

Effect of cycling on the lithium/electrolyte interface in organic electrolytes

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Abstract

The successful operation of ambient temperature secondary lithium cells is primarily dependent on the lithium/electrolyte interface properties. In this study, an attempt has been made to study the effect of cell cycling on the lithium/electrolyte interface by nondestructive methods such as a.c. impedance spectroscopy and microcalorimetry. Experimental Li-TiS₂ cells were constructed and activated with different electrolytes. The cells delivered 30 to 300 cycles at 100% depth-of-discharge depending on the electrolyte. The reactivity of both uncycled and cycled lithium towards various electrolytes was studied by measuring the heat evolved from the cells under open-circuit condition at 25 °C by microcalorimetry. Cycled cells at the end of charge/discharge showed considerably higher heat output compared with the uncycled cells. After thirty days of storage, the heat output of the cycled cells is similar to that of the uncycled cells. A.c. impedance analysis results indicate that the cell internal resistance increases with cycling, and this is attributed to the degradation of the electrolyte with cycling. The value R_f was found to decrease with cycling. The observed decrease in R_f is probably due to the increase in the surface area of the lithium anode due to cycling. The peak frequency was found to be in the range, 400 to 1000 Hz for both uncycled and cycled cells suggesting that the passivating film composition does not change significantly with cycling.

Introduction

The successful operation of ambient temperature secondary lithium cells is primarily dependent on the lithium/electrolyte interface properties. Several important cell characteristics such as voltage delay, rate capability, cycle life, and shelf life are controlled by the characteristics of the lithium/electrolyte interface. Lithium is highly reactive towards most of the electrolytes and passivating films are formed on its surface as soon as Li comes in contact with the electrolyte [1, 2]. The reactivity of the uncycled Li (with the native passivating film) towards the organic electrolytes was investigated by several researchers. During cycling, deposition and dissolution of Li occurs and this results in significant changes in the composition and morphology of the passivating film. Most of the studies reported in the literature were concerned with the characterization of the composition of the passivating films by various destructive physical and chemical analysis methods such as infrared, atomic absorption spectrophotometry,

electron spectroscopy for chemical analysis, scanning electron microscope, etc. [3, 4]. In this paper, an attempt has been made to study the effect of cell cycling on the lithium/electrolyte interface by nondestructive methods such as a.c. impedance spectroscopy and microcalorimetry.

Experimental

Sealed spiral wound 1 A h Li-TiS₂ cells were used in this study. These cells were cathode limited by design and the anode to cathode capacity ratio was 6:1. Celgard 2400 was used as the separator. Each cell contained 4 ml of electrolyte. The cells were activated with five different electrolytes: (i) 1.5 M LiAsF₆/tetrahydrofuran (THF), (ii) 1.5 M LiAsF₆/ethylene carbonate (EC)+THF, (iii) 1.5 M LiAsF₆/THF+2-methyltetrahydrofuran (2-MeTHF), (iv) 1.5 M LiAsF₆/2-MeTHF+2-methylfuran (2-MeF), (v) 1.5 M LiAsF₆/EC+2-MeTHF+2-MeF, (vi) 1.5 M LiAsF₆/THF+2-MeTHF+2-MeF, and (vii) 1.5 M LiAsF₆/dioxolane+2-MeF.

Cycle life of the cells was determined at 50% depth-of-discharge (DOD). During the cycling, cells were charged and discharged by a constant current method. The charge and discharge current densities were 0.5 and 1 mA/cm², respectively.

The reactivity of both uncycled and cycled Li towards various electrolytes was studied by measuring the heat evolved from the cells under open-circuit condition at 25 °C. A heat conduction Hart Scientific Microcalorimeter, model 5023, was used in the study.

The changes taking place at the surface of the Li electrode due to cycling was investigated by a.c. impedance spectroscopy. Measurements were made on cycled and uncycled cells after 30 days of storage at ambient conditions. A.c. impedance measurements were made in the frequency range from 0.1 Hz to 65 kHz using a Solartron 1250 frequency analyzer and a Solartron 1286 electrochemical interface controlled by an IBM AT compatible computer.

