

SULFONE-BASED ELECTROLYTES FOR LITHIUM INTERCALATION BATTERIES

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Summary

On account of their physical and chemical properties, sulfones form a very attractive group of organic solvents usable in lithium intercalation batteries. Conductivity measurements performed on various lithium salts in molten dimethylsulfone (DMSO₂) indicate that LiClO₄ and LiAsF₆/DMSO₂ are the most promising electrolytes. The two mol kg⁻¹ LiAsF₆/DMSO₂ shows a conductivity value of about $8 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 170 °C. Discharge-charge curves of some well-known intercalation cathodic materials (V₂O₅, MnO₂, TiS₂, ..) have been plotted for LiAsF₆/DMSO₂ at 100 °C. The cathode utilization of a V₂O₅ electrode has been examined as a function of cycle number. The electrochemical behaviour of V₂O₅ in various sulfone-based electrolytes (dimethylsulfone, dipropylsulfone, sulfolane) is briefly compared at different temperatures. All the results obtained proved that sulfone-based electrolytes offer suitable features for application in lithium intercalation batteries over a wide temperature range (from normal temperature up to about 200 °C).

Introduction

Considerable effort has been focused in recent years on the development of lithium batteries using aprotic solvents and a cathodic active material which can intercalate lithium ions [1 - 3]. Among these cathodic materials transition metal oxides and sulfides appear to be the most promising. One of the major impediments to the development of batteries using such solid-state cathodes is the low discharge rate of the cathode which may be partly ascribed to high solvation effects on Li⁺ ions in aprotic solvents [4]. Thus, the diffusion of Li⁺ ions into the host lattice is made more difficult. Utilization of molten salts like chloroaluminates [5] could provide a solution to this drawback. Though these solvents offer a wide temperature range, their practical application has not been achieved owing to their strong ability to dissolve oxides and sulfides compounds. Moreover, it has been proved that lithium may react with molten chloroaluminates.

Significant progress would be made in overcoming these drawbacks by the use of aliphatic or aromatic sulfones as solvents. Indeed, the sulfones form a potentially attractive group of organic solvents which present a high chemical and thermal stability. In addition, some solvents like dimethylsulfone (DMSO₂) [6] and tetramethylenesulfone (sulfolane) [6, 7] have been proved to give rise to a weak solvation effect on ions and especially on cations.

The only sulfones which have been tested as solvents in L₁ cells are as yet, cyclic sulfones. tetramethylenesulfone (sulfolane) and its alkyl-substituted derivative, 3-methylsulfolane. Indeed, sulfolane and 3-methylsulfolane, used alone or mixed with low viscosity cosolvents (propylene carbonate, dioxolane) have already been proposed for lithium batteries [8 - 12]. Among aliphatic sulfones, the high chemical [13], thermal [14] and electrochemical [15] stability of molten dimethylsulfone would give rise to the successful development of such a solvent in lithium batteries for high temperature application [16].

A part of this work reports experimental results on the conductivity of various molten DMSO₂-based electrolytes containing L₁ salts. The dependence of conductivity on temperature for the most promising electrolytes has been determined. The discharge-charge characteristics of transition metal oxides (V₂O₅, MoO₃, MnO₂, WO₃) and sulfides (TiS₂) in 1 mol kg⁻¹ LiAsF₆/DMSO₂ at 100 °C are briefly described. Furthermore, the cathode utilization (%) of a V₂O₅ electrode in 1 mol kg⁻¹ LiClO₄/DMSO₂ at 150 °C has been studied by cyclic voltammetry as a function of cycle number. Finally the effect of temperature on the electrochemical behaviour of V₂O₅ in molten DMSO₂, sulfolane (TMSO₂) and dipropylsulfone (DPSO₂) is demonstrated.

Experimental

Electrolytes

Dimethylsulfone (DMSO₂), tetramethylenesulfone (TMSO₂) and dipropylsulfone (DPSO₂) were obtained from Janssen. DMSO₂ was first recrystallized in water and then twice from absolute methanol, air dried at 90 °C for 48 h and dried again under vacuum at 30 °C for 12 h. The solvent was then conserved in an argon glove box. Under these conditions, water concentration did not exceed 5×10^{-3} mol kg⁻¹ [15]. Sulfolane (TMSO₂) and DPSO₂ were used without further purification.

