

ADVANCES IN AMBIENT TEMPERATURE SECONDARY LITHIUM CELLS

S. SUBBARAO*, D. H. SHEN, F. DELIGIANNIS, C.-K. HUANG and G. HALPERT

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

Summary

JPL is carrying out a NASA/OAST sponsored R & D program on the development of ambient temperature secondary lithium cells for future space applications. The goal of the program is to develop secondary lithium cells with a 100 W h kg^{-1} specific energy and capable of 1000 cycles at 50% DOD. The approach towards meeting these goals initially focussed on several basic issues related to the cell chemistry, selection of cathode materials and electrolytes, and component development. We have examined the performance potential of Li-TiS₂, Li-MoS₃, Li-V₆O₁₃ and Li-NbSe₃ electrochemical systems. Of these four, the Li-TiS₂ system was found to be the most promising in terms of achievable specific energy and cycle life. Major advances to date in the development of Li-TiS₂ cells are in the areas of cathode processing technology, mixed solvent electrolytes, and cell assembly. This paper summarizes these advances made at JPL on the development of secondary lithium cells.

Introduction

Ambient temperature secondary lithium batteries have several intrinsic and potential advantages, including higher energy density, longer active shelf life, and lower self discharge, over conventional Ni-Cd, Ni-H₂, Pb-acid, and Ag-Zn batteries. Successful development of these batteries will yield large pay-offs such as 2 - 3-fold increase in energy storage capability and a longer active shelf life of 2 - 4 years over these systems. A detailed analysis of the strengths and weaknesses of secondary lithium batteries has indicated that these batteries are suitable for applications requiring less than 1 kW power and limited cycle life. Some of the projected space applications of these batteries are for Mars Rover, planetary space craft/probes, astronaut equipment, and geosynchronous spacecraft.

*Author to whom correspondence should be addressed.

Several ambient temperature secondary lithium systems such as: Li-TiS₂, Li-MoS₂, Li-NbSe₃, Li-MnO₂, Li-V₂O₅, etc., are currently under development for consumer and defense applications [1]. Most of these systems are still in the research stage, while a few of them are commercially available in small capacities (less than 1 A h). The performance of those cells that are commercially available falls short of meeting the space application requirements [2].

Under a NASA OAST sponsored program, Jet Propulsion Laboratory is developing ambient temperature secondary lithium cells for future space applications. The primary objective of the program is to develop ambient temperature secondary lithium cells with 100 W h kg⁻¹ specific energy while delivering 1000 cycles at moderate depths of discharge (50%). The major thrusts of this program are to improve cycle life and safety of these cells. The approach has involved work in three areas: (i) chemistry and material research; (ii) component development and interactions; (iii) performance and safety. This paper describes the advances made to-date at JPL in these areas.

Chemistry and material research

Attempts to improve the performance capability of the state of the art secondary lithium cells have been inhibited by the unavailability of materials with the desired properties, and poor understanding of the cell chemistry [3]. For these reasons the major emphasis of this effort has been directed towards identifying candidate electrode materials and a stable electrolyte, and developing fundamental understanding of materials and cell chemistry. Some of the specific objectives in this area are:

- (i) selection of a cathode material with a theoretical specific energy greater than 400 W h kg⁻¹ providing more than 1000 cycles;
- (ii) identification of an electrolyte that is stable towards lithium and has a conductivity greater than 10⁻³ (ohm cm)⁻¹;
- (iii) evaluation of the use of lithium alloys and other materials with low equivalent weight (40 g eq⁻¹) to extend the cycle life performance and safety of the cells;
- (iv) development of concepts for overcharge/overdischarge protection of cells.

Significant progress has been made by JPL in the first three of the above topics, as described below.

