gas by IR.</td>
</tr>
<tr>
<td>2B</td>
<td>1.998g AC, 0.228g Na$_2$S$_4$ (5.25 mmol S)</td>
<td>13.0</td>
<td>1.02</td>
<td>Strong onion odor for residue. Strong H$_2$S odor for gas. Growth of new IR peak at 2050 cm$^{-1}$. Mostly COS in the gas as shown by vapor phase IR.</td>
</tr>
<tr>
<td>2C</td>
<td>1.966g AC, 0.253g Na$_2$S$_4$ (5.8 mmol S)</td>
<td>21.0</td>
<td>0.58</td>
<td>Same as above.</td>
</tr>
<tr>
<td>4</td>
<td>2.05g AC, 0.328g Na$_2$S$_2$ (4.2 mmol S)</td>
<td>18.0</td>
<td>1.01</td>
<td>Solution turned dark brown from clear. The gas formed a green precipitate with CuCl$_2$. IR spectra showed it to be NH$_3$.</td>
</tr>
<tr>
<td>6A</td>
<td>1.953g AC, 0.2664g Na$_2$S$_4$ (6.12 mmol S), 1.4M butylborate</td>
<td>11.0</td>
<td>–</td>
<td>Tube leaked.</td>
</tr>
<tr>
<td>6B</td>
<td>1.9622g AC, 0.2572g Na$_2$S$_4$ (5.91 mmol S), 2.5M butylborate</td>
<td>11.0</td>
<td>0.42</td>
<td>Dark brown solution, appeared to be more viscous. The gas was found to be H$_2$S, COS and other minor components.</td>
</tr>
</tbody>
</table>
TABLE 4
STABILITY TEST DATA FOR NMAC/Na₂S MIXTURES AT 130°C

<table>
<thead>
<tr>
<th>Tube No.</th>
<th>Reactants</th>
<th>No. of Days Heated at 130°C</th>
<th>mmoles of Gas</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>5A</td>
<td>1.982g NMAC, 0.1876g Na₂S₆.2 (4.86 mmoles S)</td>
<td>6</td>
<td>0.14</td>
<td>Dark red solution; gas was found to contain COS, H₂S and other minor products.</td>
</tr>
<tr>
<td>5B</td>
<td>1.879g NMAC, 0.1744g Na₂S₇ (4.63 mmoles S)</td>
<td>12</td>
<td>0.58</td>
<td>Same as above.</td>
</tr>
<tr>
<td>5C</td>
<td>1.85g NMAC, 0.1974g Na₂S₆.5 (5.16 mmoles S)</td>
<td>18</td>
<td>1.05</td>
<td>Same as above.</td>
</tr>
</tbody>
</table>
TABLE 5

STABILITY TEST DATA FOR DIMETHYLACETAMIDE/Na₂Sn MIXTURES AT 130°C

<table>
<thead>
<tr>
<th>Tube No.</th>
<th>Reactants</th>
<th>No. of Days Heated at 130°C</th>
<th>mmoles of Gas</th>
<th>No. of Moles of Gas/Mole Sn</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>2 ml DMAC, 0.207g Na₂S₄ (4.76 mmoles S)</td>
<td>5</td>
<td>0</td>
<td>-</td>
<td>All the Na₂S₄ dissolved and the solution had a green color.</td>
</tr>
<tr>
<td>1B</td>
<td>2 ml DMAC, 0.2161g Na₂S₄ (4.97 mmoles S)</td>
<td>12</td>
<td>0.01</td>
<td>-</td>
<td>Same as above.</td>
</tr>
<tr>
<td>1C</td>
<td>2 ml DMAC, 0.2440g Na₂S₄ (4.92 mmoles S)</td>
<td>21</td>
<td>0.01</td>
<td>-</td>
<td>Same as above.</td>
</tr>
<tr>
<td>2A</td>
<td>2 ml DMAC, 0.247g Na₂S₉ (6.64 mmoles S)</td>
<td>5</td>
<td>0.36</td>
<td>0.054</td>
<td>Solution was dark red. Major component in this gas phase was COS.</td>
</tr>
<tr>
<td>2B</td>
<td>2 ml DMAC, 0.2259g Na₂S₈ (5.942 mmoles S)</td>
<td>12</td>
<td>0.47</td>
<td>0.079</td>
<td>Dark red solution with green tinge at 130°C. Mostly COS in the gas.</td>
</tr>
<tr>
<td>2C</td>
<td>2 ml DMAC, 0.243g Na₂S₈ (6.472 mmoles S)</td>
<td>21</td>
<td>1.02</td>
<td>0.157</td>
<td>Green solution at 130°C became dark red on cooling. Mostly COS in the gas.</td>
</tr>
<tr>
<td>3A</td>
<td>2 ml DMAC, 0.344g Na₂S (4.4 mmoles S)</td>
<td>5</td>
<td>0</td>
<td>-</td>
<td>Very little Na₂S dissolved. The solution was clear.</td>
</tr>
<tr>
<td>3B</td>
<td>2 ml DMAC, 0.329g Na₂S (4.22 mmoles S)</td>
<td>12</td>
<td>0</td>
<td>-</td>
<td>Very little Na₂S dissolved. The solution was clear.</td>
</tr>
<tr>
<td>3C</td>
<td>2 ml DMAC, 0.319g Na₂S (4.10 mmoles S)</td>
<td>21</td>
<td>0</td>
<td>-</td>
<td>Very little Na₂S dissolved. The solution was clear.</td>
</tr>
<tr>
<td>3D</td>
<td>2 ml DMAC, 0.011g S (3.1 mmoles)</td>
<td>21</td>
<td>0.775</td>
<td>0.25</td>
<td>Yellow solution. The gases were a mixture of COS and CS₂ as evidenced by IR and mass spectra.</td>
</tr>
</tbody>
</table>
# TABLE 6

STABILITY TEST DATA FOR DEAC/Na$_2$S$_m$ MIXTURES AT 130°C

<table>
<thead>
<tr>
<th>Tube No.</th>
<th>No. of Days at 130°C</th>
<th>mmoles of gas</th>
<th>% Sulfur Reacted</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>L$_1$</td>
<td>7</td>
<td>0.686</td>
<td>9.8</td>
<td>Dark olive-green with brown tint.</td>
</tr>
<tr>
<td>L$_2$</td>
<td>14</td>
<td>0.739</td>
<td>11.6</td>
<td>Dark green solution at temperature. Turns dark brown on cooling.</td>
</tr>
<tr>
<td>L$_3$</td>
<td>21</td>
<td>1.00</td>
<td>15.5</td>
<td>Same as above.</td>
</tr>
<tr>
<td>X$_1$</td>
<td>7</td>
<td>0</td>
<td>-</td>
<td>Dark blue-green solution. Na$_2$S$_4$ not all dissolved.</td>
</tr>
<tr>
<td>X$_2$</td>
<td>14</td>
<td>0</td>
<td>-</td>
<td>Same as above.</td>
</tr>
<tr>
<td>X$_3$</td>
<td>21</td>
<td>0</td>
<td>-</td>
<td>Same as above.</td>
</tr>
<tr>
<td>C$_1$</td>
<td>6</td>
<td>0</td>
<td>-</td>
<td>Salmon color over Na$_2$S powder.</td>
</tr>
<tr>
<td>C$_2$</td>
<td>12</td>
<td>0</td>
<td>-</td>
<td>Same as above.</td>
</tr>
<tr>
<td>C$_3$</td>
<td>21</td>
<td>0</td>
<td>-</td>
<td>Same as above.</td>
</tr>
<tr>
<td>B</td>
<td>21</td>
<td>0</td>
<td>-</td>
<td>Remained clear.</td>
</tr>
<tr>
<td>FF</td>
<td>43</td>
<td>0.53</td>
<td>13.25</td>
<td>Reddish-yellow solution.</td>
</tr>
</tbody>
</table>
Fig. 3: Absorption spectra of DMAC or DMAC/Na$_2$S solutions before and after heating at 130°C.
Fig. 4: Vapor phase IR spectrum of the gases from $\text{AC}/\text{Na}_2\text{S}$ solution after 18 days of heating.
It appears that in an Na₂S/AC solution with an excess of acetamide, as in the present case, reactions 8 and 12 predominate. Reactions 9 and 11, leading to the formation of H₂S, probably occur only to a small extent. It may be noted that reaction 12 is analogous to the well characterized reaction of CH₃COOC₆H₅ with NaSH to form CH₃COSNa and C₆H₅OH, as depicted in Equation 13.

