

DEVELOPMENT OF AMBIENT TEMPERATURE SECONDARY LITHIUM CELLS

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Under a NASA-OAST sponsored program, JPL is developing ambient temperature secondary lithium cells for future spacecraft applications. Prior studies on experimental laboratory type Li-TiS₂ cells yielded promising results in terms of cycle life and rate capability. To further assess the performance of this cell, 5Ah engineering model cells were developed. Initially baseline cells were designed and fabricated. Each cell had 15 cathodes and 16 anodes and the ratio of anode to cathode capacity is 6:1. A solution of 1.5 molar LiAsF₆ in 2Me-THF was used as the electrolyte. Cells were evaluated for their cycle life at C/2 and C/5 discharge rates and 100 percent depth of discharge. The cells were cycled between voltage limits 1.7 and 2.8 volts. The rate of charge in all cases is C/10. The results obtained indicate that cells can operate at C/10 to C/2 discharge rates and have an initial energy density of 70 Wh/kg. Cells delivered more than 100 cycles at C/2 discharge rate. This paper describes the details of cell design, the test program, and the results obtained.

INTRODUCTION

Under a NASA OAST sponsored program, Jet Propulsion Laboratory is developing ambient temperature secondary lithium batteries for future space applications. These lithium batteries have a number of intrinsic and potential advantages such as higher energy density, longer active shelf life, lower self discharge etc. over conventional Ni-Cd, Pb-acid and Ag-Zn batteries. The main objective of the program is to demonstrate the feasibility of developing cells with greater than 100 Wh/kg specific energy while delivering 1,000 cycles at moderate depths of discharge (60-70%). The program pay-offs are 2-3 fold increase in energy storage capability and a longer active shelf life over Ni-Cd and Ni-H₂. Some of the projected applications of these batteries are for Mars Rover, planetary space craft/probes, astronaut equipment, and GEO spacecraft. To achieve these ambitious goals, we have examined the performance potential of Li-TiS₂, Li-MOS₃ and Li-V₆O₁₃ systems in detail. Among these three, the Li-TiS₂ system has shown the longest cycle life and highest rate capability. Experimental five cell Li-TiS₂ batteries (10.5V, 0.4Ah), developed in-house, have completed twelve simulated and accelerated GEO seasons successfully (1). These encouraging results prompted us to assess the performance capability of the Li-TiS₂ system in engineering model 5Ah cells. This study will serve as an intermediate step before

building prototype flight 20-35Ah cells. Development of 5Ah cells is proposed to be completed by 1989. In this paper we report the results of our preliminary work done on the development of baseline SOA 5Ah cells.

CELL DESIGN

The computer program, developed earlier (2) for the design trade-off studies of 35Ah Li-TiS₂ cells was used in the selection of a design for the 5Ah baseline engineering model cells. Some of the important design features of the cell are given in Table 1. The TiS₂ cathode is the limiting electrode and ratio of anode to cathode capacity is 6:1. This high anode to cathode capacity was chosen to accommodate the degradation of Li electrode and achieve maximum cycle life. Results of the design trade-off analysis indicate that the capacity ratio has minimal effect on specific energy of the cells (Table 1). The operating current density of the cell at C/2 discharge rate was 2 mA/cm². Operation at current densities higher than 2 mA/cm² is limited by the poor conductivity of the electrolyte. The cell contains 15 TiS₂ cathodes and 16 Li anodes. Celgard 2400, a porous polypropylene film, was chosen as the separator material. The composition of the electrolyte is 1.5M LiAsF₆/2Me-THF and each cell is activated with 40 cc of electrolyte. This electrolyte quantity is designed to fill the internal void volume of the electrodes, and separator, and other minor cell void spaces. The cell weighs approximately 230 grams, and the weight budget is given in Figure 1. It may be noted that the cell can is the major contributor to cell weight. Among the active materials, Li contributes the least to the overall weight. The collector grids contribute more to the weight than does lithium alone. The use of titanium cases and aluminum grids will reduce cell weight considerably.

TiS₂ CATHODE DEVELOPMENT

The suitability of various processing methods such as brushing, pressing, and rolling have been examined in the fabrication of TiS₂ cathodes with EPDM binder. The brushing method even though simple, was not found suitable for making large electrodes. Considerable problems were encountered in making electrodes by the pressing method due to poor flow characteristics of the electrode active material. The rolling method on the other hand, offered many advantages such as amenability to scale-up, uniform loading, incorporation of integral tabs, etc.

