Electrochemical testing of industrially produced PEO-based polymer electrolytes

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Abstract

The present report describes the results of the electrochemical tests performed on polyethyleneoxide-based polymer electrolyte thin films industrially manufactured by blown-extrusion. The polymer electrolyte composition was PEO_{20} $LiCF_3SO_3$: 16.7% $\gamma LiAlO_2$. The polymer electrolyte film was tested to evaluate the ionic conductivity as well as the interfacial properties with lithium metal anodes. The work was developed within the advanced lithium polymer electrolyte (ALPE) project, an Italian project devoted to the realization of lithium polymer batteries for electric vehicle applications, in collaboration with Union Carbide. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Rechargeable lithium battery systems, called lithium-ion or rocking-chair batteries, are commercially available on a large production scale. However, this battery system that makes use of liquid electrolyte, is not being developed rapidly for electric vehicle applications. Although the performance of lithium-ion batteries is extremely good for consumer market applications, especially because of the very long life (>2000 cycles) [1,2], the lithium-ion battery chemistry does lack of a fundamental requirement of large batteries for electric vehicle application: safety. Safety tests (for example, nail tests) have shown that the result of the thermal runaway induced by the damage of large size lithium-ion batteries is frequently dramatic. The set-up of an internal overpressure due to short circuit of the battery electrodes results in the rapid leakage of flammable liquids and/or gases that eventually proceeds in a fire or in the explosion of the battery itself.

Dry polymer electrolyte-based batteries certainly represent a solution to this problem because of the absence of liquid electrolyte. In addition, the lithium polymer system's theoretical specific energy is markedly higher than that of Li-ion systems. For example, the Li/VO_x couple offers over 600 Wh/kg while the Li-ion systems offer between 380 and 450 Wh/kg depending on the choice of positive active material. However, despite more than two decades of scientific and industrial research, the lithium-metal dry polymer electrolyte battery system is still not available commercially. Four factors are accountable for such a delay:

- the unsatisfactory reversibility of the lithium plating/stripping process which requires an excess amount of lithium to achieve adequate battery cycle life;
- the practical extent to which the positive electrode material can be utilized;
- the cost of the manufacturing processes for the large areas of very thin structures required for large batteries; and
- the somewhat less volume-efficient stack design of the thin film technology.

The first factor is not longer considered a major problem for the development of lithium polymer batteries. Recent work in our group has shown that the properties of the lithium-polymer electrolyte interface can be highly improved by the appropriate processing [3–5].

The other three factors are all correlated with the low ionic conductivity of the polymer electrolyte even at above ambient temperatures (typically lithium-polymer batteries are operated between 60 and 90°C). To have reasonable cathode utilization the use of very thin positive electrodes

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and, in turn, of any other component, is required. This introduces the need for the manufacturing of very thin components and to optimize the stack design of large batteries.

Besides the Italian project ALPE, there are two main active programs dedicated to the development of lithium polymer batteries led by Argo-Tech (Canada) and Bolloré/ EDF (France). All programs are based on the use of thin lithium-foil negative electrodes and vanadium oxide-based positive electrodes separated by a PEO-based polymer electrolyte but they substantially differ for the processing of the layers. Argo-Tech technology involves the casting of the thin positive electrode and electrolyte from solvent containing solutions or slurries, followed by the lamination of a thin (<50 μm) layer of metallic lithium. Bolloré/EDF and ALPE programs are both based on the solvent-free fabrication of thin polymer electrolyte and composite cathode films by hot-extrusion followed by calendering and lamination steps. These techniques were adopted because of the environmental restrictions as well as of their potential for high-speed, low-cost manufacturing. However, these techniques are still presenting development challenges.

The present work addresses one of these challenges. The investigations were focused on individuating an industrial process to manufacture thin films of polymer electrolytes by avoiding the use of any solvent. As it will be shown in the following, the investigation was successful and the polymer electrolyte films prepared by the industrial-like procedure showed very good electrochemical properties in terms of conductivity and stability of the lithium-polymer electrolyte interface, comparable with lab-scale produced polymer electrolytes.

