

PRACTICAL RECHARGEABLE LITHIUM BATTERIES

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Summary

Several mixed ether electrolyte solutions containing three major solvent components, designated as ternary electrolytes, have been identified for improved low-temperature performance of Li/TiS₂ secondary cells. C-size and prismatic Li/TiS₂ cells having capacities from 2 A h to 8 A h have been built and tested. These cells could be discharged with appreciable capacity at very low temperatures which, depending on the electrolyte, included -40 °C. The C-size Li/TiS₂ cells exhibited more than 150 deep discharge/charge cycles. The electrical characteristics of several AA-size Li secondary cells are compared.

Introduction

There is a great deal of current interest in the development of ambient temperature, rechargeable lithium batteries for a variety of military and civilian applications. This activity represents the culmination of a number of key advances in the basic science and engineering relevant to the technology. Recent advances include: electrolyte solutions which allow the cycling of the secondary Li electrode with high efficiency [1, 2] and discharge of secondary Li cells at very low temperatures [1], novel materials for electrolytes and electrodes spawning new battery systems [3, 4], and superior cell fabrication techniques which allow the construction of high quality cells [5, 6]. We have achieved both high efficiency Li cycling and superior discharge performance over a range of ambient temperatures, including -30 °C, in Li/TiS₂ cells with the use of a mixed ether electrolyte. It comprises a solution of LiAsF₆ in a mixture of tetrahydrofuran (THF) and 2-methyltetrahydrofuran (2-MeTHF) [1]. In order to improve the low temperature performance of Li/TiS₂ cells down to -40 °C, we have investigated LiAsF₆ solutions derived from three component (ternary) solvent mixtures. Initial results, including cycling and low temperature discharge performance for Li/TiS₂ cells containing ternary ether electrolytes, have

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been reported [7]. Conductivity and Li/TiS₂ cell cycling data recently obtained for several new ternary electrolyte solutions are presented in this paper. We also report here on the performance characteristics of several Li/TiS₂ cell and battery prototypes having capacities from 2 to 8 A h. In addition, the electrical characteristics of several AA-size secondary Li cells are tabulated in order to bring into focus the state-of-art in the technology.

Experimental

Tetrahydrofuran (THF), distilled in glass, was obtained from Burdick and Jackson. Ethylene carbonate (EC), methyltetrahydrofurfuryl ether (98%; MTE), 2-methyltetrahydrofuran (2-MeTHF) and 2-methylfuran (2-MeF) were from Aldrich. Alfa-Ventron supplied the 2-methoxytetrahydrofuran (99%; MeOT) and the 2-methoxy-1,3-dioxolane (99%, MeOD). Dimethoxymethane (DMM) was also obtained from Aldrich. Ethylene carbonate was stored over molecular sieves at 50 °C prior to vacuum distillation. The other solvents were distilled from CaH₂ under a blanket of flowing Ar. The middle 80% fraction was collected for all distillations. THF and 2-MeTHF were also passed through activated neutral alumina (Fisher, Beckman Activity 1). THF, 2-MeTHF and 2-MeF were all stored over Li in the dry box until use. The LiAsF₆ electrolyte solutions were prepared with cooling to minimize decomposition [8].

Conductivities of a number of ternary solutions were determined. Each ternary had 50 vol.% THF, 20 vol.% 2-MeTHF and 30 vol.% of the third component. Conductivities were measured as described previously [1]. Li/TiS₂ laboratory test cells and cycling techniques used for electrolyte evaluation have been described previously [1]. All solutions contained ~1 vol.% 2-MeF as an additive [1].