Anhydrous lithium perchlorate (Fluka) was dried under vacuum at 190 °C for 12 h. LiAlCl₄ and LiAl₂Cl₇ were prepared by weighing appropriate quantities of LiCl and AlCl₃, and introducing the mixture into a bulb in the presence of pure aluminium wire. The bulb was sealed under vacuum and held at 240 °C for 8 h. AlCl₃ (Fluka) was purified by vacuum sublimation, LiCl (Prolabo) was dehydrated by bubbling pure HCl at 250 °C for 3 h and then kept under vacuum for 5 h at the same temperature. LiCF₃SO₃ and

LiBF_4 were obtained from Fluka and purified by drying under vacuum at 110°C for 12 h. LiAsF_6 was supplied by USS Agri-Chemical and used as received. All the electrolytes were protected from moisture by keeping them in an argon-filled glove box.

Cathodic materials

V_2O_5 (K.K. Laboratories), MoO_3 and WO_3 (Alfa), heat-treated $\gamma\text{-MnO}_2$ (supplied by "La Société SAFT" from Poitiers) and TiS_2 (CERAC) were dried at 120°C under vacuum for 12 h and stored in a dry atmosphere. The graphite for the working electrodes was supplied by Koch-Light (purity 99.999%)

Experimental technique

The working electrode consisted of an aluminium grid, 1 cm in diameter, on which a finely powdered mixture ($\cong 15$ mg) of the cathodic active material and graphite (90% by weight) was pressed. Lithium was used as the reference and auxiliary electrodes. Though we have not undertaken studies on the cycling efficiency of the lithium electrode, we have shown in a previous paper [15] that lithium was chemically stable under our experimental conditions in sulfone-based electrolytes such as $\text{LiClO}_4/\text{DMSO}_2$.

Experiments were performed using about 15 g of electrolyte and a three-electrode galvanostatic device (Tacussel) allowing control of the current during the determination of discharge-charge curves. The instruments used for cyclic voltammetry include a Tacussel Servovit with a PRT 40-1 \times potentiostat and a IG5-LN coulometer.

The electrochemical cell has already been described [16]. The cell was thermostatted with silicone oil whose temperature ($\pm 1^\circ\text{C}$) and circulation were controlled by a Huber T 200 thermostat.

Electroactivity range

Discharge-charge curves and cyclic voltammetric curves recorded with graphite as the working electrode confirmed that no redox process occurred in the voltage window studied (1.5 - 4.5 V *versus* Li/Li^+). The electrochemical reduction of residual water occurs below 1.5 V and the limiting reaction which prevails for anodic curves beyond 4.5 V concerns the electrochemical decomposition of the solvent and/or the oxidation of the aluminium grid.

Results and discussion

Figure 1 shows the conductivity dependence on concentration of various lithium salts in molten DMSO_2 at 150°C . Except for the $\text{LiAsF}_6/\text{DMSO}_2$ and $\text{LiAl}_2\text{Cl}_7/\text{DMSO}_2$ electrolytes, conductivity increases with increasing solute concentration up to about 1 mol kg^{-1} . The best results were obtained for the $\text{LiAsF}_6/\text{DMSO}_2$ electrolyte regardless of LiAsF_6 concentration; moreover, the maximum value of conductivity was never reached

