

Investigation on lithium/polymer electrolyte interface for high performance lithium rechargeable batteries

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Abstract

Performance data of several linear and cross-linked polymer electrolytes are reported and the electrochemical criteria for the selection of electrolytes to be used in electric vehicle lithium metal batteries are discussed. Further, laboratory lithium cells with LiMn_2O_4 composite cathode were tested to ascertain the effective viability of these polymer in solid-state batteries and preliminary results are reported. This study clearly demonstrates the importance of a broad-based electrochemical characterization in selecting an electrolyte for lithium metal batteries. © 1997 Elsevier Science S.A.

Keywords: Polymer electrolytes; Gelled electrolytes; Lithium interface; Lithium batteries

1. Introduction

The success of the rocking-chair batteries does not necessarily mean that lithium metal rechargeable batteries are out of the picture [1]. In principle lithium metal batteries provide high energy density required by modern devices, so that attention should be focused on improving the lithium interface stability and enhancing battery cycle life, two crucial aspects of this very appealing energy storage system. Accordingly, we are working on the development of polymer electrolytes for electric vehicle (EV) lithium metal batteries, with lithium manganese oxide operating under 4 V as the cathode active material.

A composite polymer electrolyte based on linear poly(ethylene oxide) (PEO), $\text{Li}[(\text{SO}_2\text{CF}_3)_2\text{N}]$ salt and $\gamma\text{-LiAlO}_2$ ceramic filler, and prepared by the traditional solution-casting process, is a promising candidate for EV lithium polymer batteries [2]. Combining $\gamma\text{-LiAlO}_2$ with $\text{Li}[(\text{SO}_2\text{CF}_3)_2\text{N}]$ gives the PEO-based electrolyte an exceptionally slow recrystallization rate and enhances greatly the lithium interface stability as well as the mechanical properties of the electrolyte [2]. Scaling up to industrial polymer electrolyte manufacture would conceivably require polymer electrolytes which do not require the solution-casting procedure in which a toxic solvent such as acetonitrile has to be removed from the polymer and the salt solution. Accordingly,

two different approaches have been pursued: the first involves the use of linear PEO in gel organic solutions of lithium salts, with the addition of $\gamma\text{-LiAlO}_2$ to enhance mechanical properties, and the second involves the chemical curing by a trifunctional cross-linking agent of viscous liquid mixtures of light-weight poly(ethylene glycol) (PEG) and lithium salts with and without the addition of organic plasticizers and ceramic filler.

The present paper reports performance data of several of these newly designed polymer electrolytes and discusses the criteria of their selection for use in EV lithium batteries. The tested polymer systems are listed in Table 1, and the performance data of the composite $\text{PEO-Li}[(\text{SO}_2\text{CF}_3)_2\text{N}]$ are shown for comparison [2]. Preliminary test results of $\text{Li/LiMn}_2\text{O}_4$ laboratory cells with selected polymer electrolytes are also reported and discussed.

2. Experimental

2.1. Linear electrolyte preparations

The plasticized linear PEO-based electrolytes were prepared in a glove-box by dissolving the LiSO_3CF_3 salt in liquid poly(ethylene glycol)dimethylether (PEGDME) or γ -butyrolactone ($\gamma\text{-BL}$) under stirring at 50 °C for 2 h. After salt dissolution, the ceramic filler $\gamma\text{-LiAlO}_2$ was dispersed in

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Table 1
List of the tested polymer electrolytes

	Polymer	Salt	Plasticizer	Filler	O/Li
Linear Polymer Electrolyte	PEO ^a	Li[(SO ₂ CF ₃) ₂ N]		γ-LiAlO ₂	8
	PEO	LiSO ₃ CF ₃	PEGDME ^b	γ-LiAlO ₂	14
	PEO	LiSO ₃ CF ₃	γ-BL ^c	γ-LiAlO ₂	8
	PEG ^d -Desmodur R ^e	Li[(SO ₂ CF ₃) ₂ N]			18
Cross-linked Polymer Electrolyte	PEG-Desmodur RE	LiSO ₃ CF ₃			18
	PEG-Desmodur RE	LiSO ₃ CF ₃	PEGDME		18
	PEG-Desmodur RE	LiSO ₃ CF ₃	PEGDME	γ-LiAlO ₂	18
	PEG-Desmodur RE	LiSO ₃ CF ₃	γ-BL		18

^a PEO: poly(ethyleneoxide), mol. wt. 600 000.

