Interfacial phenomena in polymer-electrolyte cells: lithium passivation and cycleability

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Abstract

The properties of the electrode interfaces in polymer electrolytes based on the combination of poly(ethylene oxide) (PEO) and lithium salts, such as LiClO$_4$, have been investigated by impedance spectroscopy. Three main dispersion phenomena characterize the a.c. impedance spectra of the Li/PEO–LiClO$_4$ interface. The evolution of these spectra as a function of time of storage has been explained and interpreted using a solid-polymer layer (SPL) model assuming that the passivation of the lithium surface may be described by a combination of solid inorganic and polymeric layers. The time evolution of the impedance parameters indicates that a passivation film grows rapidly on the lithium surface. The kinetics of the passivation process may be controlled by incorporating into the electrolyte membrane-suitable inhibition agents.

Introduction

Research on new classes of highly conductive polymer electrolytes has been very active and substantial progress has been achieved in the last few years. From the initial, *first generation* electrolytes based on the 'simple' combination of high molecular weight polymer hosts (e.g., poly(ethylene oxide) (PEO) and lithium salts (e.g., LiX) having conductivities of 10^{-4} S cm^{-1} at 100 °C, these developments resulted in the production of *second generation* electrolytes, – based on the combination of modified, comb-shaped PEO structures (e.g., short ethylene oxide side chains attached to supporting inactive backbone chains) with Li salts – having conductivities of the order of 10^{-4} to 10^{-5} S cm^{-1} at room temperature [1], and, more recently, of *third generation* electrolytes formed by the addition of plasticizers and cross-linking agents to 'common' PEO–LiX complexes, as well as by trapping in a gel matrix liquid solutions of Li salts, both systems having conductivities as high as 10^{-3} S cm^{-1} at ambient and subambient temperatures [2].

However, a high conductivity, although crucial for assuring low IR drops across the cell, is not the sole requirement for a successful polymer electrolyte. Stability towards the electrode materials is also an essential parameter to guarantee acceptable performance in electrochemical devices, such as batteries, especially in terms of cycleability and safety.

Indeed, there are preliminary, but convincing results, that Li passivation phenomena, similar to those commonly experienced in liquid electrolytes, also occur in polymer electrolyte cells [3, 4]. However, the nature and the mechanism of the passivation phenomena are still unclear and one can only postulate that they depend in a non-

predictable manner on the type of electrolyte involved, the temperature of operation, and the residual impurities.

If studies on electrode interfaces in first generation polymer-electrolyte cells is scarce, it is practically nonexistent in second and third generation polymer-electrolyte cells, i.e., in those cells which are presently proposed as the most promising systems for the development of versatile, rechargeable Li polymer batteries. On the other hand, Li passivation in these multiphase, multicomponents electrolyte systems is expected to be even more severe than that experienced with the relatively simple binary mixtures of PEO and Li salts. In fact, third generation polymer electrolytes are commonly based on liquid additives and plasticizers (e.g., propylene carbonate (PC)) which are very unstable when in contact with Li metal. This expectation is somewhat confirmed by preliminary results reported on the characteristics of the electrode interfaces in these electrolytes, which clearly show that Li readily passivates when in contact with: common plasticizers, such as low molecular weight poly(ethylene glycol), PEG 400 [5], or with PEO–LiX, or, finally, with gel composites, such as of a $LiCF_3SO_3$ dimethylsulfoxide solutions in 2-acriloamido-2-methylpropane sulfonate [6] or $LiClO_4$–ethylene carbonate–propylene carbonate solution in polyacrylonitrile [7].

As a general conclusion, one can state that the properties of the electrode interfaces are far from being satisfactory clarified for the first generation PEO–LiX electrolytes and virtually not examined for the second and third generation polymer electrolytes, where the presence of additives and of liquid phases of various nature and properties is likely to induce fast corrosion rates for the Li electrode. Therefore, in order to evaluate the possible applications of the various classes of polymer electrolytes, there is a definite need for a better understanding of these interfacial characteristics. With this aim, we have undertaken a systematic investigation of the behaviour of passivation phenomena displayed by the Li electrode in contact with various polymer electrolytes.