\[
\text{CH}_3\text{COOC}_6\text{H}_5 + \text{NaSH} \rightarrow \text{CH}_3\text{COSNa} + \text{C}_6\text{H}_5\text{OH}
\] (13)

Stabilities of Amide/Na₂Sn, n > 1, Solutions. The tests were performed with amide/Na₂Sn solutions where n = 4 or ~8. The test solutions had a S concentration of ~2-3M/litre. The various test mixtures for the amides, AC, NMAC, DMAC and DEAC respectively are shown in Tables 3, 4, 5 and 6.

A solution of Na₂S₄ in DMAC or DEAC did not produce any gas even after heating for a period of 21 days at 130°C. The visible spectra of fresh and heated solutions, shown in Figure 5, were similar. The primary absorption in these solutions is the strong peak at 618 nm due to S₃⁻. The NMR and IR spectra also indicated no products in solution.

Longer-chain polysulfides (Sn⁻², n > 4), were found to react with DMAC or DEAC at 130°C. Both of these amides produced gases, the amount of which increased with increasing heating time. A plot of the amount of gases produced versus heating time (days) is shown in Figure 6. Vapor phase infrared spectrum (Fig. 7) indicated that the gases were the same from both of the amides and were identified as containing mostly carbon oxysulfide, COS. The visible spectra of these solutions also showed major changes after the heating. This is illustrated in Figure 8 for a solution of Na₂S₈ in DMAC. After heating for 21 days at 130°C, the absorption peak at 520 nm, characteristic of long chain polysulfides found in freshly prepared solution, has considerably decreased in intensity. The spectral properties of the solution before and after the heating suggest that during heating S⁰ present in solution with polysulfides reacts gradually with the amides to produce carbon oxysulfide and polysulfides of shorter chain lengths. It appears, thus, that the reactive species in these solutions is elemental S. The stability tests at 130°C on mixtures of S and DMAC or DEAC seem to support this. Elemental S is insoluble in N,N-dimethylacetamide or in N,N-diethylacetamide at room temperature. However, when a mixture of S and either of these amides is heated to 130°C, an orange-yellow solution is formed. No gas is formed from this reaction mixture in 16 hr at this temperature. The visible spectra of these solutions, Figs. 9 and 10, show broad absorptions with a peak at 437 nm for the DMAC-sulfur reaction product and two peaks at 500 nm and 425 nm for the DEAC-sulfur reaction product.

*The solvents alone show no absorptions above 300 nm after heating for the same period of time.
Fig. 5: Visible spectrum of a solution of Na$_2$S$_n$ in DMAC after heating for 21 days at 130$^\circ$C.
Fig. 6: A plot of the amount of gas produced vs. heating time for amide/Na$_2$S$_n$ solutions

A - AC/Na$_2$S$_n$ solution, n = 8  
B - DMAC/Na$_2$S$_n$ solution, n = 8  
C - NMAC/Na$_2$S$_n$ solution, n = 6  
D - DEAC/Na$_2$S$_n$ solution, n = 8
Fig. 7: Vapor phase infrared spectrum of gases from DMAC/Na$_2$S$_8$ solution after 21 days of heating at 130°C.
Fig. 8: Visible spectra of solutions of Na₂S₈ in DMAC.
B - After heating for 12 days at 130°C
C - After heating for 21 days at 130°C
Fig. 9: Visible absorption spectra of 1M DEAC/S reaction product in solution.

A - after 16 hours of heating at 130°C
B - After 40 days of heating at 130°C
Fig. 10: Visible absorption spectra of the DMAC/S reaction product in solution.
A - after 16 hours of heating at 130°C
B - After 21 days of heating at 130°C
Further heating of these solutions produce gases, the amount of which increases with increasing heating time. Some changes are also observed in the visible spectrum of the solution, although the gross features of the spectra are maintained. Vapor phase infrared (Fig. 11) and mass (Fig. 12) spectral data proved that the gases were a mixture of carbon oxysulfide (COS) and carbon disulfide (CS₂). About 75% of the mixture was carbon oxysulfide. It was found that the reaction of each of the four amides with S under the present reaction conditions produces a similar mixture of volatile products of COS and CS₂. The evidence that COS and CS₂ are produced considerably after the initial reaction with S, suggests that in all cases these gases are secondary reaction products. It appears that elemental sulfur reacts initially with the amides to produce long chain sulfur containing products which on continued heating decomposes to give COS and CS₂, as shown in Equations 14 and 15.

\[
\text{CH}_3\text{CON(CH}_3)_2 + n\text{S} \xrightarrow{130^\circ C} \text{CH}_3\text{COS}_n\text{N(CH}_3)_2 \quad (14)
\]

\[
\text{CH}_3\text{COS}_n\text{N(CH}_3)_2 \xrightarrow{\Delta} \text{CH}_3\text{S}_{n-1}\text{N(CH}_3)_2 + \text{COS} \quad (15)
\]

The various physical properties of the solution products are also consistent with the formation of the polysulfides I and II. For example, the visible spectrum resembles that of alkali metal polysulfides in non-aqueous solvents (10). The infrared spectrum of the orange solution from DMac and S exhibited an absorption at 1135 cm\(^{-1}\) which is in the region of C-S stretching vibrations. The \(^1\)H NMR spectrum of this solution exhibited a complex pattern. Nevertheless, the presence of new \(-\text{N(CH}_3)_2\) resonances centered at 2.9 ppm and a new-COCH₃ or -SCH₃ resonance at 1.51 ppm, are also consistent with the structures I and II.

