High-performance electrolyte membranes for plastic lithium batteries

G.B. Appetecchi, F. Croce, B. Scrosati

Sezione di Elettrochimica, Dipartimento di Chimica, Università 'La Sapienza, 00185 Rome, Italy

Received 13 May 1996; revised 4 September 1996

Abstract

The synthesis, properties, and application of new types of lithium-ion conducting polymeric membranes are reported and discussed. These ionic membranes are dimensionally stable, have a very high ionic conductivity, an acceptable lithium-ion transference number and a wide electrochemical stability window. Due to these favourable properties, these membranes are suitable for the fabrication of advanced-design, high-performance batteries and power source devices.

Keywords: Lithium batteries; Membranes; Electrolyte membranes

1. Introduction

Today, large attention is devoted to the characterization of ion-conducting membranes to be used as advanced electrolytes in new-design, solid-state, electrochemical devices. Indeed, the concept of a power source capable of combining high performance with a plastic, flexible structure is very appealing for the consumer electronic market. Accordingly, substantial work has been directed to the identification of the most suitable components for the fabrication of these devices, with particular concern on the most crucial of them, namely the electrolyte component which ideally should be a membrane of such a nature of assuring efficient electronic separation between the electrodes, high ionic conductivity and good compatibility with the electrode materials.

So far, the most successful procedure to achieve this goal appears to be the gelification of liquid electrolyte solutions in a polymer matrix. Indeed, a large number of university and industrial laboratories are involved in the development of these 'hybrid' or 'gelionic' electrolyte membranes [1–8]. In this paper we describe the characteristics and properties of some selected examples of these membranes, including a series originally developed in our laboratory, with the aim of evaluating their electrochemical behaviour and of suggesting to which type of device they can be profitably addressed.

2. Experimental

2.1. Synthesis

The electrolyte membranes were prepared by immobilizing selected lithium salt solutions in a poly(acrylonitrile)

(PAN), or in a poly(methyl methacrylate) (PMMA) matrix. The details of this procedure were reported in previous papers [6–8]. For reasons of simplicity, the membranes are hereafter indicated by writing in sequence the selected lithium salt, the liquid solvent (or solvent mixture) and the immobilizing polymer. For instance, the notation $LiClO_4$–EC–PC–PMMA refers to a membrane formed by a solution of lithium perchlorate in an ethylene carbonate–propylene carbonate solvent mixture immobilized in a poly(methylmethacrylate) matrix.

The new class of membranes originally developed in our laboratory [9] and hereafter denoted with the acronym ALPE (advanced lithium polymer electrolytes), were prepared by gelling solutions of lithium salts in combined poly(ethylene oxide) (PEO) and poly(ethylene glycol) dimethyl ether (PEGDME) mixtures.

The lithium-ion membrane electrolytes (LIMEs) were synthesized by immobilizing in a PMMA matrix a solution of an $LiN(CF_3SO_2)_2$ lithium salt in an ethylene carbonate–dimethylcarbonate, EC–DMC, solution The preferred LIME composition was (in molar ratio): $LiN(CF_3SO_2)_2$:EC:DMC:PMMA = 5:50:20:25.

All the materials and the chemicals used were of high purity. The synthesis procedures gave in most of the cases dimensionally stable membranes of a typical thickness ranging between 50 and 100 μm.

2.2. Electrochemical characterization

The conductivity of the membranes was obtained by measuring the impedance response of cells formed by sandwiching

the given electrolyte sample between two blocking (e.g., stainless-steel) electrodes.

The electrochemical stability window was evaluated by running a sweep voltammetry of cells using an inert (e.g., stainless steel) or an active (e.g., $LiMn_2O_4$) working electrode, a lithium counter electrode and a lithium reference electrode. Alternatively, the anodic stability was evaluated by monitoring the impedance response of blocking electrode cells kept under different voltage bias.

2.3. Battery prototypes

The battery prototypes were assembled in an environmentally controlled dry box by pressing into appropriate, button-type containers a sequence formed the lithium disk anode, the electrolyte membrane and the film cathode. The latter had a composite configuration which typically included the active material (e.g., $LiMn_2O_4$), carbon powder and a binder, preferably polymeric and of the same nature of that used in the selected electrolyte membrane. The cells were sealed and kept in the dry box for all the electrochemical tests. No optimization in the cell geometry or structure was attempted in this work whose main objective is demonstrating the feasibility of selected types of membrane for the development of plastic-like, lithium-metal or lithium-ion batteries.