In this work we report the first series of results comprising a comparative study of the characteristics of the Li interface in contact with three different, PEO-based systems, namely a 'classical' polymer-electrolyte complex (e.g., the PEO–$LiClO_4$ complex) and two 'composite' polymer electrolytes obtained by adding to the PEO–$LiClO_4$ complex finely dispersed ceramic powders, e.g., γ-$LiAlO_2$ or crystalline zeolites, respectively.

Experimental

Lithium metal, a Foote Mineral Co. pure compound, was used as received. In order to obtain electrodes with a 'clean' surface, i.e., with a surface as free as possible from native films, Li was scraped to metallic luster in an argon-filled dry box.

High molecular weight (mol. wt. = 4×10^6) poly(ethyleneoxide) (PEO) a pure BDH product, was used as received. The Li perchlorate ($LiClO_4$), a Fluka reagent-grade product, was melted under vacuum to allow complete dehydration.

High surface area γ-$LiAlO_2$ powder, a fine reagent-grade Foote Mineral Co. product, was dried by annealing overnight at 800 °C. The powder had a particle size of 40 μm, which were agglomerates of finer powders having a mean diameter <0.5 μm. Aldrich, type 4 crystalline zeolites (molecular sieves), having the general formula $[(Al_2O_3)_{12}(SiO_2)_{12}] \cdot 27H_2O$, with mean particle size of 3 to 5 μm, were dried overnight at 200 °C under vacuum.

Appropriate weight of $LiClO_4$ and PEO to give an O:Li ratio of 8:1 were dissolved in HPCL-grade acetonitrile (Aldrich, glass distilled, filtered through 0.5 mm filters, with a water content less than 0.003%). The solutions were then stirred for 20 h at

room temperature in a stoppered flask. The simple PEO–LiClO$_4$ electrolytes were obtained by a direct casting procedure of the solution. The preparation of composite electrolytes involved a further step consisting in adding to the solution a known amount (10 wt.%, w/o) of γ-LiAlO$_2$ or, alternatively, of a known amount (10 w/o) of molecular sieves. The solution was then stirred continuously by a high-intensity ultrasonic finger directly inserted in it, in order to break up the powder agglomerates and to facilitate PEO solubilization. After complete homogeneity of the components had occurred, the composite electrolyte samples were obtained by the same casting procedure used for the simple electrolytes, namely by pouring the solution on a flat polytetrafluoroethylene container and covering it to favour slow evaporation of the acetonitrile solvent. By this controlled casting procedure, homogeneous polymer-electrolyte films, from 50 to 75 μm of thickness, with no evidence of powders agglomeration, were routinely obtained.

The synthesis and the manipulation of all electrolyte samples were carried out in an argon-filled dry box.

The impedance measurements were performed using reciprocal cells of the Li/PE/Li type, were PE indicates the selected polymer-electrolyte sample. The cells, having two plane, metallographic grade polished, parallel stainless-steel current collectors, were kept under constant mechanical pressure (by using calibrated spring-loaded terminals) and under constant temperature (by housing them in a Buchi, model T-51 oven). The impedance values were obtained with a Solartron 1255 frequency response analyser (frequency range 10^{-2} to 10^5 Hz) coupled with a Solartron 1286 electrochemical interface, all the instrumentation being controlled by an IBM-70 PC. The testing temperature was initially raised to about 95 °C while continuously recording the impedance spectra. After a few days, the temperature was finally set to 106 °C and the impedance spectra were recorded twice a day for the entire duration of the test. Occasionally, current pulses, ranging from 25 μA cm^{-2} to 1.4 mA cm^{-2}, were passed through the cell with the aim of monitoring disruption of the passivating films.

