

Impedance study on the reactivity of gel polymer electrolytes towards a lithium electrode

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Abstract

Impedance tests have been run, during a 10-day storage, on lithium electrodes in contact with carbonate-based liquid electrolytes and gel polymer electrolytes formed by immobilizing the former in poly(acrylonitrile) (PAN) and poly(vinyl chloride) (PVC) matrices. The polymer electrolytes show higher resistances of the passivation layer and during the charge transfer process. It is suggested that this may stem from the reaction of lithium with the –CN group of PAN and the –Cl atom of PVC, because of their electron-acceptor characteristics.

Keywords: Polymer electrolytes; Lithium; Electrodes; Impedance studies

1. Introduction

The accession of the polymer electrolyte concept in the late 1970s [1], raised the expectation of a solution to the problems created by the reactivity of liquid electrolytes in contact with lithium in nonaqueous batteries. However, it was soon realized that even 'dry' polymer electrolytes, e.g. $(\text{LiClO}_4)_x$ -poly(ethylene oxide) (PEO) formed a passivating film on Li [2,3], this leading to a dendritic morphology which could not favour an extended cycling.

In recent times, the need of polymer electrolytes usable at ambient and sub-ambient temperatures, has suggested the use of gel polymer electrolytes (GPEs) where macromolecular matrices, as poly(acrylonitrile) (PAN), poly(vinyl chloride) (PVC), immobilize common liquid electrolytes, e.g. LiClO_4 -EC/PC [4–7]. With this technique, thin films are processable and allow the construction of laminate anode-electrolyte-cathode stacks. Furthermore, it was assumed that the presence of these polymeric matrices could, at least in part, diminish the Li corrosion.

Li cells with gel polymer electrolytes based on PAN and PVC have a satisfactory cycling behaviour. However, in spite of a conductivity resembling the one of liquid electrolytes, only cycling at low rates (typically, 0.1 mA/cm²) has been reported [4,7]. Studies of the Li–GPEs interfaces have evidenced the build-up of passivation layers with high resistances [5,6,8,9].

It is rather surprising that no attention has been paid to the fact that such resistances tended to be higher than those measured in liquids [10–12]. To rule out the possibility that this may just result from different experimental conditions, we have undertaken, during storage, a parallel investigation on the Li passivation in various liquid electrolytes and in polymeric electrolytes obtained by immobilizing them in PAN and PVC matrices.

2. Experimental

2.1. Materials preparation

LiClO_4 was dried by melting at 300° C under vacuum. LiBF_4 and LiPF_6 (high-purity products from Tomiyama, Japan) were used as-received.

Propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) were distilled according to standard procedures and kept in a dry box under 4 Å molecular sieves. 1 M solutions of LiClO_4 , LiBF_4 and LiPF_6 in binary liquid mixtures (see Table 1) were stored with Li chips.

PAN and PVC (from Aldrich) were used as-received. In an experiment, high-purity PVC (Aldrich) was used.

The GPEs were prepared according to the following procedures:

(i) PAN-based electrolytes. The Li salt and, then, PAN were dissolved in the EC/PC mixture (in one case EC/DEC,

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Table 1
Fundamental parameters derived from the impedance tests on symmetrical Li/Li cells with different liquid electrolytes

Electrolyte	Time (days)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	d (\AA)	i_0 (mA/cm ²)
LiBF ₄ -EC/PC	0	4	5	51	10	5	1.0
	3	1	9	20	12		
	5	1	12	27	13		
	7	1	9	20	13		
	10	2	11	25	12		
LiPF ₆ -EC/DEC	0	4	6	50	16	8	0.13
	3	12	6	173	7		
	5	18	4	249	7		
	7	11	7	194	6		
	10	7	7	198	6		
LiPF ₆ -EC/DMC	0	2	3	32	6	14	0.10
	2	3	4	70	5		
	4	2		114	5		
	6	15		265	6		
	8	20		266	6		
	9	6		251	6		
LiBF ₄ -EC/DMC	0	5	4	86	9	57	0.38
	2	4	6	44	6		
	4	2	5	52	6		
	7	1	4	47	6		
	10	3		74	7		
LiClO ₄ -EC/PC	0	6	2	37	5	14	0.34
	4	6	2	60	3		
	6	6	1	60	3		
	8	5	1	54	3		
	11	5	1	67	3		

see Table 2). The solution was stirred and some drops were poured onto a hot glass plate to give transparent films (thickness, ~150 nm). The composition was: 8 mol% LiClO₄, 28 mol% EC, 33 mol% PC and 21 mol% PAN.