The TiS₂ electrodes required for 5Ah baseline cells were fabricated by the rolling method and the details of processing are given in Figure 2. TiS₂, the active material of the cathodes, was processed in-house by a vapor transport method involving a chemical reaction between titanium and sulphur. This material had a stoichiometry of Ti_{1±0.1}S₂. The approximate composition of electrode material is 86% TiS₂, 10% conducting diluent and 4% binder. Shawinigan black was chosen as the conducting diluent in view of its chain-like structure, high conductivity and purity (3). EPDM was used as the binder material. The binder was dissolved in cyclohexane (1%) and added to TiS₂ and carbon mix. Excess solvent was removed by vacuum extraction. The resulting material was ground to a fine powder and applied onto a nickel exmet screen by rolling. Electrode active material preparation was carried out in an argon atmosphere chamber. The electrode processing was done in a dry room (humidity less than 0.5%).

Master electrodes (6" x 6" x 0.02") were fabricated and cut into required dimensions. The porosity of the electrodes is about 35 to 40% and the active material loading is $75 \pm 5 \text{ mg/cm}^2$. The surface area of the electrodes is about $12 \text{ M}^2/\text{gm}$. These electrodes have exhibited more than 90% faradic utilization initially in experimental cells (150mAh) and yielded more than 200 cycles (100% DOD) with only 20% loss in capacity.

RESULTS AND DISCUSSION

Baseline engineering model cells were evaluated for their charge/discharge characteristics, rate capability, and cycle life. Cells were charged by constant current method at C/10 rate to 2.7V. Cells were discharged at different rates to a cutoff voltage of 1.7V. Charge discharge characteristics of the cell at C/10 rate are given in Figure 3. The cell exhibits sloping charge/discharge curves which are typical for the intercalation cathodes. Discharge characteristics of the cell at C/10, C/5, and C/2 rates are given in Figure 4. At the C/10 rate cells delivered approximately 7.8Ah which is roughly equivalent to 100% capacity. Energy density of the cells at this rate is found to be about 75 wh/kg. At C/2 discharge rate, cells have exhibited approximately a capacity of 6Ah. Cells were evaluated for their cycle life characteristics at C/5 & C/2 discharge rates to 100% DOD. The capacity of the cells as a function of cycle number is given in Figure 5. The cells were found to lose capacity upon cycling. The impedance of cells was also found to increase on cycling. The cells cycling at C/2 lost approximately 0.05Ah/cycle and by the end of 100th cycle cells delivered only about 3Ah. Surprisingly the cells cycling at C/5 discharge rate failed at about 60 cycles. Probably, the cells developed "soft-shorts" as revealed by longer charge periods. Similar problems were encountered (soft shorts) while testing commercial secondary Li cells at low discharge rates (4). The low cycle life performance of the 5Ah baseline cells may be due to electrolyte degradation, starved electrolyte condition, processing of cells in the dry room, non-optimized cell design, or charge methodology. We are in the process of evaluating and optimizing these parameters. Cells with optimized design will be built and tested for their performance and safety and we are anticipating to complete this work by the end of 1989.

FUTURE DIRECTIONS

A number of areas are under investigation to improve the energy density and the cycle life performance of secondary Li cells. Some of the major areas are high energy density cathode materials, high performance electrode structures, stable electrolytes, design optimization, and improved charge methodology. Among various cathode materials, NbSe_3 appears promising and its performance potential is being assessed in experimental cells. The limited cycle life capability of rechargeable lithium cells is mainly due to the high reactivity of lithium with the electrolyte. A number of mixed solvent electrolytes are currently being evaluated for conductivity, viscosity, stability towards lithium and lithium cycling efficiency. Pulse charging and modified constant current charging methods will be examined to improve cell performance. We are planning to complete these activities by 1992 and build prototype cells for flight qualification.

ACKNOWLEDGEMENTS

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TABLE I. - INFLUENCE OF ELECTRODE CAPACITY RATIO ON SPECIFIC ENERGY

ANODE TO CATHODE CAPACITY RATIO	SPECIFIC ENERGY (Wh/Kg)
5.5	58.2
5.0	58.4
4.0	58.8
3.0	59.3
2.0	59.8
1.0	60.3

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TABLE II. - OUTLINE OF 5-Ah Li-TiS₂ CELL DESIGN

1) THEO. ANODE CAPACITY (Ah)	= 38.5
2) THEO. CATHODE CAPACITY (Ah)	= 6.6
3) ELECTRODE CAPACITY RATIO	= 5.8:1
4) NO OF ANODES (2.75"*2.5"*0.014")	= 15
5) NO OF CATHODES (2.75"*2.5"*0.025")	= 14
6) CURRENT DENSITY (mA/cm ²)	= 2.0
7) ELECTROLYTE (1.5M LiAsF ₆ /2Me-THF)	= 40
8) CELL WEIGHT (g)	= 230
9) CELL DIMENSIONS (in)	= 2.78*4*.98

