

Polymer electrolyte coatings for lithium anodes in SOCl_2 cells

K. M. Abraham, D. M. Pasquariello and M. Alamgir
EIC Laboratories, Inc., Norwood, MA 02062 (USA)

W. P. Kilroy
Materials Division, Naval Surface Warfare Center, Silver Spring, MA 20903-5000 (USA)

Abstract

Polymer electrolytes based on poly[bis-((methoxyethoxy)ethoxy) phosphazene] (MEEP) or its composites with poly(ethylene oxide) (PEO) or poly[(ethylene glycol)diacrylates] (PEGDA) have been investigated as coatings on the lithium anode to alleviate the voltage delay of Li/SOCl_2 cells. Cells with the polymer electrolyte-coated anodes exhibited significantly lower voltage delays and better capacity retention when discharged after two weeks of storage at 70 °C.

Introduction

The voltage delay and capacity loss associated with the storage of Li/SOCl_2 cells have precluded widespread applications of an otherwise energy dense power source. A variety of avenues has been pursued to mitigate voltage delay [1]. However, it remains an unresolved issue, especially in cells discharged at high rates after storage at 70 °C. In this study, we investigated the usefulness of Li^+ -conductive polymer electrolyte coatings on the Li anode for mitigating both the voltage delay and capacity loss associated with the storage of Li/SOCl_2 cells. Specifically, we have studied Li salt complexes of poly[bis-((methoxyethoxy)ethoxy) phosphazene] (MEEP) and composites of this polymer with poly(ethylene oxide) (PEO) or poly[(ethylene glycol) diacrylate] (PEGDA). A detailed account of the preparation and properties of these polymer electrolytes has been given recently [2]. These electrolytes have conductivities between 5×10^{-5} and $5 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ at room temperature. MEEP- $(\text{LiAlCl}_4)_n$, where $n = 0.13, 0.25$, etc., represents the first example of dimensionally-stable polymer electrolytes based on neat MEEP [2]. The dimensional stability of MEEP electrolytes containing other Li salts such as LiSO_3CF_3 , LiPF_6 and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ is increased by forming composites with PEO or PEGDA.

Experimental

Thionyl chloride (99+ % purity) was obtained from Fluka, distilled and stored over finely divided Li. LiAlCl_4 , purchased from Anderson Physics, was used as-received. The SOCl_2 solutions were 1 M in LiAlCl_4 .

MEEP and MEEP- $(\text{LiX})_{0.25}$, where $\text{LiX} = \text{LiAlCl}_4, \text{LiCF}_3\text{SO}_3, \text{LiN}(\text{SO}_2\text{CF}_3)_2$ or LiPF_6 , were prepared as described recently [2]. A typical procedure for coating the

Li anode with each of the electrolytes involved the following sequence of experiments. First a coating solution was prepared by adding 0.5 g MEEP to 10 ml tetrahydrofuran (THF). The Li salt was added to the THF solution in an amount adequate to give the electrolyte a composition of 4:1 molar ratio of MEEP monomer to the Li salt. The Li anode was dipped into the solution followed by drying in vacuum. The procedure was repeated thrice for each anode used in the laboratory cells (see below). The MEEP:PEO(LiX)_n and MEEP:PEGDA-(LiX)_n composite electrolyte coatings were formed with minor modifications of the procedure described above. The former composite electrolyte had the composition 70 w/o MEEP:30 w/o PEO with Li salt present at 1 mole per six moles of MEEP monomer. The ratio of MEEP to PEGDA in the MEEP:PEGDA-(LiX)_n electrolyte was 90 w/o to 10 w/o. To prepare this electrolyte appropriate amounts of the two polymers were dissolved in 5 ml THF. The Li salt was added to obtain a solution with a MEEP:salt ratio of 4:1. A drop of a photoinitiator was also added. The Li anode was dipped in this solution and each side of it then was irradiated with a UV light source for five min. The process of dipping and irradiation was repeated thrice with each anode used in the laboratory cells (see below).

Small laboratory size and 1/2 'AA'-size Li/SOCl₂ cells were used as the test vehicles. The thickness of the anode coating in the 1/2 'AA' cells was varied according to the nature of the polymer electrolyte (see Results and discussion). This was done on the basis of the results of the laboratory cell tests. The cells were filled with 1 M LiAlCl₄/SOCl₂ and hermetically sealed. Storage experiments were performed at 70 °C for two weeks. The voltage delay of stored cells containing polymer electrolyte-coated and bare Li anodes were compared with those of their fresh counterparts. The cells were discharged at 10 mA cm⁻². The voltage-time data were recorded on a Bascom-Turner Instruments Model 8000 Microprocessor-Controlled Recorder with fast data acquisition capability.

