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Publication Date

1988-10-01

Lawrence Berkeley Laboratory

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October 1988

DISCLAIMER

SODIUM/BETA"-ALUMINA/ORGANOSULFUR BATTERIES
OPERATING AT INTERMEDIATE TEMPERATURES

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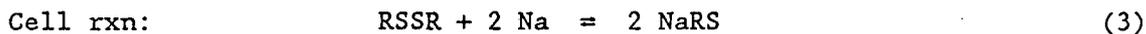
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INTRODUCTION

Concurrent with impressive advances in advanced batteries operating at high temperatures such as the Na/Na_2S_x and Li/FeS systems, have been concerns over safety and reliability of such batteries. Accordingly, various efforts have been made to offer alternative high specific energy/power batteries operating at reduced temperatures [1, 2, 3]. However, since electrode kinetics and mass transport processes in batteries are thermally activated, lower temperature systems often present a compromise between lower power output, and enhanced reliability, safety, and economic factors. Fortunately, lower temperature systems also offer far more flexibility in cell design, allowing geometries with higher electrode surface area than would be feasible with high temperature systems, thereby reducing the necessary current densities for acceptable power output.

The sodium/organosulfur cells discussed in the following paper are based on the well known $Na/beta"-alumina/Na_2S_x$ battery technology. However, in the present cells the sodium polysulfide electrode which has an operating temperature of 300 to 350°C has been replaced with an organosulfur electrode [4, 5, 6] which is limited at the low temperature limit by the melting point of sodium (≈ 100°C).

-1-

At present the majority of advanced and/or conventional batteries are derived exclusively form inorganic electrochemical couples (i.e. Na/Na_2S_x, Li/TiS_2, Pb/PbO_2, etc.). Sodium/organosulfur electrodes present a departure from this tradition in that they are based on a general redox reaction for organic disulfides,

$$RSSR + 2 \ e^- \ = \ 2 \ RS^-, \qquad (1)$$
$$2 \ Na \ = Na^+ + 2 \ e^- \qquad (2)$$

Cell rxn: $\qquad RSSR + 2 \ Na \ = \ 2 \ NaRS \qquad (3)$
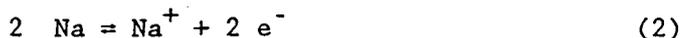
where R is an organic moiety such as CH_3, C_6H_5, $CH_3OCH_2CH_2$, etc. Among the advantages of such a generic redox couple for energy storage include the ability to control the physical, chemical, and electrochemical properties of the organosulfur species by appropriate choice of the organic R groups. Although the organodisulfides appear to share a common redox mechanism due to the presence of the disulfide linkage [6], other properties of these compounds are as different as the organic moieties attached to the sulfur-sulfur bond. The simple alkyl disulfides have melting points well below room temperature (- 85°C for CH_3SSC_3), have low viscosities, and are quite non-polar; electrodes based on these disulfides require the addition of a high dielectric constant solvent in order to dissolve the thiolate salts generated on cell discharge. The thiuram disulfides typically have melting points between room temperature and 100°C, are fairly viscous when molten, and are sufficiently polar to dissolve and partially dissociate the alkali metal thio salts generated on cell discharge [4, 5]. Chemical oxidation of dimercaptans such as $HSCH_2CH_2OCH_2CH_2SH$ generates viscous polymers having low equivalent weights and capable of dissolving sodium thiolate salts due to the presence of CH_2CH_2O groups as in the "glyme" type solvents and crown ethers; in these cases the charge/discharge of Na/RSSR cells causes reversible polymerization/depolymerization in the positive electrode.

The equivalent weight of organosulfur electrodes is of course dependent on the choice of the R groups attached to the disulfide linkage. Typical theoretical energy densities of Na/RSSR cells range from 360 Wh/Kg where R is $(C_2H_5)_2NC=S$, to 770 Wh/Kg where R is simply CH_3, assuming no solvent is incoporated in the positive electrode (table 1). Hydroxyethyl disulfide and representative alkoxyalkyl disulfides were tested in Na/RSSR cells as described below since it was expected that the hydroxy and/or ether linkages would enhance solubility of the sodium thio salts generated on cell discharge. Still, for most cases some solvent is necessary in the organosulfur positive electrode, and consequently less than the theoretical energy density is realized. Fortunately, the low temperature of operation of these cells and non-corrosive nature of the positive electrode greatly reduces the complexity of and weight of cell technology, so that practical energy densities in the range of 100 to 150 Wh/Kg are easily achieved with these electrodes.

