# Advances in Li–TiS$_2$ cell technology

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## Abstract

JPL is involved in a NASA sponsored program to develop ambient temperature secondary cells for future space missions. After several years of research on various cathode materials, titanium disulfide (TiS$_2$) was selected in view of its intrinsic reversibility and high faradaic utilization. In the last two years, efforts have been focussed on improving the cycle life of the system and developing 1 A h cells. Several approaches including the use of mixed solvent electrolytes, the operation of cells at low temperature, and the cycling of cells under different voltage limits, were initially examined to improve the cycle life performance of the Li–TiS$_2$ system. Spiral wound 1 A h cells fabricated incorporating the improvements from the above studies have delivered more than 600 cycles at 50% DOD. Work is in progress to identify alternate anode materials that can improve the cycle life of the cells to 1000 cycles at 50% DOD. This paper summarizes the advances made in the Li–TiS$_2$ technology at JPL since 1989.

## Introduction

Ambient temperature secondary lithium batteries have a number of intrinsic advantages such as higher energy density, longer active shelf life, lower self discharge, etc. Over the conventional Ni–Cd, Pb–acid and Ag–Zn batteries. The pay-offs are 2–3 fold increase in energy storage capability and a longer active shelf life of 5 to 10 times that of Ni–Cd.

Under a NASA OAET sponsored program, Jet Propulsion Laboratory (JPL) is developing ambient temperature secondary lithium cells for future space applications. The main objective of the program is to develop ambient temperature secondary lithium cells with greater than 100 W h/kg specific energy while delivering 1000 cycles at moderate depths of discharge (50%) by 1995. Some of the projected space applications of these batteries are for planetary rover, planetary spacecraft/probes, astronaut equipment and Geo-Syn-Spacecraft.

After a detailed examination of various cathode materials, TiS$_2$ was selected in view of its intrinsic reversibility and high faradaic utilization [1]. The state-of-art Li–TiS$_2$ cells have a limited cycle life performance (100–200 cycles at 100% DOD), and the cells were found to lose capacity on cycling [2]. The capacity loss in found to be mainly due to the increased cell polarization with cycling. This increased polarization is understood to be

due to the electrolyte degradation with cycling. Hence any approach, that can reduce the electrolyte degradation and/or improve electrolyte stability towards lithium will result in improved cycle life. A number of approaches such as the use of mixed solvent electrolytes, the operation of cells at low temperature, and the cycling of cells under different voltage limits, were examined to improve the cycle life performance of the Li–TiS$_2$ system. Spiral wound 1 A h cells were fabricated incorporating the improvements from the above studies. The cells have delivered more than 600 cycles at 50% DOD. Other approaches are required to achieve the goal of 1000 cycles. Lithium alloys and intercalation compounds have lower reactivity towards organic electrolyte than elemental lithium [3]. The use of these materials as candidate anode materials can result in improving the cycle life performance of the cells. A number of lithium alloys and intercalation compounds are being evaluated as candidate anode materials. This paper summarizes these advances made at JPL since 1989 in Li–TiS$_2$ technology.

## Mixed solvent electrolytes

The limited cycle life performance of the ambient temperature Li–TiS$_2$ cells is mainly due to the high reactivity of the organic electrolyte towards lithium and cathode material [4]. JPL used 1.5 M LiAsF$_6$/2-MeTHF as bench mark electrolyte for secondary Li–TiS$_2$ cells. Use of additive and co-solvents were investigated to improve the stability of THF, 2-MeTHF and dioxolane electrolytes. The additives and co-solvents investigated were 2-methyl furan (2-MeF), ethylene carbonate (EC), propylene carbonate (PC) and 3-methyl sulfolane (3-MeS). A number of electrolytes with different combinations of additive and co-solvents were evaluated for their stability towards lithium by open circuit stand, a.c. impedance spectroscopy and microcalorimetry methods [5]. Three electrolytes were selected for detailed assessment in view of their improved stability and conductivity. The selected electrolytes are 1.5 M LiAsF$_6$ EC/2-MeTHF, 1.5 M LiAsF$_6$ THF/2-MeTHF/2-MeF, and
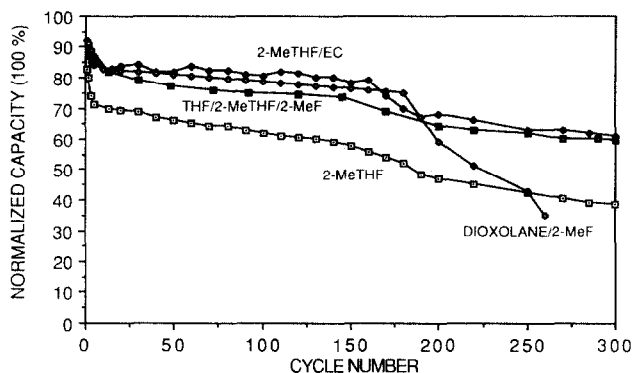


Fig. 1. Cycle life performance of experimental cells activated with mixed solvent electrolytes.