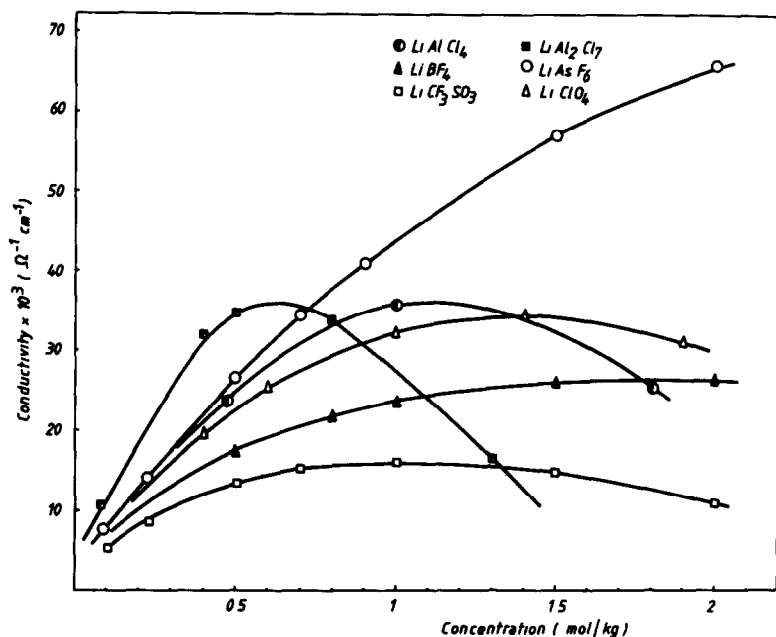


Fig 1 Conductivity of various LiX/DMSO₂ solutions at 150 °C as a function of LiX concentration

TABLE 1

Maximum conductivities ($\times 10^3 \Omega^{-1} \text{ cm}^{-1}$) for various solutions of lithium salts in molten DMSO₂ compared with electrolytes based on propylene carbonate at 60 °C

Solvent	Solute					
	LiClO ₄ ^a	LiCF ₃ SO ₃ ^a	LiBF ₄ ^a	LiAlCl ₄ ^a	LiAl ₂ Cl ₇ ^b	LiAsF ₆ ^c
PC (60 °C)	12	5	8	—	—	27
DMSO ₂ (107 °C)	21	10	18	22	23	41
DMSO ₂ (150 °C)	33	16	27	36	36	66

^a[LiX] = 1 mol kg⁻¹, ^b[LiAl₂Cl₇] = 0.7 mol kg⁻¹, ^c[LiAsF₆] = 2 mol kg⁻¹

in the concentration range studied. The maximum conductivities are summarized in Table 1 for temperatures of 107 °C and 150 °C and compared with those obtained for some common lithium salts in propylene carbonate (PC) at 60 °C.

As with PC electrolytes, LiCF₃SO₃ and LiBF₄ dissolved in molten DMSO₂ are not attractive as electrolytes. LiClO₄ and LiAlCl₄ in molten DMSO₂ look very interesting, whereas LiAsF₆ solutions give the best results. Taking the difficulty of preparation and purification of lithium chloroaluminate salts into account, LiAsF₆/DMSO₂ and LiClO₄/DMSO₂ appear to be the most promising electrolytes.

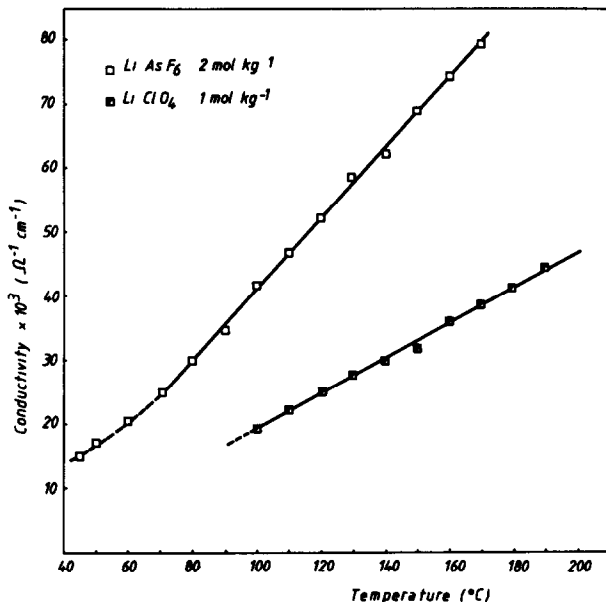


Fig 2 Dependence of conductivity in $2 \text{ mol kg}^{-1} \text{ LiAsF}_6/\text{DMSO}_2$ and in $1 \text{ mol kg}^{-1} \text{ LiClO}_4/\text{DMSO}_2$ electrolytes on temperature