In order to obtain the impedance parameters, all the experimental spectra were fitted with the NLLSQ (non-linear least square) fitting programme written by Boukamp [8]. The equivalent circuit utilized to elaborate the experimental data was derived from physical considerations based on the preferred interface model. Indeed, the selected equivalent circuit was adequate for describing the impedance spectra for all the three types of Li/PE interfaces considered here, even under situations where the occurrence of a fast-growing passivation film drastically changed the shape of the spectra. As a general rule, we terminated the fitting procedure and accepted the related results, only when the fitting parameter 'chi-squared' was $<5 \times 10^{-5}$, thus giving us assurance that the relative errors on the impedance parameters remained generally confined below 5% and, in some cases, even below 1%.

Results and discussion

A standard method for the investigation of the stability of the Li interface in polymer-electrolyte (PE) cells we have used impedance spectroscopy. Accordingly, the evaluation of the interface characteristics has been carried out by monitoring the time evolution of the a.c. impedance of symmetrical cells of the Li/PE/Li type, stored at 106 °C under open-circuit conditions for several days.

Figure 1 illustrates the results related to a cell using a 'classical' polymer electrolyte, namely the (PEO)$_8$LiClO$_4$ complex. The response reflects that typically observed for cells of this type, i.e., a progressive expansion of the middle frequency semicircle (Fig. 1(a)). As we [9, 10] and other authors [3] previously suggested, under a qualitative
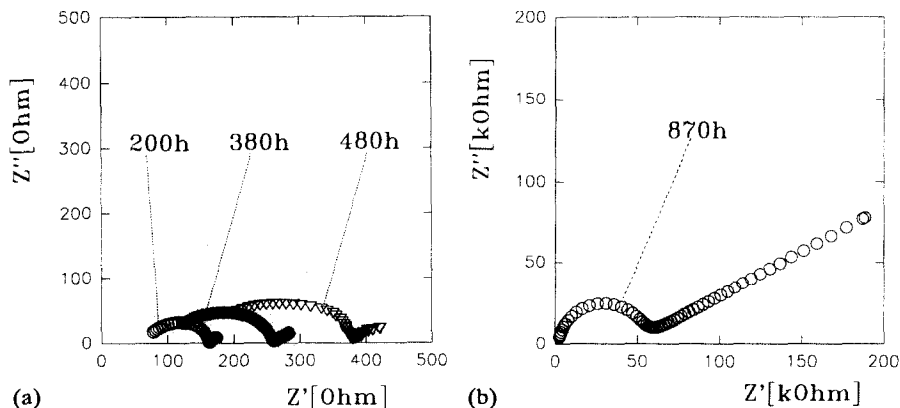
Fig. 1. Time evolution of the impedance response of a Li/(PEO)$_8$–LiClO$_4$/Li cell stored at 106 °C under open-circuit conditions: (a) the responses after 200, 380 and 480 h, and (b) after 870 h.

profile this expansion may quite likely be associated with a continuous growth of a resistive layer on the Li electrode surface, this passivation layer being the product of the corrosion reaction of Li in the electrolyte medium. However, from Fig. 1(a) we notice that the shape of the a.c. impedance spectra suggests an evolution developing in more than one semicircle, this in turn suggesting an overall impedance response based in more than one single relaxation phenomenon. Furthermore, Fig. 1(b) shows a consistent modification of the form of the response, this finally suggesting that the nature of the Li passivation process may progressively change under prolonged contact times.

Therefore, all these results concur to indicate that a proper analysis of the a.c. response requires the identification of a consistent equivalent circuit which is representative of the selected interface and which can then provide accurate values of the impedance parameters and thus a proper characterization of the relaxation phenomena associated with the passivation processes. This is not an easy operation since various equivalent circuits could in principle be used to describe the conditions of the interface examined here. Appropriate criteria for a proper selection are: (i) the definition of a model which is representative of the given interface; (ii) the design of a consistent equivalent circuit, and (iii) the testing of this circuit on experimental data by imposing limiting conditions.