The formation of the same gas products from the reactions of both elemental S and Na₂Sn, \(n > 4\), suggests a possible explanation for the observed reaction with Na₂Sn, \(n > 4\) as follows:

A variety of equilibria involving S chains and elemental S are usually present in solutions of alkali metal polysulfides in nonaqueous solvents. There is evidence, from spectroscopic and electrochemical studies (17), for the existence of equilibrium of the type 16, in solutions of alkali metal polysulfides in solvents such as dimethylsulfoxide (DMSO) or tetrahydrofuran (THF).

\[
\text{S}^{-2}_n + \text{S}^{-2}_{n-x} + x\text{S}^\circ \quad (16)
\]
Fig. 11: Vapor phase infrared spectrum of the gases from DMAC/S solution after 21 days of heating at 130°C.
Fig. 12: Mass spectrum of the gases from DMAC/S solution after 21 days of heating at 130°C.
The solution properties of \( \text{Sn}_{4}^{-2} \) in DMAC resemble strongly those of \( \text{Sn}_{4}^{-2} \) in DMSO (17). It appears that when a solution of \( \text{Sn}_{4}^{-2}, n > 4 \), in DMAC, is heated, the neutral S present in equilibrium, reacts with the amide to form I. This reaction shifts equilibrium 3 to the right until all the \( \text{Sn}_{4}^{-2} \) is converted to \( \text{S}_{4}^{-2} \). Further dissociation of \( \text{S}_{4}^{-2} \) is not observed, probably because of a unique stabilization of \( \text{S}_{4}^{-2} \) in this solvent. Spectral data suggest that \( \text{S}_{4}^{-2} \) is strongly dissociated in DMAC to form \( \text{S}_{3}^{-} \), according to Equation 17.

\[
2\text{S}_{4}^{-2} \rightarrow \text{S}_{2}^{-2} + 2\text{S}_{3}^{-}
\]  

(17)

In general, it is seen that basic solvents such as DMAC, DEAC, hexamethyl phosphoramid (HMP) or DMSO promotes the dissociation of \( \text{S}_{4}^{-2} \) in the manner shown in Equation 17. The rather high concentration of the anion radical in these solvents may indicate a unique stabilization accorded to it through solvent coordination. A common feature of all these solvents is that they possess electron-rich structural units such as C=O, P=O, or S=O. It appears that the solvent-S\(_{3}^{-}\) coordination occurs through these functional groups and may involve a five-membered ring structure, III.

\[
\begin{array}{c}
\text{X} \\
\text{S} \\
\text{O} \\
\text{S} \\
\text{S} \\
\end{array}
\]

III.

Solutions of \( \text{Sn}_{n}^{-2}, n > 4 \), in acetamide or N-methylacetamide also behave in a similar manner to the N-dialkyl substituted amides, except that the acetamide solution is much less stable. Some \( \text{H}_{2}\text{S} \) is also produced from these solutions. The formation of \( \text{H}_{2}\text{S} \) may be explained on the basis of Equations 8-11.

* Summary and Conclusion of Stability Studies

The aliphatic amides investigated in this program are thermally stable for long periods of time in the temperature range of 100 to 150°C. However, their Na sulfide solutions show varying degrees of reactivity which depend both on the nature of the sulfide and the nature of the amide. The overall stability trend is \( \text{CH}_{3}\text{CON(CH}_{3})_{2} \approx \text{CH}_{3}\text{CON(C}_{2}\text{H}_{5})_{2} > \text{CH}_{3}\text{CONH(CH}_{3})_{2} >> \text{CH}_{3}\text{CONH}_{2} \). It is also found that with the dialkyl substituted amides, the reaction is limited to \( \text{Na}_{2}\text{Sn} \), with \( n > 4 \). Thus, of the four solvents the most suitable ones are \( \text{CH}_{3}\text{CON(CH}_{3})_{2} \) and \( \text{CH}_{3}\text{CON(C}_{2}\text{H}_{5})_{2} \). With these two solvents, it might be possible to achieve a relatively stable cathode by suitably controlling the charging limit of the battery to the formation of a medium chain polysulfide such as \( \text{S}_{4}^{-2} \).
3. Sodium-Sulfur Cell Studies with CH₃CONR₂/Na₂Sn Cathodes

- **Experimental Results**

In a previous program (10), we studied the cycling behavior of the DMAC/Na₂Sn cathode, incorporated in a cell of configuration shown in Figure 13. During short-term cycling studies, this cell exhibited good reversibility between voltage limits of 1.00 and 2.70V. Typical discharge/charge curves are shown in Figure 14. The average cathode cycling stoichiometry at 130°C corresponded to

$$5S_2^- \leftrightarrow S_{10}^- + 8e^-$$

(18)

No elemental S was formed during cell charging, but only long chain, soluble polysulfides. The major system limitation was found to be the termination of discharge (sharp voltage cutoff to 1.0V) in the vicinity of a polysulfide composition of $S_2^-$. The major reasons for this appeared to be the very low solubilities of the lower order polysulfides and the consequent choking of the carbon felt current collector by the precipitated Na sulfide(s).

The carbon current collector in the above cells was fabricated from graphite felt (Union Carbide WDF felt). This has a porosity of only ~15% (1). The Teflon-bonded carbon electrode used in Li/soluble S cells (17) or in Li/SOC₁₂ cells (18) has a porosity in the neighborhood of 80%. The effect of the higher porosity Teflon-bonded carbon electrode on the discharge capacity of the DMAC/Na₂Sn cathode was assessed in the present study using a cell similar to the one shown in Figure 13, except that the graphite felt electrode was replaced with a Teflon-bonded carbon electrode. The latter electrode, 6 cm x 3.6 cm x 0.096 cm, was fabricated by Teflon-bonding 0.6g Shawinigan 50% compressed carbon black on an expanded stainless steel grid (Exmet Corp.) The electrode was wound around the $\beta$-Al₂O₃ tube and, when placed in the cell, it was firmly positioned by pressure contacting the walls of the two compartments. The cell was filled with 7 ml of 4M S as Na₂S₄ in DMAC/0.75M NaI electrolyte. The open circuit potential of the cell was 1.82V, as found previously with the graphite felt electrode, and the cell exhibited a resistance of ~7Ω at 130°C. The cell was galvanostatically discharged and charged within the limits of 1.00 and 2.40 volts. A typical charge/discharge curve is shown in Figure 15. The open circuit potential of the cell, measured at the end of discharge was 1.23V. This suggests that the discharge of Na₂Sn to a composition below $S_2^-$ was achieved with the Teflon-bonded carbon electrode as opposed to a discharge only to $S_2^-$. With graphite felt. In the latter case, the OCV of the cell at the end of discharge, corresponding to the polysulfide composition of $S_2^-$, was 1.76V. The present cell cycled five times, and the average
Fig. 13: High temperature electrolytic cell having a $\beta$-$\text{Al}_2\text{O}_3$ separator.
Fig. 14: Galvanostatic charge (C)/discharge (D) curves for a cell of configuration molten Na/β-Al2O3/Na2S4 (2.4M S) NaBF4 (0.4M), DMAC/carbon felt at 130°C. Current densities based on 12.6 cm² electrode area: 4C, 4D, 1.59 mA/cm²; 1C, 1D, 2.4 mA/cm²; 0D, 2C, 2D, 3C, 3D, 3.2 mA/cm².
Fig. 15: The third discharge (3C) and fourth discharge (4D) curves for a cell, liquid Na/β-Al₂O₃/Na₂S₄ (4M S), 0.75M NaI, DMAC/Teflon-bonded C electrode at 130°C. Current = 20 mA; current density = 2 mA/cm². The cell was tested galvanostatically.
charge utilization in discharge was just below \(1 \text{e}^-/\text{S}\). However, the lower S utilization might be due to the unoptimized current collector, especially with respect to the solution to current collector volume ratio. Since we know that the primary self-discharge reaction is the reaction of the amide with elemental S, which would occur in significant amounts only when the polysulfide composition is \(>4\), it might be possible to achieve long cycle life as well as good S utilization with an optimized cathode structure consisting of a solution of \(\text{Na}_2\text{S}_n\) in DMAC and a high porosity carbon such as a Teflon-bonded carbon current collector. Note that the reversible reaction

\[
\text{S}_4^{2-} + 6\text{e}^- \xrightarrow{\text{t}} 4\text{S}^{2-}
\]

involves \(1.5\text{e}^-/\text{S}\), and the loss of \(\approx 0.3\text{e}^-/\text{S}\) by restricting the charging limit to \(\text{S}_4^{2-}\) is minor, compared with the possible gain in cycle life.