(ii) PVC-based electrolytes. Being PVC insoluble in carbonate-based electrolytes, the polymer was first dissolved in tetrahydrofuran (THF). This solution was added to the liquid electrolytes. After stirring, the clear solution was poured into a Teflon container. The film, detached after a couple of days, had the same thickness of the PAN films. The composition was: 4 mol% LiClO₄, 39 mol% EC, and 33 mol% PC and 24 mol% PVC.

The specific conductivity of the polymer electrolytes, measured at room temperature by impedance tests with blocking electrodes, was in the 5×10^{-4} – $2 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ range.

A composite cathode film was formed by admixing LiMn₂O₄ with acetylene black and LiClO₄-EC/PC-PVC (46% active material).

2.2. Apparatus and procedure

The storage characteristics of Li were evaluated in laboratory symmetrical coin cells. The liquid electrolytes were supported on two layers of glass filter paper (Whatman GF/A, thickness 260 μm), whereas a single disc of the polymer electrolytes was used. The electrode area was 1.3 cm².

When evaluating the storage characteristics of an Li/LiMn₂O₄ cell, a Li reference electrode was located in the coin cell.

The impedance measurements were carried out with a Solartron 1255 frequency response analyser coupled to a 1286 Solartron electrochemical interface. No direct current was passed through the cell during the tests, while an a.c. perturbation of 8 mV was applied in the 100 kHz–0.1 Hz frequency range. The measurements were carried out on fresh cells (within few minutes after assembling) and after the storage periods, at room temperature, indicated in Tables 1 and 2.

3. Results and discussion

A comparison of literature impedance data for Li in contact with liquid and polymeric electrolytes is a difficult task. Indeed, the experimental conditions are often different (this being especially true for the critical Li electrode preparation [13]), the electrode area is sometimes not mentioned, the storage times may vary from a few hours to several days and, finally, the treatment of the impedance data is not uniform. However, even with these limitations, one can notice that for liquid electrolytes the impedances tend to be less than $10^2 \Omega \text{ cm}^2$ [10–15], while for gel or dry polymer electrolytes they are often in the k $\Omega \text{ cm}^2$ range [6,8,9,16,17]. The absence

Table 2
Fundamental parameters derived from the impedance tests on symmetrical cells with different polymer electrolytes

Electrolyte	Time (days)	$R_{s1}(\Omega \text{ cm}^2)$	$C_{s1}(\mu\text{F/cm}^2)$	$R_{s2}(\Omega \text{ cm}^2)$	$C_{s2}(\mu\text{F/cm}^2)$	$d(\text{\AA})$	$i_0(\text{mA/cm}^2)$
LiClO ₄ -EC/PC-PAN	0	9	0.5	48	2	143	0.074
	4	74	0.2	147	2		
	7	40	0.5	252	2		
	11	76	0.4	347	2		
LiBF ₄ -EC/PC-PAN	0			25	1	29	0.004
	3	80	1	1610	2		
	5	75	1	1315	3		
	12	80	2	6900	5		
LiClO ₄ -EC/PC-PVC	0	9	0.5	78	2	95	0.038
	3	138	0.3	552	2		
	5	122	0.6	554	2		
	10	170	0.6	670	2		
LiPF ₆ -EC/DEC-PVC	0			511	0.1	817	0.018
	5	220	0.05	1180	0.2		
	10	197	0.07	1400	0.5		
LiBF ₄ -EC/PC-PVC	0			770	0.1	0.028	
	4			1140	0.8		
	5			860	0.9		
	10			900	2		
LiPF ₆ -EC/PC-PVC	0			330	0.2	95	0.013
	3	146	0.07	950	0.2		
	5	357	0.2	1450	0.8		
	10	307	0.6	2010	1		

of papers simultaneously reporting data on the two classes of electrolyte is noteworthy.

Tables 1 and 2 and Figs. 1–3 show the evolution of the impedance characteristics of the Li electrode in several liquid and gel polymer electrolytes as a function of storage time (up to about 10 days).

