

## Feasibility study of sulphone-based electrolytes for a medium-temperature reserve cell concept

C. O. Giwa

*Materials and Structures Department, Defence Research Agency, Farnborough, Hampshire GU14 6TD (UK)*

(Received September 30, 1992; accepted December 3, 1992)

### Abstract

This paper describes a feasibility study on materials for a medium-temperature (178–270 °C) reserve primary cell, which is activated by melting lithium salt/sulphone mixture in order to provide electrical power. The aim was to define performance parameters for use as a high energy density battery capable of current density in the range 5 to 50 mA/cm<sup>2</sup>. The cathode was silver chromate and vanadium oxide (V<sub>6</sub>O<sub>13</sub>). The most promising test cell used silver chromate cathode, di-*p*-tolylsulphone/lithium perchlorate, electrolyte and lithium–aluminium alloy anode. Maximum current capability was 40 mA/cm<sup>2</sup>. It was observed that voltage drops were rather high due to the high internal resistance of some sulphone-based cells. These cells could power a heat sensor.

### Introduction

Polar aprotic solvents such as dimethylsulphoxide, and aliphatic and aromatic sulphones are becoming more and more important in modern battery research programmes [1–3]. Sulphones form a very attractive group of organic solvents for use in lithium intercalation cells, due to their chemical and physical properties. One of the fundamental requirements of an aprotic solvent for dissolving an electrolyte in a medium temperature reserve cell, where an alkali–aluminium alloy is to be employed, is its complete chemical and electrochemical stability against both the alkali-alloy anode and cathode materials. Molten sulphone/salt mixtures appear to satisfy these requirements even though they are not thermodynamically stable to lithium metal. It is well known that many aprotic solvents including sulphones solvate cations readily, and have high dielectric constants. For example, molten dimethylsulphone (DMSO<sub>2</sub>) is an inert solvent which readily dissolves many inorganic salts.

The electrochemical behaviour of some transition metal oxides in molten dimethylsulphone has been investigated [3]. Lithium salts used in this investigation were the perchlorate, tetrafluoroborate and hexafluoroarsenate. The results showed satisfactory performance from all cathode materials examined. As a result, dimethylsulphone was said to be a very promising organic solvent for use in high energy density non-aqueous lithium cells. Lithium perchlorate dissolved in molten sulphone was also examined in conjunction with a mixed transition metal oxide cathode system (CuO + V<sub>2</sub>O<sub>5</sub>) and a lithium anode [4]. The aim of this study was to develop a lithium rechargeable battery. The simultaneous presence of vanadate and unreacted CuO + V<sub>2</sub>O<sub>5</sub> in this mixed cathode materials generated an open-circuit voltage (OCV) varying

continuously from 3 to 2.5 V during electro-reduction. This system displayed only limited rechargeability, probably due to the particle-size distribution of the cathodic material.

A literature review indicated that certain sulphones could be used as solvents in reserve cells. Their selection was based on the need for their mixtures with lithium salts to remain solid and non-conducting at the maximum perceived storage temperature (70 °C). Thus, selected sulphones — dimesitylsulphone (DMS), tris(ethylsulphone)-methane (TESM) and diethylsulphonemonophenylsulphonyl methane (DESMPSM) — have been prepared. These, and the commercially-available sulphones dimethylsulphone and di-*p*-tolylsulphone were examined as potential solvents for use in a medium-temperature reserve cell, based on lithium–aluminium alloy anode. The electrolytes used were lithium trifluoromethanesulphonate, lithium perchlorate and lithium tetrafluoroborate. The effects of the above-mentioned sulphones on the conductivities of lithium salts, and single-cell tests at moderate temperatures are discussed.

