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A Novel Class of Positive Electrodes for Rechargeable Batteries

C.C. Mailhe
(Ph.D. Thesis)

October 1987

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A Novel Class of Positive Electrodes for Rechargeable Batteries

Catherine Colette Mailhe

Ph.D. Thesis

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

October 1987
A NOVEL CLASS OF POSITIVE ELECTRODES FOR RECHARGEABLE BATTERIES.

Catherine Colette Mailhe

ABSTRACT:

A novel class of organosulfur positive electrodes for intermediate temperature rechargeable batteries is described here.

High temperature batteries such as sodium/sulfur exhibit alluring and unrivaled power and energy densities but unfortunately are plagued by corrosion problems. A decrease in the operating temperature from 350°C to the 110-150°C temperature range resulted in a simplified cell technology allowing for the use of polymeric seals. The non-aggressive nature of the positive electrode lessened also considerably the corrosion issues.

A tetraethylthiuram disulfide/diethyldithiocarbamate cell was first investigated because of its attractive theoretical energy density of 360 Wh/kg and because of the low melting point of the diethyldithiocarbamate sodium salt (145°C), condition necessary to maintain the electrode in the liquid state. (Sodium and Beta" Alumina were respectively the negative electrode and the solid electrolyte). The low melting sodium salt requirement can be advantageously replaced by the use of a solvent in charge of solubilizing the sodium salt generated during discharge. Low viscosity and high dielectric constant were identified as two key factors in the solvent optimization. The addition of 20 % in weight of dimethyl sulfoxide or of sulfolane permitted the cell charge and discharge at 5 mA/cm² at 130°C. Peak current densities of 100 mA/cm² at 1 Volt were also obtained.

The perspectives opened by solvent addition, led to the concept of
"electroactive solvent" where the electroactive material itself solvates the sulfide sodium salt. In this respect, the alkoxyalkyl disulfides are promising candidates because of their combined low viscosity, high energy density and thermal stability.

The chemical versatility of these organo-sulfur compounds allows for the tuning of their properties to the battery needs and creates the uniqueness of these new class of positive electrodes.
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INTRODUCTION

The increasing importance of energy management and storage has stimulated developments in the field of rechargeable, high energy density batteries.

Utility companies have used hydroelectric pumping stations (load levelling), in order to meet the daily fluctuations in power consumption. Battery station units would advantageously replace the conventional pumping stations, because they do not require special sites and a large amount of space. More compact and therefore more easily integrated in an urban environment, their capacity could also be tailored to local needs.

The electric car constitutes another major application where high specific energy, rechargeable batteries are needed. Removing car noise and pollution from everyday life, would revolutionize our quality of living and is certainly a goal worth striving for. It may become a reality in a not too distant future.

Advanced performance batteries also find application in the space industry, particularly in the field of telecommunication satellites where high energy density is needed.

The object of this thesis is to present a new battery system or more precisely a new positive electrode material that may provide some interesting alternatives to these energy storage issues.

BACKGROUND:

The general battery characteristics are defined in appendix 1. The well known lead acid battery is the most widespread rechargeable battery system and has been the object of extensive research and optimization. This system displays very impressive peak power densities - sufficient to start a car - but its low energy
density, inherent to the high equivalent weight of the Pb and PbO electrodes, has always constituted a major drawback. The optimized lead acid battery exhibits energy densities of 40 Wh/kg which is not sufficient for electric vehicle propulsion.

Alkali metals, lithium or sodium, constitute the obvious choice for the negative electrode of a high energy density battery, because of their low equivalent weight and because of the battery high open circuit voltage.

The nature of the electrolyte is the next issue; it should be a good ionic conductor, an electronic insulator, and should be stable towards the electrodes. Aqueous liquid electrolytes, attractive because of their high ionic conductivity and low cost, seriously limit the choice of a suitable redox couple and the operating temperature range. Because of the obvious incompatibility of water with alkali metals, a new class of electrolytes had to be developed. Liquid electrolytes such as organic solvents with a dissolved sodium or lithium salt would constitute a first possibility, but suffer stability problems because of the very reducing character of sodium or lithium. Lithium or sodium molten salts are corrosive. Moreover, a fascinating class of new materials which display fast ionic conduction in the solid state were discovered. Such materials include ceramics, polymers and glasses. Beta*Alumina, a sodium aluminate, is a ceramic material, which conducts sodium ions and displays a conductivity of 3 - 5 ohms cm at 350°C (KU). Polyethylene oxide (PEO) with dissolved LiClO₄ (AR 85) is an example of a polymeric ionic conductor and lithium sulfide glasses or Nasiglass are glassy ionic conductors (MAL 80, SU 83).

The more promising and representative battery systems currently under investigation are briefly described in the following. Their performances,
theoretical and practical energy densities and power densities are listed in table 1, although this list does not pretend to be exhaustive. High temperature systems such as Na/ Beta Alumina/sulfur or Li, Al/ molten salt/ FeS or FeS$_2$ have the highest power densities and their operating temperature is around 350°C (CAI 73). Despite very impressive performances, these systems are plagued by the highly corrosive nature of their components and the related issues of reliability and degradation. Solutions to these corrosion problems have been suggested but are expensive. Yet, such systems, if costly, have alluring and unmatched characteristics and may be considered viable. Some attempts were made in decreasing the operating temperature of these batteries which would simplify the temperature management and alleviate the corrosion issues. The sulfur-molten chloroaluminate/Beta Alumina/ sodium cell developed by Mamantov (MAM 80), operates at 220°C and displays good performances, although the severe corrosive nature of the molten chloroaluminate is the major drawback. On the other end of the temperature spectrum, Li/PEO/V$_2$O$_5$ or TiS$_2$ room temperature batteries demonstrate high energy densities but have low power densities: a peak current density is of the order of 1 mA/cm$^2$ compared to 1 A/cm$^2$ for the sodium/sulfur battery.(AR 85, AB 82). The concept of a polymer electrolyte is particularly attractive because a polymer, owing to its elastomeric properties, can accomodate volume changes of the electrodes during the battery operation, and therefore can prevent the creation of gaps at the electrodes interfaces. The assembly technology of these room temperature batteries is very easy: three micron thick films are pressed and rolled together to form the battery. Similar kind of room temperature lithium batteries, using a liquid electrolyte such as propylene carbonate, are known to experience rechargeability problems: the growth of lithium dendrites while charging, can eventually lead to the short circuiting of the battery.

The operating temperature of a battery is a critical factor dictating how fast
RECHARGEABLE BATTERY SYSTEMS

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>operating temperature</th>
<th>THEORETICAL specific energy Wh/kg</th>
<th>PRACTICAL specific energy Wh/kg</th>
<th>typical electrode current density mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-Al/FeS</td>
<td>450</td>
<td>457</td>
<td>100</td>
<td>150</td>
</tr>
<tr>
<td>Li-Al/FeS₂</td>
<td>450</td>
<td>629</td>
<td>100 - 150</td>
<td>150</td>
</tr>
<tr>
<td>Na/S</td>
<td>350</td>
<td>830</td>
<td>150 - 200</td>
<td>100-200</td>
</tr>
<tr>
<td>SCI / Na₄ Molten chloroaluminates</td>
<td>220</td>
<td></td>
<td>200</td>
<td>35</td>
</tr>
<tr>
<td>RSSR/Na</td>
<td>110 - 130</td>
<td>to be discussed</td>
<td>id</td>
<td>id</td>
</tr>
<tr>
<td>Li/PEO/TiS₂</td>
<td>80</td>
<td>520</td>
<td>100</td>
<td>0.5 - 1.0 peak 6</td>
</tr>
<tr>
<td>Li/PEO/TiS₃₂</td>
<td>25</td>
<td>520</td>
<td>100</td>
<td>3-20 10⁻³ peak 300</td>
</tr>
<tr>
<td>Pb/PbO₂</td>
<td>25</td>
<td>175</td>
<td>30-40</td>
<td>peak 300</td>
</tr>
</tbody>
</table>
ions can move through the solid electrolyte or within the electrodes and therefore determines the range of power densities that can be expected. There is a trade-off between fast kinetics and high power densities of a high temperature system and the costs associated with a high temperature technology. These different battery systems obviously have to be targeted accordingly. The low cost and the ease of packaging of an all-solid-state battery may be a prime requirement for some applications which do not require high power density. On the other hand, the high power density of high temperature systems are unrivaled. The new system proposed in this thesis can operate at an intermediate temperature around 130°C and offers some interesting alternatives.
CHAPTER I
FROM SODIUM/SULFUR TO SODIUM/ORGANOSULFUR.

The battery system proposed here uses sodium as the negative electrode, Beta"Alumina as the solid electrolyte and a novel organosulfur positive electrode. Sodium and Beta"Alumina have been used in numerous battery systems and the originality of the system is constituted by the positive electrode material. The concept of a low temperature version of the sodium/sulfur battery is certainly appealing. Attempts were made to decrease the operating temperature of the battery by solubilizing the sulfur in organic solvents such as dimethylacetamide (DMAC) (AB 78). The kinetics of such systems were slow. Organosulfur compounds in the molten state, studied here, constitute another possible route to a low temperature application and have not yet been investigated as possible positive electrode materials.

1.1 THE SODIUM/SULFUR BATTERY:

The sodium/sulfur system has been the object of extensive investigations in the past twenty years. Its characteristics and problems are quickly reviewed here since some of the issues will be applicable to our system. The sodium/sulfur battery, as indicated by its name, utilizes a molten sodium negative electrode and a molten sodium polysulfide positive electrode and the solid electrolyte Beta"Alumina (Fig. 1). The operating temperature is 350°C. Upon discharge, the sodium metal is oxidized to sodium ions at the negative electrode and concurrently the sulfur is reduced to polysulfide anions at the positive electrode. The battery discharge is limited to the Na$_2$S$_3$ composition in order to maintain the positive electrode in the
SCHEMATIC OF THE SODIUM-SULFUR BATTERY

- sodium
- thermo compression bond
- alpha-alumina
- glass seal
- Beta⁺ Alumina
- sulfur electrode
- cell casing (chromized mild steel)

DISCHARGE
\[ \text{Na} \rightarrow \text{Na}^+ + e^- \]
\[ \text{Na}_2 \text{S} + 2e^- \rightarrow \text{Na}_2 \text{S}^2^- + \text{S}^2_- \]

CHARGE
\[ \text{Na}^+ + e^- \rightarrow \text{Na} \]
\[ \text{Na}_2 \text{S} + \text{S}^2_- \rightarrow \text{Na}_2 \text{S} + 2e^- \]
molten state. Sodium ions are the only species allowed to diffuse through the 
Beta"Alumina solid electrolyte from the positive electrode compartment to the 
negative electrode compartment. Upon charge, the sodium polysulfides are 
oxidized to lower polysulfides whereas the sodium ions diffuse through the Beta" 
Alumina towards the sodium compartment where they are reduced back to sodium 
metal.(TI 83),(KU 68).

This system has been the object of extensive research because of its 
impressive electrochemical characteristics and its potential application for electric 
vehicle propulsion as well as load levelling (PR 86). The highly corrosive nature of 
molten polysulfides at $350^\circ$C and the resulting corrosion and degradation problems 
so far have prevented a commercial development of this system. The main issues 
concern the current collector corrosion and the Beta"Alumina solid electrolyte 
degradation.

I.2 THE BETA"ALUMINA DEGRADATION:

I.2.1. BETA" ALUMINA STRUCTURE:

Beta"Alumina of composition $\text{Na}_2\text{O} \cdot 5.33 \text{Al}_2\text{O}_3$ exhibits a spinel block 
structure separated by planes where sodium ions are quasi free to move. (Fig. 2). 
Beta" Alumina also exhibits a range of non stoichiometry in which about 17 % of 
the conduction sodium sites are unoccupied: the ionic conduction in Beta" Alumina 
involves motions of sodium vacancies. (The activation energy for sodium ion 
conduction is very much temperature dependent which can be explained by the 
fact the sodium vacancies ordering/disordering phenomena change with 
temperature). The resistivity, at $350^\circ$C, of 3-5 ohms, is comparable to conduction 
in liquids and renders it very attractive (KU). However, Beta" Alumina is 
susceptible to catastrophic failure because of its intrinsic brittleness common to all
Figure 2. Structures of sodium beta alumina and sodium beta'' alumina.
ceramic material. The propagation of a crack through the Beta" Alumina ceramic enables the two components of the battery to react directly in a highly exothermic fashion, short circuiting the battery. The resulting temperature rise can be sufficient to damage neighboring cells.

1.2.2. MODES OF DEGRADATION:

The degradation of Beta"Alumina solid electrolyte has been the object of extensive research. Several modes of degradation have been identified, and are described here.

Mode I degradation takes place under electrolytic conditions, during the charge process, when sodium ions are flowing back towards the sodium compartment. The sodium ions being reduced to sodium metal will plate inside any crack present at the surface of the Beta"Alumina, and while flowing out of the crack, will exert a Poiseulle pressure which can lead to further opening of the crack (FE 82, DE 81 a, RI 75).

The stress induced at the crack tip depends on the current density, and a critical current density which cannot be exceeded, is obtained. The calculated value is actually unrealistically high, which indicates that other factors of degradation should be taken into account.

The mode II degradation originates in the instability of the Beta"Alumina towards sodium. The solid electrolyte can be reduced by sodium and oxygen vacancies are created with concurrent electron injection. This electron injection establishes an electronic conductivity gradient in the electrolyte and can cause internal precipitation of sodium and associated cracking (DE 81, DE 82).

Also, Beta"Alumina is water sensitive and requires adequate handling in an
inert atmosphere. Sodium ions can be exchanged by hydronium ions, producing an hydrated layer at the surface with altered ionic conductivity (BA 83). Moreover, Beta"Alumina exhibits ion exchange properties with other alkali metals or even transition elements when immersed in the proper molten salt. When present as impurities, water or calcium will cause the formation of a resistive layer and worse, potassium will even cause cracking for steric reasons.

Control of the micro-structure, homogeneity, and grain size, through an appropriate processing, improved the material performances. Dispersion of ZrO₂ particles was shown to improve the fracture toughness without being detrimental to the ionic conductivity.(GR 83).

I.3 THE CURRENT COLLECTOR:

Ideally, a current collector must be highly conductive, cheap, light and easily manufactured. When the current collector also constitutes the cell casing, good mechanical properties are required. The strongly corrosive nature of molten polysulfides at 350°C makes the search for a current collector a non-trivial materials problem.(TI)

Thermodynamically, metals are not stable to sulfur at 350°C and form the corresponding sulfide. Metals may still be considered for current collectors if the sulfide film formed at the surface is passivating and electronically conductive. A highly resistive layer will result in an unacceptably high internal resistance or poor contacts. A non-passivating layer will decrease the cell capacity by consuming irreversibly some active material which then is not available for the battery reaction. Corrosion products may also be deleterious to the electrochemical processes in the battery.
Mo, Zr, Cr display a good resistance towards corrosion; however, their high cost and the difficulty of their fabrication have prevented their use. Al forms a highly resistive layer of Al$_2$S$_3$. Graphite is stable to the polysulfides but does not provide a mechanically sound structure for a cell casing. Coatings of Cr on stainless steel produced satisfactory results. Conductive ceramics such as doped TiO$_2$ are electronically conductive and can be used as coatings on metal substrates; however, they are much less attractive than metals because of the difficulty of their processing.