Results and discussion

Lithium anodes coated with MEEP-based electrolytes

Diffuse reflectance Fourier-transform infrared (DRFT-IR) spectroscopy and scanning electron microscopy (SEM) were used to monitor the morphology and chemical identity of the Li surfaces before and after coating them with the polymer electrolytes. The DRFT-IR spectra of the surface of as-received Li foil (Fig. 1) showed prominent,

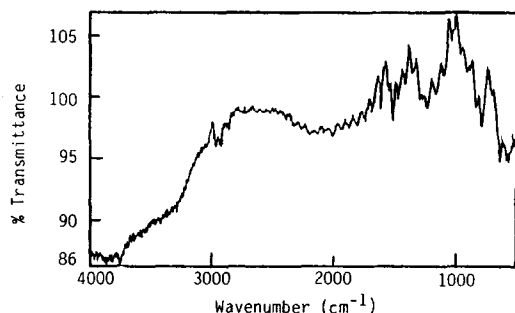


Fig. 1. DRFT-IR spectrum of the surface of fresh lithium foil.

but generally weak absorption bands at 2960, 2920, 1610, 1506, 1227, 783, 636 and 567 cm^{-1} . Peaks at 1500, 880 and 530 cm^{-1} could be attributed to Li_2CO_3 [3], ones at 680–630 cm^{-1} to Li_2O [3]. The peaks at 2960 and 2920 cm^{-1} may be associated with the C–H vibrations organic compounds. Scraping removes most of the surface impurities; however, the softness of the metal makes this a difficult task to perform efficiently. All Li/SOCl_2 cells used in this study were built with as-received Li foil.

Figure 2 depicts the DRFT-IR spectrum of a Li surface coated with MEEP. The spectrum is that expected for MEEP [2]. A SEM picture of the surface indicated a uniform coating with little cracking or peeling. The IR spectra showed little change even after storage of the coated Li for three months at room temperature followed by three months at 70 °C. The DRFT-IR spectra of Li anode surfaces coated with representative electrolytes are presented in Fig. 3.

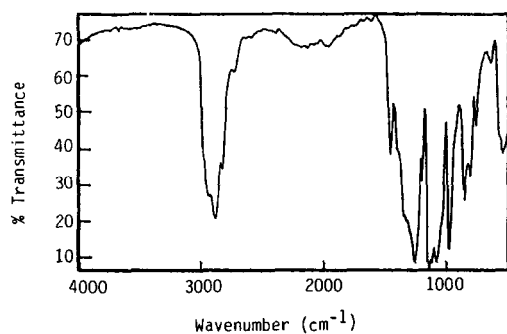


Fig. 2. DRFT-IR spectrum of the surface of lithium foil coated once with MEEP.

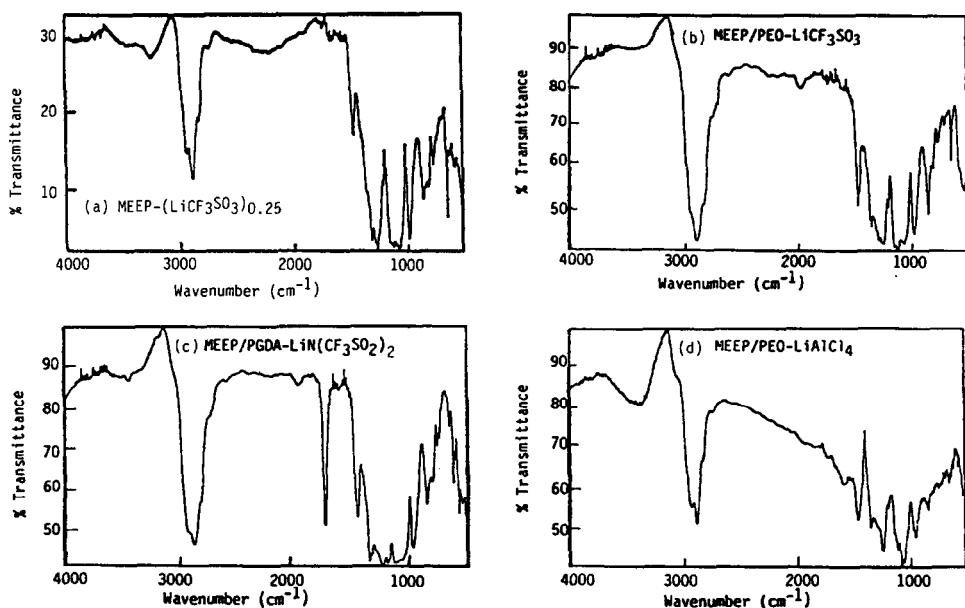


Fig. 3. DRFT-IR spectra of lithium anodes coated with polymer electrolytes. The electrolytes are identified in the spectra.