2. Experimental

The composite electrolyte tapes were prepared by following a solvent-free procedure [3,6]. All the components of the electrolyte, polyethylene oxide, P(EO) (Union Carbide, WSR-N80, MW = 200,000 and WSR-N750, MW = 300,000), $LiCF_3SO_3$ (3 M, FC122), $\gamma LiAlO_2$ (HSA, Cyprus-Foote Co.), were dried in an oven under vacuum. The materials were dried at 120°C with the exception of PEO which was dried at 50°C. After drying, all of the components were carefully sieved through 200 and 400 mesh sieves in order to break-up or eliminate macro-aggregates into smaller powder granules. Finally, they were gently mixed in the desired proportions by ball milling for at least 24 h. The composite mixture had a $EO/LiCF_3SO_3$ molar ratio (20:1). The $\gamma LiAlO_2$ content was 16.7% (w/w). The above mentioned procedure were performed at ENEA (Casaccia Research Center) in a dry-room (R.H. < 0.2%).

Blown films were made from two samples differing for the molecular weight of the polymer (PEO) used. The two samples were first extruded into strands and pelletized using a C.W. Brabender, PLASTI Corder, PL2000, 1 in. extruder,

Type DR-2072 with a 25 in. screw and L/D compression ratio of 3/1. Pelletizing was done by a Killion pelletizer, Model 46807372143-OA. The sample containing P(EO) WSR-N80 (MW = 200,000) was processed using a screen pack of 100 and 20 mesh. A temperature profile of (120, 130, 140, 145, Die 140°C) and a 20 rpm roll speed were used. The sample containing WSR-N750 (MW = 300,000) was processed using a screen pack of 100 and 20 mesh. A temperature profile of (130, 150, 170, 175, Die 170°C) and a 20 rpm roll speed were used.

The composite materials absorbed moisture during the pelletizing step. Therefore, they required drying before the blown film process. The pellets were dried and stored at ambient temperature under dry nitrogen.

The blown film in each case was fabricated on a C.W. Brabender PREP Center, Type D-72 and a C.W. Brabender 1 in. extruder, Type 2523 with a 25 in. screw and L/D compression ratio of 2/1. The film tower was a C.W. Brabender, Type BFW-100-B. The sample with WSR-80 and lithium salt was processed at a temperature profile of (120, 130, 140, 135, Die 156°C), at 25 rpm, 106 kg cm^{-2}, and film take up roll speed setting of 25. The sample with WSR-N750 and lithium salt was processed at a temperature profile of (130, 155, 170, 165, Die 189°C), at 25 rpm, 286 kg cm^{-2}, and film take up roll speed setting of 30.

The processing of both samples required a careful adjustment to balance the air flow. With the sample containing WSR-N750, the film tower bubble would collapse due to the presence of a few holes in the film. The sample containing WSR-N80 was easier to process due to its lower molecular weight and higher melt-flow. Films of both samples were obtained with thicknesses ranging from 0.1 to 0.15 mm. The pelletizing and blown steps were performed at Union Carbide (Bound Brook) in ambient air. However, particular care was taken to reduce the exposure of the materials to humid air. Blown films were dried under vacuum and stored in sealed polyethylene bags.

Then, the blown composite polymer electrolyte films were transferred at ENEA (Casaccia Research Center) in a dry-room (R.H. < 0.2%) and dried under vacuum at 50°C for 24 h. The film thickness was further reduced to 0.04–0.06 mm by cold-calendering [6].

Electrochemical tests were performed on WSR-N80-based composite polymer electrolyte calendered tapes by using two-electrode cells. The tests were performed on symmetric cells realized by hot-laminating (90°C under vacuum) a layer of composite electrolyte between two copper (foil thickness: 0.025 mm; active area: 16.0 cm^2) or two lithium (foil thickness: 0.05 mm; active area: 10.0 cm^2) electrodes. Both kind of cells were sealed under vacuum in coffee bag-like packaging.