^b PEGDME: poly(ethylene glycol) dimethylether, mol. wt. 500.

^c γ-BL: γ-butyrolactone.

^d PEG: poly(ethylene glycol), mol. wt. 2000.

^e DESMODUR RE: 4,4',4''-methylidynetrisphenylisocyanate.

the solutions and PEO added to the mixtures at 120–130 °C. The resulting polymer electrolytes had a PEO/γ-BL or PEO/PEGDME ratio of 1:4.2. The viscous mixtures were placed in a Teflon vessel or between two Teflon sheets and pressed between glass plates. The ratio O/Li was 8 (see Ref. [2], and Refs. therein) for all the electrolytes and the content of the ceramic filler was 5 wt.% of the total mixture. The electrolyte thickness was in the 0.8–0.3 mm range.

2.2. Cross-linked electrolyte preparations

Polymer films were prepared in a glove-box by chemical cross-linking of PEG-salt complexes with Desmodur RE [3] with and without plasticizer and ceramic filler. The lithium salts were dissolved under stirring in PEG or in a mixture of PEG-PEGDME or of PEG-γBL. The plasticized polymer electrolytes had a 1:1 PEG/plasticizer (PEGDME or γ-BL) ratio and the O/Li ratio was ~18. The γ-LiAlO₂ ceramic filler was dispersed in the PEG-PEGDME-LiSO₃CF₃ electrolyte before adding of the cross-linking agent. The cross-linking time was considerably reduced with γ-LiAlO₂. The electrolyte thickness was in the range 0.5–0.1 mm. More details are reported in Ref. [3].

2.3. Impedance measurements

The ionic conductivity of the polymer films and the lithium interface phenomena were evaluated by impedance spectroscopy using a 1255 Solartron frequency response analyser (FRA) coupled to a 273 PAR potentiostat/galvanostat, both interfaced with a personal computer. Blocking cells with stainless-steel electrodes were used for conductivity measurements, and lithium symmetrical non-blocking cells were used to investigate interface phenomena. A 10 mV a.c. perturbation was used and the data were collected over a frequency range from 100 kHz to 1 Hz in conductivity measurements and from 100 kHz to 10 mHz in interface investigation by recording ten points/decade. The impedance results were examined by Boukamp's fitting program [4]

using a modified Randles circuit [2] as a model for lithium symmetrical cells.

2.4. Electrochemical window

The electrochemical stability window of polymer films was evaluated on cell with stainless-steel working and lithium counter electrodes by linear sweep voltammetry at 70 °C using a computer-interfaced 273 PAR potentiostat/galvanostat.

2.5. Transference number determination

The lithium transference number was evaluated after Bruce and co-workers [5,6] by determining the a.c. impedance of a lithium symmetrical non-blocking cell and measuring the steady-state current (I^s) under d.c. polarization ($\Delta V = 10$ mV). The transference number is

$$T^+ = I^s(\Delta V - I^0 R_i^0) / I^0(\Delta V - I^s R_i^s) \quad (1)$$

where the initial current was evaluated as

$$I^0 = \Delta V / R_\Omega^0 + R_i^0 \quad (2)$$

where R_Ω^0 and R_i^0 are the bulk and the lithium interface resistances before polarization and R_i^s is the lithium interface resistance after polarization.

