

THE LITHIUM/TITANIUM DISULPHIDE SECONDARY BATTERY (EXTENDED ABSTRACT)

K. M. ABRAHAM*, G. L. HOLLECK, T. NGUYEN, D. M. PASQUARIELLO
and D. A. SCHWARTZ

EIC Laboratories, Inc., 111 Downey Street, Norwood, MA 02062 (U.S.A.)

Introduction

The availability of mixed ether electrolytes, which allow the cycling of the secondary Li electrode with high efficiency [1, 2] and the discharge of secondary Li cells at very low temperatures [3, 4], has prompted the fabrication of Li/TiS₂ cells and batteries for a variety of potential civilian and military applications [5, 6]. The performance characteristics of several Li/TiS₂ cell and battery prototypes that we have built and tested recently are reported in this paper.

Experimental

The TiS₂ electrodes were prepared from TiS₂ powder synthesized using a vapor transport technique. The composition of the TiS₂ cathode mix used in preparing the electrodes for C-size cells was 84 wt.% TiS₂, 8 wt.% C, and 8 wt.% Teflon [3]. 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 was 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 [3]. 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 [6]. 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 ×

*Author to whom correspondence should be addressed.

6.04 cm \times 1.65 cm. The electrode stack consisted of a number of alternate, parallel plate Li and TiS_2 electrodes, as in our 5 A h Li/ TiS_2 cells, reported previously [5]. The 6 A h and 8 A h cells were designed to yield 50 and 10, one hundred percent. 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/ SO_2 or the BB-590/U Ni-Cd battery.

All cells were cycled under constant current conditions using standard cycling equipment [2 - 6].

Results and discussion

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 high-rate capability of TiS_2 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 1). 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/ TiS_2

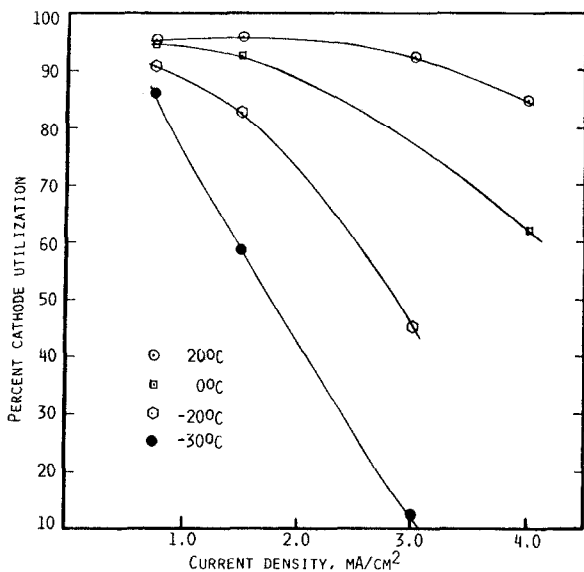
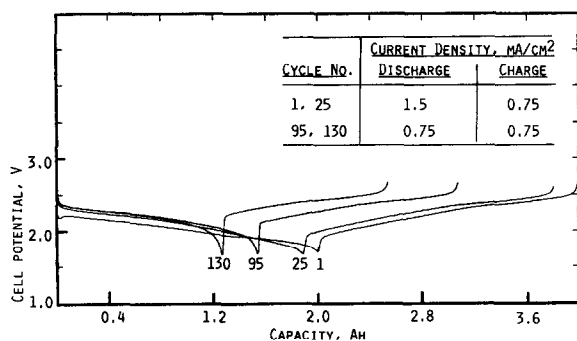


Fig. 1. Performance map of Li/ TiS_2 C-cells utilizing the standard electrolyte. One hundred percent. utilization corresponds to 2.1 A h.

TABLE 1

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

Electrolyte ^b	Cycling parameters			100% DOD cycles	F.O.M. _{Li}
	Voltage limits	Discharge current (mA) ^c	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 ^d	1.6 - 2.8	320	160	35	12

^aAll cycling at room temperature (20 °C).^bAll electrolytes contained 2Me-Furan as an additive and 1.5 M LiAsF₆.^cThe 320 mA corresponds to 1.5 mA cm⁻².^dThis electrolyte was reported in ref. 4.Fig. 2. Typical cycling curves for an Li/TiS₂ C-cell at room temperature.

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 2 and 3. 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 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.

TABLE 2

Comparison of existing batteries with the 2 A h, 24 V Li/TiS₂ 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	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 3

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

Acknowledgement

This work was supported by Contracts DAAH01-86-C-1056 and DAAK20-84-C-0391.

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