The cycling behavior of a Na/S cell with a DEAC/\(\text{Na}_2\text{S}_n\)/NaI cathode was also evaluated. A Teflon-bonded carbon electrode similar to the one discussed above was used. The cell initially contained 6 ml of a 2M S solution as \(\text{Na}_2\text{S}_4\) in DEAC/0.5M NaI electrolyte. The OCV of the cell was initially 1.84V, similar to that observed with a DMAC/\(\text{Na}_2\text{S}_4\) cathode. The cell exhibited a resistance at 130°C of 15Ω. The cell was cycled at the various constant currents of 10, 20 and 30 mA, corresponding to current densities of 1, 2 and 3 mA/cm². Cycling limits of 1.0V and 2.7V were used. The discharge/charge curves are shown in Figures 16, 17 and 18. The cell exhibited good reversibility behavior, although the discharge capacity did show a tendency to decrease with increasing cycle number, especially after the 5th discharge. Much of this loss may be attributed to the self-discharge reaction between DEAC and elemental S. In this cell, we made no attempt to restrict the charging limit to an intermediate size polysulfide chain such as \(\text{S}_4^{2-}\), the highest charge composition with minimal amounts of elemental sulfur in equilibrium.

**Summary and Discussion of Cell Cycling Studies**

The cell cycling studies indicate that DMAC and DEAC exhibit analogous behavior with respect to their solvent properties for the dissolved S cathode. The discharge capacities obtainable practically for cathodes consisting of solutions of \(\text{Na}_2\text{S}_n\) in these two solvents appear to be strongly dependent on the porosity of the current collector; the more porous the current collector, the greater the depth of discharge. This results from the fact that with a highly porous current collector, it would be possible to store larger amounts of the insoluble di- and monosodium sulfides on the electrodes, as is done in the case of Li/SOCl₂ cell (18). There is a slow self-discharge reaction in these cathode systems. However, it appears that this can be minimized greatly by restricting the charging
Fig. 16: Galvanostatic discharge/charge curves for a cell, liquid Na/β-Al2O3/Na2S4 (2M S), 0.5M NaI, DEAC/Teflon-bonded C electrode at 130°C. Current = 10 mA; current density = 1 mA/cm². Cell was discharged first, 1D. The charge curve 10C represents the last charge half cycle after the cycles shown in Figs. 17 and 18.
Fig. 17: The third discharge (3D), third charge (3C) and fourth discharge (4D) curves for the cell shown in Fig. 16. Current = 20 mA, current density = 2 mA/cm².
Fig. 18: Cycles five through ten of the cell shown in Fig. 16. The 7th and 8th charge and 8th and 9th discharge curves are not shown. Current = 30 mA, current density = 3 mA/cm².
limit of the battery to a medium size polysulfide such as $S_4^{2-}$. Comparison with the high temperature battery (1) shows that for an equivalent energy density of 60 Whr/lb, it is necessary to achieve a solubility (as Na$_2$S$_{10}$) of $\approx 1.3$M if the charged cathode is to be in solution and if a complete reduction to $S^{2-}$ is obtained. As we have seen, with a highly porous cathode it might not be necessary to achieve this much solubility for $S_n^{2-}$. The insoluble materials could be stored on the cathode current collector itself. To date only lower-rate cycling has been achieved, mostly due to ohmic drops in thick, non-state-of-the-art $\beta$-Al$_2$O$_3$ tubes.

B. Sodium-Sulfur Cell with a 1,3 Cyclohexanediol (CHD)/Na$_2$S$_n$ Cathode

Alcohols, in general, are unstable in the presence of Na$_2$S$_n$ at temperatures $>100^\circ$C. However, it was pointed out to us by Drs. W. L. Fielder and J. Singer of NASA-Lewis that 1,3 cyclohexanediol (CHD), C$_6$H$_{10}$O$_2$, was an exception. Long-term stability tests, carried out as in the case of the amide/Na$_2$S$_n$ solutions, indicated that CHD/Na$_2$S or CHD/Na$_2$S$_n$, $n = 4, 8$, were stable at $130^\circ$C at least for 21 days. The higher stability of this diol may be associated with the "cyclohexene structure". Two cells were studied using this solvent. They were: (i) cell in which the initial catholyte was CHD/Na$_2$S/0.5M NaBr, (ii) cell in which the initial catholyte was CHD/Na$_2$S$_4$/0.5M NaBr.

1. Cell with CHD/Na$_2$S/0.5M NaBr Solution as the Initial Catholyte

The cell was assembled, as described earlier. Since Na$_2$S is soluble in CHD to the extent of about 1M, the cell was initially charged with 1.1g of Na$_2$S and 7 ml of CHD/0.5M NaBr electrolyte was then added to make the solution the equivalent of $0.2$M in Na$_2$S. The Teflon-bonded carbon electrode used in the cathode compartment was identical to the one described before. The OCV of the cell initially was 1.38V. The cell exhibited a resistance at $130^\circ$C of 230. The cell was cycled at 10 mA or about 1 mA/cm$^2$. The charge/discharge curves are shown in Figure 19. The first charge curve 1C, to 2.7 volt corresponds to $\approx 0.33$ e-/S. Only about 17% of Na$_2$S was utilized in the charging process. It appears that Na$_2$S was poorly distributed on the carbon electrode so that most of it was not available for the cell process. The first discharge, curve 1D, commenced at 1.6V, but in $<20$ mAh the cell polarized to $\approx 1.1$V and further discharged proceeded at $\approx 1.1$V. This discharge voltage is considerably lower than for the Na/DMAC/Na$_2$S$_n$ cells. The second charge corresponded to $\approx 0.8$e-/S. Evidently more Na$_2$S was available for the charging process. The second discharge, curve 2D, proceeded with voltage fluctuations and the cell reached the 1V limit in about 4 hours or 40 mAh. The third charge, curve 3C, proceeded smoothly but at a considerably higher voltage, and after 34 mAh of charge the cell open circuited to the voltage of the current source. The experiment was terminated.
Fig. 19: Galvanostatic charge/discharge curves for a cell, liquid Na/β-Al2O3/Na2S (2M S), 0.5M NaBr, CHD/Teflon-bonded C at 130°C. Current = 10 mA. Current density = 1 mA/cm².
2. Cell with CHD/Na$_2$S$_4$/0.5M NaI Solution as the Initial Catholyte

The cell initially contained 9 ml of a 2M S$_2$ solution as Na$_2$S$_4$ in CHD/0.5M NaI electrolyte. All the other features of the cells were similar to those in the cell with CHD/Na$_2$S as the initial catholyte. The OCV of the cell at 130°C was 1.83V and the cell exhibited a resistance of 25Ω. The resistance was twice that found for cells with DMAC/Na$_2$Sn or DEAC/Na$_2$Sn cathodes and having the same type of β-Al$_2$O$_3$ tube. The higher resistance was probably due to the higher viscosity of CHD. The galvanostatic discharge and charge curves at 9 mA or 1 mA/cm$^2$ are shown in Figure 20. As observed previously, the discharge begins at about 1.6V, but the cell polarizes immediately to a plateau of 1.25V. This initial polarization to the 1.25V plateau is more pronounced in the second discharge (2D). The first discharge proceeded for 194 mAh (0.4e$^-$/S), at which point a malfunction of the cycler caused the cell to charge. The charge capacity to 2.7V was, however, much less than the previous discharge; i.e., only 110 mAh (0.23e$^-$/S). The second discharge (2D) proceeded for 650 mAh. After accounting for the charge utilization in the first cycle, a charge equivalent to 640 mAh would be required to reduce the Na$_2$Sn, present at the beginning of 2D to Na$_2$S. The discharge capacity of 650 mAh thus corresponds to the reaction

$$S_4^{2-} + 6e^- \rightarrow 4S^{2-}$$ (20)

This agreement, as well as the fact that a 1e$^-$ reduction of CHD would require 1.7 Ah charge, indicate that the solvent is not reduced at potentials above 1V. Nevertheless, the second charge (2C) proceeded for only 124 Ah (0.25e$^-$/S). The third discharge was less than the second charge, and the subsequent charge and discharge also showed the decreasing efficiency. The cell could not be operated after the fourth cycle.