As shown in Figs. 1–3, the main feature of the impedance plots is a large irregular semi-circle extending especially in the high and medium frequency ranges. In the literature, this element has been treated in different ways, ranging from no deconvolution (film and charge-transfer resistances summed) [6] to a rather sophisticated one leading to the recognition of 5 resistance–capacitance (RC) circuits [18]

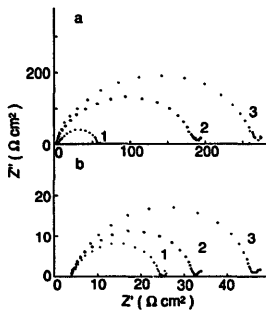


Fig. 1. Impedance plots of symmetrical Li/Li cells in: (a) LiPF₆-EC/DEC (1, fresh cell; 2, after 3 days; 3, after 5 days), and (b) LiBF₄-EC/PC (1, after 3 days; 2, after 5 days; 3, fresh cell).

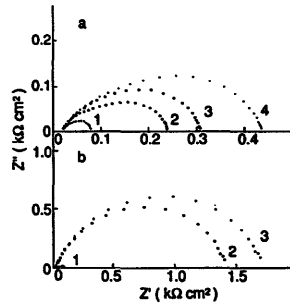


Fig. 2. Impedance plots in: (a) LiClO₄-EC/PC-PAN (1, fresh cell; 2, after 4 days; 3, after 7 days; 4, after 11 days), and (b) LiBF₄-EC/PC-PAN (1, fresh cell; 2, after 5 days; 3, after 3 days).

corresponding to a multilayer structure of the surface film covering the Li electrode. Even though it is out of the scope of the present paper to analyse the nature and structure of the Li electrolyte interface, the following considerations may be applied in any case, regardless of the experimental conditions and of the particular electrolyte used.

Three main circuitual elements (apart from the electrolyte resistance) have always to be present: (i) an RC (possibly the sum of some RC sub-elements [18]) related to the passivating film (surface layer); (ii) an RC related to the charge-transfer reaction: $\text{Li} \rightleftharpoons \text{Li}^+ + e^-$, and (iii) an element related to the Li⁺ diffusional impedance through the passivating film. It is sometimes difficult to distinguish these three main features in the plots (as also shown in Figs. 1–3),

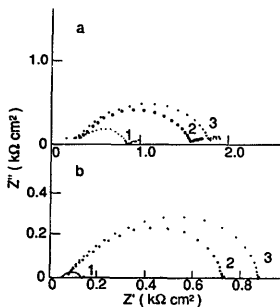


Fig. 3. Impedance plots in: (a) LiPF₆-EC/DEC-PVC (1, fresh cell; 2, after 5 days; 3, after 10 days), and (b) LiClO₄-EC/PC-PVC (1, fresh cell; 2, after 5 days; 3, after 10 days).

this explaining the variety of the interpretations [6–8,18–20]. Furthermore, in some cases, the RC of the surface layer and the RC of the charge-transfer process have not been correctly assigned. By assuming that both the surface layer and the double layer have a parallelepipedal configuration in their compact (inner) sections, the relation $C = \epsilon_0 \epsilon_r A / d$ applies, where ϵ_0 is the vacuum permittivity, ϵ_r the permittivity of the layer, A the area and d the layer thickness [10,18,19]. Therefore, a smaller C corresponds to a thicker layer. It is reasonable to state that the surface layer, C_{s1} , is thicker and includes the double layer, C_{dl} , as already found in liquid [19] and polymeric [17] electrolytes. In terms of frequency, lower C values have to be found at higher frequencies. This is why we have deconvoluted the main semicircle of Figs. 1–3 into two semi-circles and assigned the high-frequency one to the surface layer and the middle-frequency one to the charge-transfer process. The so-calculated R_{s1} , C_{s1} , R_{ct} and C_{dl} are reported in Tables 1 and 2. With the exception of a couple of values in LiPF₆-EC/DEC (with $C_{s1} = C_{dl}$), the C_{s1} is always lower than the C_{dl} , this being especially evident for the GPEs.

No attempt was made to deal with the diffusional characteristics appearing in some cases (Figs. 1(a,b) and 3(a)).

The following main results may be stressed:

(i) Both R_{s1} and R_{ct} are smaller in liquid electrolytes than in GPEs. This is also shown in Fig. 4 for LiClO₄-EC/PC and LiClO₄-EC/PC-PAN. The substantial time invariance of R_{s1} and R_{ct} for the former solution contrasts with their remarkable increase in the latter.

(ii) With the exception of the solutions containing LiPF₆, R_{ct} in liquid electrolytes are of the order of 10 Ω cm². The peculiar behaviour of LiPF₆ had already been stressed [7,15,21]. In the GPEs, R_{ct} may reach values of 10³ Ω cm² after a few days of storage.

