

LOW TEMPERATURE STUDIES ON RECHARGEABLE LITHIUM CELLS

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Summary

Rechargeable lithium cells using intercalating cathodes of TiS_2 , $\alpha\text{-MoS}_3$, and mixed $\alpha\text{-MoS}_3\text{-TiS}_2$ were studied at temperatures from 25°C to -40°C . On the basis of conductivity investigations, LiAsF_6 and LiAlCl_4 electrolytes were selected for use in a binary solvent containing 24.4 mass % 4-butyrolactone in 1,2-dimethoxyethane. The Li/TiS_2 and $\text{Li}/\alpha\text{-MoS}_3\text{-TiS}_2$ cells cycled well at 2 mA cm^{-2} down to -30°C , but at 5 mA cm^{-2} at these very low temperatures, cell capacities were significantly lower. At room temperatures all cells performed slightly better in 1 mol dm^{-3} LiAsF_6 than in 0.8 mol dm^{-3} LiAlCl_4 in 24 mass % 4-BL/DME. However, at temperatures below -10°C the latter electrolyte was found to be superior.

Introduction

A considerable fraction of recent research on rechargeable lithium batteries has focussed on the utilization of intercalating cathodes [1 - 3]. Crystalline titanium disulfide (TiS_2) is a typical example of an intercalating cathode which has excellent reversibility at 25°C and, due to its semi-conducting properties, is capable of sustaining high current densities in excess of 5 mA cm^{-2} [1, 2, 4]. Because of the moderate energy density of TiS_2 , more energetic materials such as amorphous molybdenum trisulfide ($\alpha\text{-MoS}_3$) have been developed [5]. Because $\alpha\text{-MoS}_3$ is a non-conductor, its high energy advantage cannot be realized at either moderate (1 mA cm^{-2}) or high current densities. An important concept evolved in which the inert conductor (carbon black, graphite) required for an $\alpha\text{-MoS}_3$ cathode is replaced by the active TiS_2 , thereby resulting in a highly energetic cathode possessing good reversibility and conductivity. Several studies at room temperature on mixed $\alpha\text{-MoS}_3\text{-TiS}_2$ cathodes have been reported [4, 6], but critical information on behavior at very low temperatures is not available. The major problem with cell performance below -10°C is due to electrolyte resistance. At high electrolyte concentrations ($\geq 1.5\text{ mol dm}^{-3}$) in organic

solvents, electrolyte solutions either solidify or their viscosities become so great that cell resistances are very high and capacities drop to zero.

In the present studies, the behavior of pure TiS_2 , $\alpha\text{-MoS}_3$ and mixed $\alpha\text{-MoS}_3\text{-TiS}_2$ cathodes is reported in a new, highly conductive solvent. A number of solvent mixtures were studied, and the major component of these mixtures was chosen to be an ether because of the recent success in cycling lithium in ethers [7, 8]. As a second solvent, 4-butyrolactone (4-BL) was selected because of its relatively low viscosity and high dielectric constant [9]. An interesting aspect of mixed (binary) solvents containing a low dielectric constant ether and a high dielectric constant solvent such as propylene carbonate (PC) or 4-BL is that a synergistic effect is often observed: *i.e.*, the electrolytic conductivities of several mixtures are much greater than for any of the pure solvents [10 - 13].

Experimental

Chemicals

1,2-Dimethoxyethane (DME) and propylene carbonate (PC) were Burdick and Jackson "Distilled in Glass" products, dried with type 4A molecular sieves and not treated further. 4-Butyrolactone (Aldrich "Gold Label" product) was magnetically stirred with a mixture of 4A and 5A molecular sieves for approximately 10 h with constant bubbling of purified argon, and then fractionated under vacuum. Dimethoxymethane (DMM), (Aldrich Chemicals, 97%) was refluxed for 1 - 2 h over a mixture of 4A and 5A molecular sieves followed by fractionation under a stream of high purity argon. All solvents were stored in an argon-filled Vacuum Atmosphere dry box.