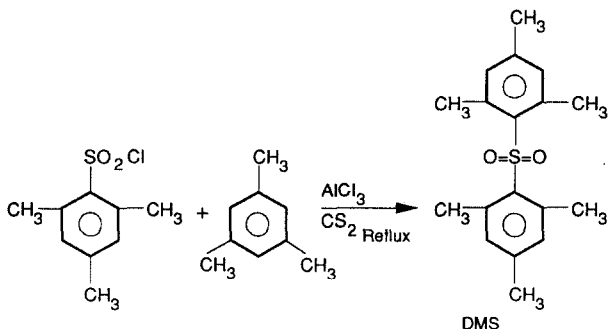
## Experimental

### Chemicals

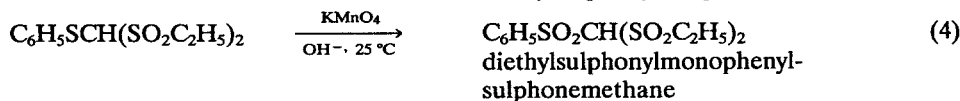
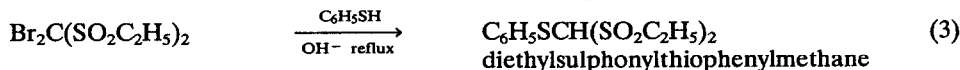
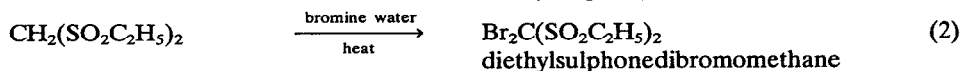
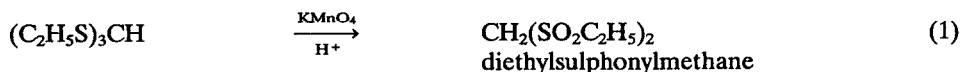
Lithium salts used as electrolytes in this study were obtained from Aldrich Chemical Co., Ltd. Silver chromate was synthesized by the metathesis reaction of silver nitrate and the corresponding sodium or potassium chromate in aqueous solution. Silver chromate was dried at 40 °C, under vacuum for 48 h before use. Tris(ethylthio)methane, di-*p*-tolylsulphone and dimethylsulphone were obtained from Lancaster Synthesis Ltd., UK.

### Preparation of sulphones and purification of di-*p*-tolylsulphone (DPTS)

Dimesitylsulphone (DMS) was prepared by a Friedel–Crafts reaction which was based on Maclean and Adam's procedure [5]. Thus, mesitylene sulphonyl chloride was allowed to react with mesitylene in the presence of aluminium chloride catalyst:



Tris(ethylsulphonyl)methane (TESM) and tris(methylsulphonyl)methane (TMSM) were obtained by peracetic acid and by permanganate oxidation of tris(ethylthio)methane and tris(methylthio)methane, respectively [6]. Diethylsulphonylmonophenylsulphonyl-methane (DESMPSM) was synthesized by alkaline-permanganate oxidation of di(ethylsulphonyl)thiophenylmethane. The yields of all three were rather low. A reaction scheme for the preparation of DESMPSM is summarized below [7]:



These products were identified not only by their melting points, but also by elemental and infrared analyses. Carbon, hydrogen and sulphur were determined microanalytically using a Hewlett Packard F and M165 analyser.

Di-*p*-tolylsulphone obtained from a commercial source was a crude product, its colour being greyish-white, which had a melting point of 156 °C. Two recrystallizations from absolute alcohol raised the melting point to 158–160 °C. Lustrous white crystals were obtained and dried in the oven at 115 °C. Finally, the purified di-*p*-tolylsulphone was stored in a dry box before use.

#### Conductivity measurements

A.c. conductivity measurements from 1 Hz to 10 MHz were made with a Solartron 1250 frequency response analyser (FRA) and the 1186 electrochemical interface to determine the bulk resistance of the molten electrolytes without binder. Ionic conductivities were calculated from the measured resistance and the geometric parameters of the cell used.

As shown in Table 1, the conductivity values obtained with a mixture of either diethylsulphonylmonophenylsulphonemethane or diethylsulphonylmethane and lithium hexafluoroarsenate were negligible. These mixtures probably reacted together to produce a polymeric compound which is thought to be responsible for the high resistance.

#### Cathode compositions

Silver chromate and vanadium pentoxide were used as depolarizer in separate single cell tests. Portions of lithium tetrafluoroborate (30%) were added to these depolarizers in order to improve their conductivities; the quantities used being shown in the respective Figures. The stability of silver chromate was investigated by thermogravimetric analysis (TGA). A DuPont thermogravimetric balance was used to heat  $\text{Ag}_2\text{CrO}_4$  in a nitrogen atmosphere from 50 to 1000 °C. Silver chromate appears to be stable between 50 and 650 °C.