The ionic conductivity was evaluated by measuring the impedance of the copper electrode cells during a cooling-heating cycle from 20 to 100°C by means of a frequency response analyzer (FRA, Solartron mod. 1260) in the 0.5–65 kHz frequency range.

The interfacial stability evaluation was performed on symmetric lithium cells in rest and in kinetic condition at 90°C. In the former case, the impedance of the cell was monitored on time by using the impedance equipment described earlier. In the latter case, a constant current was continuously passed through the cell but its polarity was changed every 3 h. The evolution of the lithium/polymer electrolyte interface was followed by recording the cell overvoltage during the test.

Both cell assembly and electrochemical tests were performed in a dry-room (R.H. < 0.2%, Corridi S.r.L.).

3. Results and discussion

As indicated in the Section 2, hole-free composite electrolyte films were obtained only by using the WSR-N80 polymer. Since the presence of holes in the polymer electrolyte was found to be one of the most common causes of polymer electrolyte cell failure (due to the growth of lithium dendrites through the cell) the characterization of the WSR-N750-based electrolyte was not further performed. All the results reported later refer to the composite electrolyte based on WSR-N80 polymer.

The ionic conductivity versus temperature behavior of the composite polymer electrolyte was evaluated by performing impedance measurements at different temperatures on symmetric Cu/polymer electrolyte/Cu cells. The experimental data, reported in Fig. 1, were analyzed with the help of a non-linear least-square (NLLSQ) fit software developed by Boukamp [7]. Only fits characterized by a χ^2 factor lower
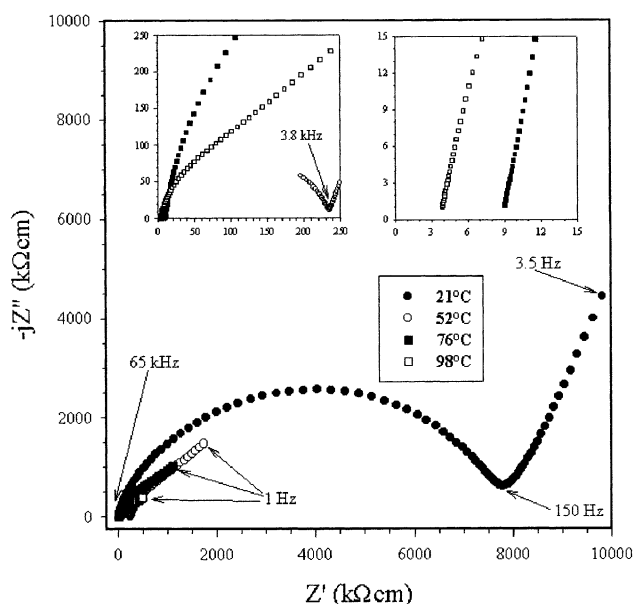
than 10^{-4} were considered acceptable. The standard model equivalent circuit [6] was used to extract the value of the polymer electrolyte ionic resistance from the raw impedance data. The spectra were normalized for polymer electrolyte thickness and copper electrode active area. The low impedance part of the spectra is enlarged in the two insets inside figure for better comparison of spectra shape at different temperatures.

Fig. 2 illustrates the results in terms of ionic conductivity versus temperature dependence (Arrhenius plot). The curve shows the standard behavior of PEO-based electrolytes containing non-plasticizing salts [3,4]. Two, well-defined conductivity versus temperature regions are seen in the Arrhenius plot of Fig. 2, separated by a steep transition around the polymer melting point ($MP_{PEO} \sim 65°C$). On heating from 20°C, the conductivity increases almost linearly with temperature. When the PEO melts (slightly above 60°C) a steep increase in the ionic conductivity is observed. Above the PEO melting temperature the conductivity still increases but at a much smaller rate. The curve is almost reversible during the following cooling cycle. The moderate hysteresis is certainly due to the presence of the γ-LiAlO$_2$ particles that were shown to prevent the polymer re-crystallization [8]. Summarizing, the ionic conductivity measurements show that the industrially manufactured composite polymer electrolyte offers the same ionic conductivity of lab-scale prepared polymer electrolytes of similar composition [4].