2.4. Equipment

Conventional electrochemical instrumentation was used for the measurements. Typically, an EEG potentiostat, Model 273, was used for the determination of voltage–current curves, a Solartron, Model 1260, frequency response analyser was used for impedance studies and an AMEL, Model 545, galvanostat was used for the battery cycling tests.

3. Results and discussion

3.1. Transport properties

Fig. 1 illustrates the Arrhenius plots for some selected examples of the gel membranes prepared and tested in our
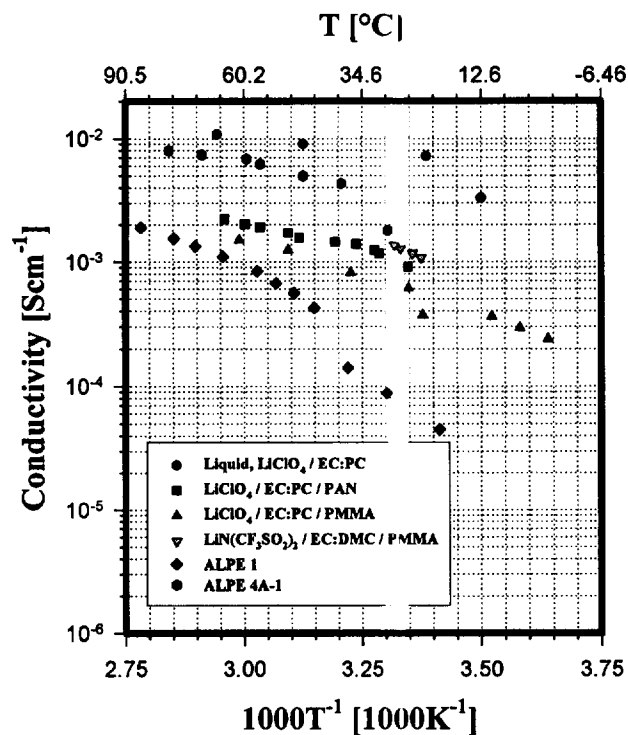

Fig. 1. Arrhenius plots of various PAN-, PMMA-based, ALPE and LIME gelionic membranes. The plot of the $LiClO_4$/PC–EC liquid solution is also reported for purposes of comparison PAN = poly(acrylonitrile); PMMA = poly(methylmethacrylate); PC = propylene carbonate; EC = ethylene carbonate; DMC = dimethyl carbonate.

laboratory. The high conductivity, which at room temperature approaches that of the liquids, is certainly the most distinctive and appealing feature of these membranes. Considering that this high conductivity is of the ionic type, we have classified these membranes with the general term 'gelionics' [8]. The fast ionic transport is accompanied by a series of other important properties (see Table 1), which include a wide electrochemical stability window and a reasonably high lithium-ion transference number.

3.2. Electrochemical stability

The determination of the electrochemical stability window of a given electrolyte is an important test for the determination

Table 1
Electrochemical properties of selected gelionic membranes at room temperature

Gelionic membrane [a]	Composition (mole ratio)	$\sigma \times 10^3$ (S cm^{-1})	Anodic stability (V vs. Li)	t_{Li^+}
$LiClO_4$–EC–PC–PAN	8:38:33:21	1.1	4.9	0.5
$LiClO_4$–EC–PC–PMMA	4.5:46.5:19:30	0.7	4.9	0.4
$LiN(CF_3SO_2)_2$–EC–DMC–PMMA	5:50:20:25	0.7	4.9	0.4
$LiN(CF_3SO_2)_2$–PEGDME–PEO [b] ALPE-1	4.8:80.9:14.3	0.1	5.0	0.3
$LiN(CF_3SO_2)_2$–PEGDME–PC–PEO [b] ALPE 4A-1	6.6:56.0:18.7:18.7	1.9	4.9	0.3

[a] PAN = poly(acrylonitrile); PMMA = poly(methylmethacrylate); PC = propylene carbonate; EC = ethylene carbonate; DMC = dimethyl carbonate; PEGDME = poly(ethylene glycol)dimethyl ether; PEO = poly(ethylene oxide).
[b] With addition of γ-$LiAlO_2$ (10 wt.%).