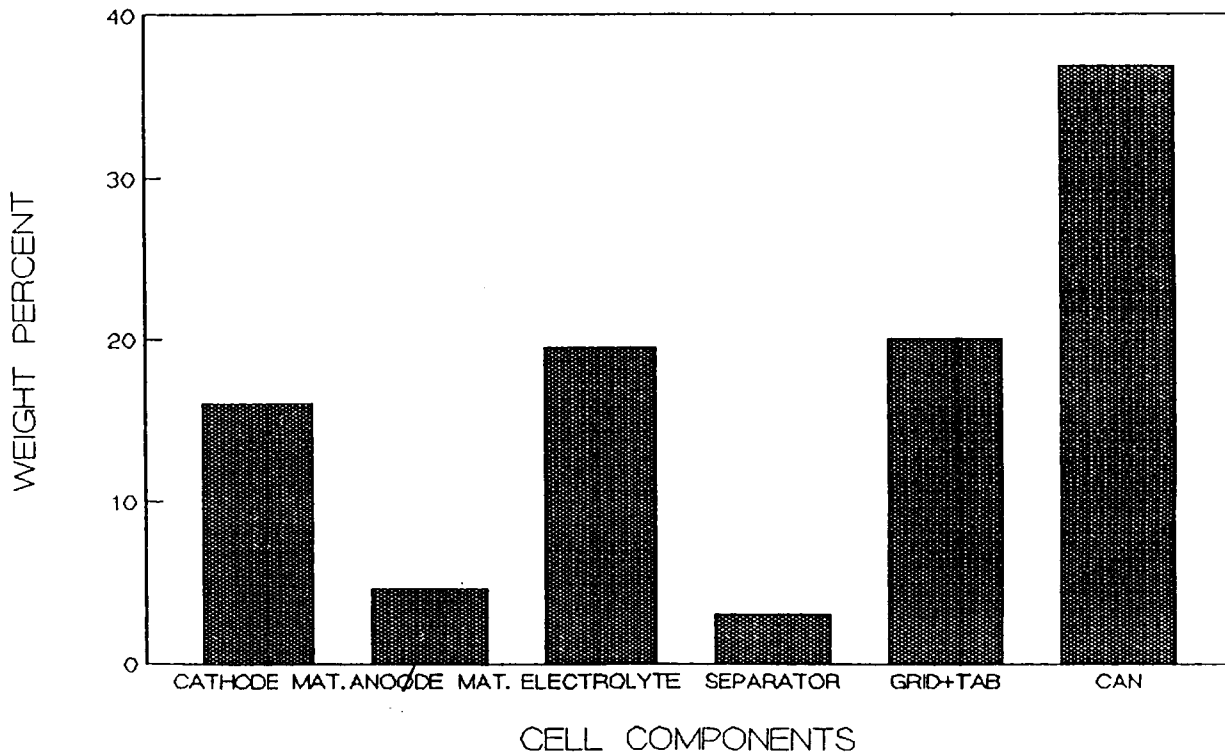


Figure 1. - 5-Ah Li-TiS₂ cell weight budget.

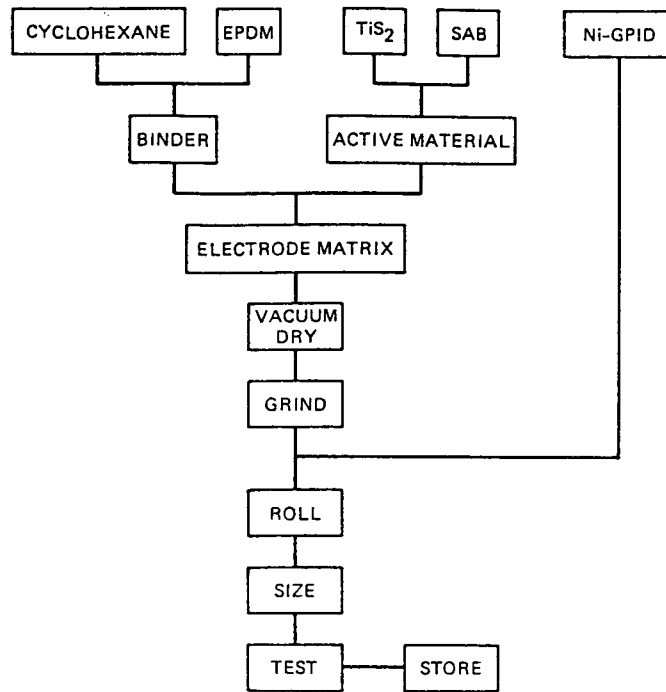


Figure 2. - TiS_2 electrode process.