I.4 AN ORGANO-SULFUR BATTERY:

If the main hurdle to be overcome for the sodium/sulfur battery is a materials problem, decreasing the operating temperature is a route to more technologically feasible battery systems. Low operating temperature in the 110-150 °C range, will allow the use of polymeric seals or epoxies and corrosion rates also should be reduced substantially. Furthermore, new perspectives in cell design are opened by a polymeric seal technology. The flat plate design, in which the Beta"Alumina has a flat plate geometry, was ruled out because the sealing method used induced unacceptable stresses. Such a design should be reevaluated in this new context since the seals could be achieved with epoxies in a much more satisfactory fashion. The flat plate design is preferable to the tube design in several respects: ease of stacking, bipolar geometry, easier electrolyte fabrication. Closed-end tubes could also be advantageously replaced by open ended tubes easily extruded and closed off by an epoxy plug. A decrease in the operating temperature will undoubtedly result in a decrease in cost and in an easier technology.

Some attempts have been made in decreasing the operating temperature by solubilizing the sulfur and the polysulfides in organic solvents such as
dimethylacetamide (AB 78). Unfortunately the kinetics of such systems were too slow and the resulting current densities were too low for a practical battery. The novel approach consists of using an organosulfur compound containing a disulfide link as the positive electrode material. Such a compound can be reduced to the corresponding sulfide sodium salt according to the cell reaction:

\[
R\text{-}S\text{-}S\text{-}R + 2 \text{Na} \rightarrow 2 \text{R} \text{-} S \text{Na}
\]

The RS-SR compounds constitute a new class of positive electrode materials and the performances of the associated battery are assessed in this thesis. The selection and the chemistry of these organosulfur compounds will be described in the following chapter.
CHAPTER II:

THE POSITIVE ELECTRODE MATERIAL: THE DITHIOCARBAMATES AND RELATED COMPOUNDS.

II.1 REQUIREMENTS:

The requirements that a suitable positive electrode material should fulfil for a low temperature, high energy density battery, can be listed as following.

a/ low melting points of the oxidized and reduced forms in order to maintain the positive electrode in the liquid state.
b/ high theoretical energy density.
c/ miscibility of the oxidized and reduced form.
d/ chemical stability at the operating temperature.
e/ electrochemical reversibility.

At first sight the number of organosulfur compounds possessing a sulfur-sulfur linkage is quite overwhelming and the selection process may seem difficult. Fortunately, the stringent requirements of a low molecular weight and a low melting sodium salt provide some guide-lines which restrict considerably the number of useful candidates. The high energy density criterion limits our investigation to compounds with a low molecular weight and therefore to rather simple molecules. The requirement of a low melting sodium salt is much more difficult fulfil as ionic species generally have high melting points (above 200°C), owing to the strength of the ionic bond. However, a big anion exhibiting a large delocalization of the electric charge is a feature which usually leads to low melting compounds. Several families of organosulfur compounds have been considered, namely the dithiocarbamates, xanthates and dithioacids.
II.2 ORGANOSULFUR FAMILIES OF INTEREST:

II.2.1 THE DITHIOCARBAMATE FAMILY:

The first family of compounds investigated, namely the dithiocarbamate family, was selected because of its attractive low melting sodium salt. The dithiocarbamate anion has the general formula:

\[ R-N-C=S \]

Where R and R' are alkyl groups.

The dithiocarbamate can be oxidized to the thiuram disulfide according to:

\[ 2 \overset{N}{R-N-C=S} \rightarrow \overset{N}{R-N-C=S} + 2 e^- \]

These compounds have found applications as complexing agents, polymerization initiators, insecticides or fungicides and even as alcohol abuse deterrents. An extensive review of the chemistry of the dithiocarbamates has been published by Thorn and Ludwig.(TH 62)

SYNTHESIS

The dithiocarbamate sodium salts are easily obtained by action of a primary or secondary amine on CS\(_2\) in the presence of NaOH.

\[ R-N-H + S=C=S + NaOH \rightarrow R-N-C=S - Na^+ + H_2O \]

MELTING POINT

This family of compounds was selected because its sodium salts exhibit low
melting points. The negative charge of the dithiocarbamate anion is largely
delocalized and the following resonance forms contribute to further stabilization.

\[ \text{R} - \dot{\text{N}} - \text{C} \equiv \text{S} \quad \text{R} + \dot{\text{N}} - \text{C} \equiv \text{S} \quad \text{R} - \dot{\text{N}} - \text{C} \equiv \text{S} \]

These salts are hygroscopic and readily form hydrates whose melting points
have erroneously been reported in the literature as being the melting points of the
pure compound. The diethyldithiocarbamate was reported to melt at 100°C,
whereas, in fact, the dry salt melts at 145°C.

The known melting points of several members of the family are listed in
table(2). No theory, as of today, can predict accurately the melting point of a
given compound, although some correlations can be pointed out. The melting
points of some thiuram disulfides are shown in table (3), (from TH 62). A
correlation exists between the chain length of the alkyl groups and the melting
points: the melting points decrease with increasing chain length as well as with
increasing asymmetry. This of course is specific to this family and cannot be
stated as a general rule.

COMPROMISES:

The two requirements of high energy density and low-melting point, which
allow for a low operating temperature, are unfortunately somewhat antagonistic.
For example, the electronic or steric effects of some substituants on the nitrogen
atom, may induce some depressing effect on the melting point by promoting charge
delocalisation but they concurrently increase the molecular weight and therefore
decrease the energy density.

The dithiocarbamate family is a good example of the kind of trade-off that
should be worked out between the different requirements. As an illustration of
SOME MEMBERS OF THE DITHIOCARBAMATE THIURAM DISULFIDE FAMILY

![Chemical Structures]

<table>
<thead>
<tr>
<th>ALKYL GROUPS</th>
<th>THIURAM DISULFIDE MELTING POINT (°C)</th>
<th>DITHIOCARBAMATE MELTING POINT (sodium salt) (°C)</th>
<th>THEORETICAL ENERGY DENSITY Wh/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = R' = CH₃</td>
<td>154</td>
<td>decomposes before melting</td>
<td>412</td>
</tr>
<tr>
<td>R = R' = CH₂₅</td>
<td>74</td>
<td>145</td>
<td>340</td>
</tr>
<tr>
<td>R = CH₃ R' = CH₂₅</td>
<td>25</td>
<td>too high</td>
<td>355</td>
</tr>
<tr>
<td>R = R' = CH O CH₃₂₅</td>
<td></td>
<td>50</td>
<td>240</td>
</tr>
<tr>
<td>R = CH₃ R' = CH₃₇</td>
<td></td>
<td>unknown</td>
<td>340</td>
</tr>
</tbody>
</table>

*table 2*
<table>
<thead>
<tr>
<th>SYMMETRICAL</th>
<th>MELTING POINT</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = R' = R = R''</td>
<td>(°C)</td>
</tr>
<tr>
<td>CH₃</td>
<td>156</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>72</td>
</tr>
<tr>
<td>n C₃H₇</td>
<td>50</td>
</tr>
<tr>
<td>i C₃H₇</td>
<td>112-4</td>
</tr>
<tr>
<td>n C₄H₉</td>
<td>viscous</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>UNSYMMETRICAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = R' R' = R''</td>
</tr>
<tr>
<td>R     R'</td>
</tr>
<tr>
<td>CH₃   H</td>
</tr>
<tr>
<td>C₂H₅  H</td>
</tr>
<tr>
<td>nC₃H₇ H</td>
</tr>
<tr>
<td>iC₃H₇ H</td>
</tr>
</tbody>
</table>
this point, methoxyethyldithiocarbamate ($R = \text{CH}_3\text{OC}_2\text{H}_5$) has a remarkably low melting point of 50°C, owing to the ability of ether oxygen to solvate internally the sodium ion, however, its energy density is too low for a high energy density application. Dimethyldithiocarbamate exhibits the highest energy density of the family but decomposes before melting. Diethyldithiocarbamate melts reasonably low at 145°C and has an energy density of 360 Wh/kg. Dithiocarbamates derived from a primary amine ($R = H, R' = \text{alkyl}$) would have attractive energy densities but they should be avoided because of their tendency to decompose to isocyanates. Preliminary synthetic work showed that methyl ethyldithiocarbamate displayed too high a melting point. Asymmetric dithiocarbamates certainly deserve a closer look; propyl-methyl-dithiocarbamate is an interesting candidate and the starting amine is commercially available.

As stated earlier, the search for an optimum electrode material has to be somewhat empirical because of the lack of theoretical understanding of the molecular structure and melting point relationship. From a more optimistic point of view, the chemical versatility of these compounds render the tailoring of these compounds to the battery requirements quite feasible.

II.2.2 XANTHATES:

The Xanthate family is similar to the dithiocarbamate family; the amine group is replaced with an alcoxy group (TO). The xanthate anions have the general formula:

$$R - \text{O - C}^-\text{S}^-\text{Na}^+,$$

where $R$ is an alkyl group.

They can be oxidized to the corresponding disulfides.
SYNTHESIS

They are synthesized in a one step reaction by action of an alcohol on CS₂ in the presence of NaOH.

\[ \text{ROH} + \text{CS}_2 + \text{NaOH} \rightarrow \text{R}-\text{O}-\text{C}-\text{S}^-\text{Na}^+ + \text{H}_2\text{O} \]

MELTING POINTS

Xanthates exhibit melting points above 150°C or decompose before melting. For this reason, they were not investigated further. It is interesting to notice that, although they have some similarities with the dithiocarbamates, they exhibit a different range of melting points.

II.2.3 DITHIOACIDS-SODIUM SALTS:

They have the following general formula:

\[ \text{R}-\text{C}=\text{S}^-\text{Na}^+ \]

They can be oxidized to the corresponding disulfides, but the oxidized form is unstable (TO). This confirms that the nitrogen atom plays an important role in the stabilization of the thiuram disulfides.

II.2.4 SUMMARY AND PRELIMINARY SELECTION:

As a summary, from these three parent families, only the dithiocarbamates have passed the preliminary screening. Most of the work presented in this thesis, is concerned with the redox couple tetraethylthiuram disulfide (TETD) and diethyl dithiocarbamate (DETC) since it constitutes, so far, the best compromise among the dithiocarbamates investigated. Yet, it is clear that the possibilities offered by this
family have not been exhausted and most likely TETD does not represent the optimal compound. However TETD will prove the validity of an organosulfur positive electrode concept. Its chemical reactivity is discussed in the following section.

II.3 CHEMICAL REACTIVITY:

The literature on the stability of the dithiocarbamates in aqueous media is abundant because of their applications as a complexing agent or as a fungicide. However, very little, understandably, is reported on the behavior of the melts. Synthetic possibilities of this family have also been explored, although an extensive review is beyond the scope of this presentation and would be quite tedious. For a positive electrode material application, from the strictly chemical point of view, the main relevant topics comprise the thermal stability at the battery operating temperature and the possible decomposition products. These topics will be discussed as well as a general presentation of the possible reactive sites of the molecule. The thiuram disulfides were intended originally to be used without any additives but it appeared that some small quantities of solvent improved considerably the cell performances; it is therefore appropriate to consider the chemical reactivity of these compounds in a broader fashion than just from the decomposition point of view.

II.3.1 THERMAL STABILITY

The disubstituted thiuram disulfides decompose upon heating to the corresponding thioureas, \( \text{CS}_2 \) and sulfur according to:

\[
RR'\text{-C}\left\{\begin{array}{c}
\text{S} \\
\text{S}
\end{array}\right\}C-NRR' \rightarrow RR'\text{-N-}\overline{C-N}RR' + \text{CS}_2 + S
\]
Another possible decomposition product is the monosulfide according to:

\[ \text{RR'N-C-S-C-N-RR'} \rightarrow \text{RR'N-C-S-C-N-RR'} + S \]

The temperature of decomposition depends on the nature of the alkyl groups. Tetramethylthiuram disulfide for example decomposes around 120°C. No data on the stability of these melts have been found. As a preliminary test, sealed ampoules of tetraethylthiuram disulfide were kept at 120°C for several weeks without showing any sign of decomposition.

The monosubstituted thiuram disulfides or the corresponding salts (one hydrogen atom is present on the nitrogen atom) decompose upon heating to give the corresponding isocyanates according to:

\[ \text{R-NH-C=S} \rightarrow \text{R-N=C=S} + \text{HSNa} \]

Although attractive because of their lower equivalent weight and their higher energy density, the monosubstituted thiuram disulfides are more prone to decomposition than the disubstituted thiuram disulfides and therefore have to be avoided. An unsuccessful attempt with ethylenediamine dithiocarbamate, which is a monosubstituted dithiocarbamate, is described in appendix 2.

11.3.2 THIURAM DISULFIDES REACTIVITY:

The reactivity of these compounds is, a priori, quite complex because of the variety of the reactive sites. The following paragraph is an attempt to describe the chemistry of this family according to its reactive sites or functional groups in a more rational fashion than a catalog of reactions. The potential reactive sites can be identified as the following:
- the sulfur-sulfur bond, which can be cleaved in an homolitic or heterolitic fashion
- the nitrogen atom, which possesses some basic and nucleophilic character
- the sulfur-carbon double bond
- the sulfur atom singly bonded to the carbon, which, in the dithiocarbamate salt, exhibits a nucleophilic character.

II.3.2.1. THE S-S BOND

The S-S bond is very labile and can be cleaved by U.V. irradiation to give radicals or by nucleophilic or electrophilic attack to give ions.

RADICALAR SCISSION:

The sulfur-sulfur bond of the thiuram disulfides can be dissociated reversibly into two radicals upon heating. The thermal dissociation of different thiuram disulfides in solution in decalin has been studied by EPR (NI 83). In the case of tetraethylthiuram disulfide an EPR signal appeared at 120°C and it increased in intensity as the dissociation became more important with increasing temperature. In the case of tetraisopropylthiuram disulfide an EPR signal appeared at 50°C, which points out the importance of the alkyl groups on the stability of the radical. The appearance of additional EPR signals, indicative of decomposition, was reported in the case of tetraethylthiuram disulfide for "higher" temperatures, the exact temperature was not reported.

One example of a reaction involving radicals is given by the action of boiling acetone on tetramethylthiuramdisulfide.

\[
(CH_3)_2 \overset{S}{\underset{S}{\text{N-}}} \overset{O}{\underset{O}{\text{CH}_3}} + CH_3 \overset{O}{\underset{O}{\text{CH}_3}} \rightarrow (CH_3)_2 \overset{S}{\underset{S}{\text{N-}}} \overset{O}{\underset{O}{\text{CH}_2}} \overset{O}{\underset{O}{\text{CH}_3}}
\]

(Several products are actually obtained; only one is mentioned here).
IONIC SCISSION:

Strong acids or strong bases can cleave a disulfide linkage. The disulfide linkage of the thiuram disulfides can be attacked by much milder reactants such as amines.

- $H_2S$ reacts with tetramethylthiuram disulfide according to:

$$\text{2} \text{H}_2\text{S} + \text{(CH}_3\text{)}_2\text{N-C-S-S-CH}_3 + \text{2(CH}_3\text{)}_2\text{N-C-SH} + \text{S}$$

$$+ \text{(CH}_3\text{)}_2\text{N-C-S}^- \text{NH}_2\text{(CH}_3\text{)}_2^+$$

ammonium salt of the dithiocarbamate

- Dimethylamine reacts with tetramethylthiuram disulfide at 100°C to give:

$$\text{(CH}_3\text{)}_2\text{N-S-S-S-N(CH}_3\text{)}_2 + \text{H}_2\text{S} \rightarrow \text{2(CH}_3\text{)}_2\text{N-S-S-N(CH}_3\text{)}_2$$

ammonium salt

$$+ \text{(CH}_3\text{)}_2\text{N-S-N(CH}_3\text{)}_2^+$$

(unstable)

- $\text{CN}^-$ ions can cause the smooth elimination of a sulfur atom according to the following reaction path, to give the monosulfide:

$$\text{RR'-N-S-S-C-N-RR'} + \text{KCN} \rightarrow \text{RR'-N-S-C-S-N-RR'} + \text{KSCN}$$

The monosulfide heated in the presence of sulfur reverts back to the disulfide.

