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STATUS OF THE DEVELOPMENT OF RECHARGEABLE LITHIUM CELLS

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ABSTRACT

The progress in the development of the ambient temperature Lithium - Titanium Disulfide rechargeable cell under development at the Jet Propulsion Laboratory is described in this paper. Originally aimed at achieving a specific energy of 100 Wh/kg, 'AA' cells have demonstrated 125 Wh/kg at the C/3 discharge rate. The results of evaluating cell design parameters are discussed and cycling test data are also included in the paper. Safety tests results at various overcharge and over discharge conditions and rates proved to be uneventful. The test results of cell with built-in overcharge mechanism proved the concept was feasible. Replacing the lithium foil electrode with a Li_xC resulted in a capacity at $1\text{mA}/\text{cm}^2$ of 200 mAh/gm and 235 mAh/gm at 0.167 mA.

INTRODUCTION

Ambient temperature Lithium - Titanium Disulfide (Li-TiS_2) rechargeable cells have been under development at the Jet Propulsion Laboratory. The effort sponsored by Code C at NASA Headquarters is aimed at high specific energy rechargeable cells that can reduce mass, and/or volume and or increase mission capability in planetary spacecraft applications. The need for a long cycle life lithium rechargeable battery has also been a goal of this effort. The program goals were 100 Wh/kg, 1000 cycles at 50% depth of discharge at the C/5 rate, 5 years of active storage life and safe under electrical abuse conditions.

The approach has been to prepare materials, components and cells to gain an understanding of how the variations in design, composition and structure affect performance and life. During the development a number of cathode materials were studied in a comprehensive evaluation process before selecting titanium disulfide for its specific energy and cycle life capability. More than seventy-five different and solvent combination electrolytes were subjected to complex impedance, microcalorimetry and electrochemical measurements before selecting a solution of 2-methyl tetrahydrofuran/ethylene carbonate/2-methyl furan (2-MeTHF/EC/2-MeF) containing 1.5 moles of lithium hexafluoroarsenate (LiAsF_6). The initial evaluation cells were a 150 mAh spiral wound design. These were scaled-up to 1 Ah size spiral wound cells. The volume of electrolyte was found to be essential to long life.

The objectives of this effort were to determine the effect of stack compression, overcharge protection and electrical abuse on the performance and safety of the Li-TiS₂ cell. Additionally an alternate Li_xC electrode prepared from commercial graphite was evaluated as a replacement for Lithium foil as the anode.

PERFORMANCE

Examples of the performance of these cells is given in Figures 1-4. Figure 1 shows the voltage on charge (C/10) and discharge (C/5). Charge is terminated at 2.5 volts and discharge at 1.7 volts. The sloping voltage has the advantage of providing a measure of state of charge. Figure 2 provides a measure of the specific energy at various discharge rates. Note that the 1 Ah cell achieved a specific energy of greater than 125 Wh/Kg at rates as high as C/2. Figure 3 illustrates 965 cycles achieved at 50% depth of discharge (to 2.2 volts) in a cell comprising the 2-MeTHF/EC/2-MeF/LiAsF₆ electrolyte and a cathode:anode ratio of 4:1. The cycle life at 100% depth of discharge (to 1.7 volts) shown in Figure 4 was 335 cycles. This is not significantly less than that achieved with commercial Ni-Cd cells.

CELL DESIGN PARAMETERS

The parameters addressed during the development process this year included: pack tightness, final selection of electrolyte composition, separator type, electrode capacity ratio and case polarity. More than 100 experimental 1 Ah spiral wrapped cells were assembled in house and 50 'AA' (1Ah) cells were procured from EIC to determine the effect of these parameters on performance.

The effect of varying the pack tightness on end of discharge voltage is given in Figure 5. The pack was tightened using a 10 mil Teflon sheet wrapped around the spiral. The tight pack utilized 2 layers around the spiral, the medium 1 layer and the loose pack did not use a Teflon layer. Although there is a significant difference in the early cycles, the performance appears to be similar after 250 cycles, probably because of the expansion of the cathode and film on the lithium foil. However, the tight pack voltage was higher throughout and therefore was judged to be a superior configuration.

Results of the evaluation of four different separators is shown in Figure 6. The Celgard microporous polyethylene (PE) and polypropylene (PP) appear to provide similar results. The microporous polypropylene was selected to minimize the lithium dendrite growth. The thermal separator, a wax-coated polypropylene material, was selected to evaluate the properties of a separator that would serve as a fuse and shut down the cell if the temperature became unsafe. These also provided more than 400 cycles at 50% DOD.