EXPERIMENTAL

All air sensitive manipulations described below were performed in argon-atmosphere glove boxes capable of maintaining oxygen and water levels below 1 ppm. Beta"-alumina tubes (L = 10 cm , OD = 1.08 cm , ID = 1.0 cm) purchased from Ceramatech were rinsed and ultrasonically cleaned in methanol, and subsequently baked out at $900^\circ C$ overnight in a soda rich enviroment prior to filling with sodium. Reagent grade sodium metal was heated to $300^\circ C$, filtered through stainless steel wool, and reacted with titanium sponge at $350^\circ C$ overnight to scavenge dissolved oxygen in the sodium melt [7]. Beta"-alumina tubes treated as described above were then filled with the highly purified sodium at $200^\circ C$, maintained at temperature for an hour to ensure thorough wetting of the electrolyte with the liquid metal, sealed with high temperature epoxy to an aluminum cap through which a stainless

steel wire contacted the sodium metal electrode, and cooled to room temper-
ature. The sodium electrode/beta"-alumina tube was then tightly wrapped in
graphite felt and inserted into a stainless steel cell having approximately
20 cm^2 of electrolyte surface area and 5 ml of free volume in the graphite
felt/cathode compartment available for injection of the organosulfur species
(fig. 1).
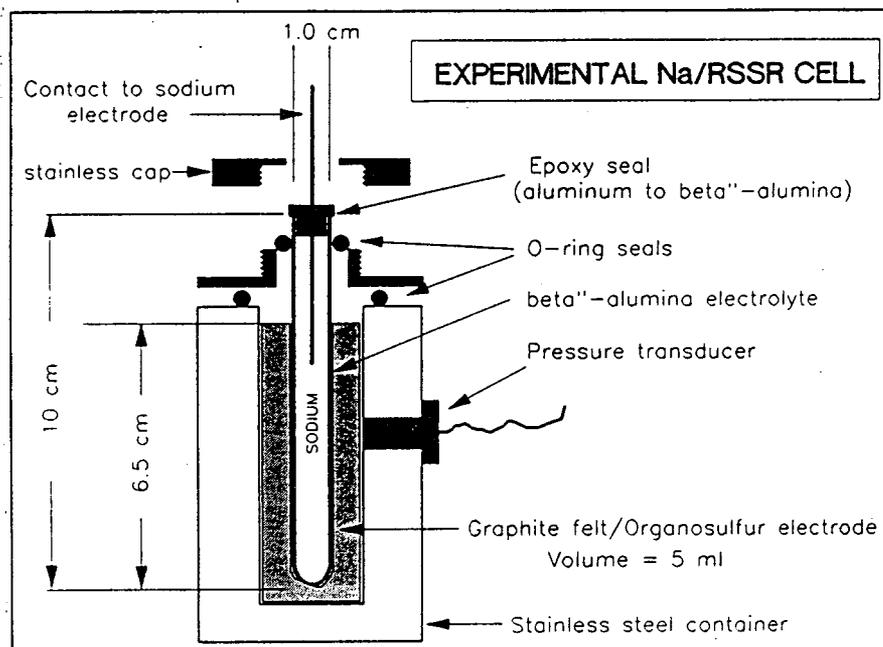
XBL 8810-3479

Fig. 1. Laboratory sodium/beta"-alumina/organosulfur cell for intermediate
temperature operation. Pressure transducer allows monitoring of positive
electrode pressure as a function of cell cycling.

The cell was sealed with silicone o-rings, and fitted with a piezo-
electric transducer to monitor the internal pressure (psig) of the
positive electrode; by monitoring the positive electrode pressure under
closed circuit conditions it was possible to detect possible irreversible
reactions giving rise to volatile side products such as mercaptans, thio
ethers, etc.

Ethoxyethyl disulfide and methoxyethyl disulfide were made by the
reaction of 2-chloroethyl ethyl ether and 2-chloroethyl methyl ether
with potassium hydrogen sulfide in methanol under pressure to yield the