Results and discussion

Cell performance

The cells were tested after 30 days of cell assembly for their cycle life performance. The cycle life performance of the cells was found to be dependent significantly on the nature of the electrolyte. The cells activated with THF, EC+THF and THF+2-MeTHF electrolytes showed poor cycle life performance (<50 cycles). Cells activated with 2-MeTHF+2-MeF, EC+2-MeTHF+2-MeF, and THF+2-MeTHF+2-MeF electrolytes showed longest cycle life (Fig. 1).

Cells were found to exhibit voltage delay in the first discharge. The voltage delay characteristics of a 1 A h cell activated with 1.5 M LiAsF₆/2-MeTHF are given in Fig. 2. The voltage drop observed in these cells is negligible compared with the data reported for Li-SOCl₂ cells. The observed voltage delay in the secondary Li cells is probably due to the native passivating film on the Li surface and/or due to the passivation of the Li anode during 30 days of storage. No such voltage delay was observed during subsequent discharges. This may be because the Li anode was not passivated heavily due to limited open-circuit stand time following the charge.

Microcalorimetric studies

Heat output from the cells was measured at various stages of cycle life (uncycled, early life, and end-of-life). Measurements were made on the uncycled cells (after 30

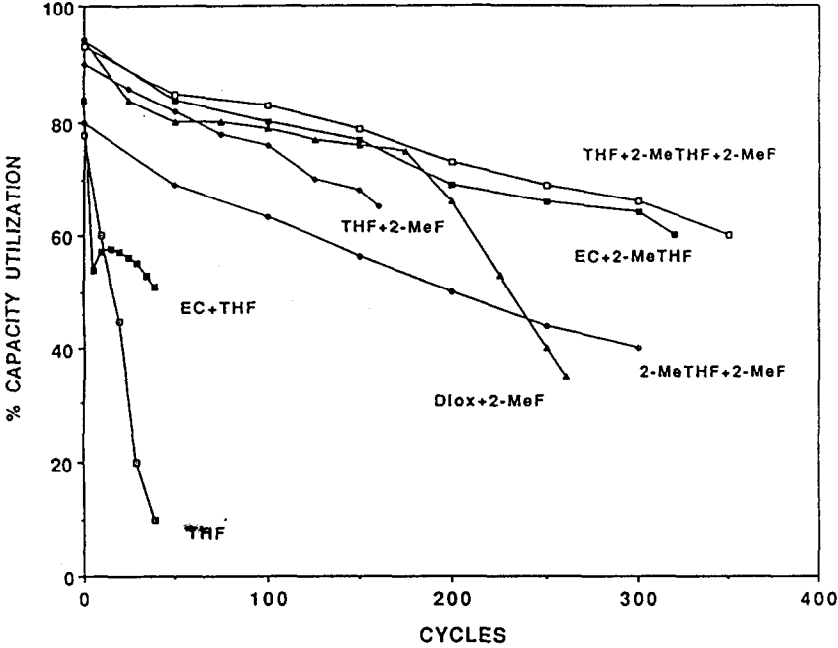


Fig. 1. Cycle life performance characteristics of 1 A h Li-TiS₂ cells.