The summary of the design parameter study, including work previously performed is given in Table 1. The anode:cathode ratio of 4:1 has been shown to provide consistent long cycle life cells. Three electrolytes including that described above have proven to be capable of providing long life. Only 6 cc of the electrolyte were found to be necessary. The optimum ethylene/propylene/diene terpolymer (EPDM) binder in the TiS₂ cathode was found to be 1%. There was little difference in performance with a floating or case positive polarity.

SAFETY EVALUATION TESTS

Experimental and EIC 1 Ah cells were subjected to short, circuit, overcharge, over discharge, and combinations thereof. The results of the short circuit test is given in Figure 7. Peak current rose to 25 amps within 2 minutes and then dropped to near zero current immediately after. The temperature followed the current, rising to 220 °F, then tapering to 95° F within 30 minutes. There were no ventings, explosions or other safety incidents during these tests. Table 2 provides a summary of the results of inadvertent electrical abuse tests which occurred during cell testing when a computer failed. Even after overcharging 5 times and over discharging 10 times the capacity after 200 - 500 cycles, the cells were in tact and did not vent.

OVERCHARGE PROTECTION STUDIES

From an operational point of view cells in a series string require overcharge protection to prevent a cell from being overcharged when degradation results in cell imbalance in the string. Ni-Cds cells utilize their inherent oxygen recombination capability to allow cells in a string to be balanced during overcharge. Lithium rechargeable cells do not inherently have this capability. Three additives were included in Li-TiS₂ cells to create a shuttle reaction that could provide overcharge protection. Tetracyanoethylene (TCNE), N-butylferrocene, suggested by EIC and JPL's tetramethylphenylenediamine (TMPD) were evaluated. Figure 8 shows the result of adding TMPD to a cell. The additive provided 10-15% capacity at 2.9 volts thus protecting the cell during that period. TCNE did not provide adequate protection. N-butylferrocene from, early measurements appears to be comparable to or better than TMPD.

LITHIUM/CARBON ANODES

Replacement of lithium foil electrodes with an alternative lithium anode to enhance safety has been of interest. The performance targets for this material were 250 mAh/g and >2mA/cm² with good mechanical stability. One of areas JPL's effort has centered on is the development of a lithium/carbon alloy (Li_xC). Several carbon materials, including pitch coke, petroleum coke, graphite fiber and graphite were evaluated as potential candidates. The rate capability of Li_xC using the graphite material is shown in Table 3. At 1 mA/cm² a capacity of 200 mAh/g was achieved. At the lower rates, higher capacities to 235 mAh/g were found. A discharge curve is given in Figure 9. As expected the voltage of this experimental cell was below the lithium foil electrode cells. The Li_xC electrode was only 72 mv below the Lithium electrode potential at the start of the discharge and increased to 264 mv at the end of the discharge. Thus, it had a discharge curve comparable to that of the lithium foil cells.

SUMMARY

Ambient temperature rechargeable Li-TiS₂ cells have demonstrated a capability of 125 Wh/kg at rates greater than C/2 and almost 1000 cycles at 50% depth of discharge. Design studies identified that a tight pack provided a more consistent and higher operating voltage. Microporous PE or PP were found to be suitable as separator material. The electrolyte and anode:cathode ratios among other parameters were also specified. Significant electrical abuse did not result in a venting or explosion. Overcharge protection was shown to be possible in these cells. A Li₆C alloy was found to be a suitable replacement for lithium foil with predictable reduction in specific energy for the loss in lithium metal.