- The sulfur-sulfur bond can insert additional sulfur atoms upon reaction with sodium polysulfides to give trisulfides or even higher polysulfides. The different equilibria to be taken into account are numerous and the reaction products are difficult to separate and to characterize.

II.3.2.2 THE C=S BOND:

The presence of a C=S bond could have been a concern for the stability of this positive electrode material, since compounds containing the C=S bond alone
are not very stable and tend to oligomerize or polymerize to give the more stable C-S bond (TO). The C=S bond is much less stable than the analogous C=O: the C=O bond is stabilized by the sp² hybridization of the carbon atom whereas such hybridization is not possible for the C=S bond.

The C=S bond exhibits a slight polarity C⁺-S⁻ and is much less polar than the C=O. The dipolar moments of the sigma bond and the pi bond are actually in opposite directions. On the other hand, the sulfur atom is much more polarizable than the oxygen and therefore much more able to stabilize a negative charge. The C=S bond is very sensitive to its environment and is strongly stabilized by substituents such as sulfur or nitrogen, as in the case of the thiuram disulfides. The C=S is therefore a rather inactive site in the thiuram disulfide molecule, which is very fortunate for our electrochemical application.

II.3.2.3 NUCLEOPHILICITY OF S⁻:

Thiolates of general formula RS⁻Na⁺ are good nucleophiles and rather poor bases. The dithiocarbamates can be expected to exhibit some nucleophilic character, although they should be less strong nucleophiles than simple alkyl thiols because of the delocalization of the negative charge over the neighboring atoms. Some examples of the nucleophilicity of the dithiocarbamates are listed below.

Ester formation:

\[ \text{R}_2\text{N-}_\text{S}^- \text{Na} + \text{CH}_3\text{I} \rightarrow \text{R}_2\text{N-}_\text{S}^-\text{CH}_3 + \text{NaI} \]

Attack on dialkylcarbamoyl:

\[ \text{RR'}\text{N-}_\text{C-S}^- \text{Cl} + \text{RR'}\text{N-}_\text{C-S}^- \text{Na} \rightarrow \text{RR'}\text{N-}_\text{C-S}^-\text{S}^-\text{N-RR'} + \text{NaCl} \]

The equivalent reaction to the thiol disulfides exchange for the dithiocarbamate/thiuram disulfide could be considered as a nucleophilic attack of the S-S bond by the dithiocarbamate ion.
II.3.2.4 BASICITY OF THE NITROGEN ATOM:

The nitrogen atom of the dithiocarbamate exhibits some basic character and can be protonated which leads to a decomposition reaction:

\[
\text{RR'}-\text{N-C-S}^{\text{Na}^+} + \text{H}_2\text{O} \rightarrow \text{RR'}-\text{N-H} + \text{NaOH} + \text{CS}_2
\]

This reaction is actually the reverse of the salt synthesis reaction. The dithiocarbamic acids are very unstable in aqueous solutions especially at low pH. They decompose to the amine and CS\textsubscript{2} in 0.3 s at pH=2 and in 35 days at pH=9. From a practical point of view, traces of water or acidic impurities in the positive electrode melt are certainly to be avoided and eliminated very carefully as they will induce some decomposition. The sodium dithiocarbamate salt, which is commercially available in the hydrated form, has to be dried thoroughly if the battery is to be assembled in a partially discharged state or, for this matter, if any kind of meaningful electrochemical measurements are to be performed.

In summary, little has been reported in the literature about the behavior of these compounds in the molten state, as the traditional applications of such compounds, as complexing agents or as insecticides, are far removed from our battery interests. As a consequence, each case should be investigated separately. However, from this chemical picture several guidelines for a successful use as a positive electrode material application can be formulated.

The operating temperature of the battery must be carefully chosen and preferably should be kept under 150°C to be compatible with the stability range of these compounds.

Acidic impurities or traces of water should be carefully removed from any cell components because they induce decomposition. If any additives, such as solvents
or catalysts are to be used, they should be carefully dried.

Any additives, if used, should also be chemically compatible with the TETD, which rules out primary or secondary amines and any hydrogen donor compounds. Acetone should also be avoided as it gives reactions involving radicals; no information is available regarding the reactivity towards other ketones. The dithiocarbamate ion has a nucleophilic character; therefore, solvents sensitive to nucleophilic attack should be avoided.
CHAPTER III: CELL DESIGN AND ASSEMBLY

The cell design evolved during the course of this investigation according to the state of understanding of this system. In retrospect, some of the first designs seem now somewhat awkward, and only the most representative designs will be described here.

An easy cell assembly and dismantling procedure is one of primary concern for experimental cells, whereas weight minimization and compactness constitute higher priorities for more practical high-energy density batteries. As a common feature, all these cells were, technologically speaking, easy to assemble. The most stringent experimental requirement was the use of two separate glove boxes, one of them being dedicated to the preparation of the sodium electrode, and the other one being reserved to the handling of sulfur compounds, cell assembly and testing.

The low operating temperature of the system allows for the use of epoxies, rubber gaskets or even rubber stoppers for the earlier tests, which are far easier to utilize than glass to metal seals. The rare cases of Beta Alumina tube rupture gave rise to non-violent catastrophic failures, undoubtedly messy but very easily contained within the dry box. These experimental conditions would be completely unthinkable for the high-temperature sodium/sulfur battery. In addition, these organo-sulfur compounds are much less corrosive and much easier to handle than molten polysulfides or molten chloroaluminates and similar molten salts used for high temperature, high-energy density batteries.

Only cells with a tube configuration for the Beta Alumina solid electrolyte were designed although, as mentioned earlier, a flat plate design would certainly be made possible and of interest now, with the possibility opened by epoxy seals. Schematically, in a typical cell, the graphite felt matrix is soaked with TETD and wrapped around the Beta Alumina tube which contains the sodium electrode. The
cell body itself constitutes the positive pole and the current collector. The
different designs will be described separately, but some procedures such as the
sodium preparation or the positive electrode preparation were common to all or
most cells.

III.1 SODIUM ELECTRODE PREPARATION:

The sodium was handled and purified in a sodium glove box where the
oxygen level was maintained below 2 ppm. Previous studies on the electrochemical
behavior of the Beta"Alumina sodium interface, have shown that oxygen­
contaminated sodium induces severe asymmetric polarization, especially in the
temperature range considered here. Our current understanding of the sodium-Beta"
Alumina interface will be described in more detail in the next chapter.

The sodium purification method is summarized here. Reagent grade sodium
is treated at 350°C with sodium oxide to precipitate any calcium present in the
form of calcium oxide according to:

\[ \text{Ca + Na}_2\text{O} \rightarrow \text{CaO} + 2 \text{Na}. \]

The sodium is then filtered at 130°C through a coarse stainless steel sponge,
an operation which eliminates most of the sodium oxide precipitate present in the
sodium. The filtered sodium is then heated at 350°C in the presence of titanium
sponge granules for several hours. Titanium sponge is an efficient oxygen
scavenger at this temperature, bringing the oxygen level in the sodium down to the
ppm level within two hours. At this point, the sodium surface appears absolutely
shiny and free from any sodium oxide film. Pure sodium also wets its stainless
steel crucible whereas impure sodium does not. The sodium is then poured into the
Beta" Alumina tube via a glass pipette and typically the wetting occurs almost
immediately. Beta"Alumina is thermal-shock sensitive and should be preheated to 350°C to avoid cracking. Additional granules of titanium sponge are added at the top of the tube in order to scavenge any oxygen that might have been introduced during the sodium transfer. The tube is then kept at 350°C to insure good wetting of the Beta" Alumina by sodium.

The Beta" Alumina tube must be sealed off to prevent any contamination of the sodium. In early cells, a serum stopper rubber cap was used to close off the Beta" Alumina tube. This simple seal initially gave surprisingly good results, but was short lived. The eventual sodium contamination led to high internal resistance and polarization.

A more reliable and efficient sealing method was needed; one component epoxy, UNISET A-359-LV, manufactured by Amicon, was used to seal an aluminum cap to the Beta"Alumina tube. This epoxy is particularly easy to use: the curing and hardening process does not give off any vapors and is achieved very quickly in 3 minutes at 300°C. This epoxy can withstand an operating temperature of 150°C indefinitely and is particularly resistant to chemical attack.

III.2 POSITIVE ELECTRODE PREPARATION:

Since some organo-sulfur compounds are air sensitive, the preparation of the positive electrode was carried out in a dry box. TETD is an electric insulator, and therefore it must be embedded in an electronically conducting matrix which provides an electronic path from the site of the charge transfer reaction to the current collector. Graphite felt and vitreous reticulated carbon were both tested as conductive matrices.

The internal resistance of the battery was found to be critically dependent on the preparation method of the positive electrode. The melts of TETD and DETC
exhibit a much lower conductivity than the molten polysulfides in the sodium/sulfur battery; for comparison purposes, molten polysulfides at 350°C have conductivities of the order of $3 \times 10^{-1}$ (ohms cm)$^{-1}$, whereas TETD/DETC mixtures at 130°C have conductivities typically around $10^{-3}$ (ohms cm)$^{-1}$. Because of the comparatively lower values of the TETD/DETC melt conductivities and also because of the higher resistivity of Beta* Alumina at 130°C than at 350°C, the internal resistance of a TETD cell is expected to be higher than the one of a Na/S cell. Moreover, since the TETD/DETC melts have lower conductivities, the presence of any gap at the solid electrolyte/carbon felt interface will result in a more substantial increase in the cell internal resistance, and consequently, will have a much more detrimental effect for a TETD cell than for a sodium/sulfur cell. The graphite matrix was slightly compressed in order to provide a snug fit on both sides, with the solid electrolyte and also with the current collector.

Several methods for inserting the graphite felt tightly, packed around the Beta* Alumina, were used. In one case, the graphite felt was tightly wrapped around the Beta* Alumina tube with a molybdenum foil. The whole assembly could then be inserted in the cell body without tearing the graphite felt. Molten TETD was then injected hot at the top of the graphite felt while the cell was maintained around 120°C, to prevent TETD from solidifying.

In the second method, the positive electrode was molded in the following fashion: the graphite felt was wrapped around a teflon rod and compressed into shape in an aluminum mold, (Fig. 3). TETD was injected hot in the preheated mold and percolated all the way to the bottom of the mold. After the mold had cooled down, the teflon rod was easily removed and a solid hollow cylinder of graphite soaked with TETD was obtained. The inner diameter of the molded electrode was made purposely smaller than the diameter of the Beta tube, giving a snug fit. (The tube had to be heated up to around 100°C in order to melt
MOLD FOR GRAPHITE FELT/TETD ELECTRODES

mold body
screws

central teflon rod
screws
mold stand

Figure 3
superficially the TETD and permit insertion)

In the case of the latest design (design 5), a much thinner and stiffer graphite felt was used which could be inserted in the cell body without any foil or premolding step.

III.3 DIFFERENT CELL DESIGNS:

DESIGN 1 (Fig. 4)

All the cell designs described here had a cylindrical symmetry because of the tube geometry of the Beta" Alumina solid electrolyte. A thick-walled hollow, aluminum cylinder constituted the cell body. The Beta" Alumina tube had a 1 cm outside diameter surrounded by a 3.5 mm thick positive electrode. In order to achieve good contacts, as mentioned before, the graphite felt was wrapped around the Beta" Alumina tube and the whole assembly, tube and graphite felt, was in turn wrapped in a molybdenum foil. The graphite felt had a flimsy texture and was very easy to tear apart. The molybdenum foil allowed for the insertion of the graphite felt nicely compressed against the Beta"Alumina tube, in the aluminum cell. The surface area of the solid electrolyte in contact with the graphite felt was 20 cm$^2$. For these first tests, the Beta" Alumina tube was only sealed off by a rubber cap. When the cell was closed, the rubber cap was pierced by a tungsten rod sealed to the glass top. The tungsten rod, dipping in the liquid sodium, established the negative electrode connection. The aluminum body constituted the positive pole. The glass top and the aluminum bottom are joined together by an O-ring seal and the appropriate clamp. This assembly procedure may seem somewhat awkward but short pulses with 100 mA/cm$^2$ current densities were obtained ( or a total current of 2 Amps for the cell). These good results exceeded our expectations at the time (especially considering the experimental
CEL DESIGN 1

Figure 4

tungsten rod

glass top

serum stopper

rubber gasket

Beta Alumina tube

graphite felt

Aluminum

cell body

(not to scale)
conditions) and therefore sharpened our interest.

DESIGN 2 (Fig. 5)

In this design, a more efficient sealing method was used for the Beta"Alumina tube as mentioned before. An aluminum cap was epoxied at the top of the tube. The positive electrode was either molded or inserted with a molybdenum sheet. The cell body was made out of thick walled aluminum. The seals were two screw caps with silicon rubber O rings. (Ordinary rubber O-rings were vulcanized by the TETD vapors, the rubber gaskets cracked and the seal was destroyed). The first screw cap is tightened at the cell top and the second one is screwed on the first around the Beta"Alumina tube preventing direct contact in between the epoxy of the top seal and the organo sulfur compound. The long term stability of the epoxy in contact with TETD is thus not an issue for this type of design.

DESIGN 3 (Fig. 6)

This cell generation was built to demonstrate the feasibility of a 100 Wh/kg cell. The cell casing was made of thin aluminum cylinder with a 1 mm wall thickness. Further cell optimization may actually show such a thickness is not necessary and could be reduced. The tube and the molded positive electrode were just slipped in the casing, and an aluminum cap was snapped in place and epoxied. The epoxy also served as an electrical insulator in between the cell body, which is the positive pole and the negative connection. The solid electrolyte area was 30 cm². This type of cell contained 13.5 g of TETD (Tetraethylthiuram Disulfide) and 4 g of sodium. The Beta" Alumina tube weighed 13 g, the cell casing and cap weighed 2.6 g and the graphite felt weighed 0.7 g.
CELL DESIGN # 2

- negative electrode
- epoxy seal
- top screw cap
- screw cap
- gaskets
- aluminum body
- Beta Alumina tube
- graphite felt

Figure 5
SODIUM/ORGANOSULFUR CELL

T = 130°C

- negative pole
- epoxy-seals
- epoxied stainless steel cap
- Beta-Alumina tube
- sodium
- graphite felt +positive electrode material
- cell casing current collector positive pole

Figure 6
DESIGN 4 (Fig. 7)

This cell design utilized a glass body which permits convenient visual inspection for volume or color changes or any bubbling indicative of decomposition. The cell is very simply constituted by a glass tubing, a glass collar on which the Beta" Alumina tube is epoxied, and a glass top pierced in its center for the negative connection. A molybdenum sheet was used as a current collector with a tab sticking out of the cell to provide the positive electrical connection. The molybdenum foil had a slit in the middle through which the wetting of the graphite felt could be checked.