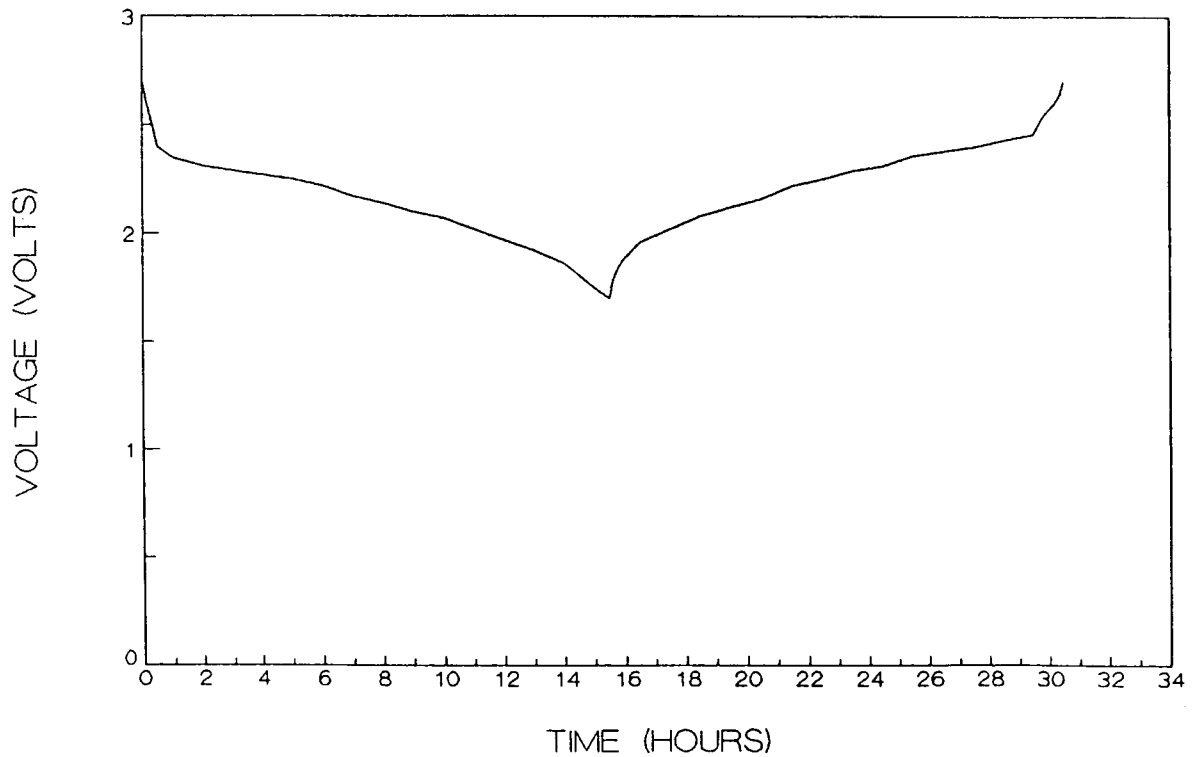


Figure 3. - Discharge and charge characteristics of 5-Ah Li-TiS_2 cells.