2.6. Lithium deposition–stripping process

The lithium–electrolyte interface was tested after deposition and stripping a large amount of lithium (comparable with that involved in battery prototypes). The cycling tests were performed on symmetrical lithium cells using different current densities at 70 °C and the interface phenomena were evaluated by impedance spectroscopy before and after cycling.

The coulombic efficiency of the lithium deposition–stripping process was investigated by cyclic voltammetry (CV) using cells with a stainless-steel or aluminium working elec-

trode and a lithium counter electrode at 70°C in the potential range from 2.0 V to –0.5 V versus Li.

The coulombic efficiency was also tested by galvanostatic deposition–stripping carried out in cells with stainless-steel working and lithium counter electrodes. A large amount of lithium ($1\text{--}2\text{ C cm}^{-2}$) was deposited on the working electrode, then 10% of the initial amount was discharged and charged, and the average efficiency of the process was calculated from the following equation [7]

$$X = [q_c - (Xq_1 - q_r)/N] / q_c \quad (3)$$

where N is the number of cycles and q_c , q_1 and q_r are the charges involved in a single deposition process, initial massive lithium deposition and final discharge, respectively. The potential of the working electrode was continuously checked and the final process was interrupted when the working electrode potential exceeded 1 V versus lithium. The equipment was a computer-interfaced 273A PAR potentiostat/galvanostat.

2.7. Electrochemical quartz crystal microbalance measurements

Electrochemical quartz crystal microbalance (EQCM) measurements were carried out to examine the lithium deposition process in liquid electrolyte PEGDME(250)– LiSO_3CF_3 (O/Li=18 and water content 135 ppm). The equipment was a (QCA917) Quartz Crystal analyser (SEIKO EG&G) connected to a computer-interfaced 273A PAR potentiostat/galvanostat. The working electrode consisted of platinum (5 mm diameter) deposited on 9 MHz, AT-cut quartz crystal, the reference electrode of a lithium rod and the counter-electrode of a lithium foil. Lithium was deposited from the solution using different current densities and the frequency variation (Δf) was related to the mass change (Δm) of the working electrode [8]

$$\Delta f = -2.26 \times 10^{-6} f^2 \Delta m \quad (4)$$

where f is the quartz crystal resonant frequency before the lithium deposition; both Δf and f are expressed in Hz and Δm in g cm^{-2} . The measurements were carried out in a MBraun argon-filled dry box (water < 1 ppm and oxygen < 1 ppm) at 30 °C.

2.8. Battery tests

The batteries were assembled by placing a thin film of polymer electrolyte between a lithium disk (0.75 mm thick, Aldrich) and a composite cathode. The composite cathodes were prepared by dry mixing and pressing lithium manganese oxides [9], graphite powder (Aldrich) and polytetrafluoroethylene (PTFE) on stainless-steel grids in the 76:9:15 weight ratio. The area and thickness of positive electrodes were 0.8 cm^2 and 0.18 mm, respectively, and the weight of cathodic mixture was in the 10–20 mg range.

Preliminary battery tests were carried out by repeating charge/discharge galvanostatic cycles at 90 °C for the batteries with cross-linked electrolytes and at 70 °C for those with the PEO-based linear electrolytes. The potential range was 2.0–3.8 V versus lithium. The current density was $70\text{ }\mu\text{A cm}^{-2}$ and the discharge rate was $C/28$; cycleability data were collected by a computer-interfaced 545 AMEL galvanostat/electrometer. All the battery prototypes were sealed in a MBraun argon-filled dry box.

3. Results and discussion

Given that the ‘ideal’ polymer electrolyte is characterized by high conductivity ($> 10^{-4}\text{ S cm}^{-1}$) at room temperature, a wide electrochemical window ($> 5\text{ V}$), a low and stable Li/electrolyte interface resistance, a unity transference number of the lithium ion, 100% coulombic efficiency of the lithium deposition–stripping process, good mechanical strength and an environmental friendly manufacturing method, selecting the best-performing polymer electrolytes involves an acceptable compromise of these requisites.