DESIGN 5 (Fig. 8)

This cell design is just a modified version of design 2. The positive electrode thickness was decreased from 3.5 mm to 2 mm which permitted faster discharge/charge cycles. The other differences are obvious from the diagram.
GLASS CELL
CELL DESIGN # 4

---
glass top

glass ring

molybdenum
connection

glass body

molybdenum foil

Beta" Alumina
tube

Figure 7
CELL DESIGN # 5

section cylindrical symmetry

negative electrode

top screw cap
cap
silicon rubber
gasket

graphite felt

Beta" Alumina tube
cell body

top screw cap
detail

Figure 8
CHAPTER IV: THE SODIUM/BETA"ALUMINA INTERFACE

IV.1. NEED TO STUDY THE DIFFERENT INTERFACES SEPARATELY:

A galvanic cell constitutes a complex system because of the variety of processes and interfaces which are involved. Such processes include mass transport of electroactive species within the electrodes or within the electrolyte, electron transfer and possible corrosion phenomena at the current collector. One or several processes can be limiting in a cell, causing polarization, and it is therefore important to determine the different contributions of each of the processes to the overall polarization.

In the case of the Na/Beta" Alumina/RSSR cell, Beta" Alumina separates completely the sodium electrode from the positive electrode, and limits their interactions to the exchange of sodium ions. It is therefore legitimate to study the two electrodes independently (There is no partial solubility of one electroactive component in the electrolyte, as it is sometimes the case for molten salts, and therefore there is no possibility for the positive electrode species to diffuse towards the negative electrode and react directly). The complexity of the system is reduced by considering separately two simpler systems, the two half cells, Na/Beta" Alumina and RSSR/Beta" Alumina.

A stable reference potential which is not affected by the passage of current is needed to single out one interface electrode/electrolyte. In our case of a sodium/Beta" Alumina/RSSR type of cell, a typical reference electrode would be constituted by a wire dipping in a droplet of sodium or a droplet of organo-sulfur compound located on the Beta" Alumina tube. It was found to be more convenient to design a sodium/Beta" Alumina/sodium cell with a reference electrode constituted by a droplet of sodium. The classical three electrode set-up used in our study is shown in fig. 9, with a working electrode, a reference electrode, and a
Figure 9

- Working electrode
- Feed-through
- Reference electrode
- Boron nitride lid
- Copper gasket
- Alumina disk
- Beta-alumina tube
- Stainless steel body (counter electrode)
- Nickel wire

Na/Na Cell
counter electrode. The potential of the working electrode is monitored with respect to the reference electrode while the current is flowing between the working and the counter electrode. The Beta"Alumina tube is partially filled with sodium. Some sodium is also present on the outside of the tube. When a difference of potential is imposed between the working and the reference electrode, sodium metal moves from one compartment to the other. The direction of movement depends obviously on the sign of the applied voltage. For example, when sodium metal from the working electrode is oxidized to sodium ions at the Beta"Alumina/sodium interface, the resulting sodium ions travel through the Beta"Alumina and are reduced back to sodium metal when exiting the Beta"Alumina and entering the counter electrode compartment. The corresponding electrons travel through the external circuit. The Beta" Alumina tube can also be filled electrolytically if a high purity sodium is needed. A thin nickel was attached to the the working electrode which provided the electrical contacts with the Beta" Alumina necessary to initiate the electrolysis process.

IV.2. THE BETA"ALUMINA/SODIUM INTERFACE AT 350°C:

The Beta" Alumina/sodium interface has been extensively studied for the sodium/sulfur application (BR 80, BR 81). The presence of impurities, such as calcium and potassium in the sodium, were reported to cause dramatic increases in the Beta" Alumina resistivity and, in the case of potassium, to cause cracking. Calcium or potassium can exchange with the sodium ions in the solid electrolyte, impeding further conduction (BR 84, YA 78). Water is also very detrimental to the solid electrolyte performances because H⁺ ions can enter the Na⁺ ion conduction planes and lead to unacceptable increases in the resistivity (BA 83).

A study was also conducted in this laboratory showing that at 350°C and at
moderate current densities of 150 mA/cm\(^2\), the Beta\(^{"}\) Alumina/sodium interface displayed a very ohmic behavior (MA 84, MA 87). (The corresponding voltage versus current curve is a straight line). The presence of sodium oxide in the sodium or the exposure of the Beta\(^{"}\) Alumina to water led to increases in the interfacial resistance attributed to the formation of a resistive layer.

In summary, provided the sodium is free of these impurities, the Na/Beta\(^{"}\) Alumina interface is well behaved.

IV.3. THE BETA\(^{"}\) ALUMINA/SODIUM INTERFACE AT 130°C:

The temperature was found to have a strong influence on the electrochemical behavior of the sodium/Beta\(^{"}\) Alumina interface: a sodium sodium cell which exhibited a perfectly ohmic behavior at 350°C, displayed an asymmetric polarization depending on the direction of sodium flow when the cell temperature was lowered. A typical current vs potential curve is shown in fig. 10 at 160°C. The experimental set-up was the same as in fig. 9. The main results are summarized here, more details can be found in the references (MA 84, MA 87).

It was observed that when sodium was flowing towards the Beta\(^{"}\) Alumina (which corresponds to discharge in the battery), the interfacial resistance increased; conversely, when fresh sodium was generated at the Beta\(^{"}\) Alumina surface, the interfacial resistance decreased.

The presence of sodium oxide, precipitated in the sodium electrode was suspected to be the culprit because it had been found to cause the formation of a resistive layer at the interface sodium/Beta\(^{"}\) Alumina in the case of the sodium/sulfur battery at 350°C. In order to investigate the effect of oxygen contamination on the electrochemical behavior of the Beta\(^{"}\) Alumina/sodium interface, the oxygen activity in the sodium working electrode was fixed at
different levels:

- electrolytic sodium which is virtually oxygen free.
- reagent grade sodium containing some sodium oxide.
- filtered sodium.
- filtered sodium treated with titanium sponge at 350°C.

The "filtered sodium" and "filtered sodium treated with titanium sponge" denominations, correspond to the successive steps of the sodium purification method which has already been described in chapter 3. The different shapes of the current vs potential curves according to the sodium purity are summarized in fig. 11. Sodium containing sodium oxide particles gave rise to the highest internal resistance. Simply filtered sodium, which may have contained some sodium oxide particles, exhibited an asymmetry behavior at 200°C, whereas it displayed an ohmic behavior at 350°C. On the other hand, electrolytic sodium gave a completely ohmic behavior from 350°C to 130°C. Filtered sodium, treated with titanium sponge, also gave the same result.

An accumulation/depletion model was proposed which accounts for this asymmetric behavior. Beta" Alumina behaves very much like a sodium-selective membrane, and constitutes a blocking interface for ions other than sodium ions. Sodium ions can travel through the Beta" Alumina whereas oxygen ions are stopped at the interface. When sodium metal flows towards the Beta" Alumina interface, any oxygen ions, present as impurities in the sodium, are stopped at the interface whereas the sodium ions resulting from the oxidation of sodium metal go through the Beta" Alumina. The concentration of oxygen ions at the interface rises, leading eventually to the precipitation of a resistive film. Similarly, sodium oxide particles, if present in the sodium, are caught in the flow of sodium and will pile up at the interface, giving rise to a resistive layer and an increase in the internal cell resistance. Conversely, when fresh sodium is generated at the surface of the
Summary of I/E curves of the Beta" Alumina/sodium interface for different sodium purities

**SODIUM CONTAINING NaO_2**

![Graph 1](image1)

**FILTERED SODIUM**

![Graph 2](image2)

**FILTERED SODIUM, CLEANED WITH TITANIUM**

![Graph 3](image3)

Figure 11
solid electrolyte, oxygen impurities or film present at the interface, are swept away and the interfacial resistance decreases.(fig. 12).

Two factors contribute to the difference of electrochemical behavior at 130°C and at 350°C. The oxygen solubility in sodium drops from 200 ppm at 350°C to less than 10 ppm at 130°C. Traces of oxygen in the sodium electrode which do not affect the ohmic behavior of the interface at 350°C, will lead to sodium oxide precipitation at 130°C and will give rise to asymmetric polarization. Also, the diffusion coefficient of the dissolved oxygen or of oxygen ions in sodium is much lower at 130°C than at 350°C. During the accumulation process at the interface, these species are less able to diffuse back, away from the interface. For these two reasons, the formation of a resistive layer at the solid electrolyte surface is far easier at lower temperatures.

The ohmic behavior of the "oxygen free sodium/Beta" Alumina" interface at 130°C is not a trivial result: Beta" Alumina is known to be wetted by sodium at 350°C, but there was some controversy as to whether this was also the case at 130°C (VI 83). It is reported that once the Beta"Alumina has been wetted at 350°C it stays wetted when the temperature is lowered to 130°C. A poor wetting of the Beta" Alumina by the sodium would have rendered impossible the idea of a low temperature battery.

Furthermore, since the sodium electrode is not subjected to polarization, it can be used as a reference electrode: any polarization arising in the battery can be attributed solely to the positive electrode side. This is valid, of course, provided the sodium side stays clean which requires good sealing methods.

In conclusion, the sodium/Beta" Alumina interface can be made to behave in a desirable ohmic fashion, provided that the sodium is properly purified.
Figure 12
CHAPTER V: THE Na/TETD BATTERY.

V.1. CELL TESTING PROCEDURE:

The cells were assembled in the fully charged state, according to the procedure described in chapter 3 and were discharged at a constant electrode current density of 5 mA/cm². The cell voltage was recorded as a function of the percentage of discharge with a P.A.R (Princeton Applied Research) model 173 potentiostat/galvanostat equipped with a digital coulometer 179. The recorder was a Bascom Turner model 4120. A typical discharge curve is shown in fig. 13. (the cell design used for a particular cell is always mentioned on the curve itself).

At various stages of the discharge process, the battery was brought back to open circuit voltage and pulsed at different current densities. The current pulses were generated with a P.A.R. universal programmer 175. The two components of the overall cell polarization, the instantaneous ohmic drop and the time dependent polarization, can be separated by studying the transient response of the cell to these current pulses. The initial vertical drop of the E versus time curve corresponds to the ohmic drop through the cell and is followed by the time dependent part of the polarization. A good separation depends obviously on the respective time constant of the phenomena, the response time of the equipment and the duration of the pulse. The Bascom turner can record up to 1000 data points per second.

The power density capability in the first third of discharge was determined by discharging the cell at half open circuit voltage for a short period of time (one minute).
Figure 13

DISCHARGE/CHARGE OF PURE TETRAETHYLTHIURAM DISULFIDE

CHARGE DISCHARGE RATE = 5 mA/cm²

T = 130°C

CELL VOLTAGE (VOLTS)

0 20 40 60 80

0 0.5 1 1.5 2 2.5 3 3.5

cell design #3

2.5 mA/cm²
V.2. RESULTS:

V.2.1. POWER DENSITIES:

The power capabilities of the battery are displayed in fig. 14. The high current densities which were obtained, generated a great deal of enthusiasm and interest in the TETD battery, as they proved that the system displayed high rate kinetics. In the early stages of this investigation, pulses of 2 A (which correspond to a current density of 100 mA/cm²), were obtained for about one minute at one volt which exceeded expectations, considering the low operating temperature of the system. The achievement of high power densities depends directly on a low value of the cell internal resistance. The latter decreased as the cell design was optimized. The highest power density obtained, so far is 80 Wh/kg which corresponds to a discharge rate of 150 mA/cm² at 1 volt, for 20 cm² of solid electrolyte. These current densities, however could only be sustained for 5 s.

V.2.2. CHARGE/DISCHARGE CURVE:

A typical charge discharge curve is shown in fig. 13. Up to 40 % discharge, the cell polarization was essentially constant, as desired; above 40% discharge however, the cell polarization increased substantially and steadily. At the beginning of charge the cell polarization was constant again but increased sharply after 60 % recharge but, the cell still accepted charge if the current density was decreased.

V.2.3. CURRENT PULSE TRANSIENTS:

The study of the current-pulse transient showed that the cell internal resistance increased as the discharge proceeded. The contribution of the time dependent polarization increased as well. At the beginning of discharge, the
Operating Temp. = 140°C
Electrolyte Area = 20 cm²
Cell Mass = 50 g

Charge Rate = 25 mA/cm²
= 0.5 AMPS

Discharge Rates

- 100 mA/cm² = 2 AMPS
- 50 mA/cm² = 1 AMP

Cell Voltage

Time (seconds)

40 W/Kg
30 W/Kg
discharge curve was flat as shown in fig. 13 and the cell internal resistance was 1 ohm. Current pulses performed at 54 % discharge, shown on Fig. 15 and Fig. 16, indicated that the internal resistance of the cell on discharge has increased to 2.5 ohms, whereas the internal resistance on charge was only 2 ohms. The transient behavior of the cell during a current pulse on a 1 s time scale demonstrated clearly the asymmetry between the discharge and the charge processes. There was very little time dependent contribution for the charge-pulse polarization whereas the phenomena taking place during the discharge-pulse are obviously much more sluggish. On recharge, for a similar composition at 47 % discharge, the shape of the transients has changed: the charge and discharge process were now much more symmetric and the internal resistance on discharge has decreased and was restored to a much more acceptable value (Fig. 17).

V.2.4. CELL INTERNAL RESISTANCE:

The cell internal resistance was considerably affected by the nature of the conductive matrix. The use of reticulated vitreous carbon (RVC) as conductive matrix instead of graphite felt resulted in a significant increase in the internal resistance, as demonstrated in fig. 18 and 19. For a 500 mA total electrode current and the same surface area, the cell internal resistance was 2 ohms for the RVC and 1 ohms for the graphite felt. The graphite felt has a much higher surface area than the RVC, which is of prime importance considering the conductivity range of these melts. RVC was a very attractive material since it can be machined easily to the cell dimensions, but had to be abandoned because of its poor cell performances. (It also was plagued by electrical bad contacts originating from the differences in thermal expansion with the aluminum casing.)

V.3. ELECTROCHEMICAL MEASUREMENTS:
TETRAETHYLTHIURAM DISULFIDE (pure)

CURRENT PULSES Figure 15

- Current density: 5 mA/cm²
- Cell design #3
- 54% discharge
- T = 130°C
- Discharge process
TETRAETHYLTHIURAMDISULFIDE (pure)

CURRENT PULSES
(transient 1s)

Figure 16

current density
5 mA/cm²

T = 130°C

cell design #3
54% discharge

DISCHARGE PROCESS

CELL VOLTAGE (Volts)

open circuit voltage

0 0.5

TIME (s)
TETRAETHYL THIURAM DISULFIDE (pure)

CURRENT PULSES (transient) Figure 17

- Current density: 5 mA/cm²
- Temperature: T = 130°C
- Cell design #3
- 47% discharge

Charge process

CELLOUTAGE (Volts)

- 3
- 2.5
- 1.5

Open circuit voltage

TIME (s)
Pure TETD

Graphite felt
influence of the current density
on the cell internal resistance

surface area = 30 cm²

Resistace, (Ohms)

Current, (A)
influence of RVC on the internal resistance

surface area = 30 cm²

Current, (A)
V.3.1. IONIC CONDUCTIVITY OF THE MELT:

The ionic conductivity measurements were performed by a coworker, Steven Visco. As pointed out earlier, the ionic conductivity of the TETD/DETC melts at 130°C are lower than the ones of the polysulfide melts at 350°C. The conductivity of these melts at 130°C ranged from $2.3 \times 10^{-7}$(ohm cm)$^{-1}$ for pure TETD to $1.4 \times 10^{-2}$(ohm cm)$^{-1}$ for pure DETC. The plot of the equivalent conductance as a function of the square root of the concentration is shown in fig. 20. Interestingly, these melts do not follow the empirical law of Kohlrausch. In our case, the equivalent conductivity increased with the square root of the concentration instead of being constant (Kohlrausch law), or instead of decreasing because of ion-ion interactions. The shape of this curve suggests the presence of ion pairs in the melt at low concentrations, which form subsequently triplet ions at higher concentrations: the ion pairs, being neutral species, do not contribute to the conductivity whereas triplet ions do.

