



Lithium–titanium disulfide rechargeable cell performance after 35 years of storage



Nathalie Pereira ^{a, *}, Glenn G. Amatucci ^a, M. Stanley Whittingham ^b, Robert Hamlen ^c

^a ESRC, Department of Materials Science and Engineering, Rutgers University, North Brunswick, NJ 08902, USA

^b NorthEast Center for Chemical Energy Storage, Binghamton University, Binghamton, NY 13902-6000, USA

^c Former General Manager, Exxon Enterprises Battery Division, Holmdel, NJ, USA

HIGHLIGHTS

- Evaluation of some of the first commercial secondary Li cells after 35-year storage.
- 25 and 100 mAh button cells retained >50% of the original capacity after storage.
- Capacity losses averaged to <2% per year with similar cycle life as original cells.
- Lithium tetraphenyl boron-based electrolyte very stable with the Li/TiS₂ chemistry.
- Hope towards ultra long life, stable lithium-electrolyte interphases development.

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ABSTRACT

Much groundbreaking research in the field of lithium batteries occurred in the 1970s. Some of “the first” rechargeable lithium cells for commercial applications were fabricated by the Exxon Enterprises Battery Division in New Jersey. A small collection of 1978-era 25 mAh and 100 mAh button cells were preserved in the personal collections of the original researchers. This presented a unique opportunity to evaluate lithium cells after 35 years of storage. Cells were characterized for capacity, cycling, rate and impedance. Results were compared with original data as recovered from historical documents.

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1. Introduction

Although research on intercalation materials for alkali metals goes back a century with the first report of intercalation of bisulfate ions into graphite in 1841 [1] and of alkali metals in 1926 [2], formation of intercalation compounds with layered dichalcogenides were not published until 1959 [3]. It took another 20 years to bring the technology to the energy storage market with the realization of what we believe were the first commercial rechargeable lithium cells which were introduced by the Exxon Enterprises Battery Division in 1976–78. These cells utilized a titanium disulfide (TiS₂) cathode technology developed by Dr. Whittingham and his group in the Exxon Research Laboratory. Their evaluation of the

electrochemical performance in various layered chalcogenides initiated in the early 1970s concluded that TiS₂ offered the best approach as a positive electrode to a rechargeable lithium battery [4]. The Exxon Enterprises Battery Division was at the time created within Exxon Enterprises, the new venture part of Exxon, upon initiation of an Advanced Battery Project.

The Exxon Enterprises Battery Division together with the Research Lab evaluated various electrolyte and anode systems to be used with TiS₂-based positive electrodes, and also developed engineering designs for small cells. In order to minimize dendrite formation and hence improve cycle life, the system's negative electrode consisted of a lithium–aluminum alloy fabricated by pressing a single layer of both lithium and aluminum foil onto the opposite surfaces of a flattened expanded nickel mesh. The positive electrode was fabricated by cold-pressing TiS₂ powder directly into the positive half of the coin cell case with about 7% porosity. The negative and positive pairs, balanced for safety (by being negative

* Corresponding author.

E-mail address: npereira@rutgers.edu (N. Pereira).

electrode limited) were assembled using a Celgard separator, developed at the Celanese Research Lab in Summit, New Jersey, into 304 stainless steel cans in a dry room located at the Exxon Enterprises Battery Division facility in Branchburg, New Jersey. The electrolyte was a solution of lithium tetraphenyl boron dissolved in dioxolane. In search for an oxygen free salt that would not react violently with dioxolane, Exxon Research Laboratory in Linden, New Jersey [5] first developed lithium tetramethyl boron. It worked very well electrochemically but it appeared that it slowly decomposed with the release of trimethyl boron that is spontaneously flammable in air. Further research effort led to the development and patenting of lithium tetraphenyl boron that proved very stable, although of lower conductivity. Finally, dioxolane enabled effective lithium plating without co-intercalating with lithium into the TiS_2 cathode. The electrolyte was added before sealing the cells. As soon as the electrolyte reached the foils, the desired Li–Al negative electrode would form in-situ directly within the can. Due to the high vapor pressure of the dioxolane and the long life desired, the cells were hermetically sealed using ceramic feed-throughs for the negative electrode and laser welding around the perimeter of the cells. Cells were cooled during welding to minimize electrolyte evaporation.