The following conclusions may be drawn about the behavior of the CHD/Na$_2$Sn cathode:

- Na-S cells with CHD/Na$_2$Sn cathodes have relatively higher resistances, probably due to the higher viscosity of CHD.
- The operating voltage of the cell is low.
- Na$_2$Sn can be reduced to Na$_2$S, but the cathode exhibits poor reversibility.
Fig. 20: Galvanostatic discharge/charge curves for the cell liquid Na/β-Al₂O₃/CHD, 0.5M NaI, 2M S as Na₂S₄ (9 ml) Teflon-bonded C at 130°C. Current = 9 mA; current density = 1 mA/cm². The cell was discharged first.
III. THE Na-TRANSITION METAL SULFIDE BATTERY

A preliminary evaluation of transition metal disulfides as possible cathode materials for the Na battery was done using the disulfides, TiS$_2$ and TaS$_2$. They were separately evaluated in a cell of the configuration, Liquid Na/β-Al$_2$O$_3$/MS$_2$, DMAC, NaI.

The DMAC/NaI solution served as the Na$^+$-ion conducting electrolyte. The experiments were conducted at 130$^\circ$C.

A. Preparation and Characterization of the Disulfides

1. Titanium Disulfide, TiS$_2$

Titanium disulfide, TiS$_2$, was prepared by the direct reaction of stoichiometric amounts of Ti metal and S vapor at ~750$^\circ$C. The reaction was carried out in a sealed, evacuated (10$^{-3}$ torr) quartz tube under a temperature gradient achieved in a tube furnace.

In a preparation, 7g Ti metal powder (100 mesh) and 9.6g S (Ventron, crystals, 99.99%) were introduced into either end of a thick-walled quartz tube of 25 mm OD and 57 cm long. The tube was evacuated (10$^{-3}$ torr) and sealed off. It was then introduced into a three-zoned furnace and heated with the temperature profile shown in Table 7. After heating, the tube was allowed to cool to room temperature and the TiS$_2$ was collected. It was a dark green solid with a distinct yellow metallic luster when spread into the form of a thin film. The X-ray diffraction pattern for a sample of TiS$_2$ prepared by the same procedure as is shown in Table 8. The experimental values are in good agreement with those calculated for hexagonal TiS$_2$.

The titanium content of the sulfide was analyzed as the oxide, according to the reaction

$$\text{TiS}_2 + 3\text{O}_2 \xrightarrow{700^\circ\text{C}} \text{TiO}_2 + 2\text{SO}_2$$  \hspace{1cm} (21)

In this procedure, 0.5235g of TiS$_2$, contained in a preweighed alumina crucible, was ignited in air at 700$^\circ$C until all the sulfide was converted to the oxide. The oxide weighed 0.3785g which was equivalent to 43.4% Ti in the disulfide sample. The formula of the disulfide was calculated to be Ti$_{1.02}$S$_2$. 
**TABLE 7**

TEMPERATURE PROFILE FOR THE PREPARATION OF TiS\(_2\) FROM Ti and S

<table>
<thead>
<tr>
<th>Time (hr) at Each Temp.</th>
<th>Zone A (15 cm long) (Titanium Metal)</th>
<th>Zone B (30 cm long) (Sulfur)</th>
<th>Zone C (15 cm long) (Sulfur)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature, °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>500</td>
<td>500</td>
<td>400</td>
</tr>
<tr>
<td>2.5</td>
<td>550</td>
<td>550</td>
<td>400</td>
</tr>
<tr>
<td>19</td>
<td>600</td>
<td>600</td>
<td>400</td>
</tr>
<tr>
<td>29</td>
<td>650</td>
<td>650</td>
<td>400</td>
</tr>
<tr>
<td>20</td>
<td>700</td>
<td>700</td>
<td>400</td>
</tr>
<tr>
<td>27</td>
<td>750</td>
<td>750</td>
<td>600</td>
</tr>
</tbody>
</table>
TABLE 8

X-RAY DIFFRACTION DATA CALCULATED FOR HEXAGONAL TiS₂ AND OBSERVED LINES OF SAMPLES PREPARED BY THE PRESENT PROCEDURE

<table>
<thead>
<tr>
<th>Calculated 2θ&lt;</th>
<th>Intensity</th>
<th>Experimental 2θ&lt;</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.6</td>
<td>500</td>
<td>not done</td>
<td></td>
</tr>
<tr>
<td>34.2</td>
<td>1000</td>
<td>34.4</td>
<td>1000</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>39.8</td>
<td>149</td>
</tr>
<tr>
<td>44.1</td>
<td>450</td>
<td>44.4</td>
<td>505</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>48.0</td>
<td>75</td>
</tr>
<tr>
<td>53.9</td>
<td>250</td>
<td>54.0</td>
<td>333</td>
</tr>
<tr>
<td>56.4</td>
<td>80</td>
<td>56.6</td>
<td>118</td>
</tr>
<tr>
<td>57.5</td>
<td>160</td>
<td>57.9</td>
<td>204</td>
</tr>
<tr>
<td>65.3</td>
<td>100</td>
<td>65.4</td>
<td>268</td>
</tr>
<tr>
<td>72.1</td>
<td>80</td>
<td>72.3</td>
<td>129</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>75.0</td>
<td>53</td>
</tr>
<tr>
<td>89.5</td>
<td>80</td>
<td>89.8</td>
<td>225</td>
</tr>
<tr>
<td>89.7</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
2. Tantalum Disulfide, TaS₂

The tantalum disulfide was purchased from Cerac Inc., Milwaukee, Wisconsin (Catalog No. T-1018). Its X-ray diffraction data, according to the manufacturer, matched the pattern* for hexagonal TaS₂. We analyzed the Ta content of the disulfide as the oxide, Ta₂O₅, using the reaction

\[ 2\text{TaS}_2 + 6\text{O}_2 \xrightarrow{700^\circ\text{C}} \text{Ta}_2\text{O}_5 + 4\text{SO}_2 \]  \hspace{1cm} (22)

In the analysis, 0.6051g TaS₂ gave 0.5482g Ta₂O₅, which corresponded to 74.2% Ta in the disulfide sample. The formula of the disulfide was calculated to be Ta₁.₀₁₆S₂.

B. Stability Characteristics of Metal Sulfide/Amide Mixtures

The long term stability characteristics of dimethylacetamide (DMAC), diethylacetamide (DEAC) or their NaI solutions in the presence of TiS₂ at 130°C were evaluated by the sealed tube technique. Titanium disulfide was insoluble in these amides both at room temperature and at 130°C. The tests were performed with mixtures of the amide or its NaI solution containing an excess of undissolved TiS₂. The various test mixtures and the results are shown in Table 9. No gases were produced from any of these mixtures even after 43 days of heating at 130°C. After the heating, the liquid was analyzed by UV-visible and infrared spectroscopy. The liquid from each of the test mixtures exhibited a weak but broad absorption beginning at ~500 nm and tailing off into the UV. This absorption pattern resembled that of the reaction products of S with the amides, described earlier and it might be due to minor products resulting from the reaction of unreacted S in the TiS₂ with the amides.