V.3.2. CYCLIC VOLTAMMETRY:

The redox couple TETD/DETC has already been the object of an electrochemical investigation because of its application as a complexing agent (SC 78, CA 73). The solvent used was acetonitrile which has a large electrochemical stability window. The DETC salt is oxidized to TETD in a two electron process at 0.05 V (versus SCE, Standard Calomel Electrode) and TETD is reduced at -1.85 V to the DETC. The proposed mechanism involves the formation of a radical by scission of the sulfur-sulfur bond; this radical is then reduced easily. The TETD can be oxidized further, at 0.80 V, and different mechanisms and intermediates have been hypothesized. Some of the steps appear to be irreversible, and one of the intermediates is an oxidized form of the corresponding monosulfide.
Molar Conductance of NaDEDC Dissolved in Molten TETD at 130°C

Figure 20

Molar Conductance (ohm·cm²·equiv⁻¹)

\[ \sqrt{c} \text{ (equiv/liter)} \]

addition of tetramethyl urea
(tetraethylthiuram monosulfide). The different peaks observed on the cyclic voltammogram and the corresponding reactions are listed below:

\[
\begin{align*}
&\text{at 0.05 V} & \text{DETC} & \rightarrow & \text{N} - \text{C} - \text{S}^- + e^- \\
&\text{C}_2\text{H}_5 & \text{S} & \text{(radical Ia)}.
\end{align*}
\]

\[
\begin{align*}
2 \text{ Ia} & \rightarrow \text{TETD} \quad \text{(proposed mechanism)}. \\
\text{at -1.85 V} & \quad \text{TETD} = 2 \text{ Ia} \\
\text{Ia} + e^- & \rightarrow \text{DETC}.
\end{align*}
\]

\[
\begin{align*}
\text{at 0.80 V} & \quad \text{TETD} \rightarrow \text{S} + 2 e^- + \text{monosulfide dication}. \\
\text{at 0.25 V} & \quad 2 e^- + \text{monosulfide dication} \rightarrow \text{monosulfide}.
\end{align*}
\]

V.3.2.1. CYCLIC VOLTAMMETRY IN DMSO:

The cyclic voltammetry of the TETD/DETC was reproduced in DMSO and was also investigated as a function of temperature. The results presented here do not intend to constitute a cyclic voltammetry study per se. For battery application, cyclic voltammetry has only a limited relevance: in a cyclic voltammogram experiment, the concentration of the electroactive species is on the order of \(10^{-3}\) M whereas in the battery, the electroactive material is used pure. Consequently, the chemical environment and the stabilization of the intermediates are quite different in the two different cases, and the validity of one mechanism in one case might not transpose so easily to the other. For this reason, no mechanism will be proposed and a detailed study is not really warranted. In addition, because of the unavailability of a carbon electrode at that time, the study was carried out with a platinum electrode. (The electron transfer in the positive electrode, in this battery, occurs at a graphite fiber). Research now in progress, conducted by coworker Meilin Liu have shown that the current exchange density on carbon is higher than
on platinum.

The potentiostat used was a P.A.R. model 173 with a universal programmer model 175 and the recorder was a Bascom Turner model 4120. The DMSO used was water free and the TETD had been recrystallised three times from butanol. The solution was degassed with dry nitrogen or argon according to the usual procedure. The supporting electrolyte was tetraethyl ammonium perchlorate at a 0.1 M concentration and the electroactive material had a 0.001M concentration. A classical three-electrode set up included a Tacussel platinum working electrode, a Ag/AgCl, Me₄NCl 1 M in water, reference electrode with a water DMSO junction bridge and a platinum counter electrode. The cyclic voltammetry of benzoquinone in dimethylformamide was performed and the tabulated values of the voltammetric waves permitted the determination of the potential of the reference electrode. (The first voltammetric wave of the benzoquinone in dimethylformamide is reported to occur at -0.15 Volts (reduction) and -0.09 (oxidation) versus the NHE, source: CRC organic electrochemistry, vol. V, table EB 22). The potential of the reference electrode was found to be 0.28 Volts.

The cyclic voltammogram of the TETD, in DMSO, at room temperature, is shown in fig. 21. The reduction of TETD to DETC occured at -1.4 volts (vs NHE) and the corresponding oxidation occured at +0.37 Volts (vs NHE) in DMSO. As a comparison, the study conducted in acetonitrile showed that the reduction occured at -1.6 Volts (vs NHE) and that the oxidation occured at +0.29 Volts (vs NHE). The prominent feature of these cyclic voltammograms, is the wide peak separation between reduction and oxidation which points out that the TETD/DETC couple is a slow system. The electron transfer is also slower in acetonitrile than in DMSO. The peak height of the anodic and cathodic wave were found proportional to the square root of the scan rate. The TETD/DETC system is such a slow system that it actually falls in the category of kinetically irreversible systems.
CYCLIC VOLTAMMETRY OF TETRAETHYLTHIURAM DISULFIDE

T = 25°C
solvent: DMSO
scan rate: 100 mV/s
200 mV/s
500 mV/s
0.5 mA sensitivity
Reduction first

Figure 21
Fig. 23 and 24 display the evolution of the cyclic voltammogram as the temperature is raised. The magnitudes of the peaks increased as the diffusion coefficients of the electroactive species increased, due to thermal activation, as could be expected. In addition, the peak separation between the reduction peak of the TETD and its corresponding oxidation peak diminished, which indicated that the system tended to become more reversible as the temperature was increased. The TETD dissociation into two radicals increases as the temperature is raised and the resulting radicals are more readily reduced than the TETD itself. Also, the reduction peak underwent a larger shift in potential, than the corresponding oxidation peak, which is consistent with a kinetically slow reduction step. Some decomposition, indicated by the appearance of a new peak, occurred around 160°C.

The cyclic voltammogram of DETC recorded under the same conditions is shown in fig. 22. The DETC voltammogram is quite different from the TETD voltammogram: the peak-height ratio \( \frac{i_{\text{p, reduction}}}{i_{\text{p, oxidation}}} \) is much higher in the case of TETD than in the case of DETC. DETC possesses a sodium cation which can be reduced to sodium metal as was pointed out in a previous study (SC 78). The reduction potential of sodium ion to sodium metal in acetonitrile was reported to be -1.4 V (vs ENH). The reduction of the TETD occurs precisely at -1.4 V and the concurrent production of sodium, in the same potential range, at the electrode would complicate the electrochemical processes. Sodium metal, for example, could react directly with TETD which would explain why the peak associated with TETD reduction is so small.

This preliminary cyclic voltammetry study points out two features of this system. The separation between the oxidation and the reduction peak indicates that the TETD/DETC system is not a fast, reversible system but a slow system. The true thermodynamic equilibrium potential of the TETD/DETC redox couple is closer to the oxidation potential of DETC to TETD than to the reduction potential.
CYCLIC VOLTAMMETRY OF TETRAETHYLTHIURAM DISULFIDE

T = 60 C
solvent: DMSO
scan rate: 500 mV/s

1 mA sensitivity
Reduction first

Figure 23
CYCLIC VOLTAMMETRY OF TETRAETHYLTHIURAM DISULFIDE

T = 130 C
solvent: DMSO
scan rate: 500 mV/s

2 mA sensitivity
Reduction first

Figure 24
CYCLIC VOLTAMMETRY OF DIETHYLDITHIOCARBAMATE (sodium salt)

T = 25 C
solvent: DMSO
scan rate: 100 mV/s

Figure 22
of TETD to DETC: the open circuit voltage of the battery is 2.2 Volts and is also equal to the difference between \( E_0(\text{Na}/\text{Na}^+) \) and \( E_0(\text{TETD}/\text{DETC}) \). The reduction potential of \( \text{Na}^+ \) to Na in DMSO could not be determined but is inferior to -1.4 Volts. If the reduction potential of \( \text{Na}^+ \) to Na is assumed to be -1.4(vs NHE), one can calculate the open circuit voltage of the battery: 

\[
-1.4 - (-1.4) = 0
\]

is indeed far from the 2.2 Volts, experimental value of the open circuit voltage, whereas 0.37 -(-1.4) = +1.77 is closer to reality. The reduction of the TETD is the limiting process whether the limitation comes from a slow electron transfer or a chemical step for example of the splitting of the sulfur-sulfur bond. Also, according to these cyclic voltammetry experiments, no detectable decomposition occured up to 160°C, although detection of decomposition, in this case, is limited to electroactive species. Although the stability of TETD/DETC at 130°C on a long term basis was not proven by this experiment, these results are nonetheless encouraging. As already mentioned, sealed tubes containing TETD were maintained for several weeks at 120°C, in an oil bath, without any signs of decomposition.

It was not intended here to investigated the mechanisms of reduction and oxidation of TETD and DETC. Some work is now in progress on the Tafel plots of concentrated solutions of TETD/DETC on a carbon electrode; concentrated solutions are more representative of the phenomena occurring in the battery. The number of electrons exchanged during TETD reduction should also be determined. Rotating disk electrode experiments and chronocoulometry would be necessary here.

V.3.2.2. CONSEQUENCES OF A SLOW ELECTRON TRANSFER ON THE CELL INTERNAL RESISTANCE:

The cell internal resistance was observed to decrease with increasing current densities and the cell internal resistance is always lower during charge
than during discharge. The plot of the internal resistance versus current density is shown in fig. 18.

The cell internal resistance and the associated voltage drop do not involve any time dependent or diffusion related components. The voltage drop through the cell includes the different ohmic drops through the solid electrolyte and the electroactive melt and also a possible over-voltage due to a slow electron transfer. The cyclic voltammetry indicated that the TETD/DETC redox couple is a slow system. The plot of the cell overvoltage vs the current density (shown in fig. 25) suggests that the electron transfer electrochemical step is an important contribution to the instantaneous voltage drop. The Butler Volmer equation describes the electron transfer in terms of an over potential. It relates the over voltage (difference in between the voltage applied and the equilibrium potential) to the current according to:

\[ i = i_0 [ e^{-\alpha f \eta} - e^{-(1-\alpha) f \eta} ] \]

where \( \eta \) : overvoltage
\( i_0 \) : exchange current density
\( f \) : Faraday F/RT
\( \alpha \) : transfer coefficient

When the overvoltage imposed on the system increases, the driving force for the reaction (oxidation or reduction depending on the sign of the overvoltage) increases, and the resulting current increases in an exponential fashion. A strict exponential dependence of \( i \) as a function of \( \eta \) is not observed here, because the total voltage drop across the cell is the sum of several terms including the ohmic drop through the Beta" Alumina. The ohmic drop through the solid electrolyte accounts for about 0.2 ohms at 130°C which is substantial with respect to a total cell resistance of 1 ohms. The sum of linear and exponential terms does not give a simple mathematical expression for the internal resistance.
Polarization Curve for the Na/TETD Battery
(5 second pulses)

Electrolyte Surface Area = 20 cm$^2$
Total Cell Mass = 50 grams

Current Density (mA/cm$^2$)  

Overpotential (volts)  

Cell Voltage

Figure 25
The lowest internal resistances which are crucial for good battery performances, are achieved only at current densities of the order 100 mA/cm$^2$ which can not be sustained for continuous battery operation. An electrocatalyst may have an important part to play here and should be investigated. It may reduce substantially the internal resistance at lower current densities which are suitable to continuous battery operation, by diminishing the activation energies of the different electron transfers.

V.3.3. STABILITY OF TETD IN OXIDATION:

The cyclic voltammetry experiments mentioned in references SC 78 and CA 73 showed that TETD could be oxidized to a dication which can be subsequently reduced to give the monosulfide. From the battery point of view such a reaction, if it actually takes place during the charge process, is disastrous because it will lead to the production of the nonelectroactive monosulfide. In order to clear some doubts on the stability in oxidation of the TETD, a Tafel plot type of experiment was set up, using pure TETD in the molten state, TEAP 0.1 M as the supporting electrolyte and the same electrode arrangement. The temperature was set at 130°C. The results are shown in fig. 26. The TETD exhibits a domain of stability in oxidation of about 600 to 700 mV. On charge, the cut-off potential should be around 3 V to prevent the possibility of any oxidative degradation of the TETD.

V.4. PROPOSED ELECTROCHEMICAL PICTURE:

The following electrochemical picture can now be proposed. At the beginning of discharge the TETD molecules closest to the Beta" Alumina interface are reduced to DETC, while the counter ions, Na$^+$, have gone through the solid
ELECTROCHEMICAL WINDOW OF TETD

TEAP supporting electrolyte

Figure 26

redirection

oxidation

I mA

T = 106 C

700

600

500

400

300

200

100

0

0

(E Volts)

(Thousands)
electrolyte. The ionic conductivity of the melt, which is originally very low since TETD is an insulator, increases as the reduction proceeds further. An ionic front develops through the positive electrode, diffusing away from the solid electrolyte.

The cell operating temperature was set at 130°C, i.e. below the melting point of the DETC sodium salt because of uncertainties on the long term stability of the dimer at 150°C. The DETC salt exhibits a good solubility in the corresponding dimer. However, it can be expected that, for advanced states of discharge, solid sodium salt will precipitate. The precipitation of a solid phase is the most likely explanation for the internal resistance increase, and the aggravated polarization observed over 40% of discharge. The results of the transient pulse experiments are consistent with a precipitation of the sodium salt near or at the Beta" Alumina interface. A solid phase present at the interface will impede mass transport and create serious polarization. Moreover, the asymmetry in the cell internal resistance on charge and discharge is consistent with the DETC salt precipitation at the solid electrolyte interface. When the cell is pulsed in discharge, further precipitation of the salt occurs and therefore the polarization worsens. On the other hand, when the cell is pulsed in charge, the picture is quite different, as much of the salt is now present at the Beta" Alumina interface and can be readily oxidized to give the liquid dimer. In addition, the production of liquid dimer will facilitate the salt redissolution. The corresponding pulse is very flat.

Although the salt precipitation constitutes the most likely explanation, another possibility which would also account for this asymmetry and resistance rise, is the contamination of the sodium electrode by sulfur. A pile-up/depletion model of sodium sulfide at the solid electrolyte interface would also lead to a resistance rise on discharge and a decrease in resistance on charge. This mechanism would be completely similar to the pile-up/depletion phenomena accompanying the flow of sodium, as encountered in the case of sodium
contamination by oxygen. Contamination of the sodium compartment occurred in the early cells where the sealing of the Beta"Alumina tube was not adequate. The behavior of these cells was different, however, and their performances deteriorated as the contamination worsened; the open circuit voltage also decreased substantially below 1.7 V. The fact that a more symmetric behavior was restored on charge, as shown by these pulse measurements, would not be consistent with the sodium contamination hypothesis. On the other hand, it supports the proposed picture of a layer of salt precipitated at the solid electrolyte interface which gets redissolved during the charge process, therefore restoring an acceptable internal resistance.

One possible solution to alleviate this precipitation problem would be to add a solvent to the positive electrode. The solvent would increase the solubility limit of the DETC salt in TETD and delay the precipitation to the very end of discharge. In the event of a positive effect, this will support more strongly the hypothesis that the salt precipitation is the culprit.

