Journal of Power Sources, 22 (1988) 269 - 275

DEVELOPMENT OF AMBIENT TEMPERATURE SECONDARY LITHIUM CELLS

S. SUBBARAO, D. H. SHEN, S. DAWSON, F. DELIGIANNIS, J. TARASZKIEWICZ and G. HALPERT

Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, MS 277-102, Pasadena, CA 91109 (U.S.A.)

Summary

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–TiS_2 cells yielded promising results in terms of cycle life and rate capability. To further assess the performance of this cell, 5 A h 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 M $LiAsF_6$ in 2-MeTHF was used as the electrolyte. Cells were evaluated for their cycle life at $C/2$ and $C/5$ discharge rates and 100% depth of discharge. The cells were cycled between voltage limits 1.7 and 2.8 V. The rate of charge in all cases is $C/10$. The results obtained indicate that cells can operate at $C/10$ - $C/2$ discharge rates and have an initial energy density of 70 W h kg^{-1}. 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 W h kg^{-1} specific energy while delivering 1000 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–H_2. Some of the projected applications of these batteries are for Mars Rover, planetary spacecraft/probes, astronaut equipment and GEO spacecraft. To achieve these ambitious goals,

0378-7753/88/$3.50

we have examined the performance potentials of Li–TiS_2, Li–MoS_3, and Li–V_6O_{13} systems in detail. Among these three, the Li–TiS_2 system has shown the longest cycle life and the highest rate capability. Experimental five-cell Li–TiS_2 batteries (10.5 V, 0.4 A h), 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–TiS_2 system in engineering model 5 A h cells. This study will serve as an intermediate step before building prototype flight 20 - 35 A h cells. Development of 5 A h 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 5 A h cells.

Cell design

The computer program, developed earlier [2] for the design trade-off studies of 35 A h Li–TiS_2 cells, was used in the selection of a design for the 5 A h baseline engineering model cells. Some of the important design features of the cell are given in Table 1. The TiS_2 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 the Li electrode and to achieve maximum cycle life. Results of the design trade-off analysis indicate that the capacity ratio has minimal effect on the specific energy of the cells (Table 1). The operating current density of the cell at $C/2$ discharge rate was 2 mA cm^{-2}. Operation at current densities higher than 2 mA cm^{-2} is limited by the poor conductivity of the electrolyte. The cell contains 15 TiS_2 cathodes and 16 Li anodes. Celgard 2400, a porous polypropylene film, was chosen as the separator material. The composition of the electrolyte is 1.5 M $LiAsF_6$/2-MeTHF and each cell is activated with 40 ml of electrolyte. This electrolyte quantity is designed to fill the internal void volume of the electrodes, separator, and other minor cell void spaces. The cell weighs approximately 230 g, and the weight budget is given in Fig. 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.

TABLE 1

Influence of electrode capacity ratio on specific energy

Anode to cathode capacity ratio	Specific energy (W h kg^{-1})
5.5	58.2
5.0	58.4
4.0	58.8
3.0	59.3
2.0	59.8
1.0	60.3

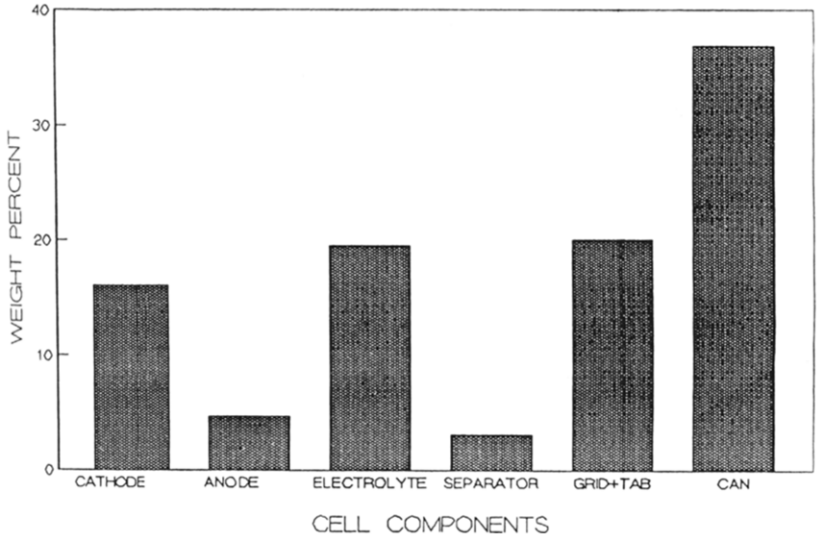

Fig. 1. 5 A h Li–TiS_2 cell weight budget.

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.