Figure 2 outlines the conductivity (χ) dependence on temperature for $1 \text{ mol kg}^{-1} \text{ LiClO}_4$ and $2 \text{ mol kg}^{-1} \text{ LiAsF}_6$ solutions in molten DMSO_2 . A linear dependence of χ on temperature is shown in both cases, except for LiAsF_6 solutions at a temperature below 70°C . For LiAsF_6 electrolytes, conductivity is found to increase more rapidly when the temperature is raised than in the case of LiClO_4 electrolytes. For example, $2 \text{ mol kg}^{-1} \text{ LiAsF}_6/\text{DMSO}_2$ showed the highest value of conductivity, about $8 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$ at 170°C . For comparison, conductivity in $1.1 \text{ mol kg}^{-1} \text{ LiAsF}_6/\text{DMSO}_2$ at 75°C is about fivefold higher than that in $1.1 \text{ M LiAsF}_6/\text{sulfolane}$ [11] at the same temperature. Having regard to these experimental results, $\text{LiAsF}_6/\text{DMSO}_2$ is the most promising electrolyte among those examined, therefore it was mainly used for the work described below.

Discharge-charge of cathodic materials

All these experiments were performed at 100°C in $1 \text{ mol kg}^{-1} \text{ LiAsF}_6$ solution in DMSO_2 at a constant current density of 1 mA cm^{-2} . Discharge-charge curves recorded under the same current density with graphite as working electrode have confirmed that no redox process occurred in the studied voltage window

V_2O_5

As mentioned in the literature [17, 18], four processes appear during the electrochemical reduction of V_2O_5 (see Fig. 3). The two first processes are quite reversible (better than 95%) according to the known schema.

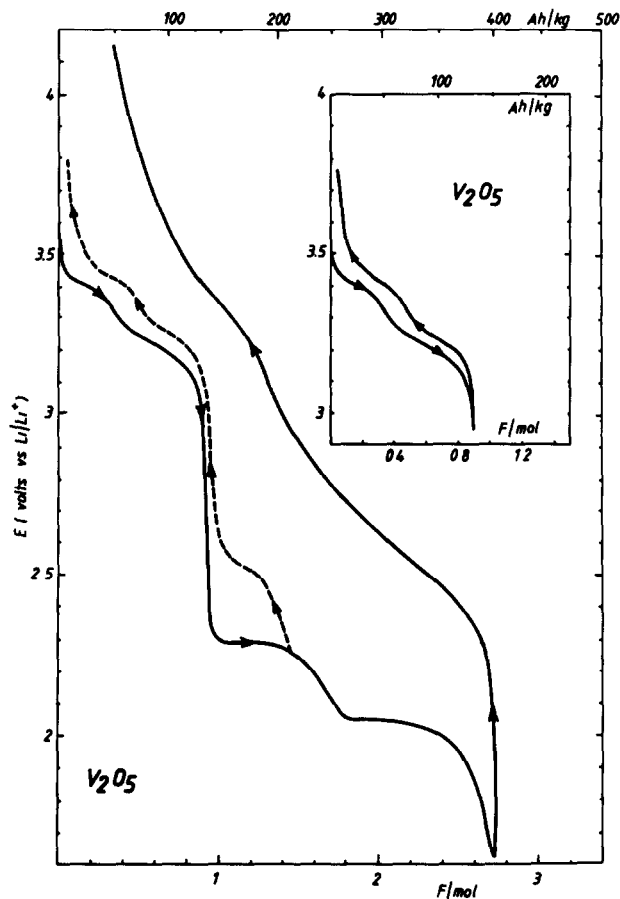
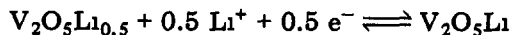
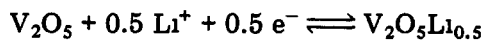


Fig 3 Discharge-charge curves of V_2O_5 in $1 \text{ mol kg}^{-1} \text{ LiAsF}_6/\text{DMSO}_2$ ($1 \text{ mA cm}^{-2} - 100^\circ \text{C}$).