of its compatibility with high-voltage cathodes, such as the lithium transition metal oxides, e.g. $LiCoO_2$, $LiNiO_2$ or $LiMn_2O_4$. Traditionally, the stability range is determined by running a sweep voltammetry of an 'inert' electrode (an electrode different from that which will actually be used in the battery) in the selected electrolyte. The onset of the current in the anodic high-voltage range is then assumed as a result from a decomposition process and, thus, the associated voltage is taken as the upper limit of the electrolyte stability range. A typical example is shown in Fig. 2 which illustrates the case of the ALPE-1 membrane.

This method, however, gives only approximate values since it may be affected by the kinetics of the probing electrode. We have then attempted to develop two new types of measuring methods. One uses inert electrode cells which, however, are tested by a low a.c. voltage (10 mV) impedance analysis run at different applied bias voltages. A typical example, again related to the response of the ALPE-1 membrane assembled in a cell using two symmetrical stainless-steel electrodes, is shown in Fig. 3. As the bias voltage increases, the trend of the impedance response changes from a linear spike to a semiarc. As well known, a linear response in the middle-high frequency impedance plot is associated with an interfacial-blocked condition while the appearance of an arc implies the ongoing of a charge-transfer process. Considering the nature of the electrode used (e.g., stainless steel), the latter may only be associated with electrolyte decomposition. Therefore, the bias voltage at which the response approaches a well-defined arc may be taken as the anodic stability limit of the electrolyte.

Up to a 4 V bias, the arc is still very wide and it does not close on the real axis (see Fig. 3), suggesting a very high interfacial resistance and thus, a negligible decomposition. On the other hand, the curvature becomes almost complete under 5 V bias, which then can be assumed as the voltage which limits the anodic stability of the electrolyte.

The second method is based on sweep voltammetry, run however at very low rates and on cells where the working

Fig. 3. Impedance spectra of a stainless-steel/ALPE-1/stainless-steel cell at room temperature and at different applied bias voltages. The curvature of the impedance response is taken as an indication of the electrolyte decomposition voltage; frequency range: 1 Hz–1 MHz.

electrode is not 'inert' but rather 'active', namely the same electrode will be eventually used as cathode in a practical battery. Fig. 4 shows a typical example, again related to an ALPE-1 membrane, tested in a cell using an established cathode material, such as $LiMn_2O_4$, as the working electrode. The current–voltage response of this electrode clearly shows an anodic peak centered at 4.75 V versus lithium, which is assumed to be related to the electrochemical lithium de-intercalation process