The TiS₂ electrodes were prepared from TiS₂ powder synthesized using a vapor transport technique. The composition of the TiS₂ cathode mix used in preparing electrodes for C-size cells was 84 wt.% TiS₂, 8 wt.% C and 8 wt.% Teflon [1]. These electrodes had a thickness of ~0.06 cm and an area of ~200 cm² for both sides. In order to assemble the C-size cells, the electrode package, consisting of the TiS₂ cathode, Celgard 2400™ separator, and Li foil anode, was spirally wound, with Li forming the outer layer of the "jelly roll", and inserted into the C-cell can. The cells were vacuum filled with the 2-MeTHF:THF/LiAsF₆ (1.5 M) mixed ether electrolyte (hereafter referred to as the standard electrolyte) described previously [1]. A few cells were also tested with other electrolyte solutions which are identified in the Results and Discussion Section. The cells were hermetically sealed.

Prismatic cells having capacities ranging from 2 to 8 A h were also built and tested. The design of a 2 A h cell has been described previously [5]. These cells formed the building blocks of a 2 A h, 24 V rechargeable Li/TiS₂ battery which has the same physical size as the BB-557/U Ni-Cd and the BA-5557/U Li/SO₂ batteries.

The larger prismatic cells had nominal capacities of 6 and 8 A h, respectively. They were fabricated in a stainless steel cell-case measuring 6.12 cm × 6.04 cm × 1.65 cm. The electrode stack consisted of a number of alternating, parallel plate Li and TiS₂ electrodes, as in our 5 A h Li/TiS₂ cells, reported previously [9]. The 6 A h and 8 A h cells were designed to yield 50 and 10, 100% depth of discharge cycles, respectively, and were intended as the building blocks of a 50 cycle or a 10 cycle, 24 V battery having the same physical size as the BB-5590/U Li/SO₂ or the BB-590/U Ni-Cd batteries.

All cells were cycled under constant current conditions using standard cycling equipment.

Results and discussion

Conductivities of solutions

Conductivities of the various ternary electrolytes, each containing 1.0 and 1.5 mole l⁻¹ (M) LiAsF₆, are presented in Table 1. The data have been obtained at 20, 0, -20 and -40 °C. Although not shown in Table 1, conductivities, in all cases, were also obtained for 0.5 and 2.0 M LiAsF₆ solutions. At 20 °C, the highest conductivity for all ternary electrolytes, except for MeOT, was found for the 1.5 M LiAsF₆ solution. For MeOT ternary, a 2.0 M LiAsF₆ solution exhibited higher conductivity at 20 °C than one

TABLE 1
Conductivities of ternary solutions

	Ternary solvent mixture ^(a)	LiAsF ₆ concentration (mole litre ⁻¹)	Conductivity ((ohm·cm) ⁻¹ × 10 ³)			
			20 °C	0 °C	-20 °C	-40 °C
i.	THF:2-MeTHF:MeOT	1.0	4.17	3.63	2.85	1.29
		1.5	6.47	5.47	4.20	2.79
ii.	THF:2-MeTHF:MeOD	1.0	7.75	6.77	5.28	3.47
		1.5	9.55	8.22	6.03	3.87
iii.	THF:2-MeTHF:MTE	1.0	8.77	6.11	0.57 ^(c)	0.15 ^(c)
		1.5	11.41	8.08	5.12	0.82 ^(c)
iv.	THF:2-MeTHF:DMM ^(b)	1.0	9.30	7.90	6.31	4.15
		1.5	10.7	8.64	6.24	3.87
v.	THF:2-MeTHF:EC	1.0	10.5	9.22	6.11	2.58 ^(c)
		1.5	13.1	9.13	5.71	(c)

^(a)In all mixtures, THF is 50 vol.%; 2-MeTHF is 20 vol.% and the third component is 30 vol.%.

^(b)These data, given previously [7], are presented here for comparison.