TiS_2 cathode development

The suitability of various processing methods such as brushing, pressing, and rolling have been examined in the fabrication of TiS_2 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 TiS_2 electrodes required for 5 A h baseline cells were fabricated by the rolling method and the details of processing are given in Fig. 2. TiS_2, 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 $Ti_{1 \pm 0.1}S_2$. The approximate composition of the electrode material is 86% TiS_2, 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 the TiS_2 and carbon mix. Excess solvent was removed by vacuum extraction. The resulting material was ground to a fine powder and applied to a nickel exmet screen by rolling. Electrode active material preparation was carried

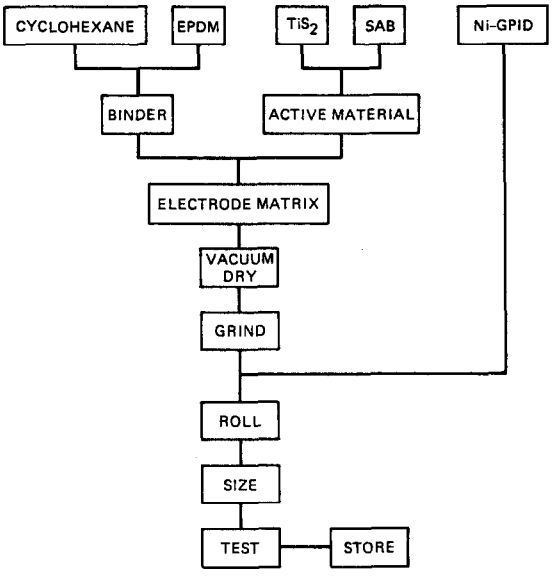

Fig. 2. TiS_2 electrode process flowchart.

TABLE 2

5 A h Li–TiS_2 cell design outline

1	Theor. anode capacity (A h)	38.5
2	Theor. cathode capacity (A h)	6.6
3	Electrode capacity ratio	5.8:1
4	No. of anodes (2.75 in. × 2.5 in. × 0.014 in.)	15
5	No. of cathodes (2.75 in. × 2.5 in. × 0.025 in.)	14
6	Current density (mA cm^{-2})	2.0
7	Electrolyte (1.5 M $LiAsF_6$/2-MeTHF)	40
8	Cell weight (g)	230
9	Cell dimensions (in.)	2.78 × 4 × 0.98

out in an argon atmosphere chamber. The electrode processing was done in a dry room (humidity less than 0.5%).

Master electrodes (6 in. × 6 in. × 0.02 in.) were fabricated and cut to the required dimensions. The porosity of the electrodes is 35 - 40% and the active material loading is 75 ± 5 mg cm^{-2}. The surface area of the electrodes is about 12 m^2 g^{-1}. These electrodes have exhibited more than 90% faradaic utilization initially in experimental cells (150 mA h) 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

a constant current method at $C/10$ rate to 2.7 V. Cells were discharged at different rates to a cutoff voltage of 1.7 V. Charge–discharge characteristics of the cell at $C/10$ rate are given in Fig. 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 Fig. 4. At the $C/10$ rate, cells delivered approximately 7.8 A h, which is roughly equivalent to 100% capacity. The energy density of the cells at this rate is found to be about 75 W h kg^{-1}. At $C/2$ discharge rate, cells have exhibited a capacity of approx. 6 A h. Cells were evaluated for their cycle life characteristics at $C/5$ and $C/2$ discharge rates to 100% DOD. The capacity of the cells as a function of cycle number is given in Fig. 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 0.05 A h/cycle and by the end of the 100th cycle cells delivered only about 3 A h. Surprisingly, the cells cycling at a $C/5$ 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 5 A h baseline cells may be due to electrolyte degradation, starved electrolyte conditions, 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 completion of this work by the end of 1989.

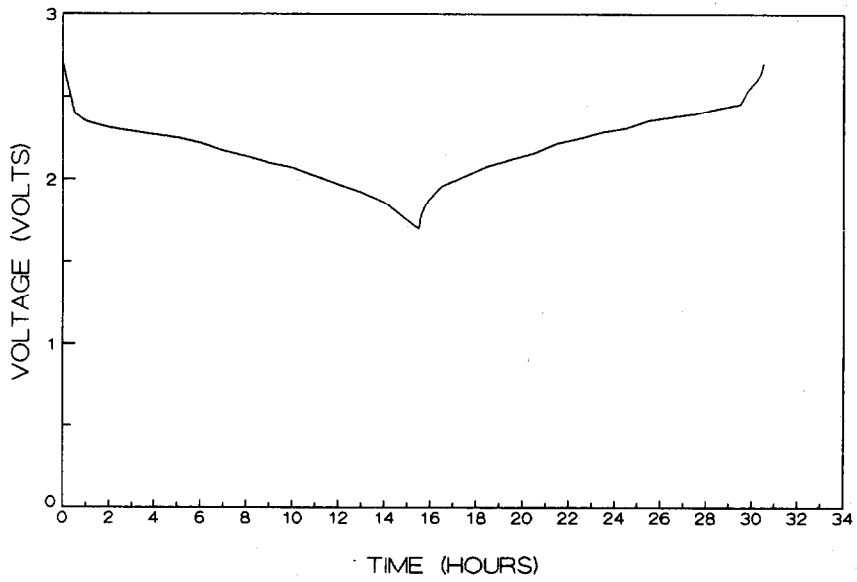

Fig. 3. Discharge and charge characteristics of 5 A h Li–TiS_2 cells.