During charge, the positive electrode in contact with the solid electrolyte gets depleted first from the DETC sodium salt, and towards the end of charge, the remaining sodium ions do not diffuse fast enough towards the solid electrolyte to maintain a uniform ionic conductivity through the positive electrode. An insulating layer of TETD forms at the surface of the Beta"Alumina which causes the polarization to rise dramatically. When the current density is lowered, the polarization decreases and stabilizes. The charge process can then proceed further until the rate of reaction cannot be sustained again and the current density has to be decreased. The positive electrode thickness of 3.5 mm may be too large with respect to the ionic conductivity of these melts. More sophisticated modelling would be necessary here.
CHAPTER VI: INFLUENCE OF SOLVENTS AND OTHER ADDITIVES ON THE TETD BATTERY PERFORMANCES:

VI.1. WHY USE A SOLVENT:

The DETC sodium salt precipitation at high percentages of discharge, certainly contributes to the degradation of the cell performances. The presence of a solid phase in a liquid system always causes the polarization to rise significantly. The obvious alternative would be to raise the cell temperature above the salt melting point, an option which was ruled out because of long term stability problems. The addition of an appropriate solvent is, a priori, a reasonable way of postponing this precipitation phenomenon to later stages of discharge.

VI.2. SOLVENT REQUIREMENTS:

A suitable solvent must exhibit the following chemical and electrochemical properties, some of which are obvious and some of which have a more subtle influence on the system behavior.

Chemical inactivity towards the positive electrode material and any part of the battery is an obvious requirement for the solvent if it is to have any beneficial effect. The solvent reacting with TETD would result in a net loss of active material as well as the production of corrosion products prone to give rise to polarization.

The solvent should also be electrochemically inert within the potential window of the charge/discharge cycle, or in other words, be able to withstand the overpotentials occurring during charge and discharge.

The solvent boiling point must be high enough as not to induce pressure
build-up incompatible with the cell design.

Solvents with a low viscosity will be preferred as they may decrease the positive electrode melt viscosity. Viscosity measurements will have to be made to further support this hypothesis; the viscosity of a mixture is not always related in a linear fashion to the viscosity of its original components. However if the melt viscosity is decreased as intended, species diffusion will be enhanced and more rapid mass transport will result. Polarization caused by a diffusion limited process will be reduced.

Solvents with a high dielectric constant are also attractive since they may help in breaking down ion-pairs and therefore in increasing the melt conductivity. Ionic conductivity measurements tend to support the existence of ion pairs in the TETD/DETC melts.

The DETC sodium salt should exhibit a high solubility in the solvent. The primary reason for adding a solvent is to postpone the precipitation phenomena to later stages of discharge.

As a summary, an appropriate solvent should be chemically and electrochemically stable, have a low boiling point, a low viscosity and a high dielectric constant, and dissolve readily the sodium salt. Among these criteria, some of them are just physicochemical quantities easy to check. The chemical stability towards the positive electrode material is harder to predict, as very little in the literature refers to the reactivity of these melts.

The addition of a solvent represents a sacrifice in energy density and the percentage of solvent added has to be kept within reasonable limits to stay within the range of interesting high energy densities.

The solvents that have been tested are shown in table 4 with their respective boiling point, viscosity and dielectric constant (SA 74).
## SELECTED ORGANIC SOLVENTS

<table>
<thead>
<tr>
<th>Solvent</th>
<th>BP °C</th>
<th>Viscosity (cP)</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diglyme ether</td>
<td>160</td>
<td>0.98</td>
<td>7.5</td>
</tr>
<tr>
<td>N,N dimethyl formamide</td>
<td>153</td>
<td>0.8</td>
<td>36.7</td>
</tr>
<tr>
<td>N-methyl pyrrolidinone (amide)</td>
<td>202</td>
<td>1.67</td>
<td>32</td>
</tr>
<tr>
<td>DMSO Dimethyl sulfoxide</td>
<td>189</td>
<td>1.1</td>
<td>46.7</td>
</tr>
<tr>
<td>Sulfolane</td>
<td>287</td>
<td>10.3</td>
<td>43.3</td>
</tr>
</tbody>
</table>

Table 4
VI.3. RESULTS:

The experimental results are shown in fig. 27 through fig. 32.

SULFOLANE: Figure 27 shows the influence of sulfolane on the discharge behavior for increasing percentages of solvent added. The addition of sulfolane improves the discharge characteristics and increases the portion of the curve for which the polarization is constant and well behaved. The improvement is the most marked for the highest percentage of sulfolane added.

DMSO: The effect of DMSO is shown in fig. 28. The improvement in the cell characteristics is somewhat better than in the case of sulfolane addition according to a comparison based on 20 % of solvent added.

DIGLYME: The effect of diglyme is shown on fig. 29. The current density is 10 mA/cm² (higher than for DMSO or sulfolane). The cell polarizes quite catastrophically at 35% of discharge.

N-METHYLPYRROLIDINONE: Partial discharge of a cell with 20 % of N-methylpyrrolidinone at a current density of 10 and 20 mA/cm² is shown in fig. 30. The addition of N-methyl pyrrolidinone did not bring any dramatic improvement with respect to the pure TETD, although it should be noted that higher current densities were used than in the case of DMSO. Polarization problems encountered at the beginning of charge were indicative of possible decomposition problems of the N-methylpyrrolidinone in the presence of the TETD/DETC mixture. The cyclic voltammogram of the positive electrode material after cell dismantlement proved that some degradation had occurred.

N-DIMETHYLFORMAMIDE: The influence of the addition of N-dimethylformamide on the cell performances is described in fig. 31. This solvent had some beneficial effect, but for the same percentage added, DMSO is more
SOLVENT EFFECT ON DISCHARGE

Figure 27

cell design # 3

- PURE TETD
- TETD + 13% SULFOLANE
- TETD + 20% SULFOLANE

5 mA/cm²
T = 130°C

CELL VOLTAGE (Volts)

% DISCHARGE

2.5 mA/cm²
SOLVENT EFFECT

COMPARISON IN BETWEEN DMSO AND SULFOLANE
ADDED TO TETRAETHYLTHIURAM DISULFIDE

T = 130 C
5 mA/cm²

CELL VOLTAGE (Volts)

20 % DMSO

20 % SULFOLANE

cell design # 3

% DISCHARGE
TETD with 20% DIGLYME

CURRENT DENSITY: 10 mA/cm²

T = 130 °C

CELL VOLTAGE (V)

Percent Discharge
TETRAETHYLTHUIRAM DISULFIDE
CELL WITH 20% N METHYL PYRROLIDINONE

$T = 130 \, ^\circ C$
current density: $10 \, mA/cm^2$
cell design #3
with vitreous carbon
TETD WITH 20% DIMETHYLFORMAMIDE

**Figure 31**

CURRENT DENSITY: 5 mA/cm²

T = 130°C
SOLVENT EFFECT ON CHARGE

Figure 32

- **PURE TETD**
- TETD WITH 13% SULFOLANE
- TETD WITH 20% SULFOLANE

**CELL VOLTAGE (Volts)**

- 5 mA/cm²
- 2.5 mA/cm²

**T = 130°C**

Cell design #3

% DISCHARGE
efficient.

INFLUENCE OF SOLVENT ON CHARGE: As indicated in fig. 32, the influence of sulfolane on charge is much less dramatic on charge than on discharge. For 20% of sulfolane added, the cell could be recharged up to 10% discharge. At the end of charge, however, the current density had to be decreased to 2.5 mA/cm² and later down to 1 mA/cm² (indicated on the curve by the dotted lines).

VI.4. DISCUSSION:

Out of five solvents tested, DMSO emerges as the most satisfactory solvent in improving the cell performances. The addition of 20% of DMSO to the positive electrode displaced the onset of the polarization from 45% of discharge for the pure TETD to 75% of discharge which constitutes a dramatic improvement. These results also support the initial hypothesis that the salt precipitation is at the origin of the increased polarization. The salt precipitate redissolved with time when the cell was allowed to rest at open circuit voltage: 1 Amp current pulses were sent through a cell containing 13% of sulfolane and discharged to 63% at different time intervals (Fig. 33). The cell internal resistance on discharge decreased, whereas the internal resistance on charge stayed constant. The solvent, by increasing the solubility limit of the salt in the positive electrode mixture delays, the precipitation phenomena to the later stages of discharge. The solvent investigation and testing have involved so far only five solvents and it is reasonable to expect that finer tuning of the physico electrochemical properties of the solvent could improve even more dramatically the cell performances. Furthermore, as has been mentioned several times, TETD/DETC is one of many
TETRAETHYLTHIURAMDISULFIDE

with 13% Sulfolane

CURRENT PULSES

current density
50 mA/cm²

T = 130 C

5:30

6:30

cell design # 3

63% discharge

Discharge process

CELL VOLTAGE (Volts)

TIME (s)

0.5
possible electrode materials and the research in this field is only starting.

The physicochemical properties chosen, a priori, as criteria of selection for the solvent proved to be the key required features. Indeed, DMSO exhibits the best combination of chemical stability, high dielectric constant, low viscosity of all the solvents tested. Sulfolane exhibits similar effects to DMSO, the slight difference in dielectric constant and in viscosity may account for the better performances of DMSO. Sulfolane is more viscous than DMSO and its dielectric constant is somewhat lower. In addition, DMSO is a better electron donor than sulfolane and therefore solvates the sodium ions better than sulfolane. The sodium ions are solvated by interaction with the oxygen atoms which have a higher electronic density in the case of DMSO than in the case of sulfolane. Diglyme seemed attractive because of its chemical stability and its low viscosity but its dielectric constant was too low. Diglyme solvates very well the sodium ion but will not dissociate the ion pair and can give rise to ion pair/solvent association. N-methyl pyrrolidinone was plagued by unstability problems or reactivity towards the TETD, problems which are not always predictable before actually trying the solvent in a cell. The five solvents studied happened to bring up a good spectrum of the possible problems, from stability problems to insufficient dielectric constant.

The dramatic solvent effect points out even more clearly that the organic nature of the positive electrode, its intrinsic flexibility and the low operating temperature, constitute big assets for this new battery system and make it unique. At the beginning of this study, the spectrum of possibilities offered by the chemical structure of the electroactive material appeared impressive. Now, the solvent capabilities have added new facets to the chemical and electrochemical picture of this new system. TETD is most probably not the best electrode material but constituted a good starting and learning experience. The concept of solvent addition is most certainly applicable to other possible organo-sulfur candidates.
The optimization of a team solvent and active material certainly lies ahead, but the new possibilities unfolding as the research progresses makes it all the more exciting.

VI.5. EFFECT OF SULFUR:

VI.5.1. CHEMICAL REACTION OF THE POSITIVE ELECTRODE WITH SULFUR:

Disulfides are known to decompose to the monosulfide and sulfur upon heating, or to insert an additional sulfur when heated in the presence of sulfur to give a trisulfide or even higher sulfides (TH 62, RE). The same mechanism is applicable to the TETD electrode material and it is quite legitimate to assume that TETD could decompose at least very partially to the corresponding monosulfide and sulfur, or even give rise to a distribution of different sulfides, monosulfide, disulfide and trisulfide during the battery operation. The possible sulfur insertion by TETD was studied by means of cyclic voltammetry and the influence of the addition of sulfur to the positive electrode on the charge discharge behavior of the battery system was investigated.

VI.5.2. CYCLIC VOLTAMMETRY EXPERIMENTS

The electrochemical set up was described in section V.3.2. The supporting electrolyte was 0.1 M TEAP (tetraethyl-ammonium perchlorate), the electroactive species had a concentration 0.001 M, and the study was conducted in Dimethylformamide. (according to ref. AB 78, sulfur and polysulfides are stable in DMF). The cyclic voltammograms of pure TETD, pure sulfur and of an equimolar solution of TETD and sulfur are shown in fig. 34, 35, 36. Since sulfur is not soluble in DMF at room temperature, the solution of sulfur in DMF had to
CYCLIC VOLTAMMETRY OF TETRAETHYLTHIURAM DISULFIDE

T = 25 C
solvent: DMF
scan rate: 100 mV/s
200 mV/s
500 mV/s
1 mA sensitivity
Reduction first

Figure 34
CYCLIC VOLTAMMETRY OF SULFUR

solvent: DMF
scan rate: 100 mV/s
200 mV/s
500 mV/s
1 mA sensitivity
Reduction first

Figure 35
CYCLIC VOLTAMMETRY OF TETRAETHYLTHIURAM DISULFIDE + SULFUR

solvent: DMF
scan rate: 100 mV/s
1 mA sensitivity
Reduction first
Successive additions of TETD to the S + TETD mixture

Figure 36
be heated up to 80°C and the cyclic voltammogram was done in the hot solution. The mixture of dimer and sulfur was also heated up in order to favor the insertion reaction if any is occurring;

The cyclic voltammogram of the equimolar mixture of TETD and sulfur exhibited two peaks in reduction and resembled the pure sulfur cyclic voltammogram with some shifts in peak potentials. The reduction peak of TETD had disappeared. However, when a known quantity of dimer was added to the mixture, the first reduction peak increased in intensity, proving that this peak could actually be attributed to the TETD reduction. Successive additions of TETD resulted in corresponding increases in the first reduction peak intensity, the second peak remained the same.

Sulfur addition caused the TETD reduction to be considerably shifted in potential; in other words, sulfur seems to have a catalytic effect on the TETD reduction and while no precise mechanism can be proposed at this stage of the investigation, this catalytic effect might be highly interesting for the battery application. TETD/DETC is a slow system and any additive which could accelerate the electron transfer or any limiting step in the process, would most certainly improve the battery performances.

V.5.3. EFFECT OF SULFUR ON THE CHARGE/ DISCHARGE PERFORMANCES OF THE BATTERY

As previously mentioned, results obtained from cyclic voltammetry experiments cannot be transposed directly to the battery for obvious concentration reasons.

Sulfur was added to two types of cells, one of them containing 20% of N-methyl pyrrolidinone and the other one containing 20% of DMSO. Both cells
contained a 1% weight of sulfur in the positive electrode.

Sulfur certainly had some beneficial effect in the case of the cell with N-methyl pyrrolidinone, as can be seen by comparing fig. 30 and fig. 37. Comparatively, high discharge rates were obtained for long periods of time in the case of sulfur addition. Problems were observed on charge, which were then attributed to decomposition reactions caused by the solvent. In the case of the cell containing DMSO as the solvent, sulfur did not bring about a significant improvement on discharge, (Fig. 38), but most definitely was at the origin of the catastrophic polarization on charge as demonstrated in Fig. 39. The conclusion of these experiments is that the presence of sulfur on charge is particularly deleterious to the cell operation, and its presence in the positive electrode has to be avoided whether or not it has some beneficial effect on discharge. Further more, the possible decomposition of the TETD to the corresponding monosulfide and free sulfur would be completely incompatible with good operation of the battery and create these severe polarization phenomena on charge. Sulfur is known to be at the origin of catastrophic polarization in the sodium/sulfur battery because of its immiscibility with the polysulfides and as a result, can create an insulating layer at the surface of the Beta" Alumina. In our case however, there are several possible solutions to this problem.