The stability of the blown composite electrolyte towards the lithium anode was investigated on symmetric Li/polymer electrolyte/Li cells by following the evolution of both the interfacial impedance in rest condition and the cell
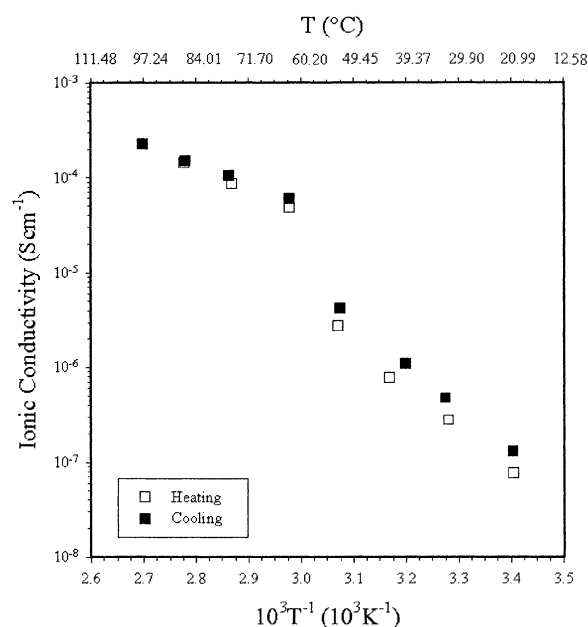

Fig. 1. Selected impedance responses of a symmetric Cu/PEO$_{20}$LiCF$_3$SO$_3$: 16.7% γ-LiAlO$_2$/Cu cell at different temperatures. PEO: WSR-N80; MW = 200,000. The spectra were normalized for polymer electrolyte thickness and copper electrode active area. The results obtained up to 50°C are enlarged in the two insets.

Fig. 2. Arrhenius plot of PEO$_{20}$LiCF$_3$SO$_3$: 16.7% γ-LiAlO$_2$ composite polymer electrolyte. Data were obtained from the impedance measurements reported in Fig. 1 by means of a NLLS-fit software. PEO: WSR-N80; MW = 200,000.
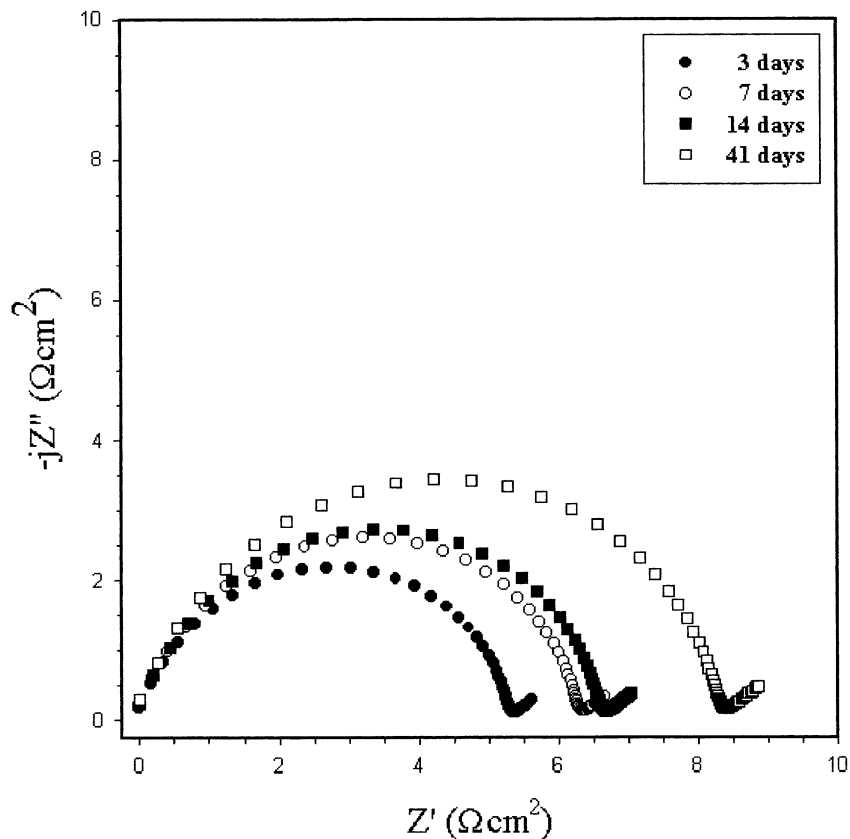
Fig. 3. Selected impedance responses of a symmetric $Li/PEO_{20}LiCF_3SO_3$: 16.7% γ-$LiAlO_2/Li$ cell at different storage time at 90°C. PEO: WSR-N80; MW = 200,000. The spectra were normalized for the lithium electrode active area. To better compare the time evolution of the spectra the contribution of the ionic bulk conductivity has been removed.