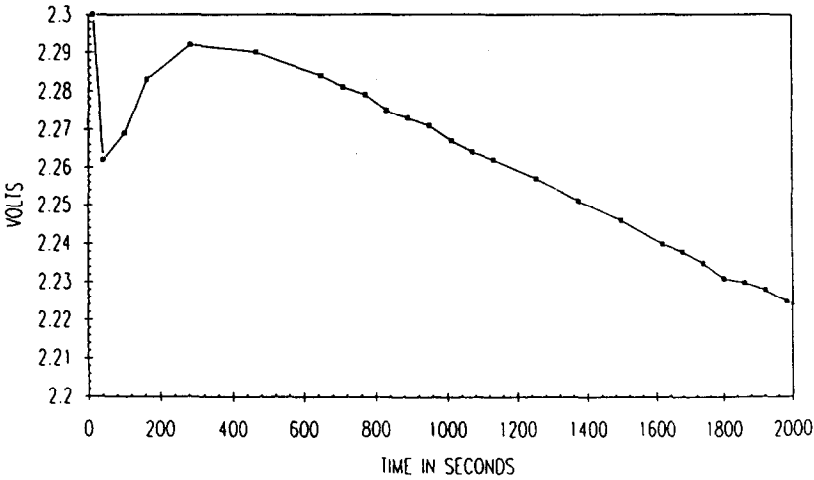


Fig. 2. Voltage delay characteristics of 1 A h Li-TiS₂ cells.

days of cell assembly) to study the reactivity of the uncycled Li towards the electrolytes. After the completion of 5 cycles, the heat output of the cells was measured during open-circuit stand for 12 h to determine the reactivity of the freshly-deposited Li towards the electrolytes. Microcalorimetry measurements were made on the heavily-cycled cells after 30 days of the termination of cycling tests to determine the reactivity of heavily-cycled Li towards electrolytes.

The heat output of the uncycled cells is given in Table 1. Based on the microcalorimetry results of the fresh cells, the electrolytes studied can be classified into two groups: (i) highly-reactive electrolytes, and (ii) low- to moderately-reactive electrolytes. The cells activated with the first group of electrolytes (THF, EC+THF and THF+2-MeTHF) showed poor cycle life performance compared with the cells activated with the second group of electrolytes (2-MeTHF+2-MeF, EC+2-MeTHF+2-MeF, and THF+2-MeTHF+2-MeF). Hence, microcalorimetry can be used as a qualitative tool for preliminary screening of the electrolytes required for long cycle life secondary Li cells.

The heat output of the cells after the end-of-cycling is not very high and is comparable with the heat output measured from the fresh cells. It is generally expected that the cycled cells will show higher heat output compared with the uncycled cells due to increase in the surface area of the Li electrode with cycling. The low heat output of the heavily-cycled cells is probably due to the extensive passivation of the Li electrode during the 30 days storage period.

The heat output of the cells after the end-of-charge was measured as a function of storage period. The heat output of the cells after 1 and 5 h of storage is given in Table 2. From the microcalorimetry data (Tables 1 and 2), it can be observed that the heat output of the cells at the end-of-charge is much higher than that of the fresh cells. The higher heat output observed after the end-of-charge is due to the high reactivity of the freshly-deposited Li towards the electrolytes.

A.c. impedance studies

The a.c. impedance spectra of the uncycled Li-TiS₂ cells containing 1.5 M LiAsF₆/EC+2-MeTHF electrolyte) as a function of storage period are given in Fig. 3. An

TABLE 1

Results of the microcalorimetric studies on uncycled Li-TiS₂ cells

Electrolyte	Heat output of uncycled cells (W/cm ²)
THF	1.51
EC+THF	1.01
THF+2-MeTHF	1.30
2-MeTHF-2-MeF	0.33
EC+2-MeTHF+2-MeF	0.30
THF+2-MeTHF+2-MeF	0.32
Dioxolane+2-MeF	0.38

TABLE 2

Results of the microcalorimetric studies on cycled Li-TiS₂ cells

Electrolyte	Heat output after 1 h (W/cm ²)	Heat output after 5 h (W/cm ²)
2-MeTHF+2-MeF	26.8	14.8
EC+2-MeTHF	1.3	0.75
THF+2-MeTHF+2-MeF	24.1	26.2

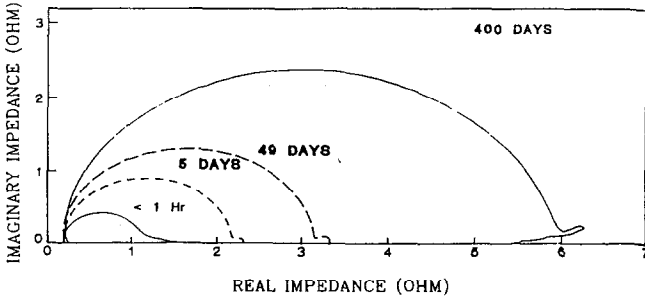


Fig. 3. A.c. impedance spectra of the uncycled Li-TiS₂ cells.