#### Pellets for electric measurements

Experimental single cells consisted of 24% lithium–aluminium alloy anode pellet pressed at about 8 tons per square inch, together with a bilayer pellet consisting of electrolyte binder (EB) and depolarizer–electrolyte layers. Silver chromate pellets were used as cathode for sulphone-based electrolytes. Vanadium pentoxide depolarizer pellets were also used during tests with molten di-*p*-tolylsulphone/lithium tetrafluoroborate. Single cell pellets were sandwiched between flat iron current collectors, which in turn were sandwiched between mica insulators. All powder handling, pelletization and subsequent discharge tests were performed in a dry box of less than 5 ppm of moisture.

TABLE 1  
Conductivities of sulphone-based electrolytes at high temperatures

Electrolyte	Melting points of sulphones (°C)	Freezing points of electrolytes (°C)	Temperature (°C)	Conductivities ( $\Omega^{-1} \text{ cm}^{-1}$ )
1 M $\text{LiBF}_4/\text{di-}p\text{-tolylsulphone}$	161-163	138-140	160	$3.2 \times 10^{-2}$
2 M $\text{LiCF}_3\text{SO}_3/\text{di-}p\text{-tolylsulphone}$	161-163	130-135	220	$1.0 \times 10^{-3}$
1.3 M $\text{LiAsF}_6/\text{di-}p\text{-tolylsulphone}$	161-163	100-110	180	$1.2 \times 10^{-2}$
2 M $\text{LiAsF}_6/\text{diethylsulphonemonomophenyl-sulphonemethane}$	170-172	120-126	220	very low (resistance $\sim 100\,000 \Omega$ )
1 M $\text{LiAsF}_6/\text{diethylsulphonylmethane}$	220-224	143-146	200	very low (resistance $\sim 100\,000 \Omega$ )
1 M $\text{LiClO}_4/\text{dimethylsulphone}$	108-110	57-60	200	(resistance $\sim 100\,000 \Omega$ ) $4.1 \times 10^{-2}$

Cells were discharged in a single cell tester at current densities of 5–40 mA/cm<sup>-2</sup> at various temperatures (178–270 °C).

## Results and discussion

### *Physical and chemical properties of sulphone electrolytes*

As mentioned above, dimethylsulphone has been considered for use as an electrolyte solvent in other types of cell. However, the melting point of 60 °C found for a solid solution of lithium perchlorate in this solvent precludes it from being used in a reserve battery which might be stored above this temperature. Therefore, synthesis of the trisulphones TESM, TMSM and DESMPSM was attempted because it was expected that these might have been better solvents for lithium salts than DPTS, on account of their higher content of the solvating sulphone groups. Preparative work had also begun on modifying some of the trisulphones to remove the active hydrogen atoms, but stopped after a combination of experimental difficulties, together with the discouraging conductivity data on trisulphone solutions.

### *Electrical discharges of test cells*

Table 2 summarizes test conditions and results of single-cell discharge tests, whilst Figs. 1 to 4 show selected discharge profiles. The aim in these discharges was to determine how far the current density for each cell could be raised before a significant fall-off in charge or energy output was observed. This would then give an indication of their likely rate capability as well as energy content. Another factor influencing the practical application of such cells would be the variability of on-load voltage for a particular application, and, if the battery should be activated on open-circuit, the size of the voltage drop on applying a load would determine the practical life of the cell to some fixed percentage, for example 70%, of peak voltage.

### *Li-Al/sulphone/silver chromate cells at 260–270 °C*

As silver chromate appeared from the above results to be the better cathode material, it alone was used in conjunction with the two sulphone electrolytes. Figures 1 to 3 show discharge curves for lithium–aluminium/silver chromate test cells in the region of 260 °C using solutions of LiBF<sub>4</sub> in either DPTS or TESM as electrolytes, immobilized on silica. V<sub>6</sub>O<sub>13</sub> was initially used as cathode in separate tests, but poor results were obtained. It is seen that the OCV for these is higher than that recorded for similar cells using nitrate electrolytes at lower temperature [8]. This is probably due to a positive temperature coefficient of the cell e.m.f., but would also possibly be due to some involvement of either nitrates or sulphone electrolyte components in the cell electrochemistry. Another general feature of discharges of cells containing sulphone electrolytes is the voltage delay phenomenon at the start of discharge, followed by a recovery later. This is not a desirable feature for practical use, and appears to depend on the nature of the sulphone and on current density. Possibly a film may have been formed within the cells during the 1 min period of the cell on open-circuit after it had reached operating temperature.