SEM and DRFT-IR analyses of MEEP and MEEP-(LiX)_n-coated Li anodes subsequent to their storage in LiAlCl₄/SOCl₂ for two weeks at 70 °C indicated possible reactions of the polymer electrolyte with the liquid depolarizer. However, significant improvement in voltage delays of the cells was observed as a result of coating the Li anode with the polymer electrolytes.

In the ideal case a polymer electrolyte coating can be viewed as replacing the poorly conductive LiCl solid electrolyte ($\sigma \leq 10^{-8} \Omega^{-1} \text{ cm}^{-1}$) with a highly conductive interphase ($\sigma \sim 5 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$) whose thickness would not change with storage [4]. The thickness of the electrolyte required for optimum cell performance will depend on the conductivity of the polymer electrolyte and the load current. It can be calculated as follows.

The resistive voltage loss (ΔE) in the polymer electrolyte coating is given by:

$$\Delta E = iR \quad (1)$$

where i is the current and R is the resistance of the film. R is given by:

$$R = \rho \frac{l}{A} \quad (2)$$

In eqn. (2), ρ is the specific resistivity (inverse of specific conductivity) of the polymer electrolyte, and l and A are the thickness and area, respectively, of the coating. When a Li/SOCl₂ cell having an open-circuit voltage (OCV) of 3.65 V is discharged at a current density of 10 mA cm⁻², an iR drop of about 0.35 V, can be tolerated in the coating. This is because with an iR drop of this magnitude, the load voltage of the cell will still be greater than 3 V. Then, the polymer electrolyte coating thickness required for this anode would be 17.5 μm . That is:

$$\Delta E = \frac{i}{A} \rho l = \frac{10^{-2}}{1} \frac{10^5}{5} l = 0.35 \text{ V}$$

$$l = \frac{5 \times 35 \times 10^{-2}}{10^{-2} \times 10^5} = 175 \times 10^{-5} \text{ cm} = 17.5 \mu\text{m}$$

The thickness of a given polymer electrolyte coating can be controlled by adjusting the concentration of the coating solution, the number of coatings, and the time the anode is held in the coating solution. The polymer electrolyte coatings used in this study had $\leq 10 \mu\text{m}$ thickness.

Voltage delay studies

The voltage delay data obtained from laboratory test cells are summarized in Table 1. In general, cells stored with uncoated anodes exhibited excessive voltage delays and were unable to recover to > 2.0 V. In contrast, those containing anode overlayers not only exhibited short voltage delays ranging from about one to a few seconds but also yielded appreciable capacities after the storage. The effectiveness of the polymer electrolyte coatings towards these two ends varied. From the point of view of voltage delay, the pure MEEP-(LiX)_{0.25} coatings showed the best performance. Their voltage delays were in the range of 0.6 to 4.0 s. The voltage delays increased when MEEP was replaced by a composite of MEEP/PEO or MEEP/PGDA, the latter being the worse of the two. The performance of a composite electrolyte coating was strongly influenced by the dopant salt. For example, the least voltage delay was observed when the salt was LiAlCl₄. When fluoride-containing salts were used, the delay times were longer. Also, considerable cell-to-cell variation was observed with some polymer

TABLE 1

Voltage delay and capacities of Li/SOCl₂ cells at 10 mA cm⁻² at 25 °C. The laboratory cells were stored for two weeks at 70 °C. All overlayers were three coats unless noted otherwise

