

THE USE OF THE REACTIVE ETHER, TETRAHYDROFURAN (THF), IN RECHARGEABLE LITHIUM CELLS

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Summary

The usefulness of tetrahydrofuran (THF) as a cosolvent with 2-methyl-tetrahydrofuran (2-Me-THF)/LiAsF₆ for improving the low temperature rate capability of rechargeable Li cells has been explored. Lithium-titanium disulphide cells utilizing 2-Me-THF/LiAsF₆ blended with 15 - 50 vol% THF have shown substantially improved rate characteristics at 0 and -10 °C. In addition, the Li electrode in such cells has exhibited practically useful cycling efficiencies.

Introduction

Practical success with normal temperature rechargeable Li cells largely depends upon the availability of suitable electrolytes for recharging the Li electrode. Considerable progress has been made recently [1 - 3]. There are at least two electrolyte systems in which the Li electrode can be recharged with high efficiency. These are the 2-Me-THF/LiAsF₆ [4 - 6] and 1,3-dioxolane/LiClO₄ [7] solutions. Unfortunately, the 1,3-dioxolane/LiClO₄ system has shown a tendency to detonate upon impact and, therefore, has been abandoned [8]. The present electrolyte of choice is 2-Me-THF/LiAsF₆ [9 - 11].

Lithium cycles very well in 2-Me-THF/LiAsF₆(1.4M) [4 - 6], typical F.O.M._{Li}'s (F.O.M._{Li} = total accumulated cell capacity/theoretical Li capacity) being 30 - 40. However, the solution is impracticable below 0 °C [6], because of a tendency of the (2-Me-THF)_n·LiAsF₆ solvate to crystallize, causing an increase in solution viscosity and a decrease in solution conductivity. A possible approach to improve the low temperature performance of 2-Me-THF/LiAsF₆ would be to use a cosolvent(s) which normally by itself is reactive with Li, but otherwise provides electrolyte solutions with a number of attractive properties required for secondary Li cells. An example is tetrahydrofuran (THF). It forms highly conducting solutions with LiAsF₆, the specific conductivity of a 1.5M LiAsF₆ solution at 25 °C being 1.60×10^{-2} (Ω cm)⁻¹. This solution maintains good conductivity from room tem-

perature down to -40°C . Tetrahydrofuran/ LiAsF_6 solutions also exhibit relatively good thermal stability. However, THF is reported to react with Li, and its solutions do not cycle Li well [12]. Despite this reactivity, when THF is used as a cosolvent with 2-Me-THF/ LiAsF_6 , the synergistic effects of the blended solution may help retard the kinetics of the Li/THF reaction. The data presented in this paper indicate practical utility for 2-Me-THF/ LiAsF_6 blended with 15 - 50 vol% THF.

Experimental

All experiments were conducted in the absence of air and moisture in a Vacuum-Atmospheres Corporation dry box equipped with a Model He-493 Dri-Train.

The purification of THF and 2-Me-THF, and preparation of LiAsF_6 solutions were carried out as described previously [5, 6, 12]. Hermetically sealed Li/ TiS_2 cells having 0.68 A h theoretical ($1\text{ e}^-/\text{TiS}_2$) capacity were used as test vehicles for electrolyte evaluation. The cells were identical with those described previously [6]. The evaluation included extensive galvanostatic cycling at various Li charge densities, rate/capacity characterization at 25, 0 and -10°C , and storage experiments at 50°C . Data collection and retrieval were undertaken with a Bascom-Turner Series 8000 Recorder equipped with microprocessor accessories. The cycling efficiency of the Li electrode was determined using the procedure described in ref. 6.

The conductivity of solutions was measured in a Jones and Bollinger-type conductivity cell. The cell was thermostatted in a Tenney Environmental Chamber prior to conductivity measurements. The solution resistance was measured with a YSI Model-31 (Yellow Springs Instruments Co., Yellow Springs, OH) conductivity bridge.

The following solutions have been evaluated: 2-Me-THF(85 vol%):THF(15 vol%)/ LiAsF_6 (1.35M); 2-Me-THF(70 vol%):THF(30 vol%)/ LiAsF_6 (1.3M); 2-Me-THF(50 vol%):THF(50 vol%)/ LiAsF_6 (1.5M). These solutions are designated, Blend 85-THF, Blend 70-THF and Blend 50-THF, respectively. The results are compared with those of cells containing 2-Me-THF/ LiAsF_6 (1.4M).