$$LiMn_2O_4 \rightarrow xLi^+ + Li_{1-x}Mn_2O_4 + xe^- \qquad (1)$$
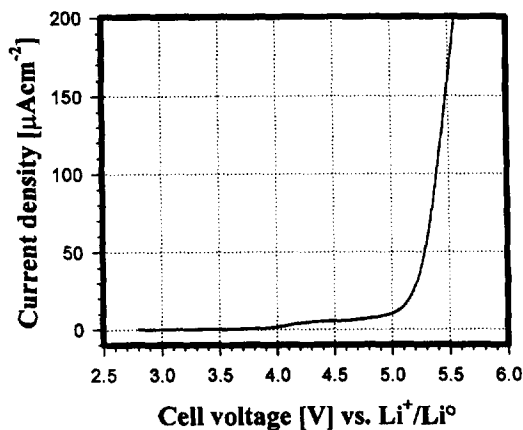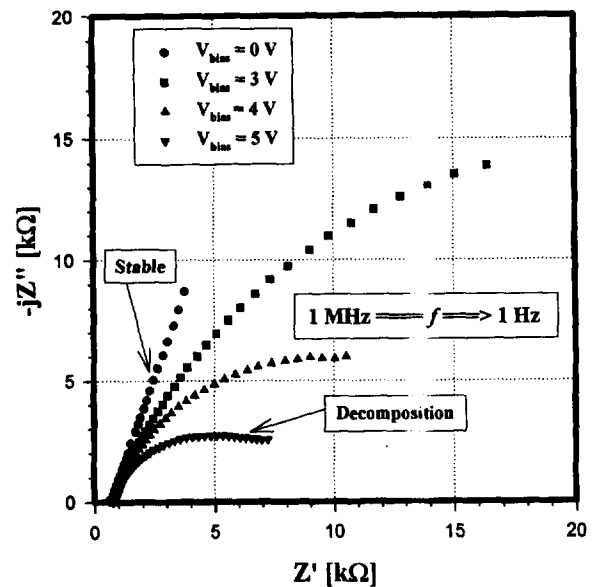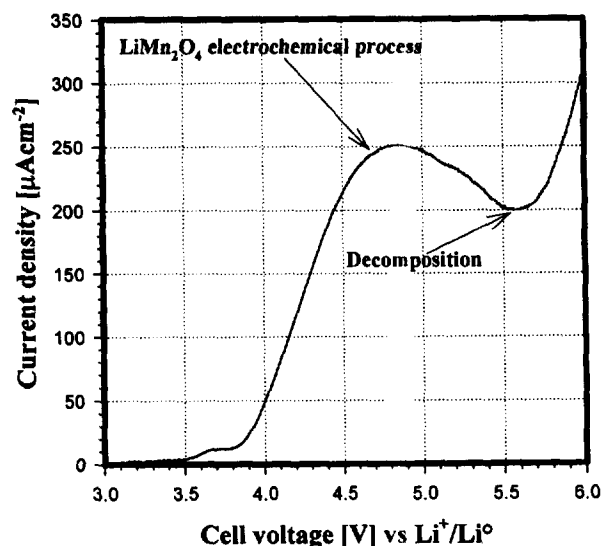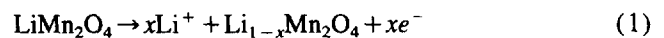
Fig. 2. Current–voltage curve for a stainless-steel blocking electrode in an ALPE-1 cell at room temperature; lithium reference and counter electrodes; sweep rate: 1 mV s^{-1}. The onset of the current gives the approximate value of the anodic stability (voltage) limit of the electrolyte.

Fig. 4. Slow-scan (0.05 mV s^{-1}) voltammetry of an $LiMn_2O_4$ electrode in an ALPE-1 cell at room temperature. Lithium counter and lithium reference electrodes. The evolution of the current–voltage trend shows that the electrolyte stability is sufficiently high to allow the electrochemical process to be completed.

Although a totally correct interpretation of this voltam-mogram would require a clear assignment of the charge involved in the various peaks, the complete evolution of the above-cited peak suggests that the electrochemical process can, indeed, be fully completed in the ALPE-1 electrolyte. In fact, a current rise, possibly related to decomposition phenomena, only occurs at voltages far more positive (around 5.5 V) than that of the end of the peak assigned to the electrochemical process.

Results obtained with the three methods (compare Figs. 2–4) are consistent in the suggestion that the stability of the ALPE-1 membrane may extend up to 5 V. A similar result has also been found for the majority of the gelionic membranes investigated in this work (see Table 1).

3.3. Stability towards the lithium-metal electrode

As well known, the lithium-metal electrode is unavoidably passivated when placed in contact with any electrolyte, and the new-generation, highly-conducting, gelionic membranes are no exceptions [8]. Possible approaches for improving the stability of the lithium electrode/gelionic membrane interface include:

(i) the selection of the most suitable solvent and/or salt and/or polymer component(s);

(ii) the addition of 'interfacial stabilizers', e.g., ceramic powders, and

(iii) the use of 'dry' membranes, i.e., plasticizer-free membranes.

A convenient method for testing the compatibility of a given electrolyte with the lithium-metal electrode is that of monitoring, by impedance spectroscopy, the time evolution of the interfacial resistance, R_i. Increases in R_i values are associated with the growth of a passivation layer on the electrode surface. Fig. 5 illustrates the evolution of R_i for lithium cells using the gelionic membranes studied in this work. The R_i of cells using an $LiClO_4$–EC–PC–PAN membrane steadily increases with time, this suggesting a poor compatibility of this membrane with the metal. Much lower is the increase in R_i in the case of cells using membranes in which PAN is replaced by PMMA or to which finely dispersed ceramic powders (e.g., γ-$LiAlO_2$ or zeolites) are added.