The two further processes require a faradaic yield of $1.5 \text{ F}/V_2O_5$ and the total balance for V_2O_5 reduction is about 2.7 F per mole of oxide. Whereas the last reduction step greatly attenuates the intercalation reversibility of Li^+ on account of excessive and irreversible distortion of the V_2O_5 crystal lattice, the third process does not give rise to an irreversible Li^+ insertion. The reversible Li^+ insertion obtained when discharge is performed beyond the three first steps (until about $1.5 \text{ e}^-/V_2O_5$) has never been observed in conventional organic solvents [17]. Such a reversibility could indicate that solvation effects of DMSO_2 on Li^+ ions are minimized.

MoO₃

The discharge-charge curves of MoO₃ electrodes are shown in Fig. 4. Two steps appear during the first discharge but only the second one is reversible. As shown in previous work [15], the first intercalation process leads to a crystal structure change of MoO₃ (MoO₃Li_x with $x \cong 0.5$) which makes further insertion of Li⁺ ions reversible. The total Li⁺ intercalation according to the reaction $\text{MoO}_3 + xe^- + x\text{Li}^+ \rightarrow \text{MoO}_3\text{Li}_x$ involves 1.5 F per mole of oxide, which is in good agreement with literature data [19, 20]. The yield of the charge process is about 80% of the capacity obtained during the second step of the first discharge, and the second discharge involves about 90% of the capacity recovered in the charge process.

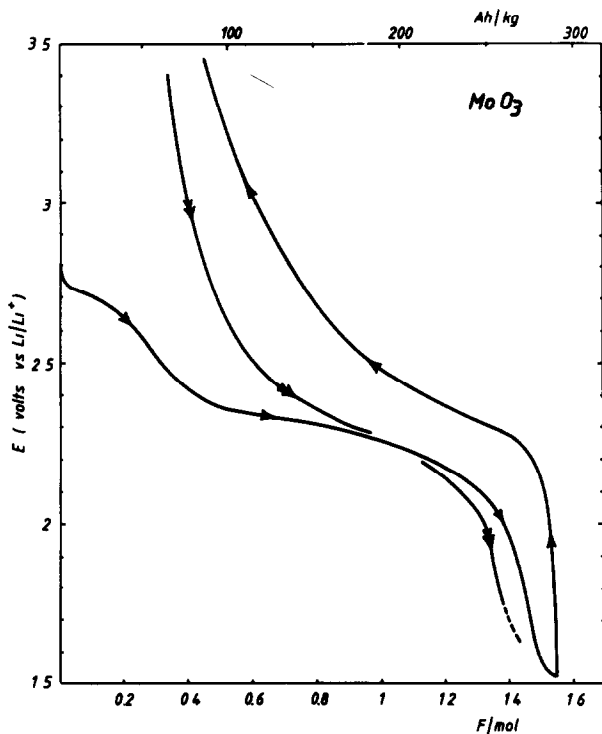


Fig 4 Discharge-charge curves of MoO₃ in 1 mol kg⁻¹ LiAsF₆/DMSO₂ (1 mA cm⁻² - 100 °C)

γ-MnO₂

Typical discharge-charge curves of electrolytic manganese dioxide are shown in Fig. 5. The discharge consists of two reduction steps, about 95% of the faradaic yield required in the discharge is recovered during the reoxidation process. The total faradaic yield of the Li⁺ intercalation into the crystal lattice of MnO₂, according to the equation $\text{MnO}_2 + x\text{Li}^+ + xe^- \rightleftharpoons \text{MnO}_2\text{Li}_x$ [21] is close to 0.6 F per mole of oxide.