The results seemed to indicate that the overall stability of the amides in the presence of the disulfides was acceptable. However, it should be noted that since the amides are basic solvents, their intercalation with the metal chalcogenide is possible. This was not investigated.

C. Electrochemical Evaluation of Transition Metal Disulfides

1. Titanium Disulfide as the Cathode

- Preparation of Pressed Electrodes

A mixture of TiS₂ and Teflon powder (90:10 w/o) was intimately mixed with a mortar and pestle for ~20 minutes. The cathode mix was bonded

*See Powder Diffraction File, No. 2-0137.
<table>
<thead>
<tr>
<th>Tube No.</th>
<th>Reactants</th>
<th>No. of Days at 130°C</th>
<th>mmoles of Gas</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.47g TiS₂, 2 ml DMAC</td>
<td>43</td>
<td>no gas</td>
<td>light brown liquid over dark grey powder</td>
</tr>
<tr>
<td>B</td>
<td>0.49g TiS₂, 0.31g NaI, 2 ml DMAC</td>
<td>43</td>
<td>no gas</td>
<td>light green liquid over dark grey powder</td>
</tr>
<tr>
<td>C</td>
<td>0.49g TiS₂, 2 ml DEAC</td>
<td>43</td>
<td>no gas</td>
<td>orange-red liquid over dark grey powder</td>
</tr>
<tr>
<td>D</td>
<td>0.46g TiS₂, 0.31g NaI, 2 ml DEAC</td>
<td>43</td>
<td>no gas</td>
<td>orange-red liquid over dark grey powder</td>
</tr>
</tbody>
</table>
to an expanded nickel screen by pressing at 4800 psi for 10 minutes at a temperature of 250°C. The pressed electrode had an average thickness of 0.56 mm. The electrode was weighed to determine the TiS$_2$ content before incorporating in the electrochemical cell.

- **Cell Studies**

  The cell setup was done as described previously for the soluble S cathode with a liquid Na/β-Al$_2$O$_3$ counter electrode. The TiS$_2$ cathode measured 6.5 cm x 2.5 cm and contained 1.42 g TiS$_2$. A solution of 1M NaI in DMAC formed the catholyte. The cell, at 130°C, exhibited an unusually high impedance of ~60Ω. The discharge was performed at 4 mA (0.2 mA/cm$^2$). The discharge and charge are shown in Figure 21. The initial OCV was 2.19V. Three plateaus are evident in the discharge curve for the sodium contents, x, of 0.41<x, 0.41<x<0.66 and 0.68<x<0.95. These values are based on the weighed amount of TiS$_2$ originally present in the cell; 1.42g or 340 mAh.

  A previous electrochemical cell study (19) also showed three plateaus for the discharge, but at slightly different ranges of the Na content, i.e., 0.45<x, 0.45<x<0.80 and 0.80<x<1. However, these were found to be dependent on the composition of the sulfide, i.e., on x in Ti$_{1+x}$S$_2$. Also, these values were obtained at room temperature and the electrolyte was propylene carbonate/NaI.

  Our data show that the three phases are formed at the higher temperature also. The different ranges of x values for the three phases in the present study may have resulted from the higher temperature condition or from the different solvent employed here.

  The charge curve also showed three regions at essentially the same ranges of Na contents. The rechargeability of the cathode was sluggish at higher rates. In one experiment, it was possible to cycle the cathode several times, Figure 22, at reasonably high discharge rates, but keeping charges at low current densities. It can be seen that the efficiency after the first cycle remained essentially constant. In general it was found difficult to charge compositions of Na$_x$TiS$_2$ with x ≤ 0.4. The exact reasons for this were not investigated. Factors such as co-intercalation of the solvent and phase transitions in the ternary system, Na$_x$TiS$_2$, are possible reasons.

  2. **Tantalum Disulfide as a Cathode**

- **Preparation of Pressed Electrodes**

  An electrode was prepared by a slightly modified procedure used for the TiS$_2$ electrodes. An intimate mixture of the disulfide and Teflon powder (92:8 w/o) was cold-pressed onto an expanded nickel screen (Exmet
Fig. 21: The discharge/charge curves for the cell liquid Na/β-Al₂O₃/DMAC (1M NaI), TiS₂ at 130°C. Current = 4 mA, current density = 0.2 mA/cm².
Fig. 22: Galvanostatic discharge/charge curves for the cell liquid Na/β-Al₂O₃/DMAC (1M NaI), TiS₂ at 130°C. D1 thru D-5 are discharge curves. Current = 20 mA (≈4 mA/cm² of β-Al₂O₃). C1 thru C5 are charge curves. Current = 5 mA or (≈1 mA/cm² of β-Al₂O₃).
Corp. 5 Ni 5 - 5/0) at 5600 psi for 6 minutes. The pressed electrode was then sintered in an argon atmosphere at 300°C for half an hour. We also prepared electrodes with NaTaS2. In this case, the cathode was cold-pressed but no sintering was done afterwards.

- **Cell Studies**

  Two kinds of experiments were carried out: (i) initial discharge and subsequent cycling of the fully charged cathode, TaS2; (ii) initial charge and subsequent cycling of the fully discharged cathode, NaTaS2. The NaTaS2 was prepared chemically from Na naphthalide and TaS2 in tetrahydrofuran as described later.

  **Tests with the TaS2 Cathode.** The cell utilized 1M NaI/DMAC electrolyte. A plot of the discharge potential (volts) vs. the degree of Na intercalation (mole Na/mole TaS2) is shown in Figure 23 (curve A). The cell EMFs corresponding to the various degrees of Na intercalation are shown in curve B, Figure 23. Both of these curves show fairly linear transitions to lower potentials as the amount of intercalated Na is increased from zero to one. At a discharge cutoff voltage of 1.00V, only 0.8 mole of Na per mole of TaS2 was intercalated. The EMF corresponding to this composition was 1.20V. The EMF value corresponding to the fully intercalated compound, NaTaS2 was obtained from a cell incorporated with this material initially as the cathode. The EMF was 0.97V at 130°C. It thus appears that in order to achieve full intercalation of the TaS2 lattice, the lower limit of the operating cell voltage has to be below 1.00V when the electrolyte is DMAC/NaI. The EMF-composition curve for the Na_xTaS2 ternary system for values of x from zero to one in DMAC/NaI at 130°C, constructed from the two sets of data, is shown in Figure 23 (curve B).

  The EMF-composition curve for the Na_xTaS2 system is different from that observed with the Na_xTiS2 ternary. The present data for Na_xTaS2 are in agreement with a previous study (20) on TaS2 at room temperature using PC/NaI electrolyte (see also inset in Figure 23). In that study, the EMF-composition data along with the X-ray results indicated a single phase ternary system for Na_xTaS2 for all values of x, 0<x<1. The present data suggest the formation of a single phase ternary system also in the DMAC/NaI electrolyte at 130°C. The EMF-composition curve does show some deviations from linearity at low and high x values. This, in the absence of X-ray data, may be attributed to the different solvent employed here. The experimental data in the previous study also showed this behavior at low x values, but X-ray revealed only one phase.