^(c)Solid phase formation.

containing 1.5 M LiAsF_6 . In the temperature range 0 to -40°C , however, the maximum conductivity in the MeOT ternary system was exhibited by the 1.5 M LiAsF_6 solution. For MeOD ternary, the conductivity maximum was found in the 1.5 M LiAsF_6 solution over the whole range of 20 to -40°C . The behavior of the other solutions varied. The conductivities of the 1.5 and 1.0 M LiAsF_6 DMM ternary solutions were about the same at -20 and -40°C . On the other hand, negligible conductivities were measured for the 1.0 M LiAsF_6 MTE ternary at -20 and -40°C , and the 1.5 M LiAsF_6 MTE ternary at -40°C . Indeed, the formation of a solid phase was observed at -20 and -40°C in the MTE ternary containing the lower concentration of LiAsF_6 . The 1.5 and 1.0 M LiAsF_6 EC ternary solutions exhibited practically the same conductivity at -20°C , while solid phases appeared in both of these solutions at -40°C . At this latter temperature, the 1.0 M LiAsF_6 EC ternary exhibited higher conductivity than its 1.5 M LiAsF_6 counterpart.

Room temperature conductivity does not appear to be an indicator of how well a solution will behave at very low temperatures. Thus, although EC and MTE ternaries are the two highest conductive solutions at room temperature, they showed phase separations and lower conductivities at -40°C compared with MeOT, MeOD and DMM ternaries. The latter three ternaries exhibited good solution fluidity and high conductivity at -40°C for the range of LiAsF_6 concentrations of 0.5 - 2.0 M. Li/TiS_2 cells utilizing MeOT, MeOD or DMM ternary could be discharged with appreciable capacity at -40°C . The differences observed in the low temperature properties of the mixed electrolytes may be ascribed to the structures of the Li^+ -solvates existing in these mixed solutions.

Li cycling efficiency

The Li electrode cycling efficiencies were determined in all five ternary electrolyte solutions. The data are presented in Table 2. Better cycling efficiencies were observed at the lower current and charge densities of 0.25 mA cm^{-2} and 1.75 mA h cm^{-2} , respectively. The best solution, based on cycling efficiency at both low and high current and charge densities, is the MeOT ternary. It should, however, be noted that the cycling efficiency in this solution is lower than that we have achieved in our standard solution composed of 1.5 M LiAsF_6 in THF and 2-MeTHF [1] (also see below for C-cell cycling data). The MeOT ternary solution appears to be more advantageous for use in cells requiring good discharge performance in the -20 to -40°C range.

Practical Li/TiS₂ cells

The capacity/rate behavior of the C-cells utilizing the standard electrolyte is shown in Fig. 1. At current densities $\leq 1.5\text{ mA cm}^{-2}$, a capacity $\geq 1.6\text{ A h}$ ($\geq 80\%$ utilization) was obtained in the temperature range 20 to -20°C . In fact, a capacity of 1.2 A h was obtained even at -30°C at 1.5 mA cm^{-2} . The performance map in Fig. 1 further illustrates the excellent

TABLE 2

Li cycling efficiency in ternary electrolytes obtained from laboratory Li/TiS₂ cells

	Electrolyte ^(a)	Discharge/charge current density (mA cm ⁻²)	Li capacity density (mA h cm ⁻²)	Li cycling efficiency (FOM _{Li}) ^(b)
i.	MeOT Ternary	1.0	1.0	17.9
		0.25	1.75	16.2
ii.	MeOD Ternary	1.0	7.0	11.8
		0.25	1.75	6.4
iii.	MTE Ternary	1.0	7.0	9.0
		0.25	1.75	14.8
iv.	DMM Ternary	1.0	7.0	7.4
		0.25	1.75	17.3
v.	EC Ternary	1.0	7.0	2.9
		0.25	1.75	4.8

(a) All solutions are 1.5 M in LiAsF₆. The solvent compositions are the same as in Table 1 and they are identified by the third solvent component in the ternary.

(b) Represents figure of merit for Li cycling; see ref. 1 for definition.