corresponding mercaptan; the β-ethoxy-alkyl mercaptans were fractionally distilled and the purified mercaptans oxidized to the disulfides which were subsequently purified by distillation under vacuum [8]. Hydroxy-ethyl disulfide (Aldrich) was distilled under reduced pressure over molecular sieves prior to use. Transition metal phthalocyanines (Pfaltz and Bauer) were used as is. Anhydrous dimethyl sulfoxide, DMSO, (Aldrich), was further dried by eluting the solvent through a column of molecular sieves and activated neutral alumina; dimethyl acetamide was dried similarly. Dimethyl sulfone (Aldrich) was recrystallized twice from methanol and dried under vacuum for 2 days. Graphite felt, GF-S5, was obtained from The Electrosynthesis Company, and dried at 250°C under vacuum overnight. To increase charge-transfer rates in the positive electrode, some samples of graphite felt were immersed in solutions of transition metal phthalocyanines dissolved in pyridine for one or two hours, air dried, and dried under vacuum as above. The use of metal phthalocyanine treated graphite felt in the positive electrode was to enhance electron transfer rates for the disulfide redox process. Metal phthalocyanines (MPc) are known to catalyze the RSSR/RS⁻ redox couple [9], and in fact representative Na/RSSR cells tested earlier in this laboratory showed up to a fivefold increase in current density upon addition of appropriate MPc's to the positive electrode.

Solutions of organosulfur compounds in various solvents were prepared at the desired concentrations and subsequently injected into the cathode compartment. Completed cells were sealed, placed in transparent quartz furnaces, and cycled under computer control with an IBM PC/AT interfaced to a PAR 373 Potentiostat/Galvanostat by means of a Data Translation 2801-A data acquisition card. Cell current was controlled from the keyboard with continuous monitoring of cell voltage, current, temperature, and pressure.

RESULTS

Sodium/Hydroxyethyl Disulfide Cells

Test tube experiments performed in the dry box indicated that hydroxyethyl disulfide (HEDS) was a very effective solvent for many sodium salts, particularly at elevated temperatures. Consequently HEDS electrodes were assembled with pure disulfide. Initial tests of Na/HEDS cells confirmed the ability of hydroxyethyl disulfide to dissolve a large percentage of the sodium thio salt generated on cell discharge; neat positive electrodes were discharged to greater than 50% of total capacity at $120^{\circ}C$ without noticeable precipitation of salt. However, polarization of these batteries as a function of current density strongly indicated slow electron transfer in the positive electrode. Consequently, cells were assembled with graphite felt treated with cobalt pthalocycanine, which was quite effective at reducing electrode polarization. A cell of this type is shown in figure 2a. At a current density of 10 mA/cm^2 (based on electrolyte surface area) the Na/HEDS cells were able to discharge at a stable voltage efficiency of about 90 to 95 % (fig. 2a). At 25 mA/cm^2 the cells were able to discharge at a stable voltage efficiency of 88 %. In fact the cells were able to sustain rates of up to 50 mA/cm^2 for about 20 minutes before appreciable time dependent polarization took place.