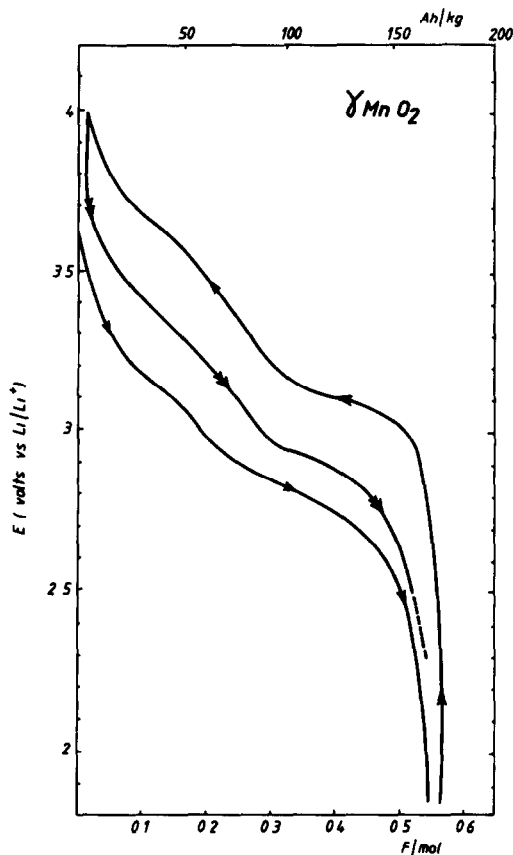


Fig 5 Discharge-charge curves of electrolytic MnO_2 in $1 \text{ mol kg}^{-1} \text{ LiAsF}_6/\text{DMSO}_2$ ($1 \text{ mA cm}^{-2} - 100^\circ \text{C}$)

WO_3

WO_3 galvanostatic discharge-charge curves are shown in Fig. 6. Two voltage plateaux (2.8 V and 2.5 V) appear during the discharge, and only one oxidation step occurs in the charge process. Li^+ intercalation according to the equation $\text{WO}_3 + x\text{Li}^+ + xe^- \rightleftharpoons \text{WO}_3\text{Li}_x$ corresponds to a maximum capacity of $0.1 \text{ Li}^+/\text{WO}_3$ for the first step and to about $0.2/0.3 \text{ Li}^+/\text{WO}_3$ for the second. The total faradaic yield agrees with that obtained by other authors in common organic solvents [22, 23]. Moreover, the total recovered capacity during the first charge is about 80% of the first discharge, whereas the full capacity is recovered when the discharge is performed to a cut-off voltage of 2.6 V.

TiS_2

The reversibility of the most typical positive electrode in lithium organic electrolyte cells, i.e. titanium disulphide, is further demonstrated by

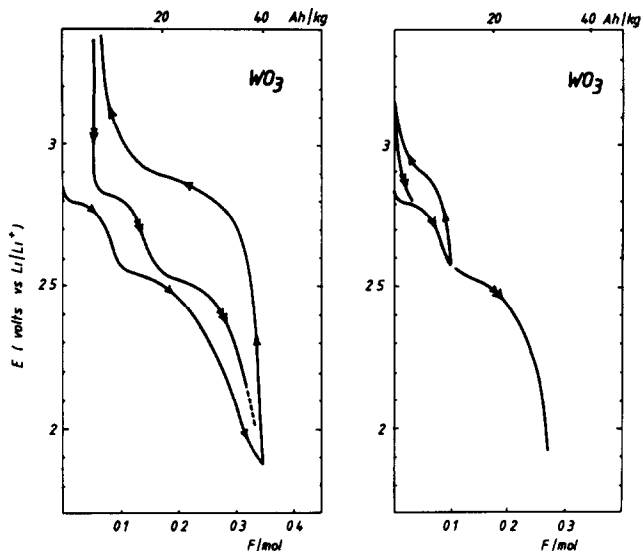


Fig 6 Discharge-charge curves of WO_3 in $1 \text{ mol kg}^{-1} \text{ LiAsF}_6/\text{DMSO}_2$ ($1 \text{ mA cm}^{-2} - 100^\circ\text{C}$)