Considering that the trend of the impedance response of the Li electrode in LiClO$_4$–PEO polymer electrolytes shows close similarities with that observed with liquid organic solutions (e.g., in the LiClO$_4$–PC solutions [9]), as a first approach one can attempt to analyse the impedance data in the polymer media on the basis of the same considerations and the assumptions successfully adopted for describing the Li interface in liquid media. Using this approach, we have considered two models as the most suitable to represent the characteristics of the interface examined in this work, namely the so-called solid-polymer layer (SPL) model and the compact stratified layer (CSL) model, both suggested by Thevenin and Muller [11] to describe nonhomogeneous passivation layers growing on a Li electrode in contact with a LiClO$_4$–PC solution. In fact, all the most relevant experimental parameters related to the electrochemical processes occurring at the Li electrode/polymer electrolyte interface, could be in

principle be derived by fitting the calculated impedance diagram spectra to the measured data (i.e., the data shown in Fig. 1) by means of the equivalent circuits related to those two models. In practice, for the CSL model, due to the large number of adjustable parameters, the fit is not sufficiently accurate to meet the imposed criteria (chi-squared $< 5 \times 10^{-5}$; relative errors of the parameters in the range of 1–5%). These conditions can instead be met with the SPL model, and, thus we selected this model and its associated equivalent circuit as the most appropriate to describe our data.

The SPL model basically describes the Li passivated surface area as consisting of a dispersion of inorganic solid compounds (possibly, the products of the reaction of metallic Li with the electrolyte impurities) in a polymer matrix (possibly resulting from the Li-initiated solvent polymerization).

It is important to point out that, even if a given model fits the experimental data satisfactorily, this does not necessarily prove its validity. However, a good fit is still a valid support for using the model, at least for achieving some insight into the electrochemical processes occurring at the interface. Under this assumption, we have used the SPL model to analyse the impedance responses obtained in this work. Figure 2 shows a typical result: one of the responses of Fig. 1 is displayed while superimposing the best fit of the dispersion data obtained by the related SPL equivalent circuit (also illustrated in the Figure). The components in this circuit are: R_e (resistance of the electrolyte), R_f (resistance of the passivation film), R_{ct} (charge-transfer resistance), Z_w (Warburg impedance), C_g (capacitance of the passivation film), and C_{dl} (double-layer capacitance).

The fitted curve reveals that the overall response may effectively be described as the combination of three-dispersion semicircles associated with different relaxation phenomena. According to the SPL circuit, the high frequency semicircle can be ascribed to the passivation layer, the middle frequency one to the charge-transfer process and the low frequency one to the diffusion process.

By using an analysis based on this equivalent circuit, it is then possible to determine the time evolution of the single circuit parameters and, in particular, of the resistance R_f of the passivation film growing on the Li electrode surface. The result, illustrated in Fig. 3, clearly shows that the resistance of the film continuously increases and thus that the Li passivation process continues upon storage. Moreover, the kinetics of this process develop in three stages: during the first stage (up to about 500 h) the resistance initially grows linearly, then increases much more rapidly until finally approaching a steady value. It is important to note that during the initial period the passivation layer may still be electrochemically disrupted, as revealed by the fact that, upon passing short galvanostatic polarization pulses across the cell, the value of the film resistance
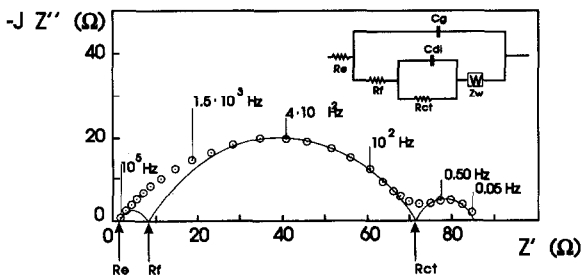

Fig. 2. Typical impedance response of a Li/(PEO)$_8$–LiClO$_4$/Li cell stored at 106 °C with superimposed the three semicircles obtained by fitting the data with the SPL equivalent circuit.