3.1. Conductivity and electrochemical window

Figs. 1 and 2 show the temperature dependence of the ionic conductivity of the linear and cross-linked polymer electrolytes evaluated during the first heating cycle from room temperature to 90 °C. Unlike the PEO–Li[(SO_2CF_3) $_2\text{N}$]– $\gamma\text{-LiAlO}_2$ composite, each new polymer electrolytes display the same conductivity values during the heating and the cool-

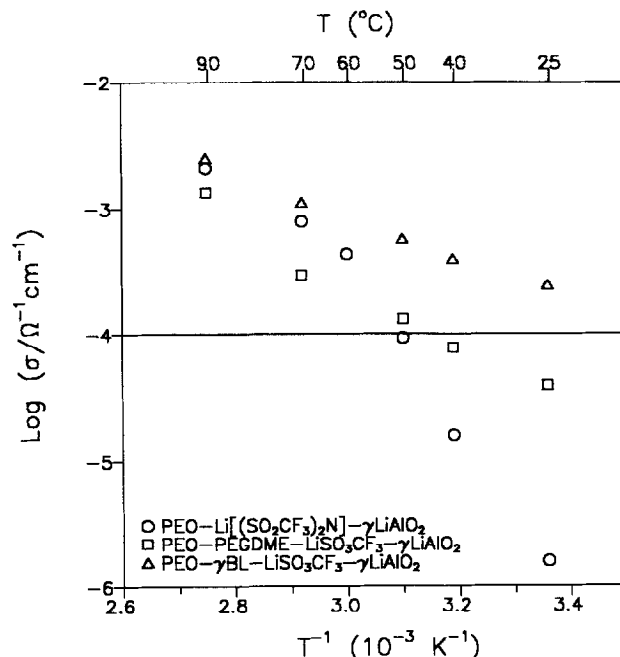


Fig. 1. Temperature dependence of the ionic conductivity of the PEO-based linear polymer electrolytes evaluated during the first heating cycle from room temperature to 90 °C.

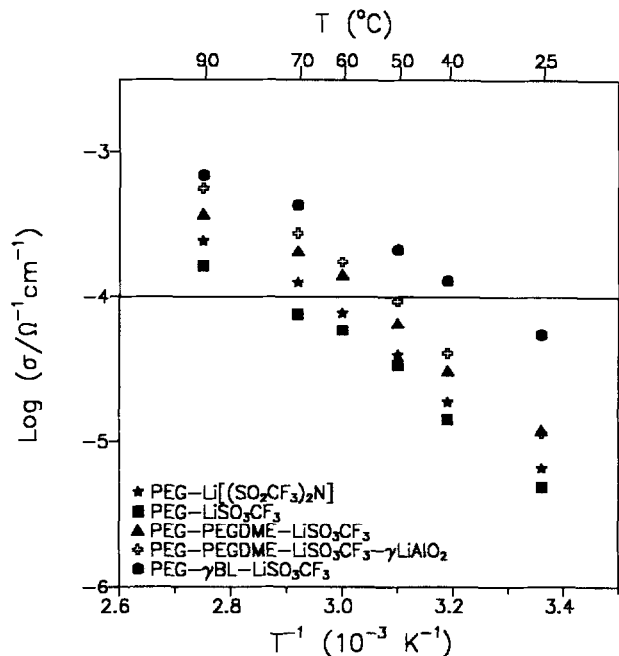


Fig. 2. Temperature dependence of the ionic conductivity of the cross-linked polymer electrolytes evaluated during the first heating cycle from room temperature to 90 °C.

ing cycles. They reach the $10^{-4} \text{ S cm}^{-1}$ conductivity value at temperatures that are easily practicable in EV batteries. As expected, the addition of a plasticizer in cross-linked polymers increases the conductivity at all temperatures and the electrolytes with γ -BL display conductivity values higher than those with PEGDME. The thermal stability of the cross-linked electrolytes is very satisfactory even at temperatures higher than 90 °C, although the use of the plasticized linear PEO electrolytes is not suggested at temperatures over 70–80 °C. The oxidation stability of these electrolytes was evaluated by linear sweep voltammetry from 2.5 to 4.5 V versus lithium; the recorded currents are negligible up to 4 V ($< 1\%$) with respect to the charge/discharge currents of Li/LiMn₂O₄ cell prototypes, so that all these polymer electrolytes are suitable for this energy storage system.