(iii) The liquid electrolytes show a C_{dl} of 3–13 mF/cm², in agreement with literature data for a passivated Li surface [10,19,22]. In the GPEs, the C_{dl} are somewhat smaller as a consequence of the presence of thicker passivation layers

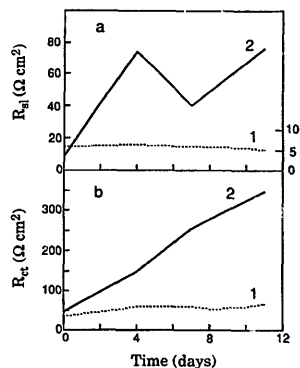


Fig. 4. (a) Evolution of R_{s1} for Li in contact with: (1) LiClO₄-EC/PC (ordinate, right) and (2) LiClO₄-EC/PC-PAN (ordinate, left). (b) Evolution of R_{ct} for Li in contact with: (1) LiClO₄-EC/PC and (2) LiClO₄-EC/PC-PAN.

(see the rather low C_{s1}). Some values of the layer thickness, calculated at the end of the storage period, are reported in Tables 1 and 2². For the liquid electrolytes, they are in excellent agreement with literature data calculated for carbonate-based solutions [18,19].

(iv) From the relation: $i_0 = RT / FR_{ct}$, the exchange-current densities may be calculated. The values at the end of storage are also reported in Tables 1 and 2. The average value for the liquid electrolytes, $i_0 = 0.4$ mA/cm², is 13 times larger than that of the GPEs, $i_0 = 0.03$ mA/cm². This may suggest rate capability problems for stored cells based on this latter class of electrolytes.

In both the liquid and the polymeric electrolytes, the resistances change with storage time in a non-regular way. This behaviour, sometimes also reported in the literature [7,18], seems to be referable to a dynamic ageing of the interfaces involving dissolution/precipitation phenomena [21].

We should now try and interpret the higher resistances shown by the GPEs. The inert nature, with respect to Li passivation, of the PAN and PVC matrices had thus far been assumed. However, the evidence of the data reported here obliges one to reconsider this aspect. The reactivity of PAN and PVC may stem from two factors: (i) impurities accompanying the commercial products, and (ii) inherent reactivity of the -CN group versus Li in PAN and of the -Cl atom in PVC. We have used pure PVC (a standard for the measurement of the mol. wt.) in one experiment. As shown in Fig. 5, in this case too a large increase in the overall resistance occurs upon storage. This seems to limit the role of impurities accompanying the polymer, but the lack of an accurate chemical analysis of the PVC used does not allow to exclude it

² The relation: $C_{s1} = \epsilon_0 \epsilon_r A / d$ was used, with the following values: $\epsilon_0 = 8.8 \times 10^{-14}$ F/cm, $\epsilon_r = 5$ [18], $A = 1.3$ cm².

completely. As for the other factor, one has to take into account that both $-\text{CN}$ and $-\text{Cl}$ have electron-acceptor characteristics. Obviously, no data on the acceptor number of PAN and PVC are available. However, useful clues may come from the acceptor number of CH_3CN , 18.9, and CH_2Cl_2 , 20.4. These values are higher than those of PC, 18.3 [23], which is known to be highly reactive versus Li.

At the present stage of this investigation, nothing can be said about the nature of the products, formed by these polymers, on Li. Given the intrinsic stability of their backbone, $-(\text{CH}_2-\text{CH})_n-$, one might speculate that only salts of the type LiCN and LiCl are formed by PAN and PVC, respectively. In carbonate-based electrolytes with LiPF_6 and LiBF_4 , the build-up of an all-inorganic surface layer has been suggested [21]. With LiClO_4 , reported to be less reactive, ROCO_2Li initially formed by EC and PC reacts with traces of H_2O to form Li_2CO_3 , ROH and CO_2 [21]. On the basis of our results, we may confirm the high reactivity of LiPF_6 in liquid electrolytes, while LiBF_4 is not more reactive than LiClO_4 . On the other hand, in the GPEs, LiBF_4 does indeed seem to be more reactive than LiClO_4 (and less than LiPF_6).

A highly passivated Li electrode cannot benefit of several plating–stripping cycles. As shown by the inset of Fig. 5, an Li electrode, after 10 days of storage in $\text{LiClO}_4\text{-EC/PC-PVC}$ (high purity PVC), even manifests higher resistances after cycling. It can be supposed that the thick film causes the formation of a highly dendritic deposit which is then more heavily corroded by the electrolyte.