Figure 1 shows that a cell containing TESM as the electrolyte solvent performed worse than one containing DPTS under comparable conditions. As the voltage collapse seen in the discharge of a further TESM cell at higher current density (Fig. 2) was also worse than equivalent cells employing DPTS (Fig. 3), further experiments were performed only with DPTS, as shown in Fig. 4. Table 2 records the durations and

TABLE 2  
Computation of energy output of Li-Al/sulphone/silver chromate cells

Sulphone	Figure ref. no.	Temperature (°C)	Current (mA)	OCV (V)	70%			60%			50%		
					Duration (min)	Voltage (V)	Energy (Wh)	Duration (min)	Voltage (V)	Energy (Wh)	Duration (min)	Voltage (V)	Energy (Wh)
TESM	1	260	10	3.45	50.0	2.95	0.024	65.0	2.9	0.029			
DPTS	1	260	10	3.45	140.0	3.05	0.071	160.0	2.95	0.079			
DPTS	3	265	50	3.45	17.8	2.8	0.041	19.8	2.7	0.044	23.0	2.5	0.048
(3% silica) DPTS	3	265	50	3.45	23.4	2.9	0.056						
(5% silica) DPTS	3	265	50	3.45	32.0	2.8	0.075						
(7% silica) DIPS		268	30	3.45	38.2	3.0	0.058	41.3	2.25	0.046	45.0	1.75	0.039
DPTS		270	50	3.45	16.0	2.95	0.039	18.6	2.1	0.033	22.6	1.50	0.028
DPTS	4	178	80	3.21	25.0	2.24	0.075	28.1	1.93	0.072	34.5	1.60	0.074
DMS	4	185	80	3.21	20.2	2.40	0.064	26.0	1.93	0.070	34.1	1.60	0.070

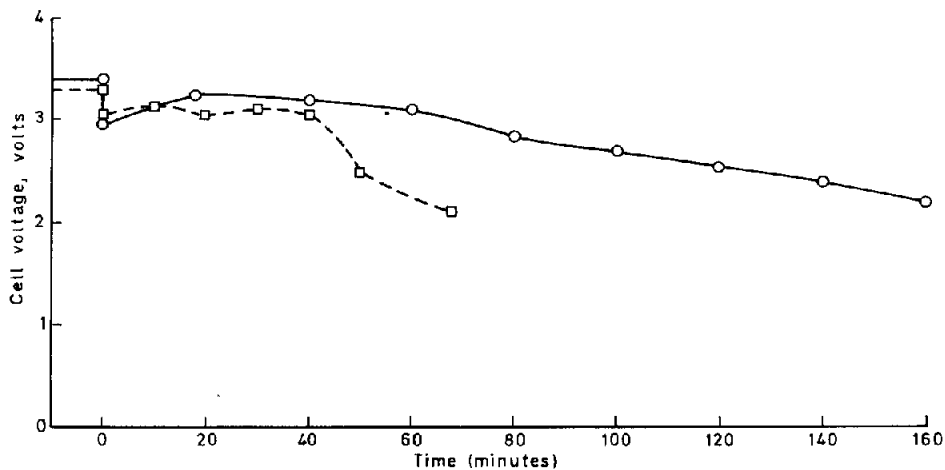


Fig. 1. The effect of trisethylsulphonylmethane on discharge performance of Li(Al)/TESM-LiBF<sub>4</sub>SiO<sub>2</sub>/Ag<sub>2</sub>CrO<sub>4</sub>. Electrolytes: (O) 2 M LiBF<sub>4</sub> in di-*p*-tolylsulphone, (□) 2 M LiBF<sub>4</sub> in trisethylsulphonylmethane; binder: SiO<sub>2</sub> (10%); anode: Li(Al); cathode: Ag<sub>2</sub>CrO<sub>4</sub> (70%), LiBF<sub>4</sub> (30%); temperature: 260 °C, and current density: 5 mA/cm<sup>2</sup>.