These evidences confirm the validity of approaches (i) and (ii), respectively. The difference between the lithium interfacial properties of PAN- and PMMA-based membranes is attributed to a difference in the reactivity of the functional groups and to a difference in the polymer-ion short-range interactions [10]. The beneficial action of the dispersed ceramics is attributed to their affinity for water and/or residual solvent traces, i.e., for those impurities which are generally considered to be very aggressive towards lithium [8]. Therefore, by trapping the impurities, the ceramic powders act as interfacial stabilizers.

Fig. 5 also reveals that lithium passivation is greatly reduced when passing from electrolyte membranes using liquid plasticizers (e.g., the ALPE 4-1 membrane which incor-
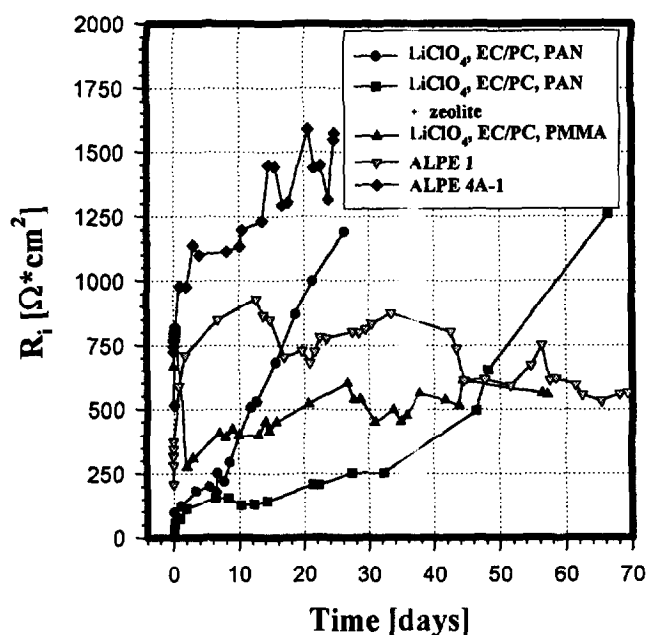

Fig. 5. Time evolution of the interfacial resistance R_i of the lithium electrode in contact with gelionic membrane electrolytes at room temperature. Data obtained by impedance spectroscopy of cells kept under open-circuit conditions.

porates DMC) to 'dry' membranes (e.g., the ALPE-1 membrane, which has no plasticizer and, in addition, contains a ceramic stabilizer), this proving the validity of approach (iii) and reconfirming that of approach (ii).

3.4. Membrane electrolytes for lithium batteries

The gelionic membranes, proved to be the most effective in terms of compatibility with the lithium electrode, have been selected for the fabrication and testing of thin-film, plastic-like, lithium batteries. Some typical examples of these batteries consider the following combinations:

1. the use of PMMA-based membranes and of thin-film polymer cathodes [11,12], and
2. the use of the ALPE-1 membrane and of a thin-film lithium manganese oxide cathodes [13].

The performance of the first type of plastic batteries has been evaluated by using a sample, button-type $Li/LiClO_4$–EC–PC–PMMA/poly(pyrrole) (pPy) cell prototypes. The results, obtained in collaboration with a research group at the Waseda University in Tokyo, Japan, are very encouraging since they show that the cell can be cycled at moderate rates for several thousands of cycles with no apparent degradation [11,12].

Fig. 6 illustrates the cycling performance of the second battery types, examplified by examining the response of an $Li/ALPE-1/LiMn_2O_4$ thin-film cell prototype. The capacity decay observed upon cycling is attributed to the cathode side which is far from being optimized, both in terms of purity of the $LiMn_2O_4$ material and of homogenization of the composite cathode structure.
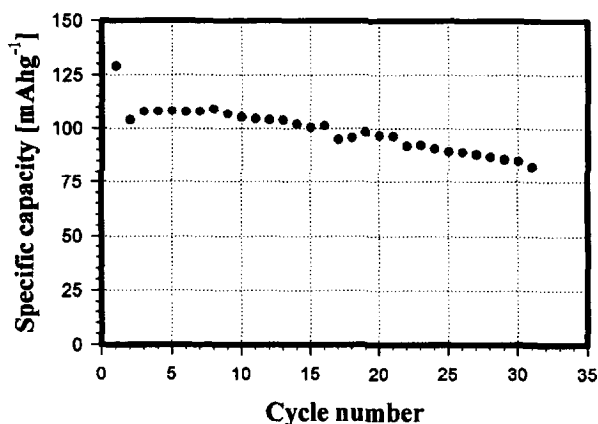
Fig. 6. Specific capacity delivered upon cycling by an Li/ALPE-1/LiMn₂O₄ cell prototype at room temperature and at $C/20$ rate.