Cathode materials

Cathode materials required for these cells must possess several desirable properties such as high specific energy, good electrochemical rechargeability, good electronic conductivity, high lithium diffusivity, and chemical compatibility towards the electrolyte. Several materials have been reported in the literature for use in secondary lithium batteries [3]. These materials can be

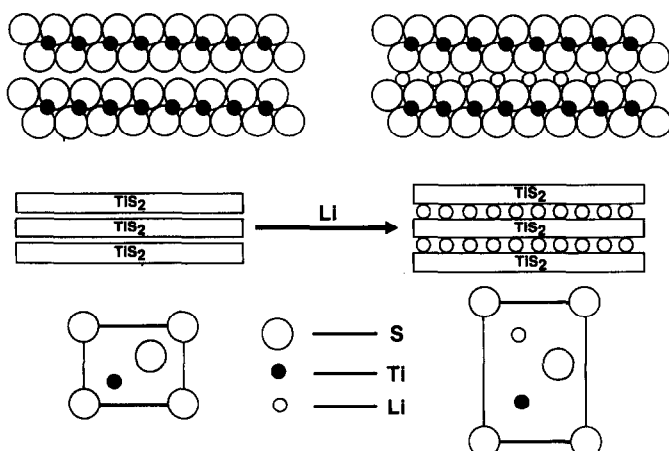


Fig. 1. Structure and intercalation of Li in TiS_2 .

TABLE 1

Performance comparison of selected cathode materials

Matl.	Op. voltage	Specific energy (W h kg^{-1})		Cycle life 100% DOD
		Theo.	Exptl.	
TiS_2	2.1	473	401	> 600
MoS_3	1.9	717	243	40 - 60
V_6O_{13} (NS)	2.15	622	323	30 - 50
NbSe_3	1.8	412	351	> 100

classified into two categories: transition metal chalcogenides (TiS_2 , MoS_3 , MoS_2 , NbSe_3 , etc.) and transition metal oxides (V_2O_5 , V_6O_{13} , MnO_2 , CoO_2 , etc.). Lithium is inserted into these host structures electrochemically during discharge (Fig. 1). Ideally, the host lattice may undergo only a minor structural change during the lithium intercalation/insertion process (discharge), and return to its original state after the charging process (the deintercalation). Four of these materials (TiS_2 , MoS_3 , V_6O_{13} , and NbSe_3) were selected for detailed examination. These four materials were evaluated for their performance (specific energy, and cycle life) in experimental cells. In order to overcome poor lithium electrode cycle life performance, a high lithium-to-positive-electrode ("cathode") ratio (6:1) was used in these experimental cells. The major emphasis of this study was focussed on determining the cycle life capabilities of these cathode materials. The results are summarized in Table 1. The results clearly indicate that the most promising cathode material is TiS_2 in view of its long cycle life performance capability and realizable specific energy. The second material of choice is NbSe_3 . Even

though MoS_3 and V_6O_{13} have higher theoretical specific energy, the materials showed poor cycle life performance and low useful specific energy. These studies led to the selection of TiS_2 as the candidate cathode material for further study with electrolytes and anode materials.

Electrolytes

The ideal electrolyte required for ambient temperature secondary lithium cells must exhibit high conductivity, a wide electrochemical operating window, a high stability towards lithium, and compatibility with cathode materials and separator, low density, and low viscosity. Some of the electrolytes that have been investigated for this application are THF, 2-MeTHF, methyl formate, and propylene carbonate [4]. These single solvent electrolytes provide only limited cycle life capability because of their reactivity towards lithium. It has been suggested [5] that the use of mixed solvent electrolytes may alleviate this problem due to the formation of a beneficial passivating film on the lithium anode and the synergistic effects associated with the use of the selected mixed solvents. A number of mixed solvent electrolytes are currently being investigated in our laboratory for use in Li- TiS_2 cells. These electrolytes contain 2-MeTHF and THF as the base solvents and ethylene carbonate (EC), propylene carbonate (PC) and 3-methylsulfolane (3-Mes) as the co-solvents. The important properties of these mixed solvent electrolytes, such as conductivity, stability towards lithium, and lithium cycling efficiency, have been evaluated. The conductivity of the electrolytes was determined by standard methods. The stability of the electrolytes towards lithium was investigated by microcalorimetry. The heat evolved from the uncycled experimental cells in open circuit condition was measured at 25 °C with a heat conduction Hart Scientific microcalorimeter. The cycling efficiency of lithium in various electrolytes was determined by cycling experimental Li- TiS_2 cells. The lithium cycling efficiency/figure of merit (FOM) was calculated using the relationship:

$$\text{F.O.M.}_{\text{Li}} = \frac{\text{total accumulated discharge capacity}}{\text{theoretical Li capacity}}$$

The comparative performance of selected electrolytes is summarized in Table 2. Among the co-solvents investigated, EC appears to be a promising co-solvent. The mixed solvent electrolytes containing EC (EC/THF, EC/2-MeTHF, EC/THF/2-MeTHF, EC/3-MeS/2-MeTHF) showed a higher conductivity and improved stability towards lithium compared with the electrolytes containing no EC (based on open circuit stand tests and microcalorimetry). The a.c. impedance and FTIR studies [6] indicated that the improved performance of EC/2-MeTHF electrolyte may be due to the formation of a thin Li_2CO_3 film on the surface of the lithium electrode. From the results it can be observed that EC-containing electrolytes yield higher FOM values than other electrolytes. An FOM of 38.5 was obtained with 10% EC + 90% 2-MeTHF electrolyte and this is 33% higher than the FOM of the

TABLE 2
Properties of selected electrolytes

Electrolyte	Conductivity $10^{-3} (\Omega \text{ cm})^{-1}$	Stability to lithium ^a (μW)	Lithium cycling efficiency ^b (FOM)
THF	13.7	90	3
2-MeTHF	3.4	25	28
10% EC + 90% THF	14.6	84	4
10% EC + 90% 2-MeTHF	6.2	16	38
20% PC + 90% 2-METHF	6.1	24	—
25% 3-MeS + 75% 2-MeTHF	3.6	—	10
50% THF + 50% 2-MeTHF	8.9	—	20

^aHeat output on OCV (microcalorimetry studies).

^bDischarge/charge current density = 2/1 mA cm⁻².

benchmark 2-MeTHF electrolyte (29.5). Although the achievement of this FOM represents a significant advance, the FOM value presently remains lower than the target objective (FOM ~ 80). Work is continuing to identify an electrolyte that can meet program targets.

Lithium alloys

The limited cycle life performance of ambient temperature lithium cells is primarily attributed to the reactivity of the lithium anode with organic electrolytes. One method of reducing the reactivity of the lithium anode towards the electrolyte is by the use of lithium alloys as anode materials. Further, the use of lithium alloy anodes may also improve the safety of the cells. Six lithium alloys were selected for preliminary experimental evaluation after a detailed review of the literature. These alloys are Li-Al, Li-Si, Li-Sn, Li-Zn, Li-Pb, Li-Cd. All these materials are basically lithium-rich alloys. They were selected based on their electrochemical potential, equivalent weight, lithium diffusivity, reversibility, and thermodynamic stability towards organic electrolytes. Some of the important properties of these alloys are summarized in Table 3. Experimental evaluation of these alloys was initiated and is in progress.

Component development and interactions

Component characteristics and cell design also play a significant role in cell performance. For this reason, work is in progress on the fabrication of TiS₂ cathodes and design analyses. Details of the progress made in these two areas are described below.