Results and discussion

Conductivity of solutions

Figure 1 depicts the conductivities, measured at 25, 0 and -20°C , of THF blended 2-Me-THF/ LiAsF_6 (1.5 M) solutions for several compositions (volume per cent.) of the two solvents. The conductivity at all three temperatures decreases in a linear fashion on going from 100 vol% THF to 100 vol% 2-Me-THF. In solutions with ≤ 10 vol% THF, the LiAsF_6 -solvate crystallizes at -20°C , resulting in considerably reduced conductivities. However, blends containing > 30 vol% THF exhibit conductivities at -20°C which are higher

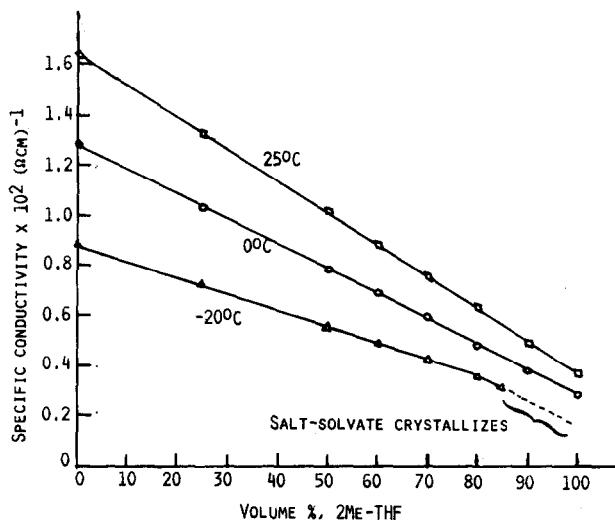


Fig. 1. Specific conductivity vs. vol% of 2-Me-THF in 2-Me-THF/THF/LiAsF₆(1.5M) electrolytes at various temperatures.

than the room temperature conductivity of 2-Me-THF/LiAsF₆(1.5M). The implication of this for rechargeable Li cells is obvious.

The lower conductivity of 2-Me-THF/LiAsF₆(1.5M) than that of THF/LiAsF₆(1.5M), despite the higher basicity and Li⁺-complexing ability of 2-Me-THF, has been attributed [5] to the 2-methyl substituent on the oxolane ring which perturbs the efficient packing of solvent molecules about Li⁺, leading to an increased number of contact ion pairs. It appears that below 0 °C the LiAsF₆·(2-Me-THF)_n complex has a rather low solubility in 2-Me-THF. In a THF(15 vol%):2-Me-THF(85 vol%)/LiAsF₆(1.5M) solution, the amount of THF is ~1.2 moles per mole of Li⁺. In this blend, probably an LiAsF₆·(solvent)_n complex with at least one THF per Li⁺, exhibiting higher solubilities in 2-Me-THF at low temperatures, is formed. In blends with larger amounts of THF, complexes with more than one THF per Li⁺ may also be present.

Based on what we know about the reactivity of Li with THF/LiAsF₆ solutions [12], it seems that blends with practical utility in rechargeable Li cells would be those containing 15 - 50 vol% THF.

Rate/capacity behavior of Li/TiS₂ cells

The significant effect expected with THF-blended 2-Me-THF/LiAsF₆ solutions, by comparison with 2-Me-THF/LiAsF₆, is improved rate capability for cells, especially at low temperatures. The data presented in Fig. 2 indicate that this, indeed, is possible. The 2-Me-THF/LiAsF₆(1.4M) cell exhibited practically no capacity at -10 °C, even at the low discharge rate of 0.5 mA/cm². On the other hand, the Blend 50-THF cell, discharging at 2 mA/cm² at -10 °C, exhibited a capacity equivalent to 70% of the theoretical cell capacity. The -10 °C capacities of the Blend 30-THF and Blend 15-THF