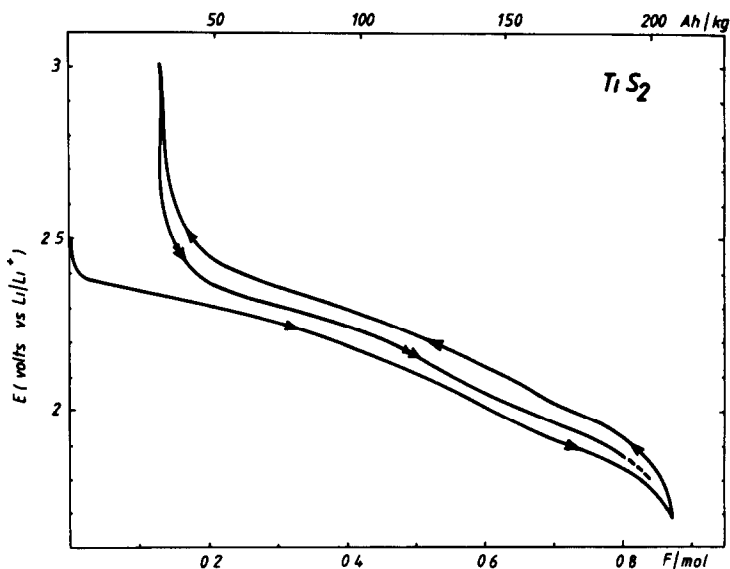


Fig 7 Discharge-charge curves of TiS_2 in $1 \text{ mol kg}^{-1} \text{ LiAsF}_6/\text{DMSO}_2$ ($1 \text{ mA cm}^{-2} - 100^\circ\text{C}$)

the galvanostatic discharge-charge curves shown in Fig. 7. The reversible Li^+ ion insertion into the crystal lattice of TiS_2 occurs with a capacity of about 0.9 F/TiS_2 under our experimental conditions (1 mA cm^{-2} ; cut-off voltage 1.7 V) according to $\text{TiS}_2 + x\text{Li}^+ + xe^- \rightleftharpoons \text{TiS}_2\text{Li}_x$ [5]. The charge process involves 85% of the faradaic yield required during reduction, whereas the second discharge corresponds to 100% of the preceding charge.