LiAsF_6 (USS Agri Chemicals "Electrochemical Grade") was dried under vacuum at 60 °C for approximately 24 h. Purified LiAlCl_4 was supplied by W. K. Behl of this laboratory, and was prepared as described in ref. 14. TiS_2 (Alfa Chemicals) was received packed under argon with a stated purity of 99+%, and was not treated further. Amorphous MoS_3 was prepared by thermal decomposition of ammonium thiomolybdate as described in ref. 5. All salts were stored in a desiccator over P_2O_5 in the dry box.

Conductivity measurements

Jones' type conductivity cells with cell constants of 5 cm^{-1} were used. The cell constants were determined with aqueous KCl solution. An Altex model RC-18A conductivity bridge was used at a frequency of 3 kHz. Stock solutions were prepared by weight in the dry box, and the Jones' cells filled and removed to the laboratory for measurements at 25 °C to -40 °C. Densities of the stock solutions were measured with a Paar model DMA density meter. Conversions of molal concentrations to volume units were made using density values calculated from $d = d_0 + Am$ where d_0 is the density of the pure solvent, A is a constant, and m is the molality.

Cell studies

Flag-type cathodes were prepared by heat pressing the cathode mix (Table 1) onto an expanded nickel screen and sintering under vacuum at 280 °C. The cathodes were sealed in Celgard 2400 separator bags and wrapped with Li anodes. This two-electrode assembly was sealed in an ST-24/40 joint which was then fitted into a Pyrex H-cell. A lithium strip served as the reference electrode. The solvent used in all cell studies was the binary mixture containing 24.4 mass % 4-BL in DME. The electrolytes used were LiAsF_6 and LiAlCl_4 at concentrations of 0.8 - 1.0 mol dm^{-3} . All solutions and cell fabrication were carried out in the dry box. The sealed cells were removed from the dry box and placed in a Tenny environmental chamber.

TABLE 1

Composition of cathodes
Composition in mass %.

Cathode	TiS ₂	MoS ₃	Carbon*	Teflon
TiS ₂	83	—	8.5	8.5
a-MoS ₃	—	70	18	12
a-MoS ₃ -TiS ₂	20	60	10	10

*Shawinigan Black.

Cells were cycled at constant current using a PAR Model 173 potentiostat with a 276 interface. The potentiostat was controlled with an HP-85 microcomputer, and anode *vs.* Li (ref.) potentials were measured with a Fluke 8502A digital voltmeter which was also controlled by the microcomputer.

Results

Figure 1 shows the electrolytic conductivities of 1 mol dm^{-3} LiAsF_6 and LiAlCl_4 in binary solvent mixtures of 4-BL/DME and PC/DMM. The curves all show a maximum or "synergistic" effect which originates from complex interactions involving viscosities, dielectric constant, and ion-solvent interactions [10 - 13, 15]. PC/DMM mixtures were rejected for continued study because of the significantly lower conductivity of LiAsF_6 in these mixtures. For the more conductive 4-BL/DME mixtures, we selected the solvent composition of 24.4 mass % 4-BL in DME for application to cell studies. In the low temperature studies, we noticed that at -15 °C LiAsF_6 solutions became highly viscous, and that small crystals of the salt were becoming visible. Therefore we also investigated the effect of decreasing the salt concentration. Table 2 shows that 0.8 mol cm^{-3} LiAsF_6 and LiAlCl_4