1.5 M LiAsF$_6$ dioxolane/2-MeF. The cycle life performance of the experimental cells (150 mA h) activated with these electrolytes is given in Fig. 1. The cells activated with 1.5 M LiAsF$_6$ EC/2-MeTHF and 1.5 M LiAsF$_6$ THF/2-MeTHF/2-MeF electrolytes showed higher cathode utilization and minimum capacity decline compared to the cells activated with 1.5 M LiAsF$_6$ dioxolane/2-MeF and 1.5 M LiAsF$_6$ 2-MeTHF bench mark electrolytes. The rate capability, operating temperature range and safety of the cells are presently being evaluated. Final selection of the electrolyte will be made based on the results of these studies.

## Low temperature operation

The reactivity of the organic electrolyte towards lithium can be reduced by operating the cells at low temperature. It was felt that the reduced reactivity of the electrolytes at low temperature can result in improved cycle life performance [6]. In the present investigation, we have evaluated the influence of temperature on the stability and lithium cycling efficiency of the electrolytes.

The electrolytes investigated were: THF, EC/THF, 2-MeTHF, EC/2-MeTHF, THF/2-MeTHF and EC/THF/2-MeTHF. All the electrolytes contained 1.5 M LiAsF$_6$. The stability of the electrolytes at three different temperatures (10, 25 and 70 °C) was evaluated by open circuit stand test method. Results of these studies are summarized in Table 1. Some of the important observations are: (i) the electrolyte showed higher stability towards lithium at 10 °C, (ii) the reactivity of electrolyte towards lithium increased with temperature, (iii) 2-MeTHF electrolytes exhibited higher stability towards lithium compared to THF electrolytes, and (iv) addition of EC improved the stability of THF, 2-MeTHF and THF/2-MeTHF electrolytes. From these results, it was expected that cycling of the cells at low temperature may result in improved cycle life performance.

TABLE 1

Effect of temperature on the stability of electrolytes towards lithium (open circuit stand test results)[a]

| Electrolyte | 10 °C | | 30 °C | | 70 °C | |
|---|---|---|---|---|---|---|
| | Li | Electrolyte | Li | Electrolyte | Li | Electrolyte |
| THF | brown | light yellow | dark brown | brown precipitate | dark brown | brown precipitate |
| EC + THF | S | C | brown spots | C | brown spots | brown |
| 2-MeTHF | S | C(ppt) | S | C | black stripes | light yellow |
| EC + 2-MeTHF | S | C | S | C | S | C |
| THF + 2-MeTHF | brown spots | light yellow | dark brown | yellow | dark brown | yellow precipitate |
| EC + THF + 2-MeTHF | S | C | S | C | brown spots | light yellow |

[a]S: shining; C:clear.

TABLE 2

Effect of temperature on the lithium cycling efficiency

| Electrolyte | Figure of merit $(FOM)^a$ | |
| --- | --- | --- |
| | 10 °C | 25 °C |
| THF | 3.3 | 3 |
| EC + THF | 4.6 | 4 |
| 2-MeTHF | | 29.5 |
| EC + 2-MeTHF | 32 | 38.5 |
| THF + 2-MeTHF | 5.1 | 4.5 |
| EC + THF + 2-MeTHF | 7.4 | 7.6 |

$^aFOM_{Li}$ = (total accumulated discharge capacity)/(theoretical Li capacity).

Cycle life performance of the cells activated with these six electrolytes was evaluated at 10 and 25 °C. These two temperatures were chosen to verify the hypothesis of benefits of low temperature cycling. Sealed 150 mA h experimental Li–TiS$_2$ cells were cycled by constant current method between 1.7 and 2.7 V. The current densities were 2 and 1 mA/cm$^2$ for discharging and charging, respectively. Cycling efficiency of lithium in various electrolytes was determined from the cycle life data. The lithium cycling efficiency/figure of merit $(FOM)$ was calculated using the relationship

$$FOM_{Li} = \frac{\text{total accumulated discharge capacity}}{\text{theoretical Li capacity}}$$

Lithium cycling efficiency $(FOM)$ in these electrolytes at 10 and 25 °C is given in Table 2. From the results it can be observed that no significant difference in $FOM$ was observed by cycling cells at 10 and 25 °C.

The lithium cycling efficiency results are not in agreement with the prediction of the open circuit stability stand tests. This is probably due to the fact that the open circuit stand test can only provide qualitative information about the reactivity of the electrolytes towards passivated lithium. During cycling, finely divided lithium is formed and the reactivity of the electrolytes towards the freshly formed lithium deposits is significantly higher.