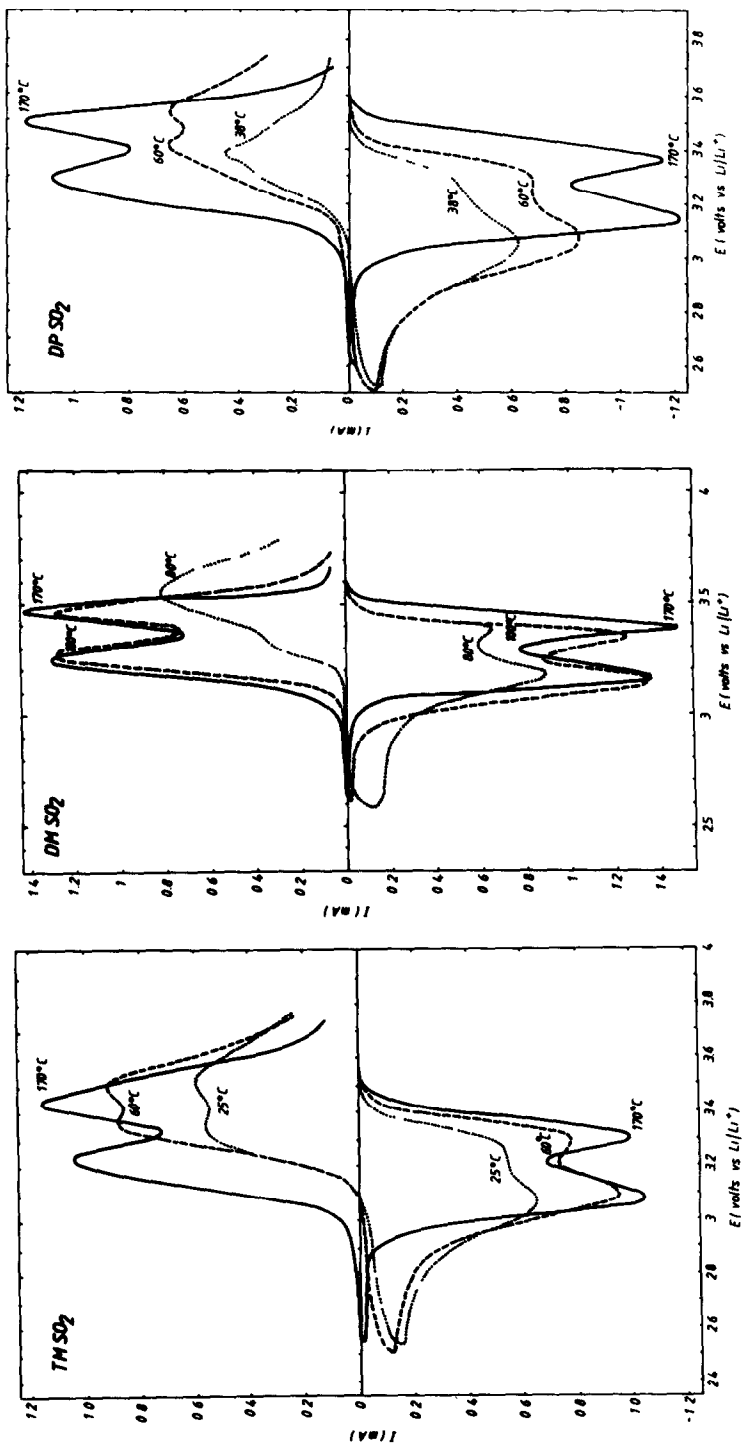


Fig 8 V_2O_5 cyclic voltammetric curves performed between cycling limits of 3.7 V and 2.5 V vs Li/Li^+ in various sulfone-based electrolytes (1.1 mV s^{-1}) TMSO₂ tetramethylenesulfone, DMISO₂ dimethylsulfone, DPISO₂ dipropylsulfone

Cathode utilization of a V_2O_5 electrode

V_2O_5 was evaluated as a rechargeable cathode in 1 mol kg⁻¹ LiClO₄/DMSO₂ at 150 °C using cyclic voltammetry. Cyclic voltammograms were performed within cycling limits of 2.8 V and 3.8 V *versus* Li/Li⁺ (*i.e.* on the two first reversible steps) and run at 1.1 mV s⁻¹. The cathode utilization of the V_2O_5 electrode was examined as a function of cycle number (theoretical capacity 0.193 mA h). The first voltammetric reduction of V_2O_5 resulted in a capacity of 0.80 e⁻/ V_2O_5 . In extended cycling of the oxide, the capacity declines rapidly in the early cycles, diminishing to 85% of the initial value by about the 15th cycle, and slowly decreasing thereafter up to 80% of the initial capacity by about the 150th cycle. With further cycling, the capacity also shows a continued but slow decline, reaching (at the 300th cycle) 50% of the capacity involved in the first discharge. Taking the high discharge rate involved in the cycling test into account (under these experimental conditions, a discharge rate of 4 - 5 C can be reached), it can be seen that reversible incorporation of Li⁺ ions into the V_2O_5 crystal lattice is strongly enhanced in DMSO₂. The total capacity recovered in this cycling test is two hundred times the theoretical capacity related to the initial weight of active material.

V_2O_5 cyclic voltammetric curves in sulfone-based electrolytes

Figure 8 shows the temperature effect on cyclic voltammograms of V_2O_5 electrodes in various 1 mol kg⁻¹ LiAsF₆/sulfone electrolytes. The tested sulfones are sulfolane or tetramethylenesulfone, dipropylsulfone and dimethylsulfone. Only the first two reversible steps in V_2O_5 reduction were examined. Figure 8 shows that the higher the temperature, the faster the rate of lithium intercalation into the V_2O_5 crystal lattice. Whatever the sulfone, electrochemical processes are very well defined, especially for DMSO₂ at temperatures above 100 °C, as we have already reported [15, 16]. Because of its high melting point (109 °C), the viscosity of the DMSO₂-based electrolyte below 100 °C is too high and reduces the sensitivity of electrochemical measurements. Other sulfones such as DPSO₂ and TMSO₂ with low melting points (28 °C and 27 °C respectively) can solve such a problem (Fig. 8). Indeed, it can be seen that TMSO₂ is the most promising sulfone for application at low temperature, whereas Li⁺ intercalation and deintercalation processes are the easiest in DMSO₂ at high temperatures. But even with TMSO₂, the sensitivity of electrochemical measurements is reduced too much at low temperatures by the high viscosity of the solvent.

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