On the basis of the discharge behavior of the Na/HEDS cells, the batteries looked quite promising. However, the charging behavior of these cells (fig. 2a) as well as the rapid buildup of internal pressure in the positive electrode implied deterioration of the hydroxyethyl disulfide electrode. As can be seen from fig. 2b, after approximately 20 % of charge there is a dramatic increase in in pressure in the positive electrode, concomitant with increasing polarization of the Na/HEDS cell (fig. 2a). Upon disassembly of the experimental cell it was obvious that the hydroxyethyl disulfide electrode had polymerized.
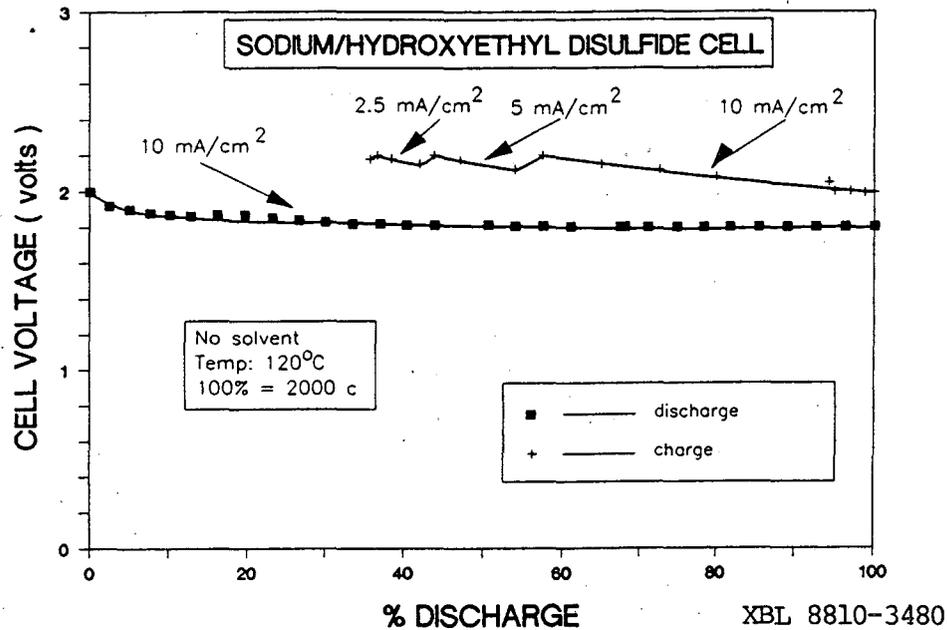
Fig. 2a. Sodium/beta"-alumina/hydroxyethyl disulfide battery. Positive electrode consists of graphite felt) w/adsorbed cobalt phthalocyanine) saturated with pure hydroxyethyl disulfide.
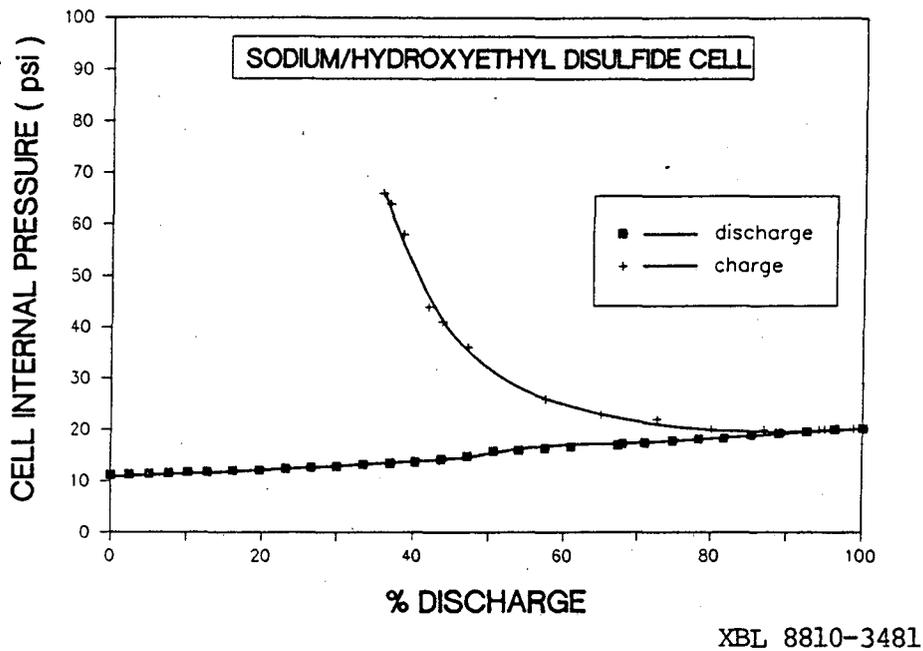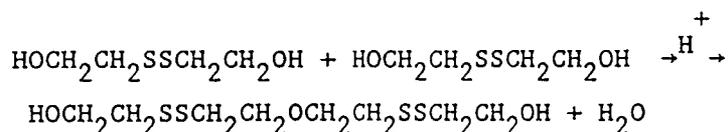

Fig. 2b. Pressure of the positive electrode in the Na/HEDS cell in fig 2a.

It is known that hydroxyethyl disulfide can undergo autopolymerization under acidic conditions according to,

$$HOCH_2CH_2SSCH_2CH_2OH + HOCH_2CH_2SSCH_2CH_2OH \xrightarrow{H^+}$$
$$HOCH_2CH_2SSCH_2CH_2OCH_2CH_2SSCH_2CH_2OH + H_2O$$

Accordingly, sealed ampoules of the hydroxyethyl disulfide electrode were kept at $120^{\circ}C$ for approximately two weeks as well as ampoules containing the electrode plus dilute HCl. In no case did the electrode show any signs of polymerization unless significant amounts of HCl were present. In fact, polymerization only occurred in the discharged electrode, implying that the polymerization process is initiated by the thio salt generated on cell discharge. It was then hypothesized that deterioration of the HEDS electrode may be due to nucleophilic attack of the thio anion on the hydroxylic end groups according to,

$$HOCH_2CH_2S^- + HOCH_2CH_2SSCH_2CH_2OH \rightarrow HOCH_2CH_2SCH_2CH_2SSCH_2CH_2OH + OH^-,$$

which of course would lead to depletion of thio salt available for charge, and polymerization of the electrode. In light of the above results, the HEDS electrode, while interesting, would not be suitable for secondary battery applications. Further, the Na/HEDS cell behavior implies that in selecting potential RSSR compounds for battery applications the presence of leaving groups such as HO^-, Cl^-, etc., in the organic R groups would not be desirable as it might similarly lead to irreversible polymerization of the electrode.