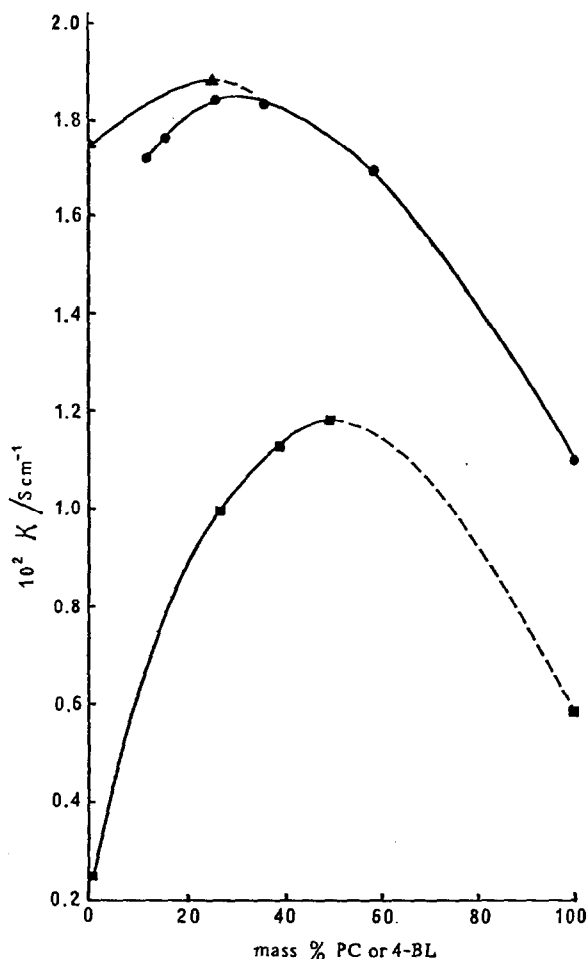


Fig. 1. Electrolytic conductivities of 1 mol dm^{-3} solutions in nonaqueous solvent mixtures. ▲, LiAlCl_4 in 4-BL/DME mixtures; ●, LiAsF_6 in 4-BL/DME mixtures; ■, LiAsF_6 in PC/DMM mixtures.

have excellent conductivities down to -50°C , and this electrolyte was also used in the experimental cell studies described below.

Figures 2 - 4 show cell discharge behavior under various conditions. All potentials recorded in these Figures are cathode *vs.* the Li reference. Figure 2 compares the room temperature discharge of the three types of cathodes at the moderately high current density of 5 mA cm^{-2} and shows the enhanced properties of the mixed $\alpha\text{-MoS}_3\text{-TiS}_2$ cathode. The mixed cathode cell was cycled at 2 mA cm^{-2} down to -30°C and typical results are shown in Fig. 3. Attempts to discharge this cell at 5 mA cm^{-2} at, and below, -30°C resulted in negligible cell capacity, and we assume this to be due to the high resistivity of both the cathode and electrolyte. The Li/TiS_2 cell was cycled at 2 mA cm^{-2} down to -40°C (Fig. 4), but at 5 mA cm^{-2} at this temperature, cell