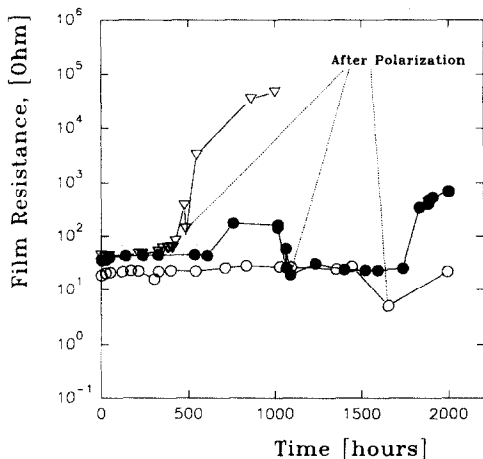Fig. 3. Time evolution of the resistance of the passivation layer at the interface of (−△−) Li/(PEO)$_8$–LiClO$_4$/Li, (−●−) Li/(PEO)$_8$–LiClO$_4$ 10w/o γ-LiAlO$_2$/Li, and (−○−) Li/(PEO)$_8$–LiClO$_4$ 10w/o zeolite/Li cells stored at 106 °C under open-circuit conditions. The modifications induced by short-current pulses across the cells are also illustrated.

decays (see Fig. 3). However, when the passivation is completed, namely in the final steady-state limit, any attempt of passing current through the cell is unsuccessful due to a very high ohmic overvoltage, this in turn suggests that the passivation phenomena may eventually lead to the almost complete inactivity of the polymer cells. Indeed, at this stage the frequency response analysis reveals a total cell resistance three orders of magnitude higher than its initial value and an impedance behaviour totally dominated by diffusion phenomena of the semi-infinite type (see Fig. 1(b)).

Further information on the characteristics of the Li passivation process may be obtained by examining the time evolution of other impedance parameters. Figure 4 illustrates the trends of the capacitance of the passivation film, C_g and Fig. 5 that of the charge-transfer capacitance, R_{ct}. After an initial increase (probably associated with thermal equilibration), the film capacitance constantly decays to reach a very low steady value. Since the capacitance may be expressed by the relation:

$$C_g = (\epsilon' \epsilon_0) A/l \tag{1}$$

where ϵ' and ϵ_0 are the dielectric constants of the film and of the vacuum, respectively, A is the film surface area and l is the film thickness, the change in capacitance observed in Fig. 4 may be due to a variation of the film thickness (increase of l) or to a variation in the film nature (changes in ϵ') or to a combination of the two. However, it is logical to assume that the progressive decay of C_g observed in the initial part of the evolution, can be mainly associated with the increase of the film thickness. On the contrary, the final part, where C_g assumes a quasi-steady value cannot obviously be explained only on the basis of further growth of the film but rather by assuming that this growth is accompanied by a change in the nature of the film.

This assumption is somewhat supported by the time evolution of the charge-transfer resistance, R_{ct}, illustrated in Fig. 5. We observe a substantial variation of R_{ct}, which increases by about two orders of magnitude during the passivation process. This indicates that this process severely affects the interfacial conditions, a fact which can
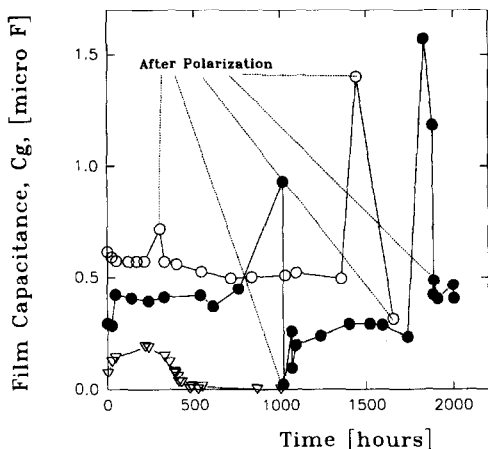
Fig. 4. Time evolution of the capacitance of the passivation layer at the interface of (-△-) Li/(PEO)$_8$–LiClO$_4$/Li, (-●-) Li/(PEO)$_8$–LiClO$_4$ 10w/o γ-LiAlO$_2$/Li, and (-○-) Li/(PEO)$_8$–LiClO$_4$ 10w/o zeolite/Li cells stored at 106 °C under open-circuit conditions. The modifications induced by short-current pulses across the cell are also illustrated.
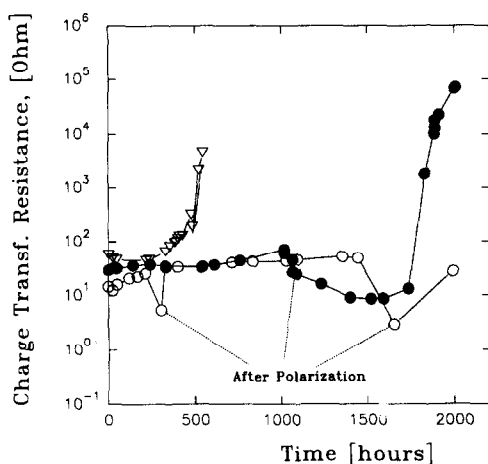