Test tube experiments with ethoxyethyl disulfide (EEDS) indicated fairly low solubility of sodium salts, implying that successful batteries would most likely need the presence of solvents in the positive electrode.

The first Na/EEDS cell was assembled without the aid of solvent. The discharge of that battery is shown in fig. 3a, and the pressure behavior is seen in fig. 3b. At the temperature of operation in the 100 % charged
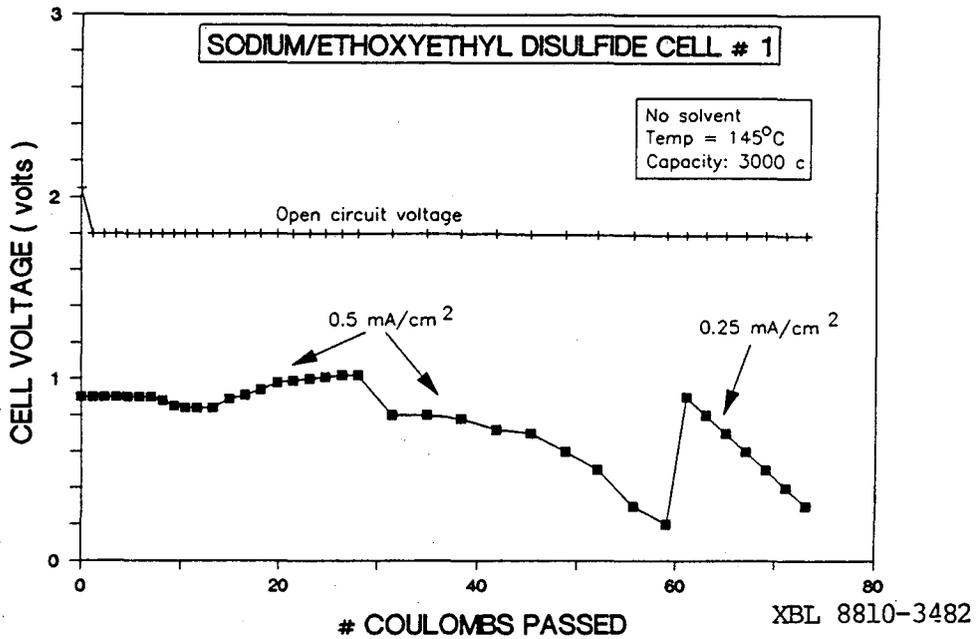

Fig. 3a. Sodium/beta"-alumina/ethoxyethyl disulfide cell # 1. Positive electrode consists of graphite felt/adsorbed CoPc saturated with neat ethoxyethyl disulfide.

SODIUM/ETHOXYETHYL DISULFIDE CELL # 1

No solvent: neat
Temp: 145°C
Capacity: 3000 c

CELL INTERNAL PRESSURE (psi)
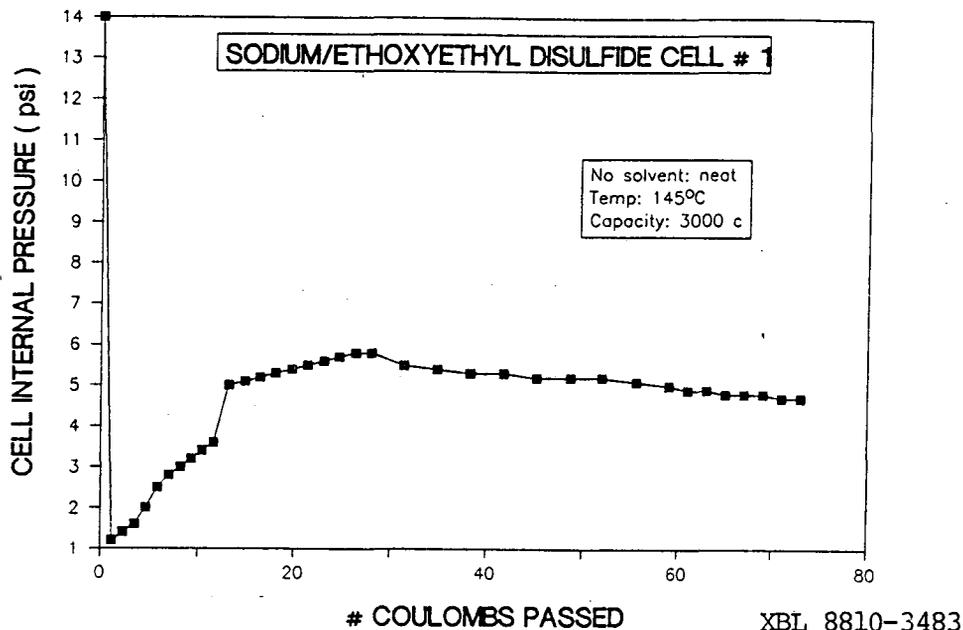
COULOMBS PASSED