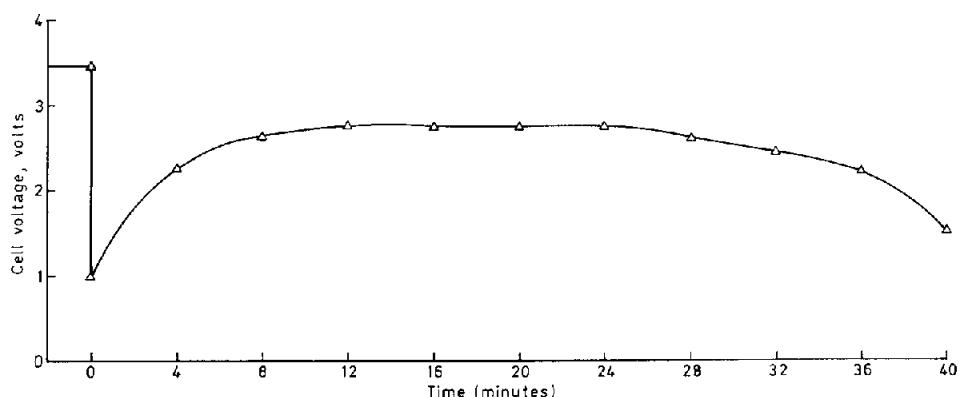


Fig. 2. Discharge curve of test cell using trisethylsulphonylmethane as medium-temperature solvent. Electrolyte: 2 M LiBF<sub>4</sub> in trisethylsulphonylmethane; binder: SiO<sub>2</sub> (7%); anode: Li(Al); cathode: Ag<sub>2</sub>CrO<sub>4</sub> (70%), LiBF<sub>4</sub> (30%); temperature: 260 °C, and current density: 25 mA/cm<sup>2</sup>.

yields of some of these cells to the same percentage voltage cut-offs. It is seen from this that an increase in binder content of the electrolyte from 3 to 7% resulting in better energy outputs of DPTS cells discharged at 25 mA/cm<sup>2</sup> at 265 °C. At 7% binder content, the yield of 0.075 Wh to a 70% cut-off approached that of some of the Li-Al/silver chromate cells using the molten nitrate electrolyte [8].

#### *Li-Al/sulphone/silver chromate at 178–185 °C*

Figure 4 shows discharge curves for cells containing di-*p*-tolylsulphone and dimethylsulphone in separate single-cell tests. When test temperatures were decreased to 178 and 185 °C, and LiClO<sub>4</sub> used as electrolyte useful discharges at higher current

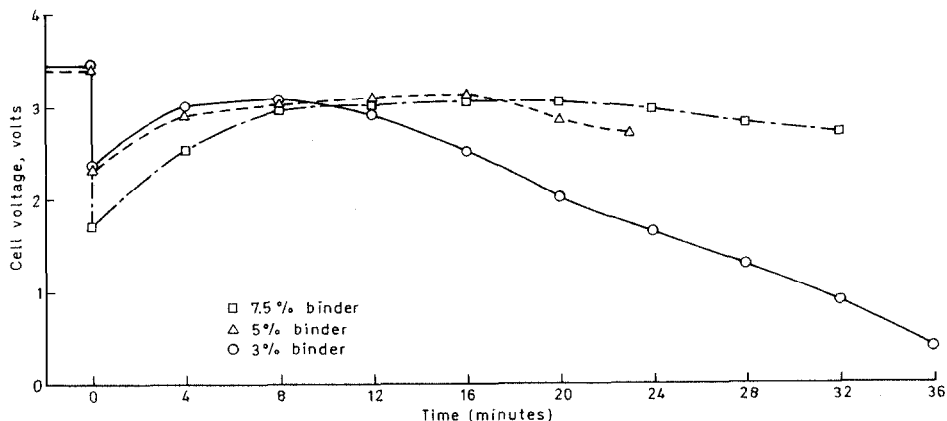


Fig. 3. Effect of binder ratios on discharge performance. Electrolyte: 2 M  $\text{LiBF}_4$  in di-*p*-tolylsulphone; anode:  $\text{Li(Al)}$ ; cathode:  $\text{Ag}_2\text{CrO}_4$  (70%),  $\text{LiBF}_4$  (30%); current density: 25  $\text{mA/cm}^2$ , and temperature: 265 °C.