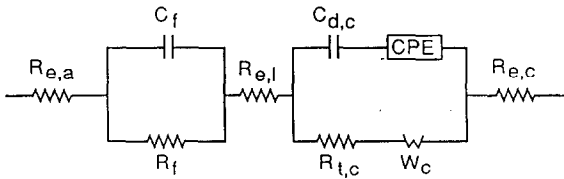


Fig. 4. An equivalent circuit model of Li-TiS₂ cells.

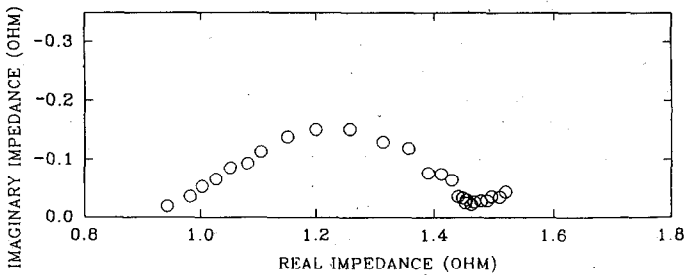


Fig. 5. A.c. impedance spectra of cycled 1 A h Li-TiS₂ cells.

equivalent circuit model given in Fig. 4 was used to analyze the a.c. impedance data. The spectra contained one clearly-defined semicircle and this corresponds to the lithium/electrolyte interface. The Li passivating film resistance was found to increase with storage time and this is attributed to the growth of the passivating layers on the Li anode.

The a.c. impedance characteristics of the Li-TiS₂ cells at various stages of cycle life (uncycled, mid-life and end-of-life) were determined. The a.c. impedance spectra of the cycled cells contained two overlapping semicircles (Fig. 5). The first semicircle corresponds to that of the lithium/electrolyte interface [5]. The cell internal resistance (R), Li film resistance (R_f) and the film capacitance (C_f) were calculated and the results were given in Table 3. From the results, it can be observed that the cell internal resistance increases with cycling, and this is attributed to the degradation of the electrolyte with cycling. The value R_f was found to decrease with cycling. The observed decrease in R_f is due to the increase in the surface area of the Li anode due to cycling. The peak frequency was found to be in the range 400 to 1000 Hz for both

TABLE 3

A.c. impedance analysis results of Li-TiS₂ cells

	Uncycled cells	Mid-life cells	End-of-life cells
Cell internal resistance (Ω)	0.12-0.16	0.13-0.2	1-2
Apparent film resistance, R_f (Ω/cm^2)	600-800	100-250	50-150
Geometric film capacitance, C_f (mF/cm^2)	0.5-1.5	2-3	1-4
Resistance-capacitance time constant (ms)	300-1200	200-750	~200

uncycled and cycled cells. This suggests that the passivating film composition does not change significantly with cycling.

Summary and conclusions

Cell cycling shows that electrolyte additives such as 2-MeF and EC improve performance of Li-TiS₂ cells. This effect could arise from the formation of beneficial passive films in the presence of the above additives. Microcalorimetry studies showed that freshly-deposited Li is most readily passivated in electrolytes containing EC/2-MeTHF. Results of microcalorimetry studies also show that the freshly-deposited Li is more reactive towards the organic electrolyte compared with uncycled Li. A.c. impedance studies show that the internal resistance of the cell at the end-of-life is ten times that of the value of the start of cycling. However, the resistance of the passive film on the anode had decreased after extended cycling. The near invariance of the resistance-capacitance time constants suggests that the composition of the passive film does not change significantly between 50 and 600 cycles.

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