3.2. Lithium interface stability

A reasonable goal under working conditions is a cell potential drop no greater than 10% of the open-circuit voltage. Thus, given the current density values required for EV applications, the cell internal resistance (including bulk, interface and diffusion resistances) should not exceed a few hundred $\Omega \text{ cm}^2$. Yet it is also well known that the stability over time of the lithium interface resistance is a critical factor, and particular attention was focused on it. Symmetrical, freshly prepared Li/electrolyte/Li cells continuously stored at room temperature were heated to 70 °C for impedance spectroscopy and then returned to room temperature for further storage time. These conditions were tested because room temperature was assumed to be the most common storage temperature and 70 °C to be a standard working temperature. Figs. 3 and

4 compare the evolution over time of a single lithium interface resistance as well as the bulk resistance for the linear and cross-linked polymer electrolytes, respectively. For a better comparison, the bulk resistance values have been scaled to a cell of 1 cm² area and 100 μm thickness. The data of the cross-linked polymer with LiSO₃CF₃, PEGDME and γ -LiAlO₂ are not reported in the figure because, even if its lithium interface resistance remains almost constant at a low value, the bulk resistance sharply decreases over storage time, leading to short circuits of the cells. Given the good mechanical strength of these rubber-like cross-linked electrolytes, this behaviour is due to a degradation process of the polymer electrolyte by the lithium metal catalysed by the γ -LiAlO₂.

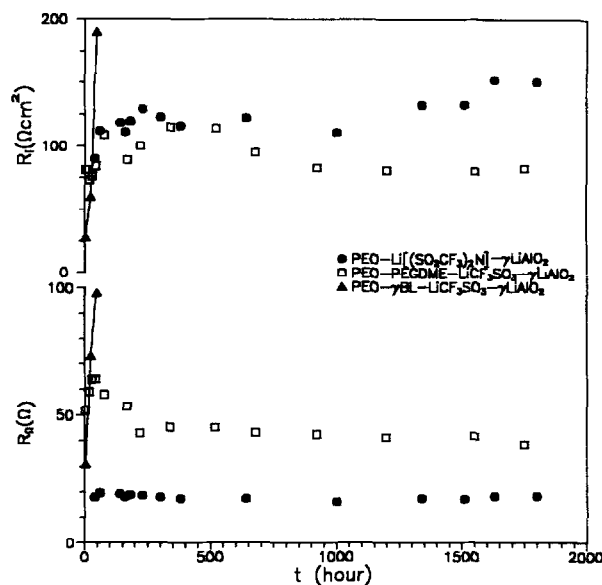


Fig. 3. Time evolution at 70 °C of the bulk (R_b) and Li/electrolyte interface (R_i) resistances for the linear polymer electrolytes. R_b have been scaled to a cell area of 1 cm² and a thickness of 0.1 mm.