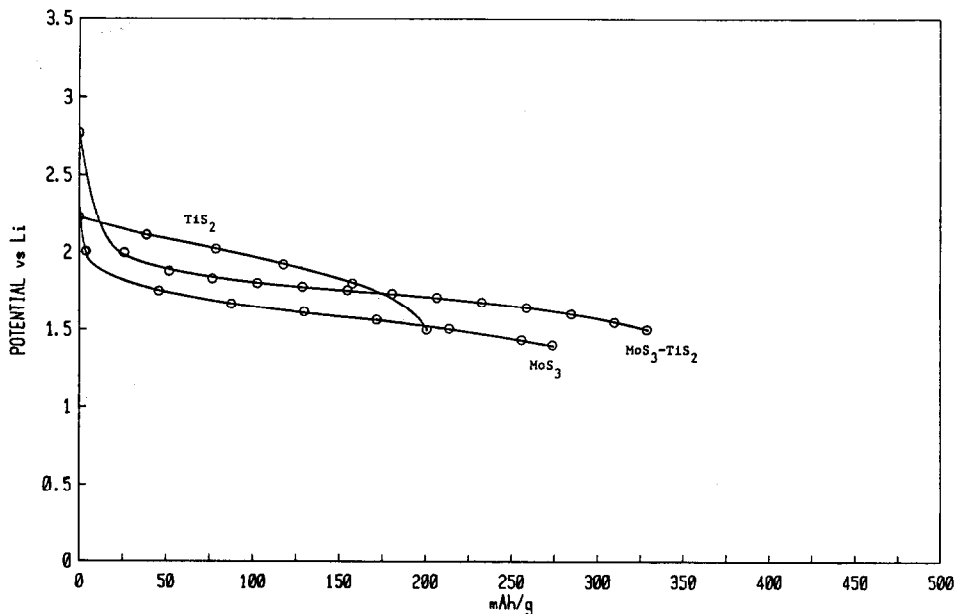
TABLE 2

Electrolytic conductivities of 0.8 mol dm⁻³ solutions*

<i>T</i> (°C)	LiAsF ₆ (κ/S cm ⁻¹)	LiAlCl ₄ (κ/S cm ⁻¹)
25	0.018	0.0185
0	—	0.0122
-10	0.0097	0.0101
-20	0.0070	0.0082
-30	0.0044	0.0064
-40	0.002**	0.0049
-50	—	0.0034

*Solvent is 24.4 mass % 4-BL in DME.

**Extrapolated value.

Fig. 2. Discharge curves at 25 °C and 5 mA cm⁻² for different cathodes in 1 mol dm⁻³ LiAsF₆ in BL/DME.

capacities were close to zero. Again we attribute this behavior to a combination of cathode and solution resistance. Numerical data for results at 2 mA cm⁻² are compared in Table 3.

Discussion and conclusion

Our data suggest that at room temperature, all cells perform slightly better in 1 mol dm⁻³ LiAsF₆ than in 0.8 mol dm⁻³ LiAlCl₄. However, at low

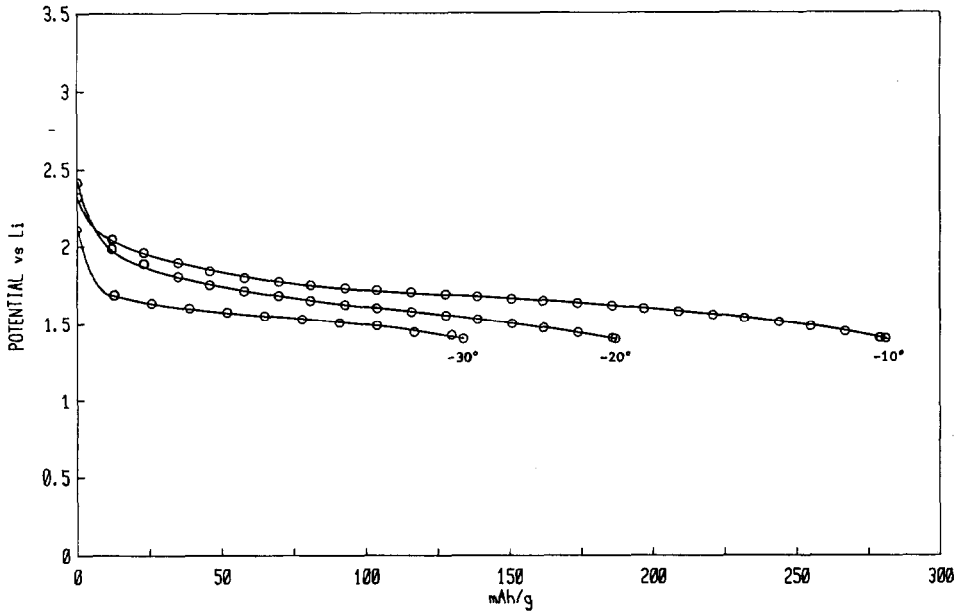


Fig. 3. Discharge curves at 2 mA cm^{-2} and different temperatures for $\text{MoS}_3\text{-TiS}_2$ cathode in $0.8 \text{ mol dm}^{-3} \text{ LiAlCl}_4$ in BL/DME.