ACKNOWLEDGMENT

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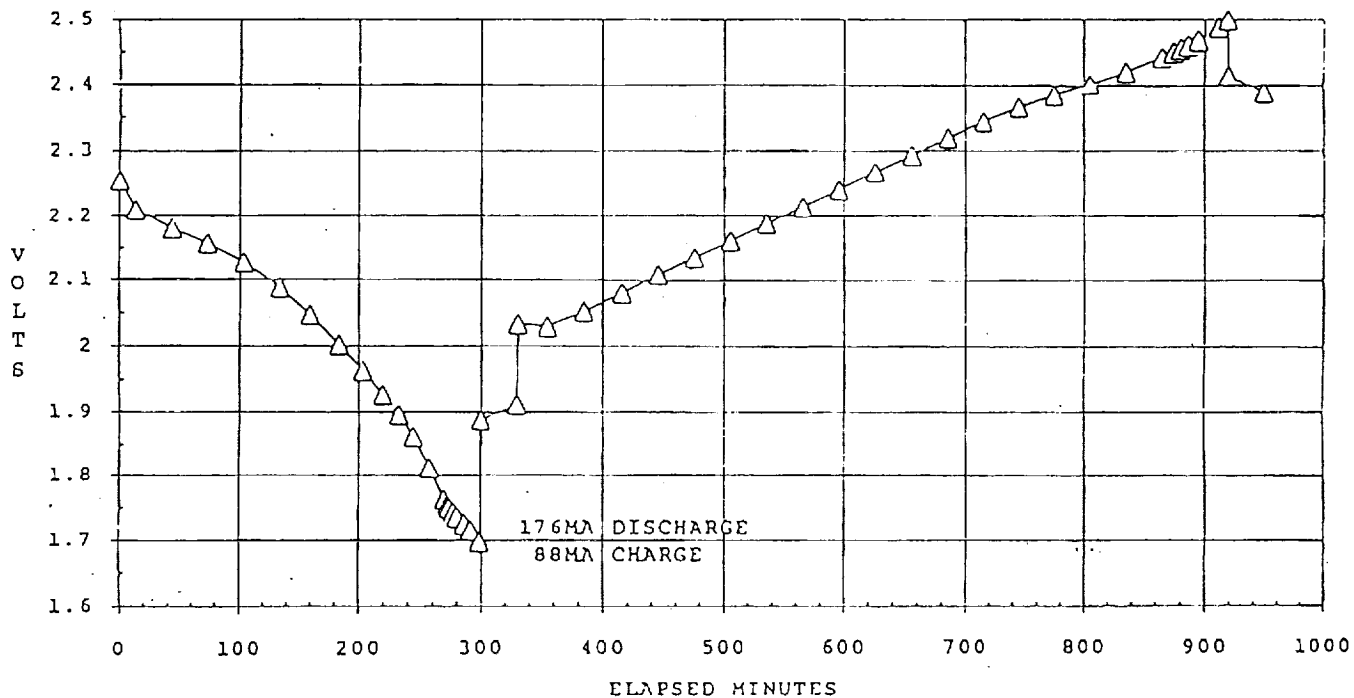