**Operating voltage limits**

It is known that at voltages lower than 1.5 V, the salt LiAsF$_6$ undergoes reduction and at voltages higher than 3 V, some solvents undergo oxidation. Thus, the degradation of the electrolyte can be minimized by selecting optimum cycling limits (end of charge and discharge voltages). To investigate this phenomenon, 1 A h Li–TiS$_2$ cells obtained from a commercial source were cycled under three different voltage regimes (1.7–2.7, 1.9–2.7, 1.9–2.5 V). These cells were activated with 1.5 M LiAsF$_6$ 2-MeTHF/THF/2-MeF.
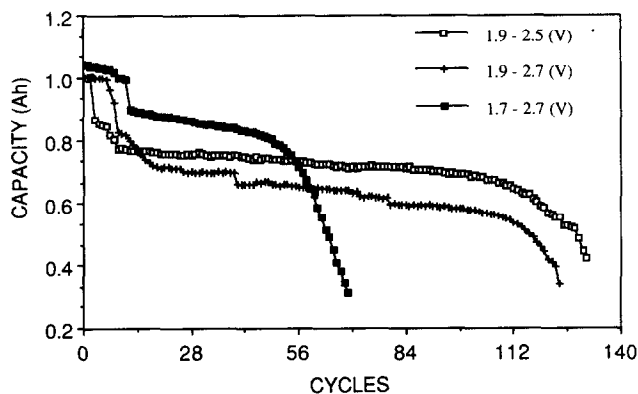
Fig. 2. Cycle life performance of Li–TiS$_2$ cells operated under different voltage limits.

Cycle life performance of these cells under three different voltage regimes is given in Fig. 2 [7]. From the results, it can be observed that the cycle life performance of the cells is significantly dependent on the cycling voltage limits. The lower voltage limit seems to have a higher influence on the cycle life performance. Detailed cycling studies are needed for each electrolyte to identify the optimum operating limits and the degradation mechanisms involved.

## 1 A h cell development

Experimental cells (150 mA h) were used until 1989 for the performance evaluation of electrolytes and cathode materials. Spiral wound 1 A h cells were developed in 1990 for design optimization studies and performance evaluation of components. These cells had an electrode capacity ratio of 6:1 (Li:TiS$_2$) and were activated with 1.5 M LiAsF$_6$ EC/2-MeTHF electrolyte. This electrolyte was selected in view of its higher stability and lithium cycling efficiency compared to the other mixed electrolytes investigated at JPL. The cycle life performance of the cells at 50% and 100% DOD was evaluated at $C/10$ charge and $C/5$ discharge. The cells had delivered more than 600 and 350 cycles at 50% and 100% DOD, respectively (Figs. 3 and 4). Even though the cycle life performance of these cells is attractive for many commercial applications, it is still inadequate for space applications. Alternate anode materials are being examined to achieve the desired cycle life performance goal.

## Anode materials

Lithium alloys and intercalation components have lower reactivity towards organic electrolytes than elemental lithium [3]. The use of these materials
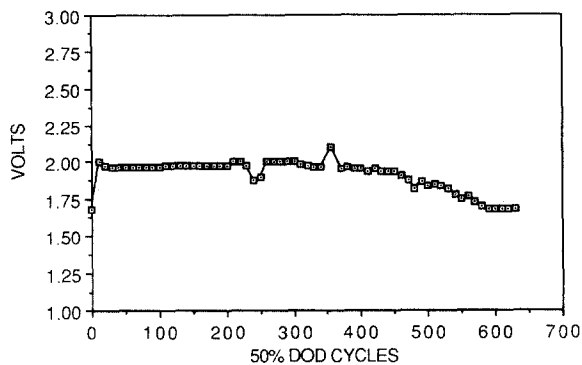
Fig. 3. Cycle life characteristics of 1 A h Li–TiS$_2$ cell at 50% DOD.
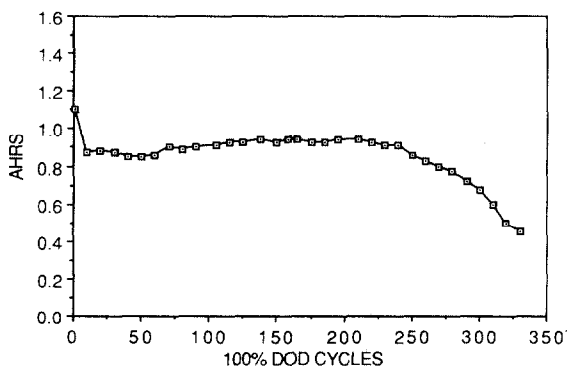


Fig. 4. Cycle life characteristics of 1 A h Li–TiS$_2$ cell at 100% DOD.

as candidate anode materials can result in improving the cycle life performance of the cells. Further, the use of lithium alloy anodes may also improve the safety of the cells.