TABLE 3

Properties of lithium alloys

Alloy	Eqn. wt (g eq ⁻¹)	<i>E</i> vs. Li (mV)	A h g ⁻¹	Diffusivity (cm ² s ⁻¹)	Sp. energy ^a (W h kg ⁻¹)
Li	6.9	0	3.86	—	473
Li _{2.5} Al	18.3	141	1.46	10 ⁻⁴ b	403
Li ₂ Si	21.0	332	1.28	10 ⁻⁵ b	356
Li _{4.5} Pb	68.1	400	0.39	10 ⁻⁸ c	253
Li _{5.6} Sn	34.2	263	0.78	10 ⁻⁵ b	337
Li _{1.5} Zn	68.9	106	0.39	10 ⁻⁹ c	295

^aCalculated for Li-TiS₂ system.^b400 °C^c25 °C.

TABLE 4

Properties of TiS₂ raw material

Source	Stoichiometry (S:Ti)	Impurities	Ap. density (g cm ⁻³)	Faradaic utilization (% theo.)
JPL	1.99	O	0.80	95
Degussa	1.97	Cl	0.48	75
Cerac	2.18	Cl, S	0.32	60

TiS₂ cathode processing

The rate capability and faradaic utilization of the TiS₂ cathode are dependent on the chemical composition of TiS₂, the nature of the binder, additives/conducting diluents, as well as the thickness and porosity of the electrode. TiS₂ processed by the vapor transfer method was found to show higher faradaic utilization compared with the TiS₂ materials procured from commercial sources (Table 4). This improved performance was found to be associated with the purity and stoichiometry of the material. Hence, it was decided in our subsequent studies to use TiS₂ prepared "in-house" by the improved vapor transport method.

During cycling the cathode undergoes a volume change due to the intercalation/deintercalation of Li into/from the TiS₂ crystal lattice. The electrode structure must be capable of accommodating these changes, otherwise it will disintegrate during cycling. Studies carried out on various binder materials identified EPDM as the most suitable binder material for the construction of TiS₂ cathodes [7]. Three methods: brushing, rolling, and pressing were examined for the fabrication of TiS₂ cathodes. The brushing method was found to be suitable for the fabrication of small electrodes in the glove box. The rolling, and pressing methods offered several advantages

TABLE 5
Properties of TiS_2 cathodes

Property	Brushing	Rolling	Pressing
Thickness (mil)	15 + 2	20 + 2	16 + 2
Loading (mg cm^{-2})	48 + 5	66 + 5	54 + 5
Porosity (%)	56 + 2	56 + 2	54 + 2
Capacity (mA h cm^{-2})	12 + 1	16 + 1	13 + 1

including amenability to scale up, and uniform loading. Typical characteristics of the electrodes fabricated by various methods are given in Table 5. Work is in progress to understand the relationships between electrode properties and performance.

Design trade off studies

Some of the important parameters to be considered in the design of secondary lithium cells are the ratio of electrode capacities, operating current density, electrolyte composition and quantity, case and grid materials, and cell size. A computer program was developed [8] to understand the influence of these parameters on specific energy and to optimize the cell design. The results of these studies indicated that a specific energy of 80 - 100 W h kg^{-1} is achievable for high capacity cells ($> 20 \text{ A h}$). The negative-to-positive electrode capacity ratio has minimal effect on the specific energy of the cells. A high anode-to-cathode capacity is required to account for the degradation of the Li electrode and to achieve maximum cycle life. Cells cannot operate at current densities higher than 2 mA cm^{-2} because of the poor conductivity of the electrolyte. The cell case is the major contributor to cell weight (Fig. 2). Of 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. Experimental work is in progress to determine the influence of some of the important parameters on the cycle life performance of the cells.