The above results suggest that the selected PMMA and ALPE gelionic membranes are in principle suitable for lithium battery applications. However, no conclusive evidence has been so far obtained to assure that full rechargeability and total reliability under prolonged and diversified cycling conditions can be effectively achieved.

3.5. Lithium-ion membrane electrolytes

Gelionic membranes which are excluded or not totally suitable for lithium metal batteries, may prove to be of great value for the development of lithium-ion batteries. Typical is the case of plasticizer-added membranes in which a certain liquid release, which is detrimental for lithium passivation (see above), may be highly beneficial in favouring wettability in high-surface, carbon electrodes.

Considering the present importance of the lithium-ion concept in the advanced battery technology, it appears to be of particular importance to optimize these 'wet' electrolyte membranes in view of their use of extending the concept to plastic-like configurations. Indeed, this idea is attracting large interest and many industrial [2,14] and university [13] laboratories are presently engaged in its exploitation in the fabrication of versatile and new-design lithium-ion batteries.

As well known, the most successful electrolytes in common lithium-ion batteries are liquid solutions of a lithium salt in an EC–DMC solvent mixture [15]. In order to keep this favourable combination also in our advanced, lithium-ion membrane electrolytes (LIMEs) we have immobilized this type of solution (i.e. a solution of LiN(CF₃SO₂)₂ in EC–DMC) in a polymer matrix (i.e., a PMMA matrix). The resulting LIME, which hereafter will be simply indicated as LiN(CF₃SO₂)₂–EC–DMC–PMMA, has a very high and stable conductivity at room temperature. This is demonstrated in Fig. 1, which shows the Arrhenius plot, and in Fig. 7 which reports the values of the conductivity at room temperature monitored for 120 days. The results confirm that the LIME has a high conductivity (Fig. 1) which, apart from oscillations due to small temperature variations (the test cell, although kept closed in the dry box, was not thermostated),
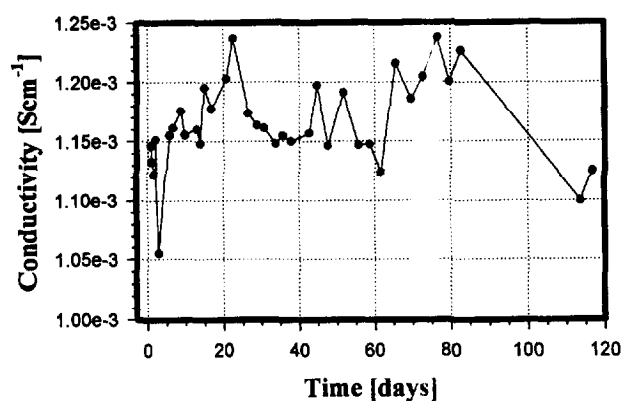

Fig. 7. Conductivity of the LiN(CF₃SO₂)₂–EC–DMC–PMMA lithium-ion membrane, at room temperature in a not thermostated, closed cell.
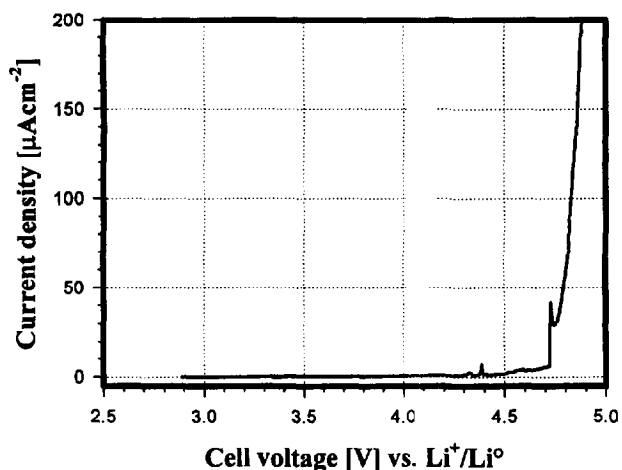