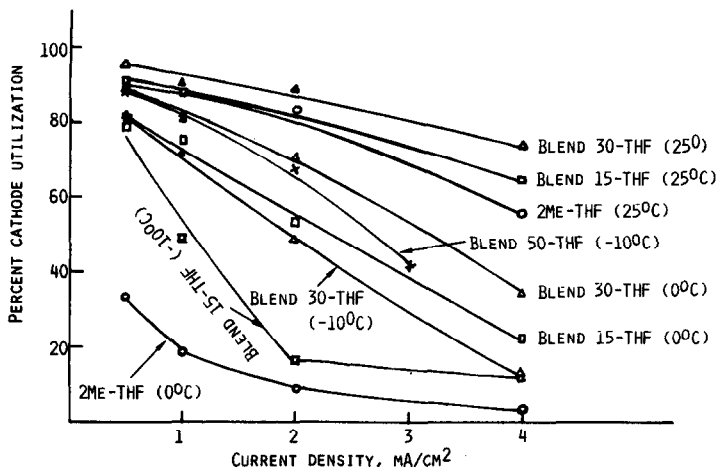


Fig. 2. Rate/capacity data for Li/TiS₂ cells at 25, 0 and -10 °C.

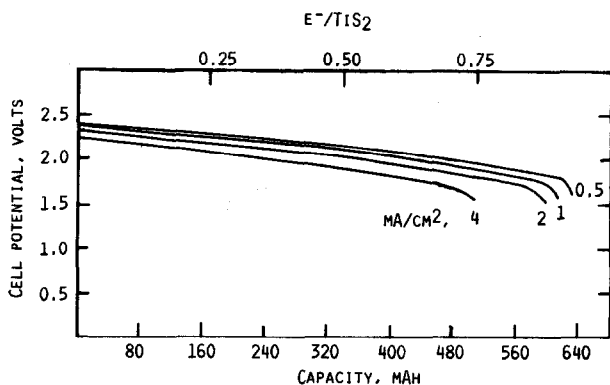


Fig. 3. Cathode utilization vs. current density in a Li/Blend 70-THF/TiS₂ cell at 25 °C.

cells at 2 mA/cm² were 50 and 16% of the theoretical cell capacity. These higher rate capabilities of cells utilizing the THF blends seem to correlate with the solution conductivities.

At room temperature, the cells with all of the solutions exhibited similar rate capabilities for each current density ≤ 2 mA/cm². At higher current densities, however, the THF blends yielded slightly better utilization; the capacity being higher the higher the solution conductivity. The discharges at various current densities for a Blend 30-THF cell at room temperature are shown in Fig. 3.

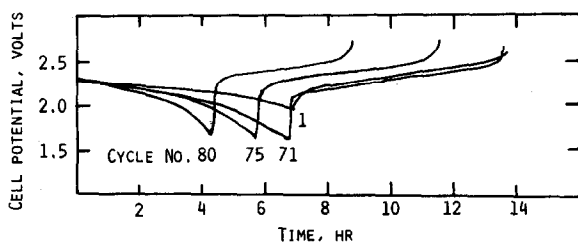
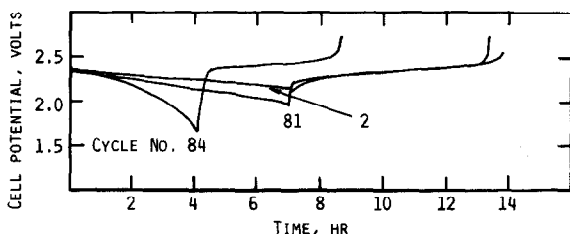
Lithium cycling efficiency

The cycling efficiencies of the Li electrode achieved in cells utilizing the various blends are summarized in Table 1. The data correspond to Li charge densities of 7 and 10.5 mA h/cm². Typical cycling curves are given

TABLE 1

Lithium cycling efficiency in Li/TiS₂ cells with 2-Me-THF/LiAsF₆ and related solutions

Electrolyte	Current density (mA/cm ²)	Li charge density (mA h/cm ²)	Li cycling efficiency (F.O.M. _{Li})
2-MeTHF/LiAsF ₆ (1.4M)	{ 1	7	40
	{ 1.5	10.5	32
THF/LiAsF ₆ (1.5M)	{ 1	7	3
	{ 1.5	10.5	23
Blend 15-THF	{ 1	7	20
	{ 1.5	10.5	14
Blend 30-THF	{ 1	7	13
	{ 1.5	10.5	13
Blend 50-THF	{ 1	7	14
	{ 1.5	10.5	14