Cell No.	Coating	OCV (V)	Voltage delay (s)	Minimal potential before recovery to 2 V (V)	Normalized capacity ^a (A h/g of carbon)
1	None	3.63	^b	< -0.5	0.0
2	None	3.66	^b	1.15	0.0
3	MEEP/LiAlCl ₄	3.71	0.6	1.15	0.53
4	MEEP/LiAlCl ₄	3.70	1.0	1.70	0.69
5	MEEP/LiCF ₃ SO ₃	3.66	2.1	1.10	0.80
6	MEEP/LiCF ₃ SO ₃	3.68	0.8	1.22	
7	MEEP/LiN(CF ₃ SO ₂) ₂	3.70	1.6	0.20	0.71
8	MEEP/LiN(CF ₃ SO ₂) ₂	3.66	3.3	-0.20	0.71
9	MEEP/LiPF ₆	3.68	4.0	0.95	0.71
10	(MEEP/PEO)-LiAlCl ₄	3.70	1.9	-3.50	0.44
11	(MEEP/PEO)-LiCF ₃ SO ₃	3.68	12.9	-3.00	0.84
12	(MEEP/PEO)-LiN(CF ₃ SO ₂) ₂	3.69	30.0	-3.10	0.48
13	(MEEP/PEO)-LiN(CF ₃ SO ₂) ₂ ^c	3.66	4.3	0.20	0.73
14	(MEEP/PEO)-LiPF ₆ ^c	3.65	4.5	0.15	0.50
15	(MEEP/PGDA)-LiAlCl ₄	3.65	8.4	0.40	0.64
16	(MEEP/PGDA)-LiCF ₃ SO ₃	3.71	38.8	-0.73	0.89
17	(MEEP/PGDA)-LiN(CF ₃ SO ₂) ₂	3.70	10.8	-0.09	0.88
18	(MEEP/PGDA)-LiPF ₆	3.66	2.15	1.20	1.09

^aFresh cells delivered a capacity of ~1.5 A h/g carbon to 0.0 V.

^bDid not recover to 2 V.

^cOne layer of coating.

electrolyte coatings. It appeared that, in laboratory cells, we did not achieve the optimum coating thickness required to produce the best voltage delay behavior.

The ability of the electrolyte overlayers to retain the capacity of stored cells appeared to follow a trend opposite to that seen in relation to voltage delay. That is, the lowest capacity after storage was found in cells utilizing LiAlCl₄-based electrolyte while the highest capacity was found in cells in which the electrolyte overlayers used fluoride salts. Also, the overlayers based on the composite electrolytes of (MEEP/PEGDA)-(LiX)_n, where LiX = LiPF₆, LiCF₃SO₃ and LiN(CF₃SO₂)₂, appeared to be the best materials for capacity retention, in spite of the fact that with three layers of coatings their use led to longer voltage delays compared with pure MEEP-(LiX)_n. The results obtained in laboratory test cells suggested that two layers of MEEP-(LiX)_n or one layer of MEEP/PEO-(LiX)_n composite would be preferred to minimize voltage delay and maximize discharge capacity. Accordingly, 1/2 'AA'-size cells were built with anodes containing two coatings of MEEP-(LiAlCl₄)_{0.25} or one coating of MEEP/PEO-(LiPF₆)_{0.13}. The results of voltage delay and discharge tests are presented in Figs. 4 and 5. The cells containing the coated anodes exhibited only short delays of less than 10 s. Further, they exhibited a remarkable ability for capacity retention during high-temperature storage.

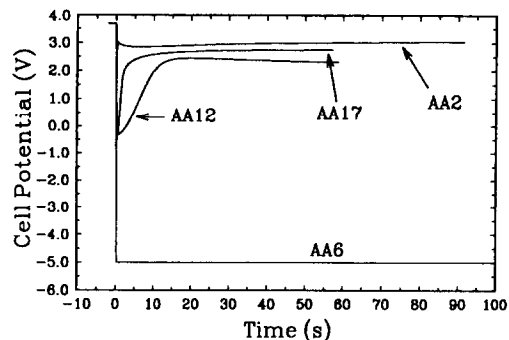


Fig. 4. Comparison of voltage delays of 1/2 'AA'-size cells. The anodes in Cell AA2 and AA6 were uncoated. Cell AA2 was discharged immediately after fabrication. AA6 was stored for two weeks at 70 °C. Two coats of the MEEP-LiAlCl₄ electrolyte were used in cell AA17. A single coat of MEEP/PEO-LiPF₆ was used for cell AA12. Those latter two cells were also stored for two weeks at 70 °C. Current density was 10 mA cm⁻².

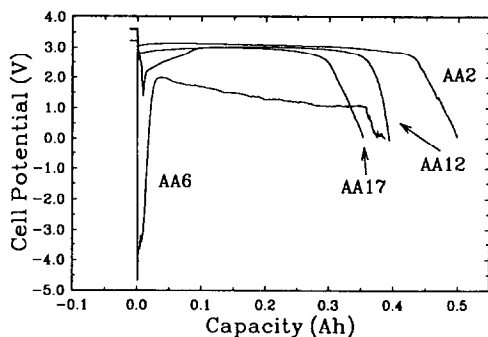


Fig. 5. Comparison of the discharge curves for the 1/2 'AA'-size cells shown in Fig. 4. Current density was 10 mA cm⁻².

The results we have obtained indicate that polymer electrolyte coatings based on MEEP and its composites are useful materials to alleviate the voltage delay of Li/SOCl₂ cells.

Acknowledgement

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