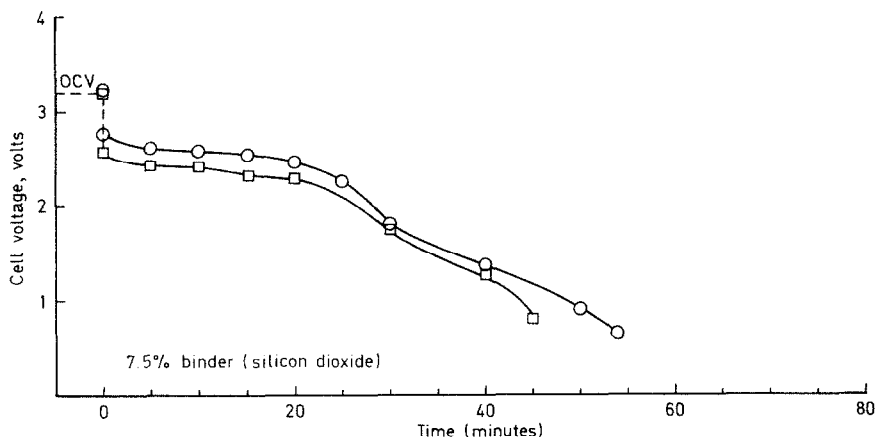


Fig. 4. Li-Al/sulphone/silver chromate cells discharged at 178 and 184 °C. Electrolyte: (O) 2 M  $\text{LiClO}_4$  in dimethylsulphone, (□) 2 M  $\text{LiClO}_4$  in di-*p*-tolylsulphone; anode:  $\text{Li(Al)}$ ; cathode:  $\text{Ag}_2\text{CrO}_4$ ; current density: 40  $\text{mA/cm}^2$ , and temperature: 185 °C, 0–178 °C.

densities of 40  $\text{mA/cm}^2$  were obtained. Details of durations and yields are given in Table 2. The yield of 0.066 Wh from Li-Al/DPTS-2 M  $\text{LiClO}_4/\text{Ag}_2\text{CrO}_4$  cell translate to a specific energy of about 320 Wh/kg of cathode weight and is therefore promising.

#### Extended storage

Accelerated storage test demonstrated that a laboratory Li-Al/DPTS- $\text{LiClO}_4/\text{Ag}_2\text{CrO}_4$  cell suffered negligible discolouration or degradation over six months at storage temperatures up to 70 °C. This is an important part of any assessment of manufactured prototype reserve batteries.



## Conclusions

1. The major advantage of using sulphones as solvent for electrolytes is that it combines a fairly high dielectric constant with moderate solvating power and outstanding resistance to electrolyte oxidation and reduction; also resistance to chemical degradation.

2. Solid organic sulphones may be usable as electrolyte solvents for medium-temperature reserve batteries, but their rate capabilities are lower than those of nitrate eutectic [8].

3. Di-*p*-tolylsulphone was found to be the most suitable material of those tested. Other sulphones with a high sulphone group content appeared to be unstable under cell test conditions.

4. It can be concluded that 7.5% silicone dioxide binder used during the discharge of the electrochemical couple based on  $\text{Li(Al)/C}_8\text{H}_{10}\text{SO}_2\text{-SiO}_2\text{-2 M LiClO}_4/\text{Ag}_2\text{CrO}_4$  displayed reasonable cell performance in terms of cell capacity and initial voltage drop.

## References

- 1 J. P. Pereira-Romas, R. Messina and J. Perichon, *J. Power Sources*, 16 (1985) 193–204.
- 2 C. Facheur, R. Messina and J. Perichon, *J. Electrochem Soc.*, 136 (1988) 1871–1874.
- 3 J. Sarradin, R. Messina and J. Perichon, *J. Power Sources*, 21 (1987) 157–164.
- 4 A. Tranchant, R. Messina and J. Perichon, *J. Electroanal. Chem.*, 242 (1988) 181–190.
- 5 M. E. Maclean and R. Adams, *J. Am. Chem. Soc.*, 55 (1933) 4685.
- 6 W. Von E. Doering and L. K. Levy, *J. Am. Chem. Soc.*, 77 (1955) 509.
- 7 E. Fromm, *Anneheim*, 253 (1889) 166–174.
- 8 C. O. Giwa, *Mater. Sci. Forum*, 73–75 (1991) 699–706.