Fig. 4. Typical cycling curves of a Li/Blend 85-THF/TiS₂ cell. Current density, 1.5 mA/cm². Li charge density, 10.5 mA h/cm². Theoretical Li, 45.5 mA h/cm².Fig. 5. Typical cycling curves of a Li/Blend 70-THF/TiS₂ cell. Current density, 1 mA/cm². Li charge density, 7 mA h/cm². Theoretical Li, 45.5 mA h/cm².

in Figs. 4 and 5. The cycling ability of the Li electrode is reduced by a significant fraction by the introduction of 15 vol% THF into 2-Me-THF/LiAsF₆. However, on going from blends with 15 - 50 vol% THF, the reduction in cycling efficiency owing to added THF does not follow a linear relationship. Thus, the Li cycling efficiency in both the Blend 50-THF and the Blend 30-THF cells is practically the same. It appears that the 2-Me-THF/LiAsF₆ solution properties, which enable high efficiency Li cycling in that solution, dominate the solution properties of the THF/2-Me-THF blends.

The F.O.M._{Li}'s achieved in the blended solutions are in the range useful for practical considerations. Cells with attractive low temperature character-

istics, although with some sacrifice in cycle life, would be of considerable practical interest.

Cell storage at 50 °C

A knowledge of the storage capability of the cells at elevated temperatures is essential for practical consideration of the solution. The data in Table 2 indicate little effect of storage at 50 °C on the cyclability of the cells. The exceptional storageability shown by 2-Me-THF/LiAsF₆ cells is in agreement with the good thermal stability of the electrolyte [5]. Prior studies [5] of the thermal stabilities of THF/LiAsF₆ solutions in the presence of Li at 70 °C have shown them to be considerably less stable than 2-Me-THF/LiAsF₆. The present findings in cells with the THF blends indicate that either the degradation reactions involving THF are significantly suppressed at 50 °C or that the favorable properties of 2-Me-THF help retard the kinetics of these Li-THF reactions. Our prior studies [6] with 10 vol% THF-blended diethyl ether (DEE)/LiAsF₆ solutions show that the Li cycling efficiency of cells stored at 50 °C was markedly lower than that of fresh cells. We ascribed that to the thermal instability of DEE/LiAsF₆ as well as to the increased solubility in polar THF/DEE blends of the LiOC₂H₅ film on the Li electrode surface. A chemically different Li surface film, probably with low solubility properties, is indicated in 2-Me-THF/LiAsF₆-based solutions.

Conclusions

The low temperature rate capabilities of rechargeable Li cells with 2-Me-THF/LiAsF₆(1.4M) can be improved by blending the solution with THF. Cells utilizing the blended solutions, despite the reactive THF component, cycle with practically useful Li electrode cycling efficiencies. This is believed to be due to a dominance of the desirable properties of 2-Me-THF/LiAsF₆ helping to retard the kinetics of the Li-THF reactions. Cells utilizing

TABLE 2

Storage test results of Li/TiS₂ cells

Electrolyte	Days stored at 50 °C	OCV		Capacity (e ⁻ /TiS ₂) at 1 mA/cm ²		Li cycling efficiency* (F.O.M. _{Li})
		Initial (V)	Final (V)	Typical fresh cell	After storage	
2-Me-THF/LiAsF ₆ (1.4M)	33	2.4	2.4	0.90	0.90	35
Blend 15-THF	17	2.4	2.4	0.92	0.84	20
Blend 30-THF	17	2.4	2.4	0.95	0.90	13.5

*Cycling efficiency obtained at 1 mA/cm² and 7 mA h/cm².

the blended solutions have also shown appreciable storage capabilities at 50 °C, indicating practical utility for these solutions.

A general conclusion of the present study is that electrolytes based on mixed solvents at proper ratios may exhibit more desirable solution properties than solutions based on the individual solvents. Our results also indicate that many of the so-called reactive solvents may be useful for improving the solution properties of less reactive electrolytes.

Acknowledgement

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