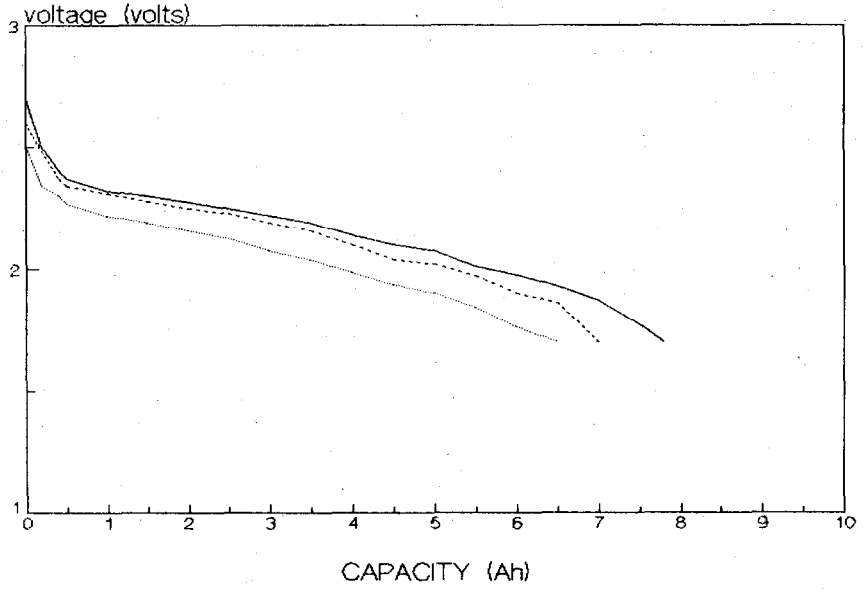

Fig. 4. Discharge characteristics of 5 A h Li–TiS_2 cells. ——, 2.5 A; - - - -, 1.0 A; ·····, 0.5 A.

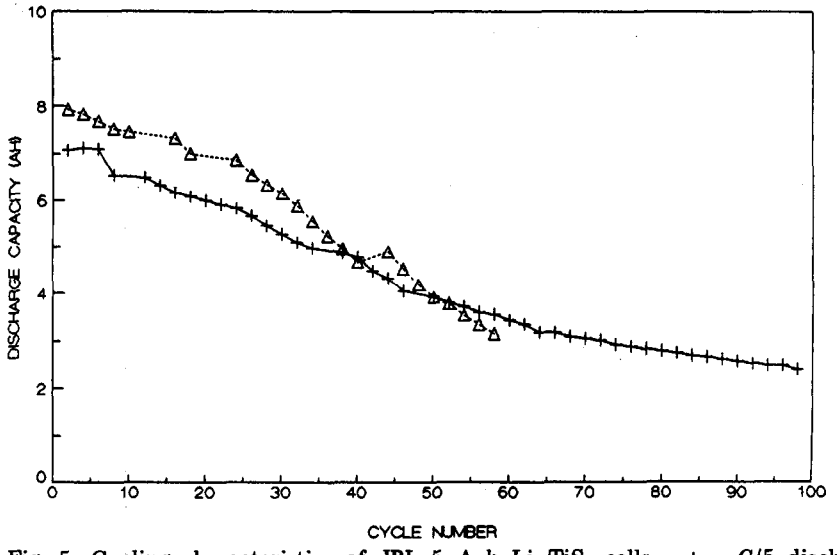

Fig. 5. Cycling characteristics of JPL 5 A h Li–TiS_2 cells. —+—, $C/5$ disch., $C/10$ ch.; ...△..., $C/2$ disch., $C/10$ ch.

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

This work represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under contract NAS-7-918.

References

1 B. Otzinger, 1984 GSFC Battery Workshop, *NASA Conf. Publ. 2382*, 1985, p. 95.
2 D. H. Shen, S. Subbarao, S. P. S. Yen and R. B. Somoano, *J. Power Sources, 18* (1986) 127 - 131.
3 D. H. Shen, S. Subbarao, S. P. S. Yen, B. J. Carter and R. B. Somoano, *ECS Ext. Abstr., 84-2*, 1984, p. 190.