Fig. 8. Current–voltage curve for a nickel-blocking electrode in an LiN(CF₃SO₂)₂–EC–DMC–PMMA cell at room temperature; lithium reference and counter electrodes; sweep rate: 0.5 mV s⁻¹. The onset of the current gives the approximate value of the anodic stability limit of the electrolyte.

remains stable around the $\sigma = 1.1 \times 10^{-3}$ S cm⁻¹ value at room temperature (Fig. 7).

Fig. 8 shows a typical current–voltage curve of a stainless-steel electrode in an LiN(CF₃SO₂)₂–EC–DMC–PMMA membrane cell. The onset of the current at 4.7 V evidences an acceptable stability window of the LIME and thus, its compatibility with high-voltage, lithium metal oxide cathode materials.

These favourable properties suggest that LIMEs may be suitable for lithium-ion battery applications. Further tests confirming this interesting expectation include the evaluation of the response, (e.g. in terms of cycleability and capacity delivery) of lithium-ion electrodes — plasticized graphite anodes and lithium metal oxide cathodes — in these electrolyte membranes. These tests are in progress in our laboratory.

Acknowledgements

          G.B. Appetecchi et al. / Journal of Power Sources 66 (1997) 77–82

assembling and testing the Li/pPy batteries, the ENEA 'ALPE Project' for in part supporting the work on the Li/LiMn$_2$O$_4$ batteries and the NEDO's International Joint Research Program 'Fundamental Researches on the Development of Advanced Batteries using New Electrode/Electrolyte Materials' for supporting the work on LIMEs.

References

[1] K.M. Abraham and M. Alamgir, *J. Electrochem. Soc.*, *136* (1990) 1657.

[2] K.M. Abraham and M. Alamgir, *J. Power Sources*, *44* (1993) 195.

[3] G. Nagusabramanian, A.I. Attia and G. Halpert, *J. Appl. Electrochem.*, 2 (1994) 298.

[4] C. Schmultz, J.M. Tarascon, A.S. Gordz, P.C. Warren and F.K. Shokoohi, *Ext. Abstr., Meet. The Electrochemical Society, Miami, FL, USA, 9–14 Oct. 1995*, Abstr. No. 109.

[5] K.M. Abrahams, in B. Scrosati (ed.), *Applications of Electroactive Polymers*, Chapman and Hall, London, 1993, p. 75.

[6] G.B. Appetecchi, F. Croce, G. Dautzenberg, S. Passerini, and B. Scrosati, *Electrochim. Acta*, *39* (1994) 2187.

[7] G. Dautzenberg, F. Croce, S. Passerini and B. Scrosati, *Chem. Mat.*, *6* (1994) 538.

[8] G.B. Appetecchi, F. Croce and B. Scrosati, *Electrochim. Acta*, *40* (1995) 991.

[9] G.B. Appetecchi, G. Dautzenberg and B. Scrosati, *J. Electrochem. Soc.*, *143* (1996) 6.

[10] E. Cazzanelli, G. Mariotto, F. Croce, G.B Appetecchi and B. Scrosati, *Electrochim. Acta*, *40* (1995)2379.

[11] S. Kakuka, T. Momma, T. Osaka, G.B. Appetecchi and B. Scrosati, *J. Electrochem. Soc.*, *142* (1995) L1.

[12] H. Ito, Y. Veda, T. Momma, T. Osaka and B. Scrosati, *Proc. 35th Battery Symp. Japan, Kyoto, Japan, 1995*, p. 313.

[13] G.B. Appetecchi, F. Croce, G. Dautzenberg, S. Panero and B. Scrosati, in J. Bates (ed.), *Proc. Thin Film Solid Ionic Devices and Materials*, The Electrochemical Society, Princeton, NJ, USA, 1996.

[14] F. Shokoohi, *13th Int. Seminar on Primary and Secondary Battery Technology and Application, Boca Raton, FL, USA, 4–7 Mar. 1996*.

[15] S. Megahed and B. Scrosati, *J. Power Sources*, *51* (1994) 79.