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Fig. 3b.   Pressure of the positive electrode in Na/EEDS cell # 1.

state, the positive electrode pressure was about 14 psi, which fell
rapidly to essentially zero psi after discharge of a few coulombs. As
can be seen in fig. 3a the internal resistance of Na/EEDS cell # 1 was
quite high, between 70 and 90 Ω for the first 30 coulombs, and then
increasing as the cell polarized with further discharge. The high internal
resistance of this cell is most likely attributable to low solubility and
association of the thio salt in the neat positive electrode. The pressure
behavior indicates that the EEDS electrode is stable on discharge and at
high overpotentials; after an initial pressure drop and rise, the pressure
steadily dropped with increasing discharge. Further, the cell was left
in the discharged state for 5 days at temperature with no change in pres-
sure or performance, and on disassembly appeared unchanged. However, the
performance of the neat electrode clearly indicated the need for solvent
in the EEDS electrode for a viable battery.

The subsequent EEDS electrode was diluted with 50 wt % dimethyl
sulfoxide (DMSO). As shown in fig. 4a, the performance of Na/EEDS cell

2 was far improved over the above Na/EEDS battery. The internal resistance of the cell was reduced from 70 Ω to approximately 0.5 Ω, and the voltage efficiency of the flat discharge at a current density of 5 mA/cm^2 was close to 97 %. The Na/EEDS cell also performed well on charge at 5 mA/cm^2, but polarized when the current density was boosted to 10 mA/cm^2 towards the end of charge.
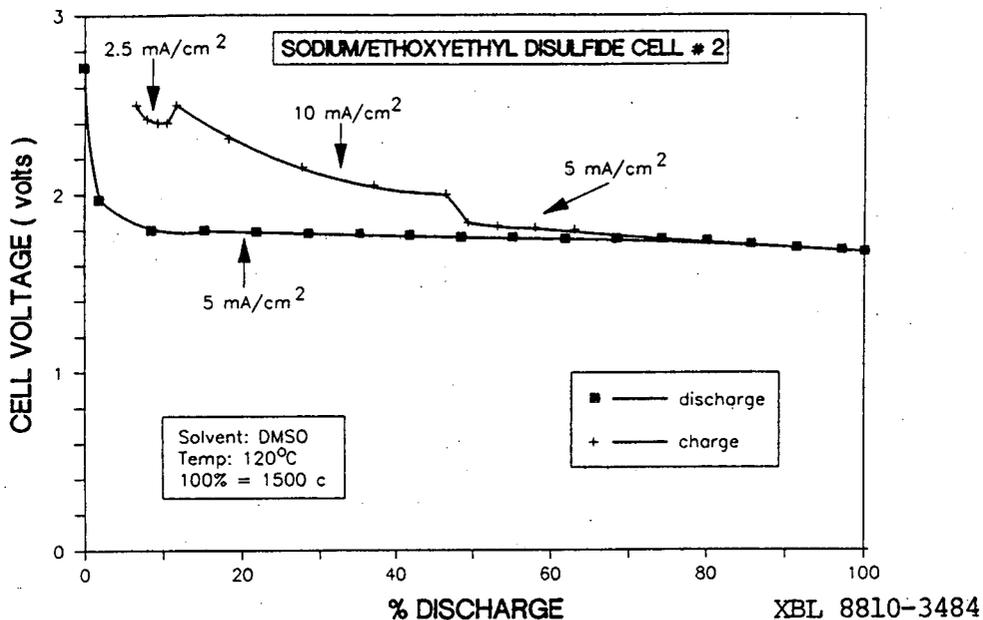