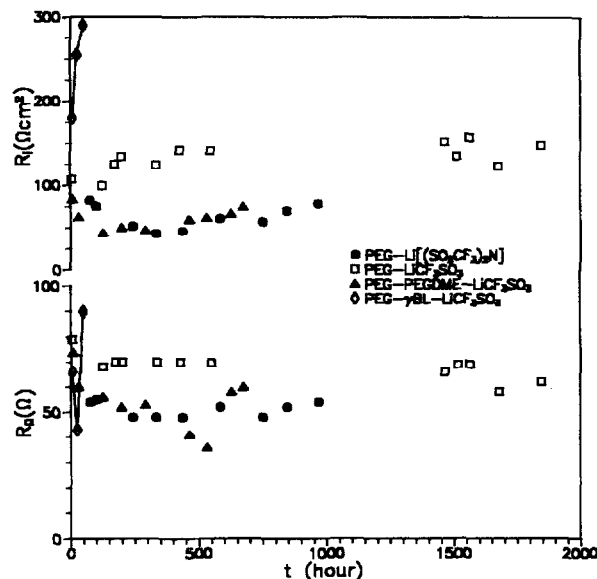


Fig. 4. Time evolution at 70 °C of the bulk (R_b) and Li/electrolyte interface (R_i) resistances for the cross-linked polymer electrolytes. R_b have been scaled to a cell area of 1 cm² and a thickness of 0.1 mm.

Indeed, where the polymer is cross-linked in the presence of the same salt and plasticizer without the ceramic filler, it is very stable with respect to the lithium electrode. The linear and cross-linked polymer electrolytes having γ -BL as plasticizer are not feasible in lithium metal batteries as both R_{Ω} and R_i dramatically grow over storage time. By contrast, all the other polymer electrolytes are stable and their low lithium interface resistance values compare well with that of the composite PEO-Li[(SO₂CF₃)₂N]- γ -LiAlO₂ [2].

3.3. Transference number

The transference numbers (T^+) were evaluated for the electrolytes that demonstrated satisfactory lithium interface stability and the data are reported in Table 2.

The T^+ value of the cross-linked polymer electrolyte with Li[(SO₂CF₃)₂N] salt is surprising low, while those polymer electrolytes with LiSO₃CF₃ salt compare well with at of the conventional PEO-linear LiSO₃CF₃ [10]. Favourably high is the transference number of the PEO-LiSO₃CF₃-PEGDME- γ -LiAlO₂. Table 2 also summarizes characteristics of these polymer electrolytes such as mechanical appearance, cross-linking time, the temperature at which polymer conductivity reaches the minimum value (10^{-4} S cm⁻¹) for battery applications (i.e. the minimum operating temperature T_{op}), lithium interface resistance, and whether the interface resistance remains stable during more than 700–1000 h. On the basis of all these characteristics the two most promising polymer electrolytes are PEO-LiSO₃CF₃-PEGDME- γ -LiAlO₂ and PEG-PEGDME-LiSO₃CF₃. They have comparable T_{op} , lithium interface resistance (R_i) and lithium interface stability, and the linear electrolyte PEO-LiSO₃CF₃-PEGDME- γ -LiAlO₂ has the advantage of a higher transference number. However, the cross-linked electrolyte has the advantage of a high mechanical strength even at high temperatures (> 70 °C), so that a battery with PEG-PEGDME-LiSO₃CF₃ could work at temperatures higher than 70 °C with the further advantage of a reduction of the interface resistance (10 Ω cm² at 90 °C).

3.4. Lithium deposition–stripping process

This selection was based on parameters determined in quasi-static conditions. To evaluate if the selected polymers can successfully sustain the transfer of a large amount of charge, impedance spectroscopy was employed to investigate how the internal resistance of the symmetrical lithium cells is modified by repeated galvanostatic cycles at 0.07 to 0.14 mA cm⁻² involving 3.5 C cm⁻², which corresponds to about 50% of the theoretical capacity of the selected cathode material (LiMn₂O₄ composite). The comparison of the impedance spectra recorded before and after deposition–stripping cycles evinced no variation of the internal resistance (bulk and interface) after cycles at a high current density but a significant increase at the low one.