A suitable lithium alloy anode material must have several desirable properties such as high Li diffusivity, low equivalent weight (molecular weight/ no. of Li reversible), high reversibility, and low voltage ($E°$ versus Li). In addition, the material must have good thermal and chemical stability in the cell environment. Detailed analysis of the variables that control the specific energy of the Li alloy–TiS$_2$ system resulted in establishing selection criteria. The equivalent weight and voltage (versus Li) of the alloy must be less than 60 g/equiv. and 200 mV, respectively, to achieve a practical specific energy of 70–80 W h/kg. The equivalent weights of different alloys were calculated assuming that 80% of the lithium in the alloy is available for reaction. This assumption was made because of the lack of actual experimental data in the literature. The properties of several lithium alloys and the corresponding theoretical specific energy of the Li alloy–TiS$_2$ system are summarized in Table 3. Among the various alloy systems examined, only Li–Si and Li–Cd alloys were found to satisfy the above criteria. The Li–Al alloy, with a voltage

TABLE 3

Properties of alternate Li anode material (theoretical)

| Material type | $E$ vs. Li (mV) | MW (g/mole) | No. of Li reversible | Specific (W h/kg) |
|---|---|---|---|---|
| Li | 0 | 6.941 | 1 | 472 |
| $\beta$-LiAl | 385 | 35.32 | 1 | 312 |
| $Li_{1.1}Zn$ | 191 | 73 | 0.6 | 220 |
| $Li_{4.3}Sn$ | 411 | 148.5 | 2 | 243 |
| $Li_{4.5}Pb$ | 388 | 238.4 | 3.5 | 254 |
| $Li_{2.85}Cd$ | 140.6 | 132.2 | 2.6 | 322 |
| $Li_{0.15}C$ | 200 | 13.05 | 0.15 | 255 |
| LiAlMn | 386 | 36 | 1 | 311 |
| LiAlCr | 386 | 36 | 1 | 311 |
| LiAlCdPb | 200 | 96.5 | 1 | 247 |

TABLE 4

Properties of alternate Li anode material (experimental)

| Material type | Stability[a] | Av. $E$ vs. Li (mV) | No. of Li reversible[b] | Specific energy (W h/kg) |
|---|---|---|---|---|
| $Li_{1.2}Al$ | good | 380 | 0.9 | 300 |
| $Li_{2.85}Cd$ | poor | 0 | | |
| $Li_{3.0}Pb$ | good | 449 | < 1.5 | 167 |
| $Li_{0.13}C$ | good | 200 | < 0.08 | 186 |
| $Li_{4.4}Si$ | poor | | | |
| $Li_{2.5}Sn$ | good | 520 | < 1.0 | 171 |
| $Li_{0.5}Zn$ | good | 256 | < 0.12 | 62 |

[a]Microcalorimetric and OCV measurements.
[b]Galvanostatic cycling studies.

higher than 200 mV versus Li, has a theoretical specific energy of more than 300 W h/kg because of its lower equivalent weight. In practical cells, Li–Al, Li–Si and Li–Cd alloys are projected to provide greater than 75 W h/kg (1/4 of theoretical). Li–C, Li–Pb and Li–Sn appear to be the next best among the alloys considered.

Li–Al, Li–Cd, Li–Pb, Li–C, Li–Si and Li–Sn materials were evaluated for their stability and reversibility. The stability of the alloys was evaluated by microcalorimetry and open circuit voltage measurement techniques. Among the alloy materials examined Li–Si and Li–Cd were found to be unstable towards 1.5 M $LiAsF_6$/EC + 2-MeTHF electrolyte. The usable capacity and reversibility of the remaining four alloy materials were evaluated in experimental cells by galvanostatic cycling. The realizable specific energy of the Li alloy–$TiS_2$ system was also calculated. The results of these studies are summarized in Table 4. From the results it can be observed that Li–Al and Li–C alloys are the only materials that can be considered for further evaluation

in view of their reversibility and higher specific energy. Detailed assessment of these materials in experimental Li–alloy/TiS$_2$ cells is in progress.

## Conclusions

Several approaches were examined to improve the cycle life of ambient temperature secondary Li–TiS$_2$ cells. Some of the important findings of the study are: (i) Li–TiS$_2$ cells activated with 1.5 M LiAsF$_6$/EC + 2-MeTHF electrolyte showed improved cycle life performance compared to the cells activated with other mixed solvent electrolytes investigated; (ii) the cycling of the cells at low temperature did not result in improving the cycle life of the cells; (iii) charge and discharge voltage limits were found to have significant influence on the cycle life of the cells. Spiral wound 1 A h cells activated with 1.5 M LiAsF$_6$/EC + 2-MeTHF electrolyte have delivered more than 600 cycles at 50% DOD. Work is still in progress to improve the safety and cycle life performance of the cells through the use of alternate anode materials.

## Acknowledgements

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