Fig. 5. Time evolution of the charge-transfer resistance at the interfaces of (-△-) Li/(PEO)$_8$–LiClO$_4$/Li, (-●-) Li/(PEO)$_8$–LiClO$_4$ 10w/o γ-LiAlO$_2$/Li, and (-○-) Li/(PEO)$_8$–LiClO$_4$ 10w/o zeolite/Li cells stored at 106 °C under open-circuit conditions. The modifications induced by short-current pulses across the cells are also illustrated.

be explained assuming a progressive and irreversible variation of the electronic structure of the film, this being necessarily associated with a modification of its chemical nature.

The impedance results described above, which have been confirmed by testing various different Li/(PEO)$_8$–LiClO$_4$/Li sample cells, lead to the important conclusion that the passivation of the Li electrode may eventually produce the formation of thick, highly-resistive layers, whose structure is of a such nature to block the transport of Li ions, and thus, any passage of current through the cell. Here, in accordance with the selected SPL model of the interface, we propose that the passivation layer reaches such a 'blocking condition' when the dispersion of the inorganic solid compounds

becomes homogeneous on the electrode surface. Furthermore, we also suggest that the inorganic compounds are mainly the products of corrosion reactions exerted by the electrolyte impurities, such as water or residual casting solvent. It follows that Li batteries, assembled by using, low-cost, directly available PEO commercial products — such as those used in our tests — may indeed be affected by severe operation problems, especially if maintained on shelf for long periods or even when run under intermittent charge/discharge cycles.

Therefore, it appears of crucial importance to improve the characteristics of the common PEO–LiX polymer electrolytes in order to control passivation of the Li electrode. With this in mind, we have considered a new class of composite electrolytes recently developed in our laboratory [12]. These electrolytes are obtained by dispersing finely divided ceramic powders into the common PEO–LiX complexes. If the nature of the dispersoid (e.g., γ-LiAlO$_2$), its particle size (e.g., around 1 μm) and its content (e.g., 10 wt.%, w/o), are properly controlled, one obtains membranes having improved mechanical and electrical properties with respect to those of the pure PEO–LiX electrolyte [4, 12]. Moreover, there are expectations that the use of the composite electrolytes could be beneficial also in terms of interfacial characteristics. This assumption is based on the following two points:

(i) The composite electrolytes maintain an overall quasi-rigid structure also in the high conductivity temperature range (i.e., around 100 °C) where instead the pure electrolytes behave as highly viscous liquids. Therefore, replacement with the composite electrolyte should prevent a flow of corrosive agents to the electrode interface.

(ii) The composite electrolytes are based on ceramic powders which have high affinity for water impurities. Therefore, being finely dispersed in the polymer structure, the powders can trap these impurities and thus remove them from the interface, this finally avoiding the formation of the homogeneous 'current-blocking' layer.

To verify this assumption, we have again used frequency response analysis and run stability tests similar to those described in the previous cases. The evolution of the a.c. impedance of symmetrical cells of the Li/(PEO)$_8$–LiClO$_4$ 10w/o γ-LiAlO$_2$/Li type, stored under open-circuit conditions at 106 °C has been monitored for almost three months. Figure 6, which illustrates the result, indicates a trend qualitatively similar to that of the pure (PEO)$_8$–LiClO$_4$ electrolyte (compare Fig. 1). However, a basic difference does exist in quantitative terms: the expansion of the middle frequency and the modification of the overall impedance response are much more limited in the former than in the latter case, even under a more prolonged storage test.