The reactivity of GPEs based on PAN and PVC versus Li does create some concern in terms of stability and reversibility of this electrode. As a matter of fact, this concern has already been expressed in the literature, but emphasis was placed on the presence of common salts and solvents [3,8,9]. On the other hand, recent results in laboratory Li cells with these electrolytes and 3 V Mn spinel cathode show that a good cycling behaviour may be achieved [7]. A good rate capability is also reported [7]. However, one has to note the rather low current densities used in the cycling tests (0.1 mA/cm^2) in spite of a conductivity similar to the one of the parent liquid electrolytes. As for the rate capability, the results refer to fresh cells [7]. As shown in Tables 1 and 2, some of the GPEs have initial interfacial resistances comparable with

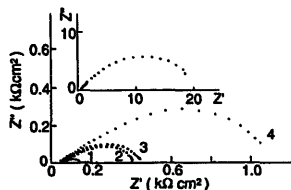


Fig. 5. Impedance plots in a $\text{LiClO}_4\text{-EC/PC-PVC}$ electrolyte prepared with high-purity PVC (1, fresh cell; 2, after 3 days; 3, after 5 days; 4, after 11 days). The inset shows the impedance recorded after cycling the cell (Z' , Z'' in $\text{k}\Omega \text{ cm}^2$).

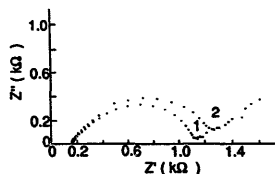


Fig. 6. (1) Impedance plot of the Li electrode in a $\text{Li/LiClO}_4\text{-EC/PC-PVC/LiMn}_2\text{O}_4$ (composite) cell, after 4 h of storage; (2) Impedance plot of the same complete cell.

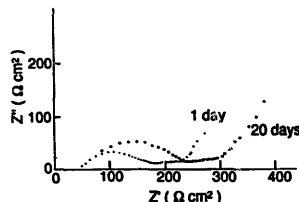


Fig. 7. Impedance plots of a composite cathode (LiMn_2O_4 + polymer electrolyte + acetylene black) in contact with $\text{LiClO}_4\text{-EC/PC-PVC}$.

those of the liquid electrolytes, both a rapid growth upon storage is observed.

The Li–electrolyte interface plays a fundamental role in determining the cell behaviour in terms of cyclability, rate and safety. For instance, this is depicted in Fig. 6, where the impedance characteristics of the Li anode and of a complete cell (with a composite Mn spinel cathode) are compared. As can be seen, the Li impedance largely determines the one of the total cell. The cathode gives a minor contribution after 4 h of storage and after a prolonged storage as well, as shown in Fig. 7. The very limited resistance increase, after 20 days, is noteworthy, especially in comparison with that shown by the Li electrode. The cell had an open-circuit voltage just greater than 3 V, so one might object that in a 4 V cell the electrolyte stability could be not so good. However, the donor numbers of the carbonates and of PAN and PVC are sufficiently low to foresee a high cathodic stability, as also confirmed by literature data [8].

4. Conclusions

The reactivity of gel polymer electrolytes versus Li based on the most common polymer matrices, i.e. PAN and PVC, is enhanced by these molecules. As a consequence, the liquid-like resistance of these electrolytes is obscured by high interfacial resistances. Because of this, cycling of Li cells with these GPEs may only be carried out at low current densities [7] and the cycle life and safety are points of serious concern. Problems of cyclability and/or mechanical stability have

also been met with other polymers, such as poly(methylmethacrylate) and poly(vinylidene fluoride) [24].

We do not intend to draw negative conclusions of general character of the polymer electrolytes. It has been ascertained that the use of low-crystallinity dry polymers, in association with appropriate Li salts, may produce electrolytes fairly stable versus Li [25]. Such electrolytes, to be used at 50–60 °C, show very limited capacity losses after long storage at high temperatures (e.g. less than 3% per year at 80 °C [25]). Recently, the use of polymer alloys has also been suggested. A polymer would show a high stability at the cathode, while the other would be anodically stable [26].

However, also in view of the excellent results emerging from the tests on Li-ion polymer batteries [27,28], one should conclude that the future of the Li-polymer technology could be limited to some applications, e.g. those requiring small cells to be used at low rates for a reduced number of cycles.

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