overvoltage during consecutive plating-stripping cycles. Several impedance measurements were taken over a long storage time on a hot-laminated symmetric Li/polymer electrolyte/Li cell held at 90°C. The results are reported in Fig. 3. The spectra were normalized for lithium electrode active area and for the interfacial resistance, i.e. the contribution of the electrolyte ionic resistance was removed. Fig. 3 shows that the interfacial impedance of the cell changed only slightly on aging.

The resistance of the lithium-polymer electrolyte interface was extracted from the experimental data with the help of a NLLS-fit software [7] by using a previously developed equivalent circuit [4,5]. The results of the fit are shown in Fig. 4. The initial value of the interfacial resistance of the composite electrolyte-lithium anode interface (1 h after cell assembling) was approximately 5 Ω cm^2 (data not shown). After 3 days time storage at 90°C it decreased to about 3 Ω cm^2 as a result of the thermal and mechanical stabilization of the interface. Such an excellent performance appears to be very stable on time. After 41 days of storage, the interfacial resistance increased to only about 4 Ω cm^2 to remain stable on further aging. This result clearly supports for a very good stability of the lithium-polymer electrolyte interface. It allows to predict that batteries using such an industrially manufactured polymer electrolyte would show

high storage stability even at the operating temperature, with a very moderate "corrosion" or loss of the lithium electrode.

The stability of the blown composite polymer electrolyte towards the lithium anode was also evaluated in kinetic conditions, i.e. during the oxidation and the plating of lithium at the anode, at 90°C by means galvanostatic plating/stripping tests. Fig. 5 illustrates the overvoltage
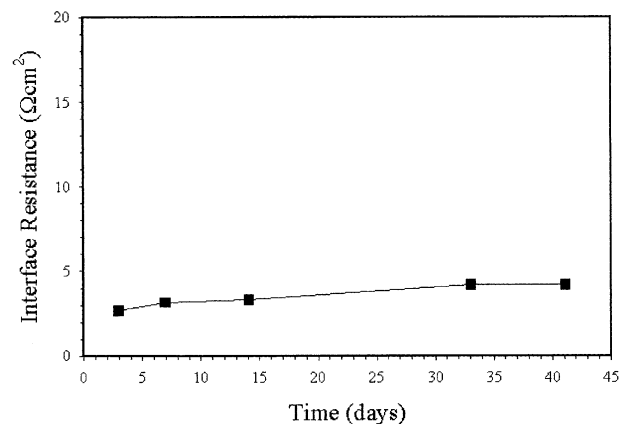