Button cells were produced in two sizes with capacities of 25 mAh and 100 mAh, respectively. Both cells are depicted in Fig. 1 with the corresponding weights and sizes in Table 1. Fig. 2 provides the specifications of each cell obtained from the original 1978 product brochure from Exxon, the Preliminary Application Guide 0578-1 [6]. This document reveals the capacity of the larger cell to be rated at 90 mAh but the (more accurate) 100 mAh value was used herein to remain on the more conservative side. The brochure specification also provided smoothed data extracted from actual voltage profiles that were obtained for a complete discharge/charge under a wide variety of operating conditions showing an almost linear variation of the voltage upon intercalation/deintercalation of lithium into/from the TiS_2 layered structure. The continuous voltage profile demonstrated that the cells could be coupled directly to several solar cells in series without any control electronics. The initial targeted applications consisted of low drain



Fig. 1. 25 mAh and 100 mAh Li– TiS_2 Cells fabricated by Exxon in 1978: (top) top of the cells, and (bottom) bottom of the cells.

Table 1

Weight and sizes of the 25 and 100 mAh cells.

	25 mAh cell	100 mAh cell
Weight	1.2 g	4.9 g
Thickness	0.33 cm	0.36 cm
Case diameter	1.1 cm	2.3 cm
Rim diameter	1.3 cm	2.7 cm

devices requiring low cycle numbers such as solar rechargeable watches and clocks, where the battery remains essentially at an intermediate stage of discharge. A photo of the solar rechargeable clocks fabricated in the 1970s is shown in Fig. 3. These solar clocks, approximately 4 inches square, consisted of a 100 mAh Li– TiS_2 cell, a miniature 10-cell photovoltaic panel, and an LCD watch unit. The functionality of the LCD is continuous in the absence of the use of the photovoltaic. The picture in Fig. 3 was taken recently and demonstrates the clock is still operational after 35 years and with its original battery. The resilience of the Li– TiS_2 system over 35 years of storage was further quantified herein upon testing of 25 mAh and 100 mAh cells fabricated in 1978 for capacity, rate, cycling and impedance. Results were also compared to the cells' original performance obtained from historical documents.

2. Experimental

A total of four cells, two 25 mAh cells and two 100 mAh cells, were obtained from the personal collection of team members of the original Exxon research group from the late 1970s. To the best of the historical knowledge, these cells were never discharged during the period of storage and represented fresh cells. Reasonable care was taken such that the storage temperatures did not exceed ambient temperatures exhibited in the state of New Jersey.

Custom cell holders were fabricated to accommodate the unorthodox design of the Exxon cells and to ensure low impedance electrode contacts. Electrochemical Impedance Spectroscopy (EIS) was performed with both types of cells before discharge from 1 mHz to 100 kHz at 20 mV amplitude. Further electrochemical tests were conducted using a Maccor Series 4000 battery test system to evaluate capacity, rate and cycling capabilities. Each type of battery was submitted to two different cycling protocols. One protocol involved a signature curve in the first discharge comprising C/50, C/100, C/250, C/500, C/1000 and C/5000 rates based on the 100 mAh and 25 mAh capacities respectively with a 15 min rest period between rates. The goal was to evaluate the cell ability to respond to high rates but also to decrease the applied current in order to quantify the absolute cell capacity remaining after 35 years of storage without rate limitation. After the first discharge to 1.3 V, the rate was maintained constant at C/125 between 1.3 and 2.6 V at 24 °C. The second protocol consisted of a slower constant cycling at a rate of C/250 based on the initial battery capacities for the first 3 cycles, and at C/500 thereafter. The focus of the latter was the study of the impact of the long storage on cycle life.

3. Results & discussion

Fig. 4 presents the first discharge voltage profile of one of the 25 mAh cells obtained today at a C/250 rate and 24 °C, after 35 years of storage. While the cell discharge capacity is about half of the initial rated capacity of 25 mAh with 12.2 mAh (Table 2), the voltage decreases in a continuous slope down to 1.3 V typical to single phase lithium intercalation into the layered structure of TiS_2 . The observed capacity represents a self discharge of 0.12% per month over a period of 35 years.

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