Figure 1: Li-TiS₂ Charge/Discharge Curve

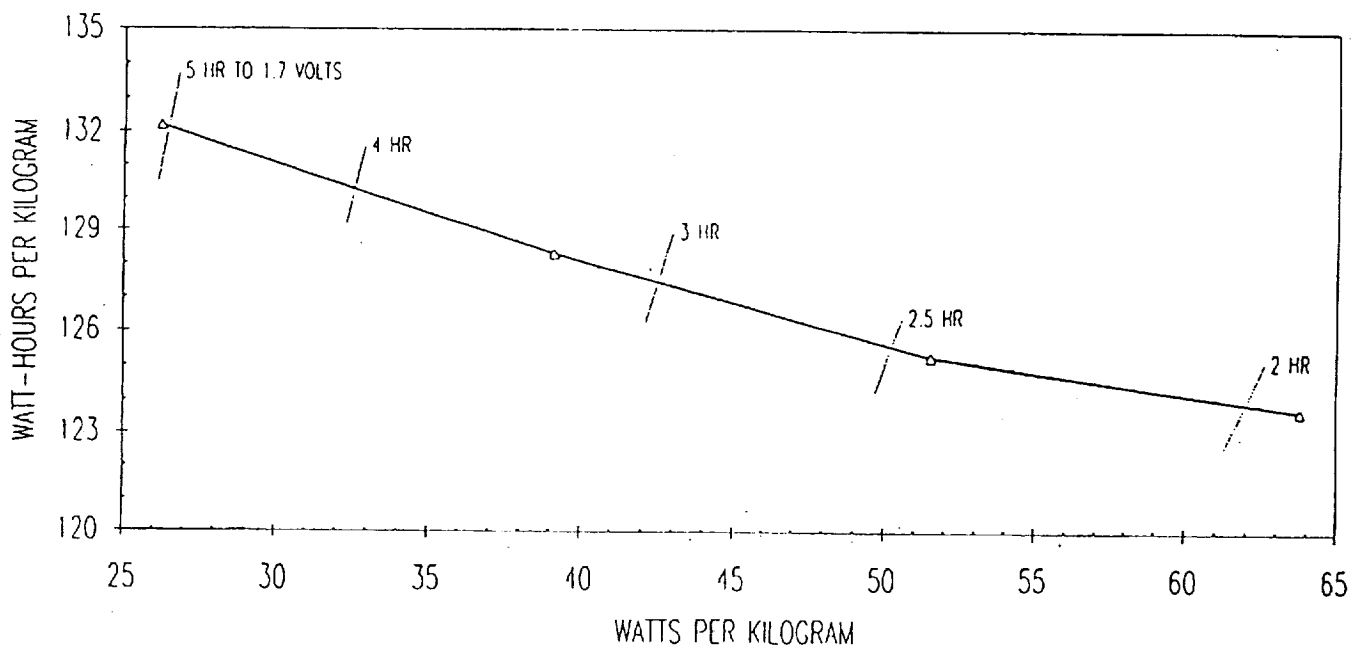


Figure 2: Performance of a Typical 1 Ah Li-TiS₂ Cell

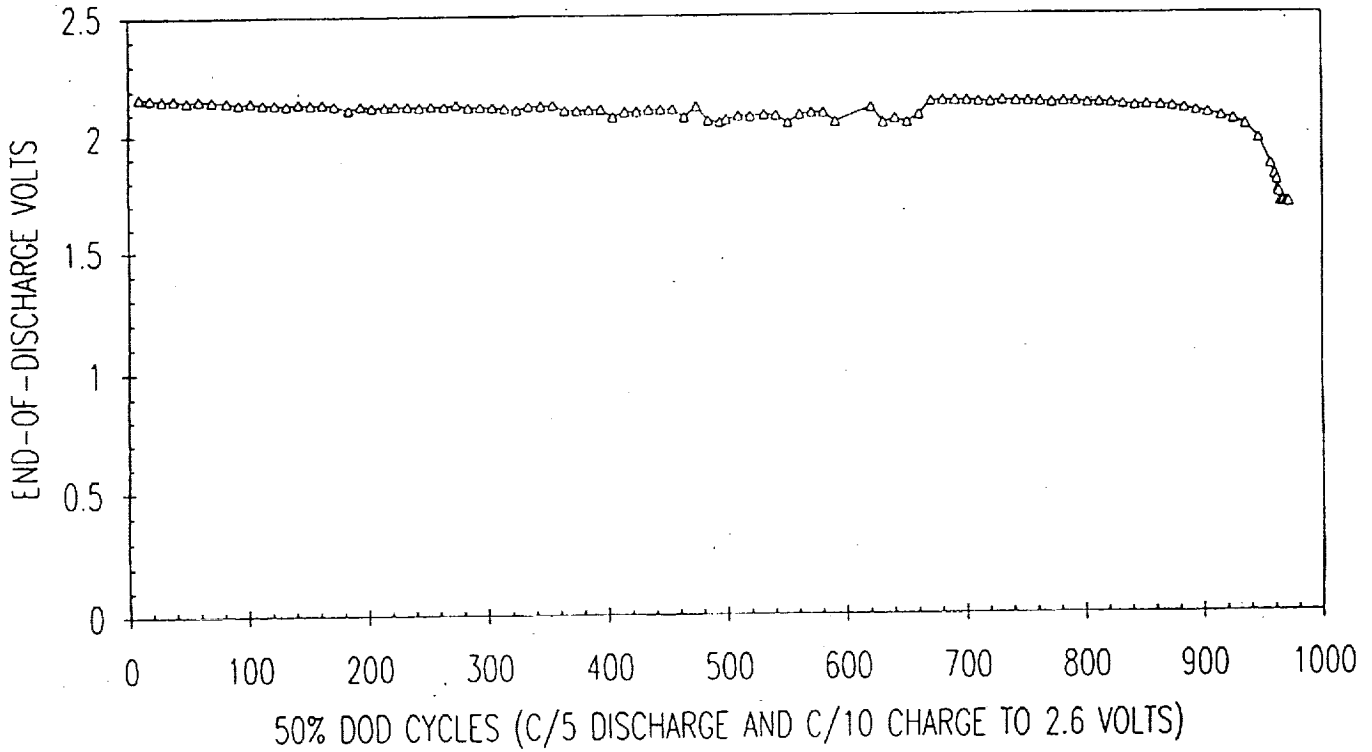


Figure 3: Cycle Life of a Li-TiS₂ Cell at 50% Depth of Discharge