Table 2
Principal characteristics of the tested polymer electrolytes

	Electrolyte	Mechanical appearance	Cross-linking time	T_{op} (°C)	R_i (Ω cm ²)	Interface stability	T^+
Linear	PEO-Li[(SO ₂ CF ₃) ₂ N]- γ -LiAlO ₂	Film mechanically stable		50	50 (70 °C)	Yes	
	PEO-LiSO ₃ CF ₃ -PEGDME- γ -LiAlO ₂	Film homogenous		50	80 (70 °C)	Yes	0.66 (70 °C)
	PEO-LiSO ₃ CF ₃ - γ -LiAlO ₂ - γ -BL	Film sticking		<25	900 (25 °C)	No	
Cross-linked	PEG-Li[(SO ₂ CF ₃) ₂ N]	Rubber-like	2 h	70	30 (70 °C)	Yes	0.14 (90 °C)
	PEG-LiSO ₃ CF ₃	Rubber-like	1.5 h	80	25 (70 °C)	Yes	0.41 (90 °C)
	PEG-PEGDME-LiSO ₃ CF ₃	Rubber-like	1 h	55	120 (70 °C)	Yes	0.44 (90 °C)
	PEG-PEGDME-LiSO ₃ CF ₃ - γ -LiAlO ₂	Rubber-like	10'	50	70 (70 °C)	Yes	0.44 (90 °C)
	PEG-LiSO ₃ CF ₃ - γ -BL	Rubber-like	> 3 h	40	10 (90 °C)	No	0.44 (90 °C)
					280 (70 °C)	No	

Correctly evaluating the coulombic efficiency of the lithium deposition–stripping process so as to estimate the excess metal lithium needed is a very difficult task. Although CV is not exactly representative of the process in a battery, it did show that coulombic efficiency depends on the substrate type as well as on the sweep rate. High efficiency values (90–97%) were recorded for aluminium electrodes at 20 mV s^{-1} . The decrease in the efficiency values as the sweep rate decreases has been explained [11] by a competitive rate of lithium deposition and lithium passivation processes. The efficiency values were also determined by galvanostatic deposition–stripping cycles (see the experimental part) and proved to be dependent on current density: at 0.18 mA cm^{-2} the values did not exceed 60%.

To gain insight into the processes leading to lithium passivation the mass changes during galvanostatic deposition of lithium at different current densities were monitored by EQCM. Preliminary experiments were carried out in PEGDME, which is a common component of the two most promising electrolytes, and we used the polyether having 250 mol. wt., which is liquid at room temperature. An example of the results at 0.4 mA cm^{-2} , scaled as mass variation Δm (by Eq. (4)) against the amount of the charge passed (scaled

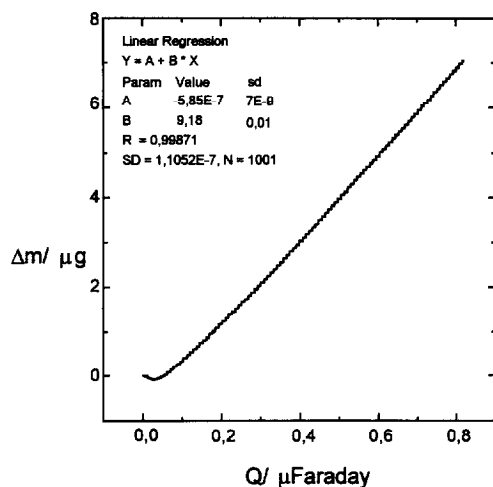


Fig. 5. Mass variation vs. amount of charge galvanostatic lithium deposition at 0.4 mA cm^{-2} in a PEGDME 250– LiSO_3CF_3 solution.

as electron mole by dividing by the Faraday constant) is shown in Fig. 5. The slope value of the curve as derived from linear regression (see the inset in the figure) is higher than 7 g/F , the value for metal lithium deposition, and the values obtained at the lower current densities are significantly higher (15 g/F at 0.25 mA cm^{-2}). These findings, even if very preliminary, are in line with all the results reported above. EQCM measurements could be a fundamental aid in optimizing the working conditions of lithium metal batteries in addition to being very useful in checking the effect of additives designed to reduce the lithium passivation rate.