The relevant impedance parameters may be obtained by assuming that also the Li/(PEO)$_8$–LiClO$_4$ 10w/o γ-LiAlO$_2$ interface can be described on the basis of the SPL model and thus by the related equivalent circuit. The evolution of the resistance of the Li passivation layer during the time of the test is compared in Fig. 3 with that related to the Li/(PEO)$_8$–LiClO$_4$ interface. The improvements achieved using the composite electrolyte are evident: the growth rate of the passivation layer is consistently reduced and the passage of current is always attainable through the cell with consequent disruption of the layer itself, thus confirming that the addition of the ceramic dispersoid is indeed beneficial for controlling the extent of the passivation process at the Li interface.

This conclusion is supported by the trends in the evolution of the capacitance of the film and of the charge-transfer resistance, which again are compared with those related to the Li/(PEO)$_8$–LiClO$_4$ interface (Figs. 4 and 5). First notice that the value of the capacitance of the passivation film growing in the PEO–LiClO$_4$–γ-LiAlO$_2$ composite polymer electrolyte is, starting from the beginning of the test, higher than
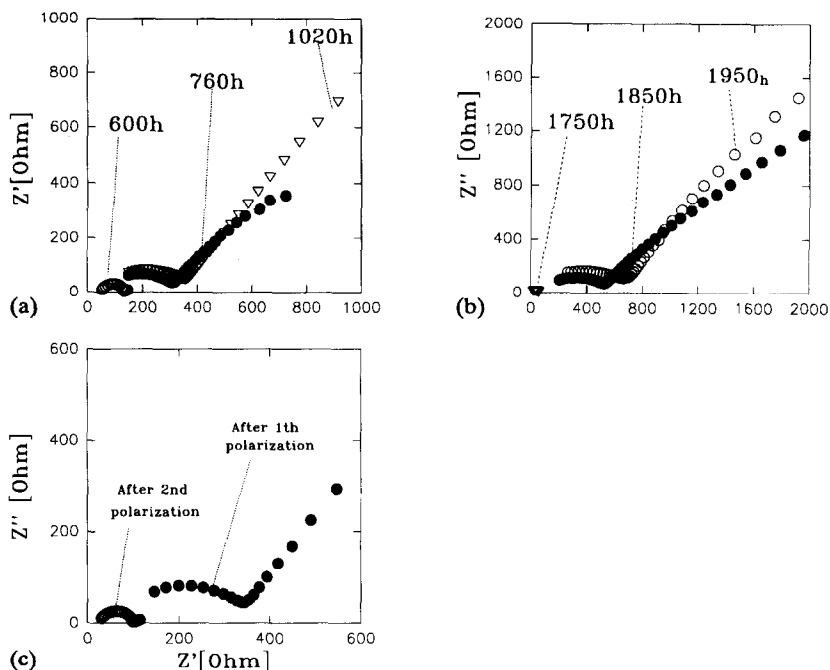
Fig. 6. Time evolution of the impedance response of a Li/(PEO)$_8$–LiClO$_4$ 10w/o γ-LiAlO$_2$/Li cell stored at 106 °C under open-circuit conditions: responses (a) after 600, 760 and 1020 h; (b) 1750, 1850 and 1950 h, as well as (c) the responses following short-current pulses (1 mA cm^{-2} for 10 min) across the cell.

that of the film growing in the ordinary PEO–LiClO$_4$ electrolyte. Since in this initial part of the test we may exclude substantial changes in the film dielectric constant and in the film surface, we may conclude, on the basis of eqn. (1), that the growth rate in the composite electrolyte is considerably lower than that in the plain electrolyte. Furthermore, Fig. 4 also shows that the capacitance changes are much less severe over comparable storage periods (ᴧ large increase occurs only after a very long storage time, i.e., about 1800 h) and that passage of current through the interface can always restore the conditions of an 'electrochemically-cleaved' interface. Also illustrative is the comparison between the evolution of the charge-transfer resistance in the two electrolyte media (Fig. 5). We notice that the sharp increase in R_{ct}, indicative of a change in the nature of the passivation film, does take place after a period of storage which is at least three times longer than that experienced in the plain polymer electrolyte.