  **Tests with NaTaS2 Cathode.** The fully Na intercalated disulfide, was prepared according to the reactions,
Fig. 23: The galvanostatic discharge curve for the cell liquid Na/β-Al2O3/DMAC (1M NaI), TaS2 at 130°C. Curve A is the plot of cell potential vs. degree of Na intercalation. Curve B is the plot of open-circuit voltage of the cell as a function of Na intercalation. C is the open-circuit voltage obtained with NaTaS2 as the cathode. Current = 10 mA or ~2.0 mA/cm² of β-Al2O3. Inset is the data from Ref. 3.
In a preparation, 2.61g (20.4 mmoles) of naphthalene and 0.47g (20.4 mmoles) of Na were mixed in ~50 ml THF and stirred overnight at room temperature to obtain a dark green solution of the naphthalide anion radical. The exact Na concentration of the solution was analyzed by treating an aliquot of the solution (2 ml) with an excess of standard HCl and then back-titrating the unreacted HCl with a standard solution of NaOH using phenolphthalein as the indicator. To 48 ml of the naphthalide solution, 4g (16.3 mmoles) of TaS$_2$ were added, and the mixture was stirred for 2 days. The Na$_x$TaS$_2$ product was filtered, washed with THF and finally dried in vacuum. The Na$_x$TaS$_2$ product was collected as a very shiny dark grey material. The filtrate was analyzed for its Na content. The composition of the intercalated material was calculated to be Na$_{1.05}$TaS$_2$. The EMF value of 0.97V vs Na$^+$/Na for this material also suggests a composition with x very close to one. This material was used for testing the rechargeability of the TaS$_2$ cathode.

Rechargeability of TaS$_2$ Cathode. The rechargeability of the cathode in DMAC/NaI electrolyte appeared to be kinetically limited as evidenced by data from cells in which the cathode initially was either TaS$_2$ or Na$_x$TaS$_2$. In general, the efficiency of rechargeability increased with decreasing current density. It was also found that the EMF-composition curve during charge showed considerable deviation from that during discharge for the same degree of Na intercalation, Figure 24. The galvanostatic charge curves, obtained from the two different initial cathode compositions, however, showed analogous voltage-composition behavior.

The work carried out herein suggests that transition metal disulfides present good possibilities as cathode materials in moderate temperature Na batteries. Further work should concentrate on a search for suitable electrolytes that can accommodate high rate battery operation and on selection of cathode materials with minimum phase transition. A most important issue is the inter-relationship between phase changes during Na intercalation and the rechargeability of the cathode. This needs to be systematically explored.
Fig. 24: Galvanostatic discharge/charge curves A and B for the cell liquid Na/β-Al₂O₃/DMAC (1M NaI), TaS₂ at 130°C. Current = 10 mA (∼2 mA/cm² of β-Al₂O₃). Curve C is the charge curve for a cell with NaTaS₂ initially in the cathode, current = 5 mA (∼1.0 mA/cm² of β-Al₂O₃).
IV. SUMMARY AND CONCLUSIONS

The feasibility of a moderate temperature Na battery having the configuration

\[
\text{Liquid Na} / \beta\text{-Al}_2\text{O}_3 / \text{Dissolved Na}_2\text{Sn} \quad \text{or}
\]

transition metal disulfide

has been investigated. The operating temperature of the battery is 130°C. Two kinds of cathode were investigated (i) a soluble S cathode consisting of a solution of Na\textsubscript{2}Sn in an organic solvent and (ii) an insoluble S cathode consisting of a transition metal dichalcogenide in contact with a Na\textsuperscript{+}-ion-conducting electrolyte.

A series of aliphatic amides was investigated in an attempt to find a suitable solvent for the soluble S cathode with special emphasis on long term stabilities in the presence of Na\textsubscript{2}Sn. The dialkyl substituted amides were found to be the most stable. They did show some reactivity during long term heating with Na\textsubscript{2}Sn, n > 4. However, isolation studies indicated that the reactive species in these solutions was the elemental sulfur present in equilibrium. The stability studies also indicated that relatively longer cycle life could be obtained for the CH\textsubscript{3}CONR\textsubscript{2}/Na\textsubscript{2}Sn cathode if the cell operation is limited to the cycling regime.

\[
S_{n}^{-2} + 6e^{-} \xrightarrow{\Delta} 4S^{-2} ; 1.5e^{-}/S
\]

Cell cycling studies using the solutions CH\textsubscript{3}CON(CH\textsubscript{3})\textsubscript{2}/Na\textsubscript{2}Sn or CH\textsubscript{3}CON(C\textsubscript{2}H\textsubscript{5})\textsubscript{2}/Na\textsubscript{2}Sn indicated that these cathodes were reversible and that the reduction of Sn\textsubscript{2} to S\textsuperscript{-2} could be achieved with a highly porous cathode current collector structure.

The suitability of 1,3-cyclohexanediol as a solvent for the soluble S cathode was also investigated. It was found that this solvent is stable with respect to Na\textsubscript{2}Sn for long periods of time and that it dissolves moderate amounts of Na\textsubscript{2}S. However, the electrochemical reversibility of 1,3-cyclohexanediol/Na\textsubscript{2}Sn solutions was poor.

A limited amount of study was carried out to determine the suitability of transition metal dichalcogenides as possible cathodes for the Na battery. Our results of studies with TaS\textsubscript{2} or TiS\textsubscript{2} indicated that the phase transitions during intercalation of Na into the transition metal dichalcogenides are strongly dependent on the structure of the dichalcogenide themselves. In general, transition metal disulfides present good possibilities as cathode materials for the moderate temperature Na battery.
V. REFERENCES


DISTRIBUTION LIST

Dr. Ted Beck
Electrochemical Technology Corp.
3935 Leary NW
Seattle, WA 98107

Dr. Doug Bennion
Energy and Kinetics Department
School of Engineering & Applied Science
University of California
Los Angeles, CA 90024

Dr. A. Donald Galbraith
Globe-Union, Inc.
60 Chestnut Street
Livingston, NJ 07039

Dr. Jose Giner
Giner, Inc.
144 Moody Street
Waltham, MA 02154

Dr. Jack Brown
Research Laboratory
Westinghouse Electric Corp.
1310 Beulah Road
Pittsburgh, PA 15235

Dr. Ralph Brodd
Research Laboratories
Union Carbide Corp.
Parma, OH 44129

Dr. Earl Carr
Eagle Picher Industries, Inc.
Electronics Div., Couples Dept.
P.O. Box 47
Joplin, MO 64801

Dr. David Douglas
Vice Pres., Contract Research
Gould, Inc.
40 Gould Center
Rolling Meadows, IL 60008

Dr. Morris Eisenberg
Electrochimica Corp.
2485 Charleston Road
Mountain View, CA 94040

Dr. D. Thomas Ferrell
ESB Technology Center
19 West College Avenue
Yardley, PA 19067

Dr. A. Donald Galbraith
Power Cell Program Office
Lockheed Palo Alto Research Lab
3251 Hanover Street
Palo Alto, CA 94304

Dr. Jose Giner
Giner, Inc.
144 Moody Street
Waltham, MA 02154

Dr. Gilbert Goodman
Globe-Union, Inc.
Milwaukee, WI 53201

Dr. Robert Huggins
Stanford University
Center for Materials Studies
Stanford, CA 94305

Mr. Henry Jensen, V.P.
C&D Batteries
3042 Walton Road
Plymouth Meeting, PA 19462

Dr. Charles A. Levine
Dow Chemical Research Labs
Walnut Creek Center
2800 Mitchell Drive
Walnut Creek, CA 94598