3.5. Battery tests

The four new electrolytes showing lithium interface stability were also tested in $\text{Li/LiMn}_2\text{O}_4$ cells (Fig. 6). For a better comparison, these prototypes had composite cathode materials with PTFE as the binder. The figure shows their discharge capacity as a percentage of the theoretical capacity over the first ten cycles at $C/28$ discharge rate. Note that the cycleability performance of these four batteries follows the same order as the electrolyte (σT^+) values, indicating that the main part of the internal resistance of these cells is due to ion transport phenomena (bulk and diffusion resistances). Given that cycleability tests on the same composite cathode material in PEGDME(250)– LiSO_3CF_3 liquid electrolyte at room temperature and at $C/10$ showed about 70% of the theoretical capacity [9] the results for the battery with PEO–PEGDME– LiCF_3SO_3 – γ – LiAlO_2 are very promising. In the solid configuration the battery performance was expected to be lower because neither cathode composition nor film thicknesses were optimized. However, we can compare the electrolyte influence by the performance of the battery.

4. Conclusions

The present study clearly demonstrates the importance of a broad-based electrochemical characterisation in selecting an electrolyte for lithium metal batteries. Two polymer elec-

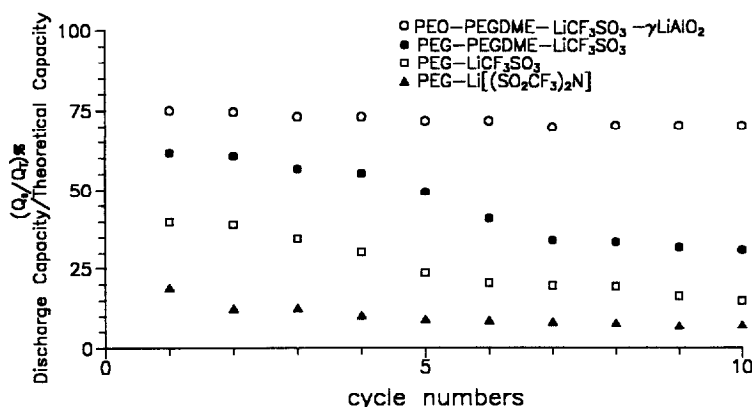


Fig. 6. Discharge capacity as a percentage of the theoretical capacity vs. cycle number for the $\text{Li/LiMn}_2\text{O}_4$ batteries based on the linear and cross-linked electrolytes.

trolytes with an environment-friendly manufacturing method proved to be promising candidates for lithium metal batteries.

The lithium deposition–stripping process, an important aspect of these batteries, still remains an open question. The EQCM technique appears to be a useful tool for process optimization and is currently being tested in our laboratory.

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References

- [1] B. Scrosati, *Nature*, 373 (1995) 557.
- [2] M.C. Borghini, M. Mastragostino, S. Passerini and B. Scrosati, *J. Electrochem. Soc.*, 142 (1995) 2140.
- [3] M.C. Borghini, M. Mastragostino and A. Zanelli, *Electrochim. Acta*, 41 (1996) 2369.
- [4] B.A. Boukamp, *Solid State Ionics*, 20 (1986) 31.
- [5] P.G. Bruce, M.T. Hardgrave and C.A. Vincent, *J. Electrochem. Soc.*, 130 (1992) 1517.
- [6] J. Evans, C.A. Vincent and P.G. Bruce, *Polymer*, 28 (1987) 2324.
- [7] D. Aurbach and Y. Gofer, *J. Electrochem. Soc.*, 130 (1989) 3195.
- [8] S. Bruckenstein and M. Shay, *Electrochim. Acta*, 30 (1985) 1295.
- [9] M.C. Borghini, M. Mastragostino and A. Zanelli, unpublished data.
- [10] R. Koksang, I.I. Olsen and D. Shackle, *Solid State Ionics*, 69 (1994) 320.
- [11] G.B. Appetecchi, G. Dautzenberg and B. Scrosati, *J. Electrochem. Soc.*, 143 (1996) 6.