Fig. 4a. Sodium/beta"-alumina/ethoxyethyl disulfide cell # 2. Positive electrode same as in fig. 3a but diluted with 50 wt % DMSO.
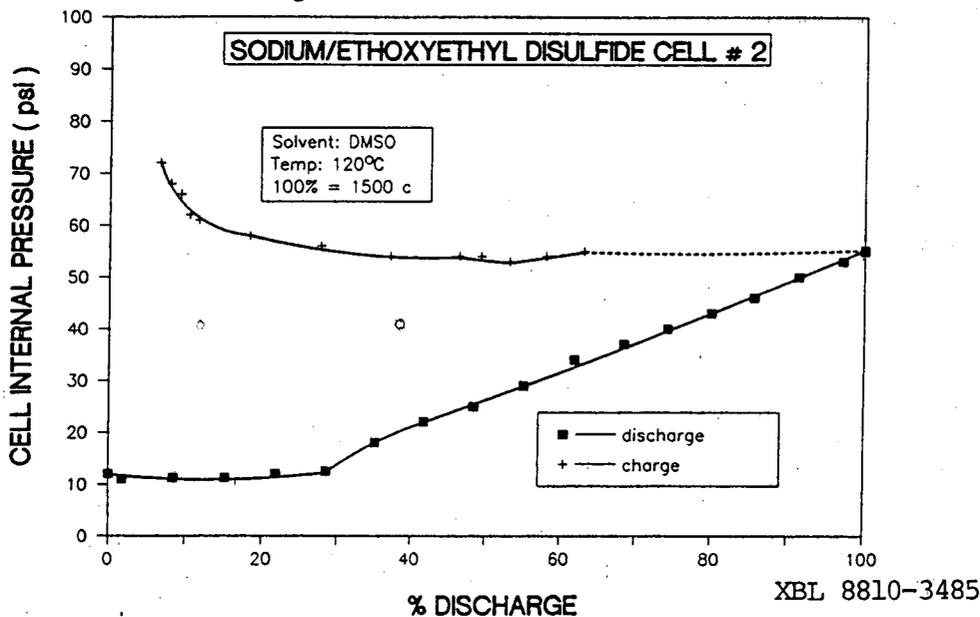

Fig. 4b. Pressure of the positive electrode in Na/EEDS cell # 2.

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Unfortunately, as is seen in fig. 4b, after approximately 30 % of cell discharge, there was an almost linear increase in cell pressure for the remainder of discharge, indicating that DMSO is probably not a suitable solvent for this system. Interestingly, the pressure behavior of this system on charge (fig. 4b) was relatively flat up to about 85 % of charge, implying that the instability occurs under reducing conditions. In fact, it is reported that DMSO can be reduced electrochemically to dimethyl sulfide (CH_3SCH_3), which has a boiling point of $34^\circ C$, and would certainly lead to pressure rise in the EEDS electrode [10].