Cell performance and safety

An assessment was made of the status of secondary lithium cells by experimental evaluation of Li-MoS_2 , Li-NbSe_3 and Li-TiS_2 cells. Li-MoS_2 and Li-NbSe_3 cells (AA) were procured from the industry. The Li-TiS_2 cells were fabricated "in-house" with non-optimized cell design and cell hardware. These cells were evaluated for their charge/discharge characteristics, rate capability, and cycle life; the results are summarized in Table 6. These cells have a cycle life of 100 - 250 cycles at moderate discharge rates ($C/5$). Li-NbSe_3 cells exhibited high specific energy and Li-MoS_2 cells showed long

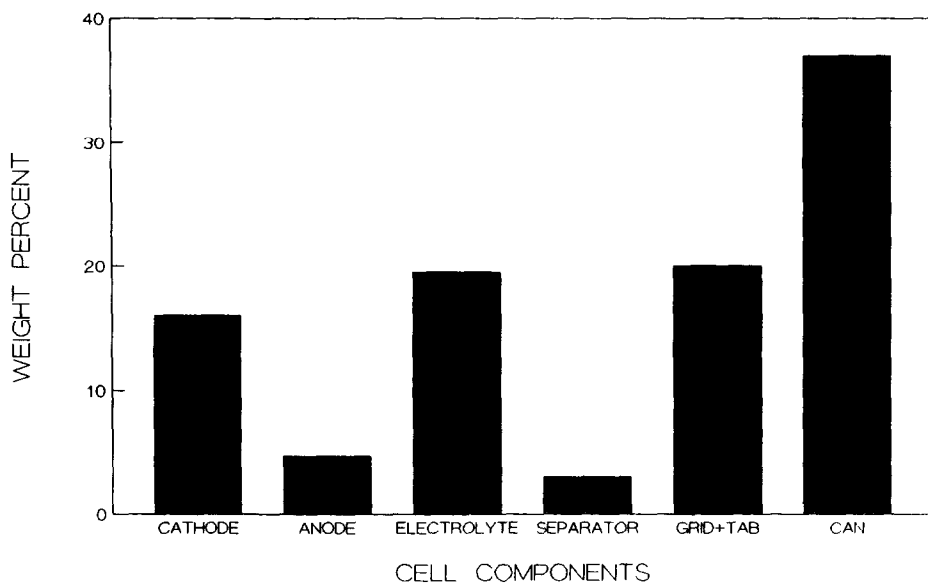


Fig. 2. 5 A h Li-TiS₂ cell weight budget.

TABLE 6

Summary of performance characteristics

	Li-MoS ₂	Li-NbSe ₃	Li-TiS ₂
Size	'C'	'AA'	PRIS.
Capacity (A h) (CYC #5)	2.20	1.20	7.5
Voltage (T/2) (V)	1.80	1.80	2.10
Discharge rate	C/5	C/5	C/5
Charge rate	C/10	C/10	C/10
Cycle life	260	105	80
Weight (g)	69	20.5	230
Specific energy (W h kg ⁻¹)	65	110	75 ^a

^aUnoptimized cell hardware.

cycle life. The low specific energy and cycle life of 5 A h cells may be due to the non-optimized cell design and cell hardware. Two of the important problems identified are: formation of soft shorts during cycling at low discharge rates (C/10) and inferior performance at low depth of discharge in the Li-MoS₂ system. An evaluation of the safety of these cells is in progress.

Conclusions

The Li-TiS₂ system appears to be the most promising of the ambient temperature secondary lithium systems examined in view of its higher realizable specific energy and cycle life. Use of mixed solvent electrolytes

was found to improve the cycle life of this system. Of the various electrolytes examined, 1.5 M LiAsF₆/EC + 2-MeTHF mixed solvent electrolyte was found to be more stable towards lithium. Experimental cells activated with this electrolyte exhibited more than 300 cycles at 100% DOD. Design trade off studies of this system indicated that a practical specific energy of 80 - 100 W h kg⁻¹ is achievable in 20 A h cells and above. The technology of these cells is still far below the requirements of planetary space missions. Significant progress is still needed, particularly with regard to cycle life, tolerance to over-charge and over-discharge, safety, and cell size. Many of these key problems require significant scientific and technological innovations in the areas of electrolyte technology, alternative lithium-based anode materials, new additives, and cell design.

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