The possibility of a decomposition reaction of TETD to the monosulfide and to sulfur needs to be investigated in more details. It is an equilibrium reaction, and displacing it strongly towards TETD would solve the problem. One possibility would be to fix the activity of the sulfur to a high value by adding a sulfur activity buffer system such as FeS/FeS\textsubscript{2}. This possibility has not been explored yet but is certainly worth investigating. The other approach is to consider other thiuram disulfides or even other disulfides as positive electrode material if there is an intrinsic stability problem with the TETD.
TETRAETHYLTHIURAM Disulfide Cell
With 20% N Methylpyrrolidinone and 1% Sulfur

Figure 37

Charge

5 mA/cm²
10 mA/cm²
15 mA/cm²
20 mA/cm²

Discharge

25 mA/cm²
15 mA/cm²
10 mA/cm²

Constant voltage = 2.6 V

T = 130°C
Design # 4

3000 C = 50% discharge

Cell Voltage (Volts)

0 0.5 1.0 1.5 2.0 2.5 3.0 3.5

0 0.4 0.8 1.2 1.6 2.0 2.4 2.8

(Thousands)

Number of Coulombs
INFLUENCE OF SULFUR ON DISCHARGE

TETD + 20% DMSO + 1% Sulfur

T = 130°C

DISCHARGE RATE = 5 mA/cm²

Cutoff voltage = 1.2 V

CELL VOLTAGE Volts

2.5 mA/cm²

5 mA/cm²

% DISCHARGE

90%
INFLUENCE OF SULFUR ON CHARGE

Figure 39

Cell with 20% DMSO, 1% S

- Cut off voltage: 2.8 V
- Discharge: 0 to 95%
- Charge: 95% to 61%
- Cell design #5
The idea of a catalyst is still valid and transition metals could be considered as they are known to catalyse the oxidation of thiols to disulfides. Caution should be advised though, as transition elements are known to enter the Beta"Alumina structure and to impede conduction.

V.6. CONCLUSIONS ON THE DITHIOCARBAMATES/THIURAM DISULFIDES:

The study on the TETD/DETC as positive electrode material showed very encouraging results, and demonstrated that the concept of an organosulfur positive electrode is rich in possibilities. One major drawback of this system, however, is the lack of stability of the TETD above the melting point of DETC. The cell had to be operated below the DETC melting point, and polarization phenomena were experienced at the end of discharge due to the salt precipitation. Yet, this issue led to the use of solvents which proved to be quite successful in postponing the polarization to the later stages of discharge. These solvents were shown to add significant, new degrees of freedom to the system. Already at this point, the search for a positive electrode material had been shifted from a low melting sodium salt to a team solvent and sodium salt, in which the solvent is to prevent precipitation of a solid phase. The search for a positive electrode could be reoriented in several directions.

One possible direction of investigation would be to lower the battery temperature around 110°C and test other dithiocarbamates such as the tetramethylthiuram disulfide or the asymmetric di(methylpropyl) thiuram disulfide. At this stage of the investigation, it would be very premature to rule out the dithiocarbamate family as possible electrode material.

If it appears that a low melting sodium salt is always linked to molecular
structures too costly in energy density and too prone to decomposition, the criteria of selection for the positive electrode should be redirected to much simpler compounds such as disulfides. They are much more stable (for example propyl disulfide can be heated up its boiling point of 193°C without any decomposition) and give much higher energy densities. The higher energy densities would then allow for a substantial percentage of solvent in the positive electrode composition. A solvent chosen adequately could take care of solvating the sodium salt generated during discharge. Ideally, the disulfide itself should also be a good solvent for its own salt, which was the case for the TETD/DETC couple.

The last section of this thesis is devoted to the preliminary results on some disulfides tested as positive electrode material.
CHAPTER VII: DISULFIDES AND RELATED COMPOUNDS.

VII.1 REACTIVITY OF DISULFIDES:

The disulfides of general formula R-S-S-R where R represents an alkyl group can be reduced to the corresponding sulfide according to:

\[ \text{R-S-S-R} + 2 \text{e}^- \rightarrow 2 \text{R-S}^- \]

At first sight, owing to its molecular simplicity, the disulfide/sulfide couple reactivity can be expected to be far simpler than the reactivity of the thiuram disulfide/dithiocarbamate couple. The disulfides are also much more stable compounds and can be distilled under reduced pressure. For example, propyl disulfide can be heated up to 200°C without any decomposition. Disulfides generally decompose first to the corresponding monosulfide, and, in this case, the decomposition would occur largely above the allowable battery operation temperature. Disulfides of low molecular weight are usually liquid at room temperature, making the battery assembly all the more easy: the positive electrode could be injected at room temperature in the graphite felt. The main reactive site of the disulfide molecule is the sulfur sulfur bond, which can be cleaved homolitically to give radicals or heterolitically to give ions. The sulfide ions, R-S\(^-\), have a strong nucleophilic character. The reactivity of these compounds will be discussed in more details in the following sections (PR, RE, KH).

VII.1.1. THE DISULFIDE BOND:

HOMOLITIC SCISSION:

The disulfide bond can be cleaved under the influence of heat or light or in the presence of radical initiators to give two radicals. The presence of these
radicals has been evidenced by EPR. The alkyl sulfide radicals are much less
stabilized than the dithiocarbamates radicals because of the absence of neighboring
groups participating in the different resonance forms. The change of color
observed upon heating of the disulfides is not always indicative of a radical
dissociation.

HETEROLIC SCISSION:

Strong acids, strong bases or strong nucleophiles can attack and cleave the
disulfide bond (or sulfur-sulfur link).

a/ Basic attack:

\[ R-S-S-R + OH^- \rightarrow RSOH + RS^- \]

The sulfenic acid, RSOH, is unstable and transformed to the more stable sulfinic acid and thiol.

b/ Acid attack:

Disulfides are cleaved in concentrated sulfuric acid or hydrochloric acid to
give the corresponding sulfonium ion according to:

\[ RSSR + H^+ \rightarrow RS^+ + RSH. \]

Regarding the battery application, disulfides are attacked only by strong acids
or bases, which will not be present in the chemical environment of the
electrochemical cell. By comparison, the thiuram disulfides could be cleaved by
weak acids or bases such as amines.

c/ Nucleophilic attack:

Strong nucleophiles such as carbanions, another sulfide, or CN- can react with
the sulfur-sulfur linkage. An order of increasing "thiophilicity" is given by:

\[ (C_2H_5O)_3P / R^-, HS^-, C_2H_5^- / C_6H_5S^- / CN^- / I^- \]

Carbanion attack:
\[
\text{C}_6\text{H}_5^- + \text{C}_6\text{H}_5\text{-S-S-C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{-S-C}_6\text{H}_5 + \text{C}_6\text{H}_5^-\text{S}^-. \\
\text{Sulfide attack:}
\]
\[
\text{RS}^- + \text{R}^-\text{-S-S-}\text{R}^- \rightarrow \text{R}^-\text{-S-S-R}^- + \text{RS}^-
\]
This reaction corresponds in the battery to a mere disulfide and sulfide exchange reaction and does not amount to any net reaction.

\[
\text{CN}^-\text{, cyanide ions can smoothly eliminate one sulfur from the disulfide bond to give the monosulfide according to:}
\]
\[
\text{RSSR} + \text{CN}^- \rightarrow \text{RSCN} + \text{RS}^- \rightarrow \text{RSR} + \text{SCN}^-.
\]
Here again, cyanide ions are not normally present in the battery.

d/ sulfur insertion:

As mentioned before in the case of the thiuram disulfides, sulfur insertion in the disulfide is possible and gives trisulfides or even higher polysulfides.

VII.1.2. NUCLEOPHILICITY AND BASICITY OF THE MERCAPTIDE RS^-:

Unlike the corresponding alkoxide RO^-, mercaptides are good nucleophiles but rather weak bases. RS^- can attack a variety of carbonyl compounds and some examples are given here:

\[
\begin{align*}
\text{R-C-X} + \text{SR}' & \rightarrow \text{R-C-SR}' + \text{X}^- \\
\text{O} & \rightarrow \text{O} \\
\text{X} & = \text{Cl, OR, } \text{O}_2\text{CR}
\end{align*}
\]

VII.2. APPLICATION AS A POSITIVE ELECTRODE MATERIAL:

Alkyl disulfides are attractive positive electrode material because of their chemical stability; the disulfide is only sensitive to attack by strong acids or bases attack. This extreme chemical environment will never be present in the battery.
The sulfide has a nucleophilic character, which should be taken into account if a solvent is to be used.

However, as positive electrode material, the alkyldisulfides have a major drawback: the sulfide sodium salts $\text{RS}^-\text{Na}^+$ have a limited solubility in the corresponding disulfide as could be expected. The sodium salts exhibit a pronounced ionic character as the negative charge is not delocalized on the rest of the alkyl chain and therefore these salts are not readily solvated by the corresponding disulfides which are very non-polar.

A cell was put together with pure propyl disulfide as the positive electrode: the cell exhibited a very high internal resistance, and polarized dramatically at a very early stage of discharge. The current densities attainable were very low (below 0.1 mA/cm$^2$). Most probably, the ionic conductivity of the positive electrode was very low and the precipitation of the sulfide sodium salt occurred very rapidly during discharge. The difference in behavior between the propyl disulfide cell and the TETD, if logical, is nonetheless striking: once again, it appears that the physicochemical properties of these compounds have dramatic consequences on the battery characteristics.

The solubility of the sulfide salt in the disulfide should be increased and several possibilities will be described here: one alternative is to add a solvent which will solubilize the sodium salt, the other one is to modify the chemical structure of the disulfide in order to increase its ability to solvate the sulfide salt.

According to the first alternative, some DMSO was added to the propyl disulfide because DMSO had shown to dissolve readily sodium thiomethoxide ($\text{CH}_3\text{SNa}$) but the two liquids appeared to be immiscible. The solvent properties of DMSO could be tested only with sodium thiomethoxide as the latter is the only sodium alkyldisulfide salt available commercially. Some research now in progress has indicated that a mixture of solvents, such as DMSO and an ether, is miscible with
the disulfide and therefore may be a possible positive electrode candidate.

The other alternative is to modify the chemical structure of the alkyl chain and for example to induce some polarity by adding some electronegative heteroatoms such as fluorine or by inserting an oxygen to form an ether linkage. The modified disulfide will be much more polar and therefore much more able to dissolve the corresponding reduced sodium sulfide.

The idea of introducing one or several ether linkages in the alkyl chain is particularly attractive because the structure of the resulting disulfide is reminiscent of the one of crown ethers. Such a structure is shown in fig. 40, the sodium ion sits in the middle of the ring and is solvated by the different oxygen atoms. The size of the crown ether ring can be tailored to solvate specifically lithium at the exclusion of sodium for example. Along the same line, polyethylene oxide is known to solvate lithium and sodium salt and exhibits fast ionic conduction in the solid state. The ether linkage is particularly stable and can be cleaved only by strong acids or strong bases; the resulting alkoxy disulfide presumably will exhibit a good thermal stability.

Some alkoxydisulfides are listed in table 5 and their high energy densities make them very attractive candidates. Unfortunately, these alkoxy disulfides are not available commercially. The reason is certainly not because of a difficult synthesis: the latter has been referenced in the literature for some compounds and seems reasonable as far organic chemistry methods go. Rather, they have appeared, so far, as a laboratory curiosity without any specific application, and their pungent odor have constituted a strong enough deterrent from further investigation. Actually, to be fair concerning the olfactif aspect, thiols are usually the culprit and well purified disulfides do not seem to be as offensive, everything being relative at this point.

The only parent compound available commercially is the hydroxyethyl
METHOXY(ETHOXY ETHYL)DISULFIDE

SOLVATION OF Na BY DIMER

INTERNAL SOLVATION OF Na⁺

Figure 40
Alkoxyalkyl Disulfides and Related Compounds
( Energy densities based on sodium/organosulfur cells )

<table>
<thead>
<tr>
<th>Disulfides</th>
<th>Theoretical Energy Density Whrs/Kg (OCV = 2.2 volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃OCH₂S)₂</td>
<td>590</td>
</tr>
<tr>
<td>(CH₃OCH₂CH₂S)₂</td>
<td>517</td>
</tr>
<tr>
<td>(CH₃OCH₂CH₂OCH₂CH₂S)₂</td>
<td>373</td>
</tr>
<tr>
<td>(HOCH₂CH₂S)₂ (HEDS)</td>
<td>590</td>
</tr>
</tbody>
</table>

Table 5
disulfide \((\text{HO-S-S-C}_2\text{H}_4\text{-OH})\). Although, the OH group seemed troublesome, cells were assembled with the hydroxyethyl disulfide in order to demonstrate the validity of the concept of modified disulfides as positive electrode material.

VII.3. THE HYDROXYETHYL DISULFIDE (HEDS) BATTERY:

VII.3.1. HYDROXYETHYL DISULFIDE:

Hydroxyethyl disulfide is a colorless liquid at room temperature. It boils at 158-163°C under 3.5 mm Hg. The hydroxyethyl disulfide available commercially has a very potent smell. An impurity was in fact at the origin of this inconvenience since, after vacuum distillation, the smell had almost completely disappeared.

VII.3.2. CYCLIC VOLTAMMETRY:

Cyclic voltammetry of the hydroxyethyl disulfide (HEDS) was performed in DMSO, under the same experimental conditions as for the TETD (Chapter 5). The two cyclic voltammograms exhibit very similar features (fig. 41). The HEDS is also a slow system. The oxidation occurs at -0.4 V and reduction peak occurs at -2.05 V for HEDS (barely distinguishable from the solvent limit) whereas the oxidation and reduction occurred at +0.09 and -1.67 respectively for TETD. (All the potentials are referenced with respect to the Ag/AgCl, Me\textsubscript{4}NCl, 1 M reference electrode). The reduction and oxidation potential for HEDS are shifted towards more negative values than for TETD which corresponds to a lower value of the open circuit of the HEDS battery, 2 V instead of 2.2 V for the TETD battery. The irreversible reduction of the alcohol functional group to give the alcoholate and hydrogen was not observed most probably because of solvent window limitations.
CYCLIC VOLTAMMETRY OF HYDROXYETHYLDISULFIDE

solvent: DMSO
scan rate: 100 mV/s
200 mV/s
500 mV/s
1 mA sensitivity
Reduction first

1/10 sensitivity

Figure 41
VII.3.3. CELL TESTING:

Several types of cell design were used. Reticulated vitreous carbon seemed an attractive choice for the conductive matrix because of the ease of cell assembly. It had to be ruled out however, as it gave rise to high internal resistances and poor contacts with the aluminum casing. A graphite felt conducting matrix was preferred and the electroactive material had to be introduced with a syringe. Good wetting appeared difficult to obtain as some argon bubbles tended to stay trapped on the graphite surface. The syringe needle was inserted all the way to the bottom of the cell in order to eliminate as many bubbles as possible.

One of the designs used a glass cell casing (design # 4) and proved to be very helpful in checking volume and color changes and the wetting of graphite felt. Upon heating, the HEDS expands somewhat, which has to be taken into account for the filling of the cell at room temperature. The cell assembly was considerably simplified by the fact that HEDS is liquid at room temperature and therefore that the cell can be assembled cold.

Partial discharge curves are shown in fig. 42 and in fig. 43. By comparison with the TETD system, these cells exhibited higher internal resistances but were able to sustain high discharge rates (2 hours at 500 mA which corresponds to 25 mA/cm² current density) for longer periods of time with a quasi constant polarization.

Unfortunately, all the cells tested showed the same sharp polarization in the early stages of charge. Upon dismantling, the positive electrode appeared to have degraded into a reddish insoluble polymer. One likely mechanism of polymerization is the formation of an ether linkage by elimination of water; the
HYDROXYETHYL DISULFIDE

CURRENT PULSE Figure 42

Glass cell
design#4

E (Volts)

<table>
<thead>
<tr>
<th>3</th>
<th>2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

500 mA
25 mA/cm²

0 1 2 time (hours)
HYDROXYETHYLDISULFIDE
(partial discharge)

E (Volts)

2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0

Open Circuit Voltage

Discharge

Glass cell
design#4

10 mA/cm²

5 mA/cm²

7000 C = 38 % discharge

Figure 43
ether formation from alcohol seemed at first sight a rather unlikely reaction however this unusual reactivity was reported in the literature and was attributed to the presence of a sulfur atom in beta of the oxygen (WO 59). The water production is of course very deleterious to the Beta" Alumina and the internal resistance-rise or asymmetric polarization occurring during discharge are not worth investigating any further, as the presence of water itself is sufficient to explain all these features.