Sulfones are reported to be more resistant to reduction and oxidation than sulfoxides. Accordingly, a third EEDS electrode was prepared approximately 60 wt% mixed solvent composed of 50 wt% DMSO and 50 wt% dimethyl sulfone (DMSF); EEDS electrodes made with pure dimethyl sulfone are relatively difficult to assemble in the dry box due to the high melting point of DMSF ($\approx 107^\circ C$). In this way, the effect of diluting DMSO with DMSF on the pressure behavior of the positive electrode could be observed as a function of cell polarization. The behavior of Na/EEDS cell # 3 is displayed in figs. 5. Clearly, the pressure stability of the EEDS electrode has been greatly enhanced by the dilution of DMSO by DMSF. At the end of the first discharge of Na/EEDS cell # 3 the pressure had gradually increased to about 15 psi, as opposed to the rapid increase of cell # 2 to 55 psi. The internal resistance of cell # 3 was 0.5 Ω, as was the case for cell # 2, and the cell was similarly able to maintain a flat discharge at 5 mA/cm^2 with a voltage efficiency of over 95 %. As seen above, during the first charge cycle there was less increase in pressure (5 psi) than during discharge. However, as the cell was further cycled (fig. 5) the pressure was observed to rise continually until the third discharge during which time the pressure actually decreased in the cell. It is clear that although much improved, there were still parasitic reactions in the cycling of Na/EEDS cell # 3, as evidenced by the increasing open circuit voltage of the cell towards the end of charge, and by the pressure behavior of the positive electrode.
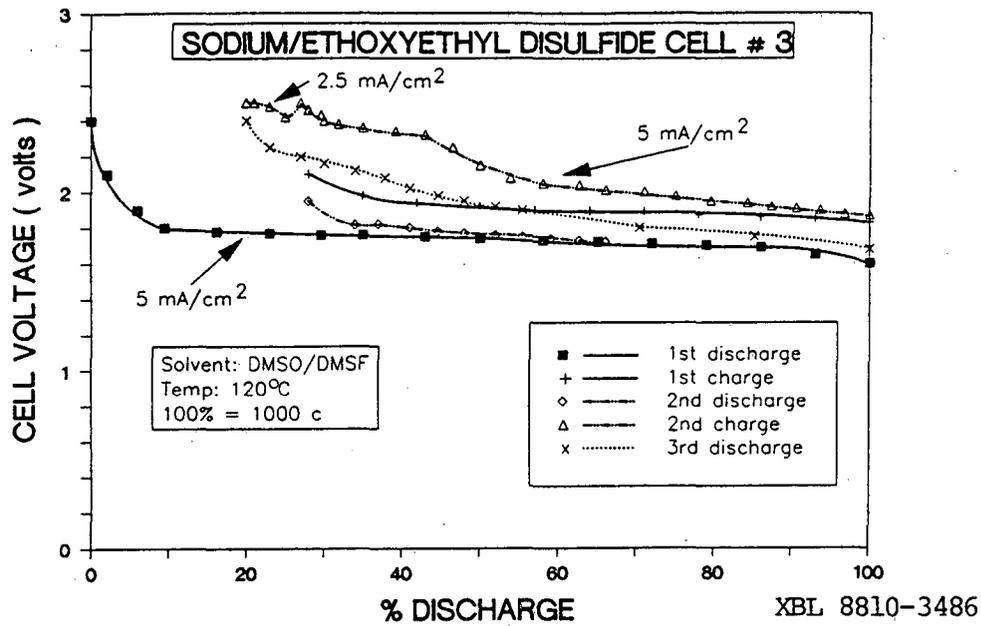
Fig. 5a. Sodium/beta"-alumina/ethoxyethyl disulfide cell # 3. Positive electrode same as in fig. 3a but diluted with 30 wt % DMSO and 30 wt % DMSF.
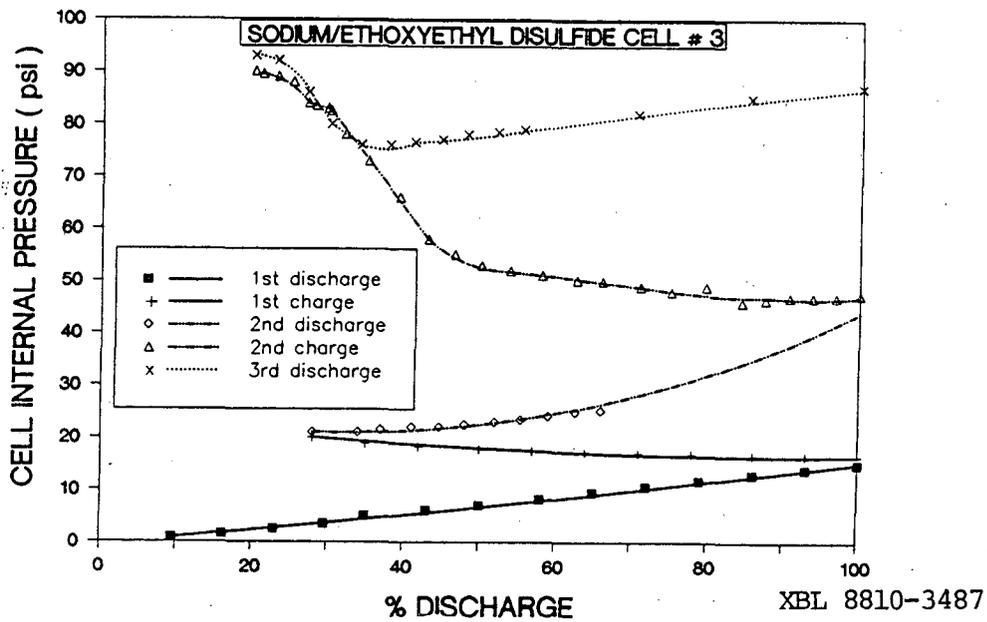

Fig. 5b. Pressure of the positive electrode in Na/EEDS cell # 3.

CONCLUSIONS

Sodium/hydroxyethyl disulfide cells can be discharged at high rates without the aid of solvents in the positive electrode. However, the HEDS electrode is irreversibly polymerized in the discharged state and consequently will not accept full charge.

Sodium/ethoxyethyl disulfide cells cannot be discharged appreciably unless the electrode is diluted with a high dielectric constant solvent such as dimethyl sulfoxide. The cells can be cycled at reasonably high rates but there is evidence of electrolysis and/or chemical reaction with DMSO. The dilution of dimethyl sulfoxide by dimethyl sulfone serves to increase the stability of the postive electrode, indicating that electrodes assembled with pure sulfone solvents should exhibit more stable cycling behavior (preliminary results with EEDS/DMSF electrodes support this conclusion).

Organodisulfide electrodes such as the alkoxyalkyl disulfides offer attractive alternatives to high temperature systems. Although extended cycling behavior has not yet been demonstrated for the alkoxyalkyl disulfides, improvement of the performance of the positive electrode with stable solvents such as the sulfones should lead to viable energy storage devices.

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