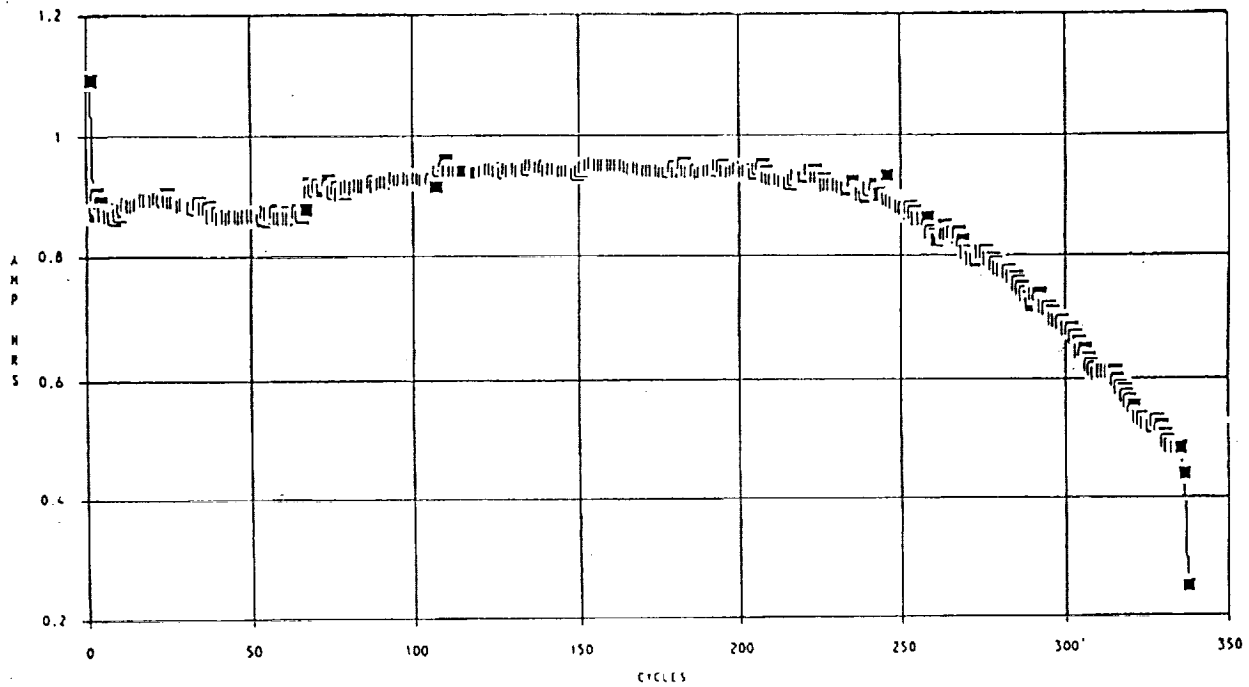


Figure 4: Cycle Life of a Li-TiS₂ Cell at 100% Depth of Discharge

EFFECT OF PACK TIGHTNESS ON END-OF-DISCHARGE VOLTAGE

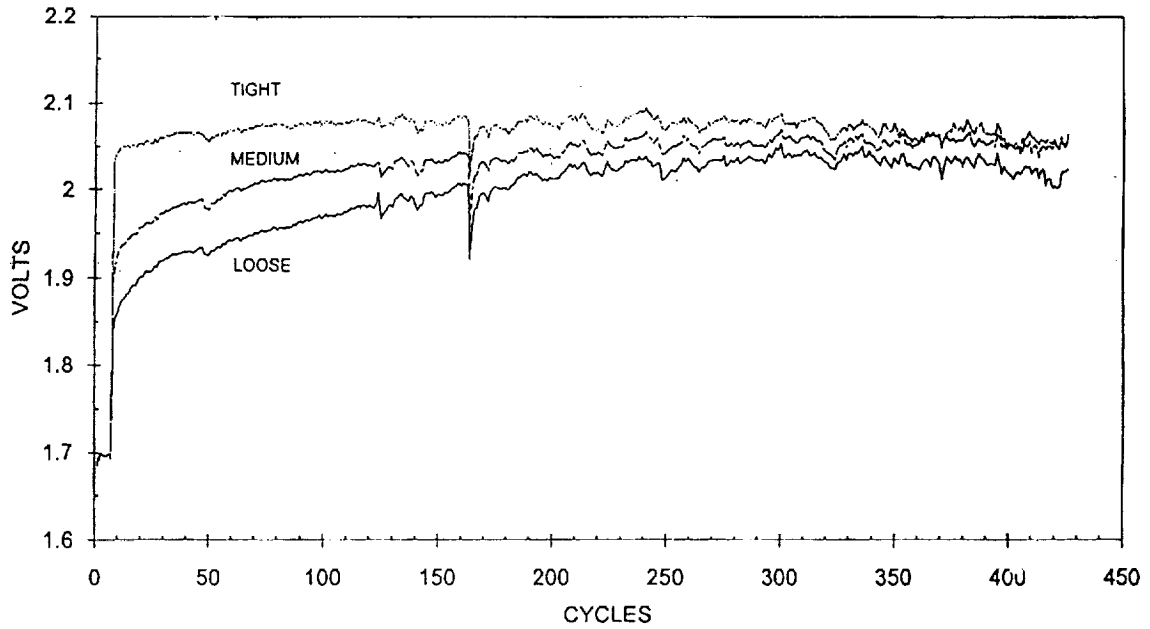