Prof. Prem Mahendroo
Department of Physics
Texas Christian University
Fort Worth, TX 76129

Dr. John Newman/Dr. Charles Tobias
Department of Chemical Engineering
University of California
Berkeley, CA 94720
Dr. Arthur Fleischer  
466 South Center Street  
Orange, NJ 07050  

Furukawa Battery Co., Ltd.  
NO. 246, 2-Chome  
Hoshikawa-Cho  
Hodogaya, Yokohama, Japan  
Attn: K. Shimizu  

Gates Energy Products, Inc.  
999 S. Broadway  
Denver, CO 80217  
Attn: E. Seo  

General Dynamics  
Convair Aerospace Division  
Dept. 623-2  
P.O. Box 80847  
San Diego, CA 92138  
Attn: R. P. Mikkelsen  

Battery Business Dept.  
General Electric Company  
P.O. Box 114  
Gainesville, FL 32602  
Attn: M. Kronenberg  

General Electric Company  
Space Systems  
Room M-2700, P.O. Box 8555  
Philadelphia, PA 19101  
Attn: K. L. Hanson  

General Electric Company  
777 14th Street, NW  
Washington, DC 20005  
Attn: D. F. Schmidt  

General Motors Research Labs  
Electrochemistry Department  
Warren, MI 48090  
Attn: R. G. Gunther  

General Motors Research Labs  
Electrochemistry Department  
Warren, MI 48090  
Attn: E. J. Cairns  

Globe-Union, Inc.  
Corporate Applied Research  
5757 North Green Bay Avenue  
Milwaukee, WI 53201  
Attn: W. L. Towle  

Grumman Aerospace Corp.  
OA0 Project  
Plant 35  
Bethpage, Long Island, NY 11714  
Attn: S. J. Gaston  

G&W H. Corson, Inc.  
Plymouth Meeting, PA 19462  
Attn: L. J. Minnick  

Chrysler Corp.  
Space Division  
Department 2730  
P.O. Box 29200  
New Orleans, LA 70189  
Attn: C. E. Thomas  

Communications Satellite Corporation  
Comsat Laboratories  
P.O. Box 115  
Clarksburg, MD 20734  
Attn: R. Strauss  

Delco Remy Division  
General Motors Corp.  
2401 Columbus Avenue  
Anderson, IN 46011  
Attn: J. A. Keralla  

E. I. DuPont de Nemours & Co.  
Engineering Materials Lab  
Building 304  
Wilmington, DE 19898  
Attn: J. M. Williams  

Dynatech Corp.  
17 Tudor Street  
Cambridge, MA 02139  
Attn: R. L. Wentworth  

Exxon Research & Engineering Company  
Government Research Lab  
P.O. Box 8  
Linden, NJ 07036  
Attn: L. Berkowitz  

ESB, Inc.  
Box 6266  
Cleveland, OH 44101  
Attn: G. Hobbib
Monsanto Research Corp.
1515 Nicholas Road
Dayton, OH 45407
Attn: I. O. Salyer

North American Aviation, Inc.
12214 Lakewood Blvd.
Downey, CA 90241
Attn: B. M. Otzinger

North American Rockwell
Aeronetics Division
P.O. Box 4192
Anaheim, CA 92803
Attn: R. F. Fogle (GA28)

North American Rockwell Corp.
Rocketdyne Division
6633 Canoga Avenue
Canoga Park, CA 91304
Attn: Library

Philco-Ford Corp.
3939 Fabian Way
Palo Alto, CA 94303
Attn: D. C. Briggs

Power Information Center
University City Science Center
3624 Science Center
Philadelphia, PA 19104
Attn: Library

Rensselaer Polytechnic Institute
Department of Chemistry
Troy, NY 12180
Attn: G. J. Janz

Southwest Research Institute
P.O. Drawer 28510
San Antonio, TX 78228
Attn: Library

Stanford Research Institute
333 Ravenswood Avenue
Menlo Park, CA 94025
Attn: Librarian

Texas Instruments, Inc.
P.O. Box 5936
Dallas, TX 75222
Attn: I. Trachtenberg

TRW Systems, Inc.
One Space Park (R-1/2094)
Redondo Beach, CA 90278
Attn: H. P. Silverman

Union Carbide Corp.
Parma Laboratory
P.O. Box 6116
Parma, OH 44130
Attn: Library

University of Maryland
Dept. of Mechanical Engineering
College Park, MD 20742
Attn: F. Morse

University of New Mexico
Technology Applications Center
Albuquerque, NM 87131
Attn: K. E. Cox

University of Pennsylvania
113 Towne Building
Philadelphia, PA 19104
Attn: National Center for Energy Management & Power

Englehard Industries, Inc.
Menlo Park
Edison, NJ 08817
Attn: J. G. Colin

Union Carbide
Development Laboratory Library
P.O. Box 6056
Cleveland, OH 44101
Dr. Judith H. Ambrus  
WR-33, White Oak Laboratory  
Naval Surface Weapons Center  
Silver Springs, MD 20910

NASA-Lewis Research Center  
21000 Brookpark Road  
Cleveland, OH 44135  
Attn: G. M. Ault, MS 3-5  
V. Hlavin, MS 3-10  
Tech. Util. Office, MS 7-3  
L. Rosenblum, MS 49-5  
C. E. May, MS 106-1  
J. S. Fordyce, MS 302-1  
D. G. Soltis, MS 309-1  
N. T. Musial, MS 500-113  
J. E. Bolander, MS 500-312  
Library, MS 60-3  
Report Control, MS 5-5

National Aeronautics & Space Admin.  
Washington, D.C. 20546  
Attn: L. Holcomb, Code RP-6  
S. V. Manson, Code NT  
P. R. Miller, Code NE  
R. LaRock, Code NE  

NASA-Goddard Space Flight Center  
Greenbelt, MD 20771  
Attn: F. Ford (Code 711.2)  
G. Halpert (Code 711.2)

NASA-Langley Research Center  
Instrument Research Division  
Hampton, VA 23365  
Attn: J. E. Zanks, MS 488

NASA-George C. Marshall Space Flight Center  
Huntsville, AL 35812  
Attn: C. B. Graff, Code EO-11

NASA-Johnson Space Center  
Houston, TX 77058  

NASA-Ames Research Center  
Moffett Field, CA 94035  
Attn: J. Ribenzer, MS 24408

Jet Propulsion Laboratory  
4800 Oak Grove Drive  
Pasadena, CA 91103  
Attn: As. A. Uchlyama, MS 198-22

Douglas Barron  
Dept. 120  
Delco-Remy Division GMC  
2401 Columbus Avenue  
Anderson, IN 46014

Commanding Officer  
US Army Mobility Equip. R&D Center  
 Ft. Belvoir, VA 22060  
(Code SMEFB-EE)

Commanding Officer  
Picatinny Arsenal  
Code SMUPA-F-S-P  
Dover, NJ 07801  
Attn: M. R. Merriman

Office of Naval Research  
Arlington, VA 22217  
Attn: Director Power Program  
(Code 473)

Naval Ship R&D Center  
Annapolis, MD 21402  
Attn: J. H. Harrison  
(Code 2724)

Commanding Officer  
US Naval Ammunition Depot  
Crane, IN 47522  
Attn: D. G. Miley  
(Code QEWE)

US Naval Observatory  
4301 Suitland Road  
Suitland, MD 20390  
Attn: H. E. Ruskie  
(NISC-4321)

NAVAL Ordnance Laboratory  
Silver Springs, MD 20910  
Attn: P. D. Cole  
(Code 232)