Fig. 4. Time evolution of the lithium-polymer electrolyte interface resistance in a symmetric $Li/PEO_{20}LiCF_3SO_3$: 16.7% γ-$LiAlO_2/Li$ cell stored in OCV condition at 90°C. PEO: WSR-N80; MW = 200,000.
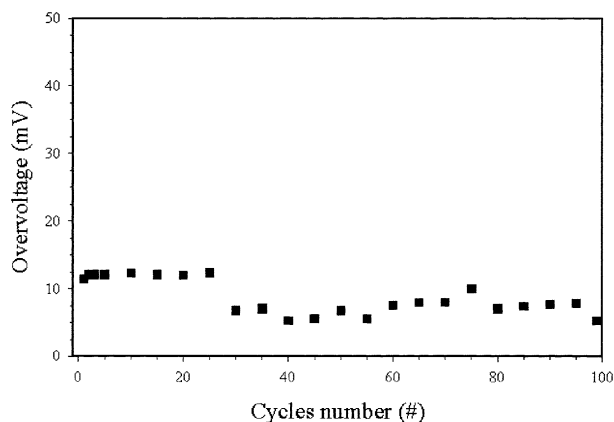
Fig. 5. Evolution of the lithium plating-stripping overvoltage upon galvanostatic cycles ($J = 0.1$ mA cm^{-2} for 3 h) of a symmetric Li/PEO$_{20}$LiCF$_3$SO$_3$: 16.7% γ-LiAlO$_2$/Li cell operating at 90°C. PEO: WSR-N80; MW = 200,000.

evolution associated with galvanostatic cycle test on symmetric hot-laminated cell composed by two lithium electrodes sandwiched around the composite electrolyte. The test was performed by passing a constant current ($J = 0.1$ mA cm^{-2}) through the cell for 3 h in each direction. The current density was selected within the applicability range of the composite electrolyte determined in previous work [3]. The overvoltage plotted in Fig. 5 is the cell voltage, i.e. it is associated with the contemporaneous lithium reduction and oxidation at the two Li electrodes. Initially, the overvoltage was about 12 mV but it dropped to 6–8 mV after 25 cycles. Such a behavior is probably due to the passive layer disruption [4]. However, a passive film is continuously formed during cycling as shown by the slow increase of the cell overvoltage after each disruption. Nevertheless, the overvoltage remained always very low and within the 6–8 mV interval. Such a low value of plating/stripping overvoltage is a clear indication of the lithium good cyclability at the anode.

4. Conclusions

In this report were described the fabrication and the characterization of PEO-based lithium polymer electrolyte which showed a reasonable conductivity at moderate temperature (80–100°C). The work has been focused on the determination of important "application" properties of the polymer electrolyte, i.e. the properties of the polymer electrolyte in real systems and in true operating conditions.

First, it has been shown that processing that is characteristic of manufacturing gives a composite polymer electrolyte with very good performance, at least comparable with lab-scale prepared ones. For example, its ionic conductivity at 70°C is about 10^{-4} S cm^{-1}. The industrially produced polymer electrolyte showed very good performance also in terms of stability and lithium cyclability at lithium-polymer electrolyte interface. Impedance measurements have confirmed a good stability of such an interface under rest conditions. Finally, lithium plating-stripping processes were seen to have a reversible character.

References

[1] S. Passerini, B.B. Owens, F. Coustier, J. Power Sources 89 (2000) 29–39.
[2] S. Passerini, F. Coustier, B.B. Owens, J. Power Sources 90 (2000) 144–152.
[3] P.P. Prosini, S. Passerini, R. Vellone, W.H. Smyrl, Solid State Ionics 75 (1998) 73–83.
[4] G.B. Appetecchi, S. Passerini, Electrochimica Acta 45 (2000) 2139–2145.
[5] G.B. Appetecchi, S. Scaccia, S. Passerini, J. Electrochem. Soc. 147 (2000) 4448–4452.
[6] G.B. Appetecchi, M. Carewska, F. Alessandrini, P.P. Prosini, S. Passerini, J. Electrochem. Soc. 147 (2000) 451–460.
[7] B.A. Boukamp, Solid State Ionics 20 (1986) 31.
[8] M.C. Borghini, M. Mastragostino, S. Passerini, B. Scrosati, J. Electrochem. Soc. 142 (1995) 2118–2121.