Figure 5: Effect of Pack Tightness on End-of-Discharge Voltage

EFFECT OF SEPARATOR ON END-OF-DISCHARGE VOLTAGE

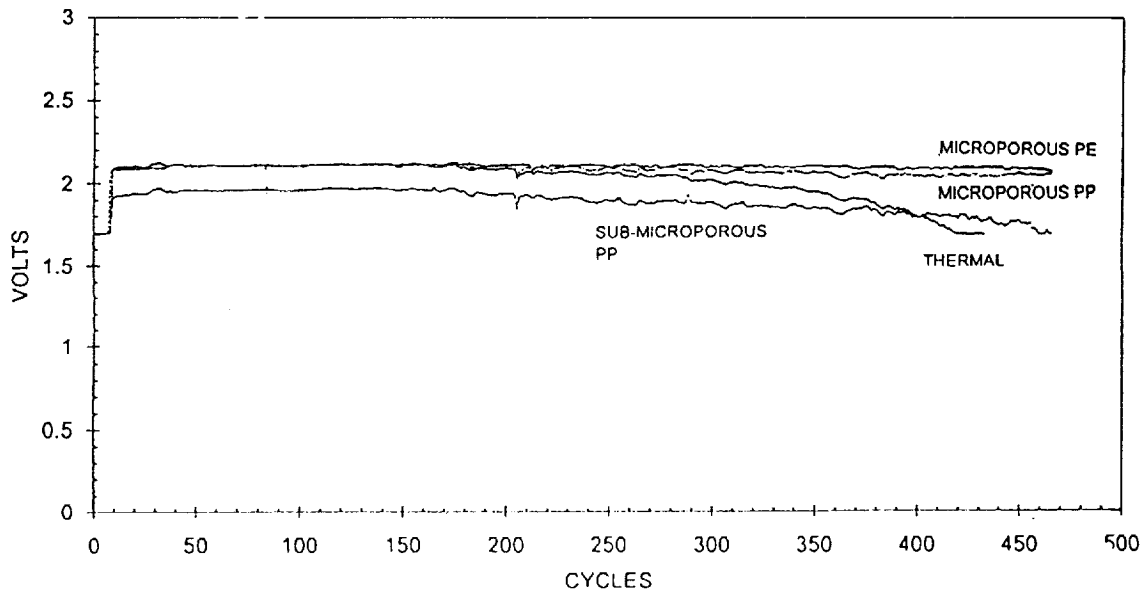


Figure 6: Effect of Separator on End-of-Discharge Voltage