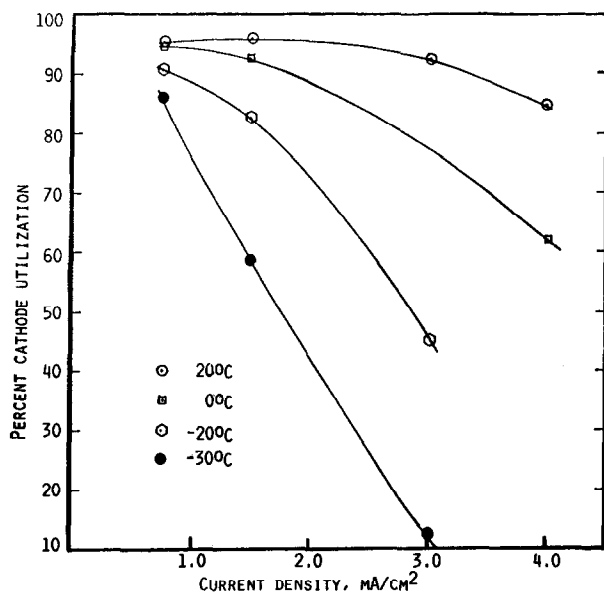
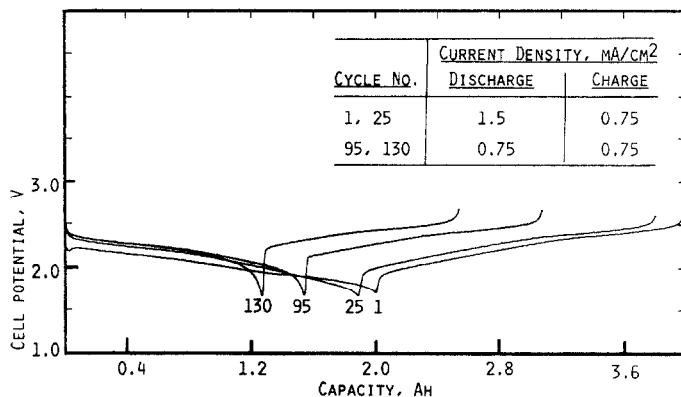


Fig. 1. Performance map of Li/TiS₂ C-cells utilizing the standard electrolyte. One hundred percent utilization corresponds to 2.1 A h.

TABLE 3

Effect of electrolyte on the cycle life^a of Li/TiS₂ C-cells

Electrolyte ^b	Voltage limits (V)	Cycling parameters		100% DOD cycles	FOM _{Li}
		Discharge current (mA)	Charge current (mA)		
Standard electrolyte	1.6 - 2.8	320	160	160	37
THF	1.6 - 2.8	320	160	50	19
THF:2-MeTHF:DMM	1.6 - 2.8	320	160	35	12
THF:2-MeTHF:MeOT	1.6 - 2.8	320	160	60	18

^aAll cycling at room temperature (20 °C).^bAll electrolytes contained 2-Mefuran as an additive and 1.5 M LiAsF₆.^cThe 320 mA corresponds to 1.5 mA cm⁻².Fig. 2. Typical cycling curves for an Li/TiS₂ C-cell at room temperature.

high-rate capability of TiS₂ cells. Thus, the discharge capacity at 20 °C decreases by only a small amount when the current is increased from 0.75 to 4 mA cm⁻².

The cycle life of the C-cells was determined by the electrolyte they contained (Table 3). The cells containing the standard electrolyte exhibited the longest cycle life, yielding > 150 cycles (Fig. 2). The Li cycling efficiency in these cells was equivalent to an F.O.M._{Li} of ~ 37. The Li/TiS₂ C-cell has a specific energy of 95 W h kg⁻¹ and an energy density of 175 W h l⁻¹, which are significantly better than the values realized in Li/MoS₂ (60 W h kg⁻¹ and 135 W h l⁻¹) and Ni-Cd (40 W h kg⁻¹ and 110 W h l⁻¹) C-cells.