Considering the substantial improvements obtained by passing from the ordinary to the composite electrolyte and the idea that these improvements are related to an *in situ* ' purification' action exerted by the ceramic dispersoid, it became obvious that the selection of an additive with enhanced trapping capabilities for water and solvent impurities, such as for instance zeolites molecular sieves, should give composite electrolytes capable of assuring an even better control of the Li interface conditions in the polymer-electrolyte cell.

To confirm these expectations we have selected 4 Å molecular sieves having the general formula [(Al$_2$O$_3$)$_{12}$(SiO$_2$)$_{12}$]·27H$_2$O to form a new series of composite polymer electrolytes of the (PEO)$_8$LiClO$_4$ 10w/o [(Al$_2$O$_3$)$_{12}$(SiO$_2$)$_{12}$]·27H$_2$O type, which will be
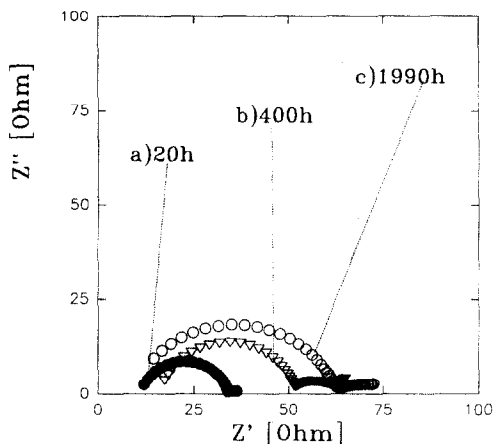
Fig. 7. Time evolution of the impedance response of a Li/ICPE/Li cell stored at 106 °C under open-circuit conditions: (a) the responses immediately after assemblage, (b) after 400 h, and (c) after 1990 h of storage.

here concisely (and perhaps overenthusiastically!) indicated as ICPE (interfacial controlling polymer electrolytes). Figure 7 illustrates the time evolution of the a.c. impedance response of Li/ICPE/Li cells stored under the usual testing conditions, namely at 106 °C for almost three months.

Figure 7 clearly shows that both the shape and the width of the impedance semicircle remain practically unchanged over the entire testing period. Indeed, this result is impressive especially when compared with those obtained with the two previously described cells, as further confirmed by the comparative analysis of the relevant impedance parameters. The resistance of the passivation film (Fig. 3) remains unchanged over the entire period of the test with a slight decrease after galvanostatic polarization. This behaviour suggests that the ICPE entirely prevents the growth on the Li electrode surface of the second porous inorganic layer which, according to the SPL model, constitutes the passivation film. This is further supported by the analysis of the comparative trend of the film capacitance (Fig. 4): the value of C_g is the highest in the case of the ICPE cell, thus confirming that in this cell the thickness of the passivation remains at its lowest value. Finally, also the trend of the charge-transfer resistance (Fig. 5) confirms the high interfacial stability obtained when the 'conventional' PEO-based electrolytes are replaced by the improved ICPE media.

Conclusions

On the basis of the results described above, one can derive the following conclusions:

(i) Passivation of the Li electrode is an active phenomenon in low cost, unpurified PEO-based polymer electrolytes and, if not properly controlled, it can lead to complete failure of the electrode performance.

(ii) Passivation phenomena in polymer-electrolyte cells can be adequately described by the SPL model developed for liquid organic electrolyte cells. The model appears particularly suitable for describing the time evolution of the impedance data even during the fast film growth which induces a rapid modification of the spectra.

(iii) Addition to the 'conventional' PEO–LiX electrolytes of finely dispersed ceramic powders, such as γ-LiAlO$_2$ and, particularly, molecular sieves of the zeolite type, effectively controls the morphology and the growth of the passivation layer on the Li electrode.

(iv) In view of the widespread utilization of rechargeable Li batteries these ceramic composite electrolytes should be preferred over other classes of polymer-electrolyte media.

Acknowledgements

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