The results obtained with the HEDS should be regarded, nevertheless, as very encouraging and let us project favorably the performances of the alkoxy disulfides. The latter obviously will not be plagued by the same polymerization issue.

VII.4. ALKOXYDISULFIDES:

VII.4.1. THE ALKOXYDISULFIDE CANDIDATES:

The alkoxy disulfide family comprises several interesting candidates. They are summarized in table 5 with their respective energy densities.

The methoxy ethyl disulfide possesses only one ether linkage, and one can imagine mimicking the crown ether or diglyme structure more closely by introducing more oxygen atoms (fig. 40).

A bidentate structure such as NaS-CH₂-CH₂-O-CH₂-CH₂-SNa constitute also a fascinating possibility: upon oxidation, a polymer, will be obtained (the other possibility is a seven membered ring which is not very stable). The corresponding thiol happens to be commercially available. Very preliminary testing has shown that after oxidation of this thiol by iodine, a polymer is obtained which is soluble in diglyme. Furthermore one can imagine adding terminating agents such as a
simple disulfide or the methoxyethyl disulfide to limit the length of the polymer.

Only very sketchy results are presented in the following section. Methoxyethyl disulfide is the only alkoxy compound which has been tested in a cell.

VII.4.2. METHOXYETHYLDISULFIDE:

VII.4.2.1. SYNTHESIS:

The following synthesis has been reported in the literature in 1930 for the ethoxyethyl mercaptan (SW 30):

$$C_2H_5-O-CH_2CH_2Cl + KHS \rightarrow C_2H_5-O-CH_2CH_2-SH \text{ (in } CH_3OH) + KCl$$

The Betachloroethylether is added to potassium hydrosulfide in methanol. The potassium hydrosulfide is 100% in excess. The solution is then heated at 65°C for 24 hours in a pressure vessel. When water is added to the solution, the mercaptan separates out as an oily phase. The ethoxyethylthiol yield was 74%. The ethoxyethylthiol boils at 125.5°C. Oxidation by iodine gives the corresponding disulfide which is reported to boil at 161°C under 33 mm Hg. A more detailed description can be found in reference SW 30.

The methoxyethylsulfide sodium salt used in our experiments was synthesized by Columbia Chemicals.

VII.4.2.2 CYCLIC VOLTAMMETRY:

The cyclic voltammogram of the methoxyethylsulfide sodium salt in DMSO is presented in fig. 44. The same experimental set-up described in previous sections, was used. The oxidation to the disulfide occurs at -0.025 V, by comparison, the DETC oxidation occurs at +0.09 V and the Hydroxyethyl sulfide sodium salt oxidation occurs at -0.4 V. The ether oxygen group proved effective in withdrawing some of the electronic density on the sulfur which becomes then more
CYCLIC VOLTMETRY OF METHOXYETHYL SULFIDE (SODIUM SALT)

T = 25 C
solvent: DMSO
scan rate: 50 mV/s
100 mV/s
200 mV/s

Reduction first

1 mA sensitivity

1 mA

1/10 sensitivity

E Volts

Figure 44
METHOXYETHYLDISULFIDE + DMSO

Figure 45

CELL OVERVOLTAGE (Volts)

charge

discharge

CURRENT PULSES

Cell in discharged stage

area: 20 cm²

CURRENT (A)

0 200 400 1 mA
oxidizing, in the methoxyethyl disulfide, than in the hydroxyethyl disulfide. It is interesting to speculate on the possible oxidation potential of the methoxymethyl sulfide salt as the electron withdrawing effect of the oxygen should even be stronger. It can be surmised that electronegative elements such as fluorine would also have the same effect. The corresponding increase in the cell open circuit voltage boosts quite interestingly the energy density.

The presence of an impurity is indicated clearly by the additional peak at 0.4 volts (vs reference). The reduction process could not be observed: the solvent limit appeared to be displaced, masking any possible reduction peak. The surface of the platinum electrode was polished carefully before any experiment, but did not affect the results. The reduction of Na⁺ to Na metal or of K⁺ impurities to K metal could also occur in this potential region, complicating the electrochemical processes.

CHARGE-DISCHARGE BEHAVIOR: PRELIMINARY RESULTS.

The cells were assembled in the fully discharged state and the type of cell used corresponded to the design # 5. The methoxyethyl sulfide sodium salt had to be dissolved in a solvent and injected hot into the cell. The cell assembly in the fully charged state with the corresponding disulfide would have been the obvious route, but the direct chemical oxidation of the sulfide salt to the disulfide was not attempted because of the small amount of active material available. The solvent was DMSO, and the solubility of the methoxyethyl sulfide salt in DMSO is close to 30 % weight at 120°C. The positive electrode had a 70 % solvent composition and the cell contained about 1000 Coulombs. This first rudimentary attempt, however, led to very interesting results. The results are summarized in fig. 44, 45.

Figure 45 showed that the methoxyethyl disulfide exhibits the same asymmetric behavior as TETD: the oxidation is easier than the reduction process or, in other
Figure 46

METHOXYETHYLDISULFIDE CELL CHARGE

Figure 46

control current

area: 20 cm²
Cell design #5

control potential

% discharge x 10
METHOXYETHYLDISULFIDE CELL DISCHARGE

Figure 47

CELL VOLTAGE (VOLTS)

15 mA/cm²

10 mA/cm²

cell design #5

imposed voltage

current density

% DISCHARGE X 10

number of coulombs
words, splitting the sulfur-sulfur bond is harder than oxidizing the sulfide anion. One full cycle was completed, and the charge-discharge process displays good kinetics (Fig. 46, 47): the average current density on charge is around 10 mA/cm$^2$. These results are very encouraging considering the experimental conditions, for example the purity of the electroactive material. The possibilities opened by the alkoxydisulfides are only sketched here and a more thorough study is underway.
CONCLUSIONS:

A novel class of positive electrode materials has been identified for battery use. The new generation of batteries offers attractive features including a low operating temperature, a cheap cell assembly technology, high theoretical and practical specific energy, and an unmatched chemical flexibility for the positive electrode design.

The low operating temperature of this new class of batteries simplified successfully the cell technology. Silicon rubber gaskets or epoxy seals are considerably easier to fabricate than glass-to-metal seals. The non-aggressive nature of these organic salts at 130°C - at least comparatively to the molten polysulfides at 350°C - allowed for the use of aluminum as a positive current collector and cell casing (at least for our short term testing). The use of epoxy seals and of an aluminum cell casing would decrease considerably the cost of the battery, and Na-Beta" Alumina remains the only expensive component.

The theoretical specific energy ranges from 340 Wh/kg to 590 Wh/kg depending on the positive electrode material. The practical specific energy, considering the actual cell design, can be estimated to be 100 Wh/kg or above. The TETD/DETC displayed interesting peak current densities of 100 mA/cm² at 1 Volt.

The chemical versatility of these organosulfur compounds constituted one of the most fascinating aspects of this investigation and also one of its strong points. A variety of organosulfur appeared to be suitable candidates and two main classes have been identified at this stage: in the first class, the organosulfur sodium salt
is characterized by a low melting point and the battery is operated above the salt melting point and in the second class, the battery is operated below the salt melting point and an appropriate solvent is added to the electroactive material.

The diethyldithiocarbamate belongs to the first class but the long term stability of the corresponding disulfide, tetraethylthiuram disulfide at 150°C was not satisfactory. The battery was operated below the melting point of the diethyldithiocarbamate. However, the search for a low-melting sodium salt along with a thermally stable disulfide should be pursued because the synthetic possibilities of the dithiocarbamate family have not been exhausted: methylpropylthiuram disulfide or ethylpropylthiuram disulfide are some suggestions.

The investigation conducted on the tetraethylthiuram disulfide and diethyldithiocarbamate which constitutes the bulk of this work was a fruitful and necessary experience, although TETD is not the best organo-sulfur positive electrode. The specific issues related to this type of systems were identified such as the compromises which must be achieved between low melting points, high specific energy and thermal stability. The results obtained with TETD involved only one charge/discharge cyle; obtaining cycling data is one of the priorities for future work.

The second class of electrode materials originated from the perspectives opened by the use of solvents as additives and from the resulting improvements in cell performances. Since a solvent had to be used with TETD, there was no sense in restricting our search to the dithiocarbamate family, and compounds such as the alkoxyalkyldisulfide family appeared very attractive owing to their simplicity, their stability and their high specific energy. The results obtained with hydroxyethyldisulfide were very interesting despite an intrinsic instability due to the OH group. The sketchy results obtained with the methoxyethyldisulfide were
very encouraging.

The alkoxyalkyl disulfides constitute the most promising system for further investigation. Emphasis should be put on the optimization of a solvent, or of a mixture of solvents, which will solubilize the sodium salt readily, and on the search for an electrocatalyst. The high specific energy of this family allows for a substantial amount of solvent (50%). In addition, the alkoxyalkyl disulfide will also solvate the corresponding sodium alkoxyalkyl sulfide salt. Since the cyclic voltammetry of all the disulfides studied showed that these systems are slow, an electrocatalyst would advantageously improve the cell performances.
APPENDIX I

BATTERY CHARACTERISTICS:

A battery is composed of a positive electrode and of a negative electrode, separated by an electrolyte. When the battery is connected to an external load, electron transfer occurs within the electrodes, and electrons travel from one electrode to the other through the external circuit. Concurrently, ionic transport occurs through the electrolyte. The important quantities which characterize a battery performances are listed below.

THEORETICAL SPECIFIC ENERGY:

The theoretical specific energy represents the ratio of the energy per weight and takes into account only the mass of the electroactive materials.

\[ \text{Theo. } W = \frac{n \times E_{oc}}{m} \text{ in Wh/kg (Theo. } W = \text{ Theoretical specific energy)} \]

where \( n \): number of coulombs

\( E_{oc} \): open circuit voltage

\( m \): mass of electroactive material in kg.

In our case of a RSSR/Beta"Alumina/Na type of battery, the cell reaction is

\[ \text{RSSR} + 2 \text{ Na} \rightarrow 2 \text{ RS Na}. \]

The expression for \( W \) becomes:

\[ \text{Theo. } W = 2 \frac{F \times E_{oc}}{M_{RSSR} + 2 M_{Na}} \times 3.6 \]

where \( F \): Faraday
M: Molecular weight of RSSR or of Na in g.

3.6: unit conversion factor.

For the TETD, Theo W is = 2 x 96500 x2.2 / (346 x 3.6) = 341 Wh/kg

PRACTICAL SPECIFIC ENERGY:

The practical specific energy takes into account the actual weight of the battery including the cell casing, the seals, the thermal insulation, etc..., in addition to the electroactive material. This quantity as indicated by its name, is much more representative of reality. As a rule of thumb, the practical specific energy usually represents one fourth of the theoretical specific energy. Optimization of the cell design obviously plays the key role. The ratio of the practical over theoretical energy is expected to be improved in our case with respect to the sodium sulfur battery: less thermal insulation will be needed for example.

SPECIFIC POWER, AND PEAK POWER:

The specific power P is given by:

\[ P = \frac{E \times I}{m} \text{ Watts} \]

where \( E \): cell voltage, Volts
\( I \): cell current, Amps
\( m \): cell weight, kg

The peak power represents the maximum power the battery can deliver for
a given short time period. (The time needed for an acceleration for an electric car application for example).

The peak power varies during the discharge of the battery, the battery usually performs less well at the end of discharge, the state of discharge at which the peak power is measured should therefore be defined.

INTERNAL RESISTANCE:

The electrochemical process within the battery occurs with some unavoidable ohmic losses. The resulting ohmic drop is given by:

\[ E = E_0 - E_{oc} = r I \]

where \( E \): cell voltage
\( E_{oc} \): cell open circuit voltage
\( r \): cell internal resistance
\( I \): cell current

COULOMBIC EFFICIENCY:

The coulombic efficiency relates the mass of active material in the battery to the number of coulombs actually available on discharge and on charge. For exclusively faradic processes the efficiency is of 100%, but in real life some corrosion or some loss of activity always occur.

ENERGY EFFICIENCY:

The energy efficiency relates the energy delivered on discharge to the
energy necessary to recharge the battery.

\[ \text{efficiency} = \frac{W_{\text{discharge}}}{W_{\text{charge}}} \]

\[ = \frac{E_{oc} - r_d I_d}{E_{oc} + r_c I_c} \]

where: 
- \( r_{c,d} \): internal resistance on charge or discharge
- \( I_{c,d} \): current on charge or discharge.

E or I or r may vary during the discharge and charge and should actually be integrated with respect to time. It appears that \( r \), the internal resistance should be minimized not only to minimize the ohmic drop through the cell, but also to maximize the energy efficiency.

**NUMBER OF CYCLES:**

It determines the life time of the battery.
ETHYLENEDIAMINE DITHIOCARBAMATE

In an effort to increase the energy density and to lower the sodium salt melting point, the ethylenediamine dithiocarbamate was tested as positive electrode material. This compound exhibited attractive features: the sodium salt was reported to have a melting point of 80 C and the bidentate molecular structure of two CS₂ functionnal groups per molecule led to a substantial increase in the energy density (the energy density for the ethylenediamine dithiocarbamate is 480 Wh/kg versus 340 Wh/kg for TETD). The sodium salt also happens to be commercially available and is very cheap. It is used industrially as a fungicide to prevent algae growth in distillation towers.

CELL REACTION:

Upon oxidation, the ethylene diaminedithiocarbamate can give rise to several products. In the case of an intra molecular reaction, the two CS₂ terminal groups react with each other to create the disulfide bond, giving rise to a cyclic compound. In the case of an intermolecular reaction, two different molecules react with each other to give a dimer molecule which in turn can react to give eventually a polymer.

Ring Closure:

\[ \overset{-S_2C{-NH-CH_2-CH_2-NH-CS_2}^-}{\rightarrow} \overset{\text{HN}}{\text{CH}}_2-\text{CH}_2-\text{NH} + 2e^- \]

Inter molecular reaction:

\[ n(\overset{-S_2C{-NH-CH_2-CH_2-NH-CS_2}^-}{\rightarrow} \overset{\text{HN}}{\text{H}}_2-\text{C}_4-\overset{\text{NH-C-S-S-C-NH-C}_2H_4-NH-CS_2^-}{\text{HN}} + n \text{ e}^- \]
RESULTS:

The ethylene diamine dithiocarbamate disodium salt proved to be actually a hydrate which melted around 80°C, however, as soon as the water of hydration was removed, the salt underwent decomposition without melting. This compound is particular prone to decomposition, as was found out later, because of the presence of hydrogens on the nitrogen atom and gives readily the corresponding thioisocyanate $S=\text{C}=\text{N}-\text{C}_2\text{H}_4\text{N}=\text{C}=\text{S}$.

The hydrate was nevertheless tested in a battery with DMSO as a solvent and the cell could be charged. The presence of water, which ruins the Beta"Alumina, prohibits any really meaningful testing. The similar compound with a saturated nitrogen ($\text{S}_2\text{C}-\text{N(}\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-N-(CH}_3\text{)CS}_2\text{)}$ should be kept in mind as it is much less likely to undergo decomposition. Its melting point most probably will be higher than the 110 -130°C range but its higher energy density, compared to TETD allows for more solvent while keeping the same energy density. One can also imagine adding some TETD as a terminating agent to control the length of the polymer chain if the polarization mechanism proves to be the predominant one. This compound is not available commercially although its synthesis can be carried out in a straightforward fashion, namely by action of $\text{CS}_2$ on the methyl 1,4 ethyldiamine in the presence of NaOH.
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