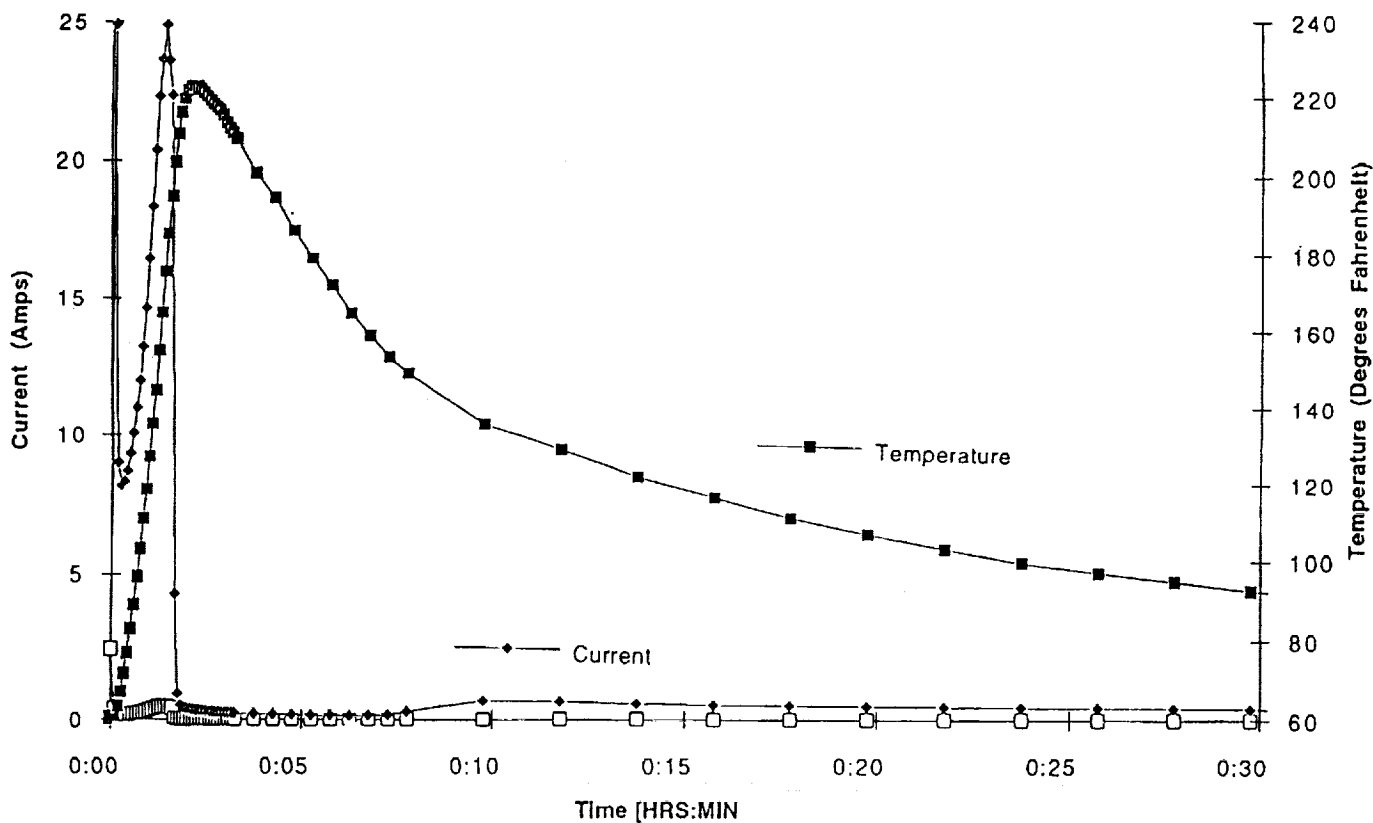
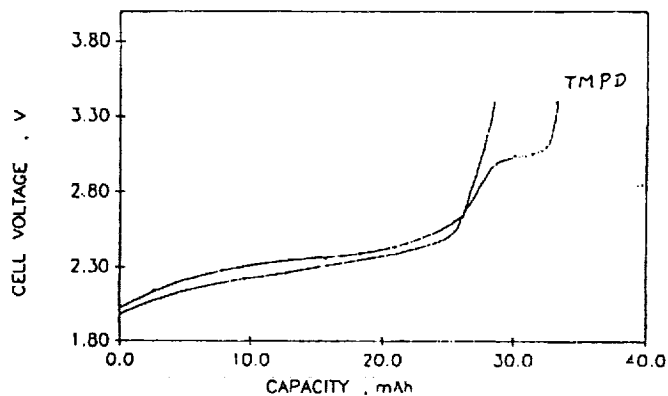


Figure 7: Short Circuit of a 1Ah 'AA' Li-TiS₂ Cell

- 70-75% OF THEORETICAL CAPACITY (STABILIZED IN 5 CYCLES)

- OVERCHARGE PERFORMANCE:



- 25 CYCLES WITH STABILIZED CAPACITY

- * COMPATIBLE WITH THE CELL
- * 10-15% OVERCHARGE PROTECTION AT THE NORMAL CHARGE RATE

Figure 8: Results of adding TMPD to a cell for Overcharge Protection

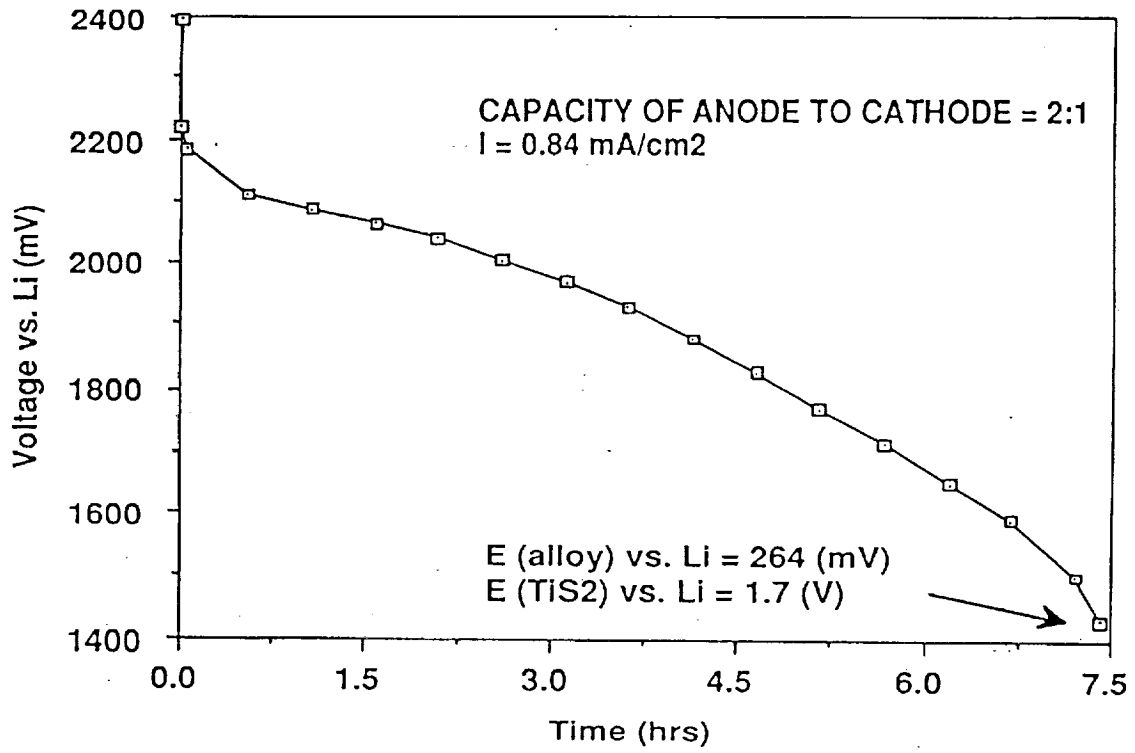


Figure 9: Discharge Curve of a $\text{Li}_x\text{C-TiS}_2$ Cell

Table 1: Cell Design Parameters

DESIGN PARAMETERS	VARIATIONS
ANODE TO CATHODE CAPACITY RATIO	4 : 1
PACK TIGHTNESS	Tight
TYPE OF ELECTROLYTE Salt: 1.5 M LiAsF ₆	10% EC + 88% 2-MeTHF + 2% 2-MeF THF + 2-MeTHF + 2% 2-MeF, DIOX + 2-MeTHF + THF + 2% 2-MeF
QUANTITY OF ELECTROLYTE	6 c. c.
SEPARATOR	Microporous Polypropylene Microporous Polyethylene
BINDER CONCENTRATION	1 % by weight
CASE POLARITY	floating or positive.

Table 2: Results of Electrical Abuse Tests on Li-TiS₂ cells

CYCLE #	TYPE OF ABUSE	RATE	ABUSE %	EVENT
200	OVERCHARGE	C/10	400	NONE
400	OVERCHARGE	C/10	500	NONE
550	OVERCHARGE	C/10	500	NONE
400	OVERDISCHARGE	C/5	1000	NONE
500	OVERDISCHARGE	C/5	1000	NONE

Table 3: Rate Capability of a Li_xC Anode

CURRENT (mA/cm ²)	CAPACITY (mAh/gm)
0.167	235
0.333	214
0.667	208
1.000	200