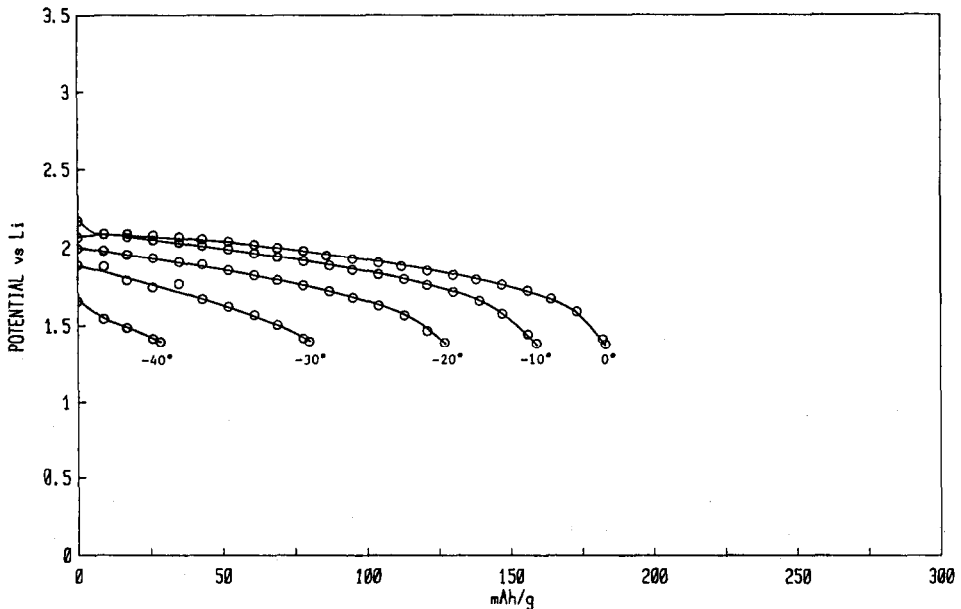


Fig. 4. Discharge of Li/TiS_2 cell at 2 mA cm^{-2} at different temperatures and in an electrolyte of $0.8 \text{ mol dm}^{-3} \text{ LiAlCl}_4$ in BL/DME.

temperatures the latter electrolyte is clearly superior. In addition, a Li/TiS_2 cell in $0.8 \text{ mol dm}^{-3} \text{ LiAlCl}_4$ was subjected to over 40 full 2.0 mA cm^{-2} discharge cycles with only small capacity losses, thus demonstrating encour-

TABLE 3

2 mA cm⁻² discharge data in 24.4 mass % 4-BL/DME

Cathode	T (°C)	Solute	W h/kg (active material)	e ⁻ /equiv. (active material)
TiS ₂	25	1M LiAsF ₆	413	0.86
a-MoS ₃	25	1M LiAsF ₆	754	2.99
a-MoS ₃ -TiS ₂	25	1M LiAsF ₆	723	2.30
TiS ₂	25	0.8M LiAlCl ₄	358	0.77
a-MoS ₃	25	0.8M LiAlCl ₄	723	2.88
a-MoS ₃ -TiS ₂	25	0.8M LiAlCl ₄	644	2.16
TiS ₂	-10	1M LiAsF ₆	364	0.79
a-MoS ₃ -TiS ₂	-10	1M LiAsF ₆	389	1.40
TiS ₂	-10	0.8M LiAlCl ₄	280	0.66
a-MoS ₃ -TiS ₂	-10	0.8M LiAlCl ₄	481	1.70
TiS ₂	-30	0.8M LiAlCl ₄	130	0.33
a-MoS ₃ -TiS ₂	-30	0.8M LiAlCl ₄	209	0.81
TiS ₂	-40	0.8M LiAlCl ₄	42	0.12

aging cyclability of lithium in LiAlCl₄ containing electrolytes. At room temperatures, both the Li/TiS₂ and Li/a-MoS₃-TiS₂ cells cycled well at 5.0 mA cm⁻², but at and below -30 °C, cell capacities fell significantly. However, the same cells when cycled at 2.0 mA cm⁻² showed far improved low temperature performance, with the Li/a-MoS₃-TiS₂ cells showing the highest capacities. The major cause of failure at 5.0 mA cm⁻² is the high internal resistance of the solid cathodes, and current investigations are addressing this problem. Although very low temperature performances of these cells at high rates are currently only nominal in view of practical applications, these results are certainly encouraging when compared with other results [1 - 8] for cells based on comparable characteristics and cycling regimes.

Acknowledgement

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