

CAPACITY-CYCLE LIFE BEHAVIOR IN SECONDARY LITHIUM CELLS

R. B. SOMOANO, B. J. CARTER, D. SHEN and S. P. S. YEN

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

Summary

The practical utilization of high energy density rechargeable lithium cells is dependent upon maintaining high capacity for the duration of the required cycle life. However, a critical, yet generic problem with room temperature lithium systems is that the capacity often declines considerably during the early stages of cycling. We report the results of our studies on electrolyte degradation which we observe after cells have undergone 300 and 700 deep cycles with 3-methylsulfolane- and 2-methyltetrahydrofuran-LiAsF₆ electrolytes, respectively.

1. Introduction

Room temperature rechargeable lithium cells hold promise as advanced energy sources for future space applications. In particular, NASA has need of a secondary battery that can deliver >100 W h/kg for ten years of geosynchronous earth orbit (GEO) operation. However, lithium cell research and technology are in an early stage of development with only hand or custom made cells available.

To achieve the above performance, studies have been carried out to identify and understand the fundamental physical and chemical processes which govern (and limit) cell processes. The emphasis of this work has consisted of elucidating the all important lithium-electrolyte interaction which is responsible for electrode passivation and electrolyte degradation. Lithium arsenic hexafluoride (LiAsF₆) dissolved in either 2-methyltetrahydrofuran (2-MeTHF) or 3-methylsulfolane (3-MeS) have been the electrolytes chosen to investigate the cell chemistry and demonstrate cycle capability. Figure 1 illustrates the cycle life achieved in hermetically sealed, cathode-limited Li-TiS₂ laboratory cells. High cycle life is clearly possible. However, the capacity is seen to decline at a rapid rate during the early stages of cycling prior to levelling off, especially with the 3-MeS electrolyte. Capacity decline is a serious problem in room temperature rechargeable lithium cells that must be resolved prior to practical utilization. We have investigated the

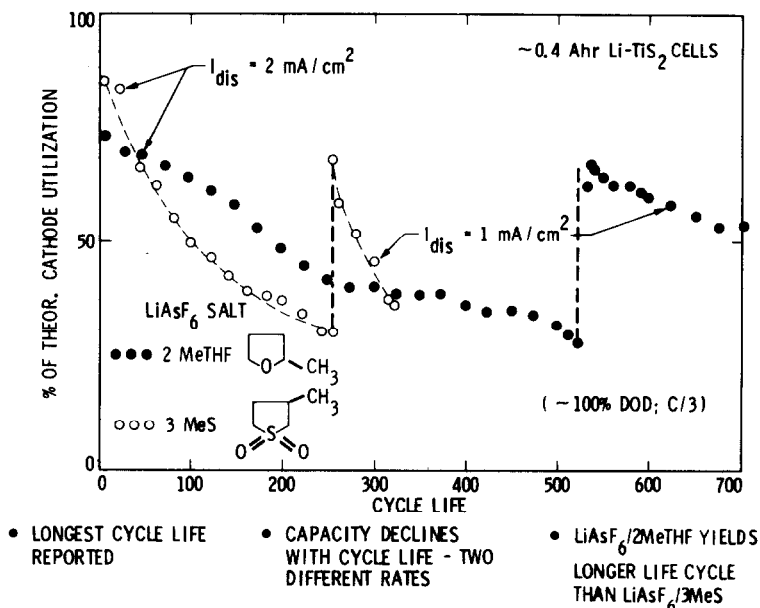


Fig. 1. Capacity vs. cycle life for approx. 0.4 Ah cathode limited Li-TiS₂ sealed laboratory cell. The cell using the 3-MeS electrolyte was cycled at 60 °C.

lithium-electrolyte chemistry in Li-TiS₂ cells which utilize the LiAsF₆/3-MeS electrolyte in hope of assessing the contribution of specific chemical processes to capacity decline.

2. Lithium-electrolyte reactions

Our earlier studies of the LiAsF₆/2-MeTHF electrolyte indicated that solvent reduction by lithium leading to ring-opened products is a dominant degradation mode [1, 2]. To achieve improved electrochemical stability, we have examined sulfolane-based electrolytes. We have cycled an Li/1.3M LiAsF₆-3-MeS/TiS₂ cell at 60 °C for over 350 cycles before the cell capacity dropped to less than 30% of initial theoretical capacity (Fig. 1), at which point the test was voluntarily terminated. The capacity declines with cycle-life although the rate of decline decreases with cycling. The cells were opened after 350 cycles for *post-mortem* analysis. The lithium passivation film was exhaustively washed with purified 3-MeS to remove unreacted LiAsF₆. Subsequently, the film material was washed with cyclohexane (purified and dried from Li-amalgam) and vacuum dried to ensure removal of all solvents (3-MeS, cyclohexane).

Scanning Electron Microscopy (SEM) showed that the surface of the lithium electrode was covered by a porous film after cycling. X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) were employed to identify the solid state chemical species formed on

the lithium anode surface after 350 cycles. The principal results of the XPS study are:

(i) the observation of two different oxidation states of sulfur, indicative of two solid state, sulfur-containing lithium salts with binding energies at 162.8 eV (R'SLi) and 166.2 eV (RSO₂Li) [3, 4];

(ii) the observation of only one valence state of arsenic, As³⁺, at 42.3 eV corresponding to an As³⁺-S polymer [3]. The results of an FTIR study of Nujol mulls of the lithium passivating film indicate the presence of sulfonic acid functional groups and sulfonic acid-lithium salt at 1115 cm⁻¹ and 1150 cm⁻¹, respectively [4]. These data support the XPS assignments.

In order to account for the experimental results, a reaction scheme suggesting degradation pathways of the solvent (3-MeS) and solute (LiAsF₆) in the presence of lithium in an electrochemical environment at 60 °C is proposed. The mechanism proposes that the solute, LiAsF₆, is reduced by Li to yield AsF₃ [5]. The solid-liquid reaction of freshly replated lithium and 3-MeS results in the formation of the salt (RSO₂Li). The presence of this salt after 350 cycles suggests that it is relatively stable. Since fresh lithium is continuously formed during charging, RSO₂Li undergoes solid-solid reaction, first to the sulfoxide, RSO, then to the sulfide, RS, and finally to the ring-opened unsaturated mercaptan salt, R'SLi. Since the rate of the solid-liquid reaction is faster than the solid-solid process, we suggest that the former occurs during early cell cycling, and possibly contributes to the rapid initial decrease in cell capacity. The solvent degraded species, R'SLi, can further react with AsF₃ to yield (-As³⁺-S-)_n. The latter compound is the sulfur analog of (-As³⁺-O-)_n reported by Koch in his studies on the degradation of 1.5M LiAsF₆-2-MeTHF [5].

Conclusion

Our results indicate that the LiAsF₆/3-MeS electrolyte is unstable at 60 °C in the presence of lithium under prolonged cell cycling. Degradation products of both the solvent and solute have been identified and may be contributing to capacity decline. Work aimed at elucidating the chemistry as a function of cycle life is in progress in order to determine the impact of the degradation processes on cell performance. The 3-MeS solvent may still hold promise if a more stable solute is found for this cell system.

Our results demonstrate that room temperature Li-TiS₂ laboratory cells can be cycled extensively, although there are certainly problems that must be solved. Our understanding of the fundamental processes and degradation modes in rechargeable lithium cells must improve substantially.

Acknowledgement

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, Contract NAS7-918.

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