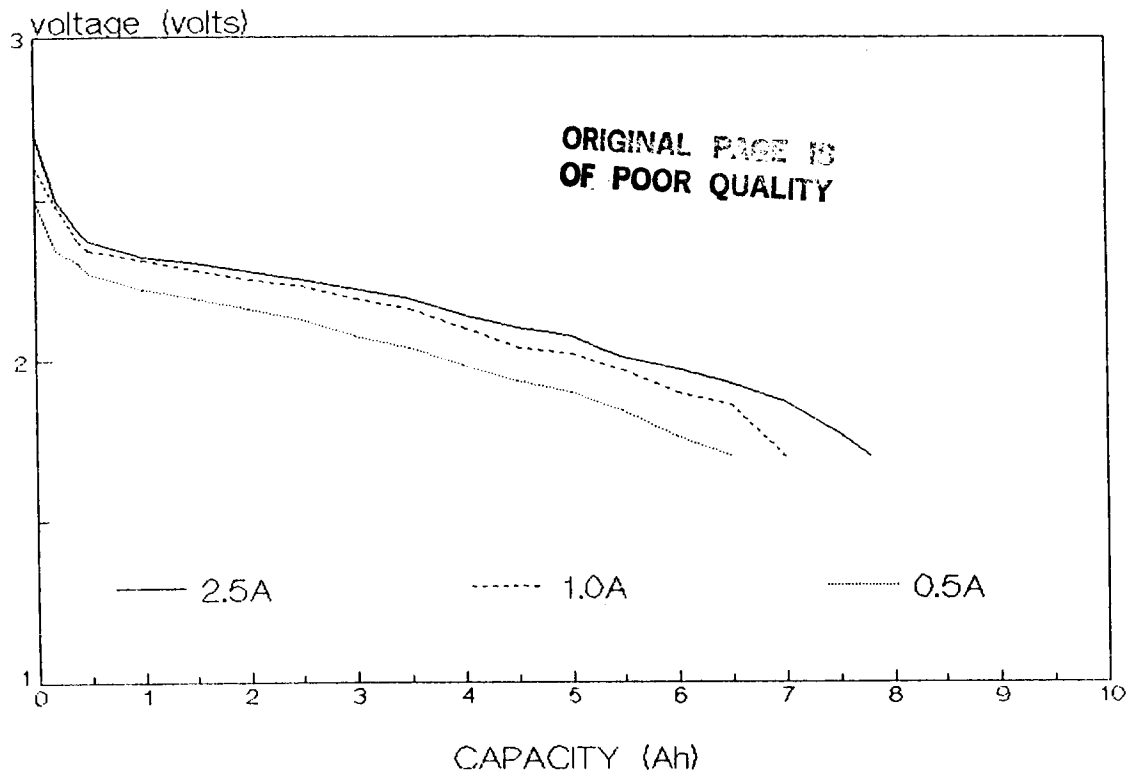


Figure 4. - Discharge characteristics of 5-Ah Li-TiS₂ cells.

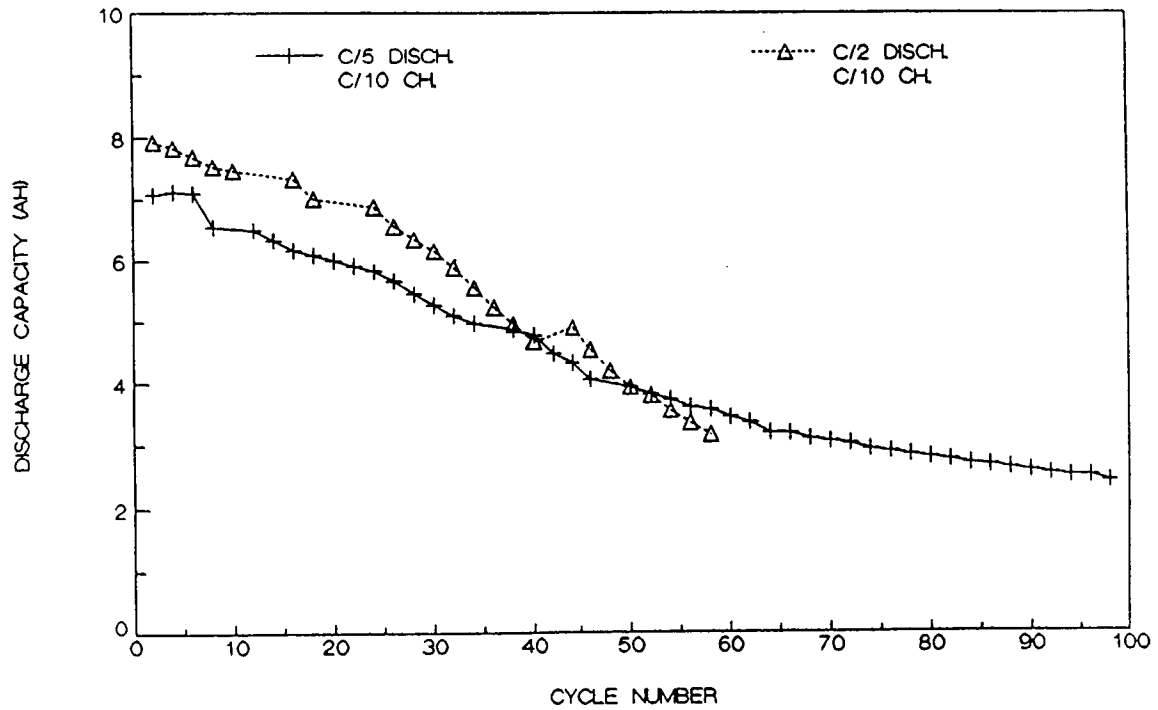


Figure 5. - Cycling characteristics of JPL 5-Ah Li-TiS₂ cells.