Comparisons of the various 24 V Li/TiS₂ batteries with existing Army Ni-Cd and Li/SO₂ batteries are presented in Tables 4 and 5. The 50 cycle Li/TiS₂ batteries yield about 40 times more energy than the Li/SO₂ primary batteries, without significantly compromising the specific energy and

TABLE 4

Comparison of existing batteries with the 2 A h, 24 V TiS_2 battery

Chemistry	Li/SO ₂ (BA5557/U)	Ni-Cd (BB557/U)	Li/TiS ₂
Type	Primary	Rechargeable	Rechargeable
Rated capacity (A h)	2.25	0.5	2.00
Rated discharge current (A)	0.65	0.1	0.4
Capacity at 0.65 A discharge (A h)	2.25	0.4	1.80
Cycle life	1	224	50
Cumulative discharge capacity (A h)	2.25	81	83
Battery weight (lb)	1.1	1.5	1.6
Wt. energy density (W h lb ⁻¹)	49	8	32
Volumetric energy density (W h in ⁻³)	2.42	0.52	2.17

TABLE 5

Characteristics of larger batteries

Battery designation	Li/TiS ₂ 10 cycles	Li/TiS ₂ 50 cycles	Ni-Cd BB590/U	LiSO ₂ BA5590/U
Rated capacity (A h)	8.5	6.5	1.5	6.9
Rated discharge current (A)	1.5	1.5	1.5	2.0
Capacity at 2 A discharge (A h)	8	6	1.3	6.9
Cycle life	10	50	224	1
Cumulative discharge capacity (A h)	70	280	270	6.9
Battery weight (lb)	2.92	2.88	4.01	2.25
Weight energy density (W h lb ⁻¹)	70	54	9	74
Volumetric energy density (W h in ⁻³)	3.8	2.9	0.67	3.1

volumetric energy density of the latter. The Li/TiS₂ batteries, while giving the same cumulative capacity as the Ni-Cd batteries, require fewer recharges than the latter and show significantly better charge retention on storage and low temperature discharge performance.

Other practical secondary lithium cells

Because of the great military interest in high energy density secondary Li batteries, early prototype cells were large, *e.g.*, 5 A h Li/TiS₂ [9], 10 A

TABLE 6

Electrical characteristics of some ambient temperature rechargeable lithium cells

Cell type	Cell size	Nominal capacity (A h)	Mid-disch. voltage (V)	Volumetric energy density (W h l ⁻¹)	Specific energy (W h kg ⁻¹)	Cycle number
Li/TiS ₂	AA	0.9	2.10	235	95	> 100
Li/MoS ₂	AA	0.6	1.75	135	50	> 200
Li/NbSe ₃	AA	1.1	1.95	270	107*	> 200
Li/MnO ₂	AA	0.71	2.80	264	122	> 200
Li/SO ₂ -CuCl ₂	AA		3.2	210	75	> 100
Ni/Cd	AA	0.70	1.2	105	35	500

*Estimated for a cell weighing 20 g.

h Li/Cr_{0.5}V_{0.5}S₂ [10] and 20 A h Li/MoS₃ [11]. Recent efforts have been devoted to the development of small cells, *e.g.*, AA-size Li/TiS₂ [12, 13], Li/MoS₂ [6], Li/NbSe₃ [14] and Li/MnO₂ [15] cells, and 2/3 A- and AA-size Li/SO₂ cells [16, 23]. Electrical characteristics of some of these small cells are compared in Table 6 with those for the Ni/Cd cell. A number of Japanese companies including Hitachi-Maxell, NTT and Matsushita have developed button size secondary Li cells [17]. A 50 A h Li/MoS₂ cell has been developed with potential applications in electric vehicle propulsion [18]. It is clear that the future prospects of rechargeable Li battery technology are very good. However, a number of issues must be resolved before the technology can be expected to receive widespread acceptance. These issues include: safety aspects, mechanisms for overcharge and overdischarge protection [19, 20], and satisfactory performance over a wide range of environmental conditions. We have recently identified a class of organic compounds which are very useful as redox additives to the electrolyte for overcharge protection of Li/TiS₂ cells [20]. Substantial improvements in cell safety, if not completely eliminated, may be achieved with reductions in cell size. This may be a reason for the present focus on AA-size cells. Future developments may include alternative anode cells [21, 22] for improved safety, mixed electrolytes for environmentally stable batteries, and new additives for higher efficiency Li cycling.

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