



# Impedance spectroscopy of lithium and nickel electrodes in propylene carbonate solutions of different lithium salts

## A comparative study

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### Abstract

This paper reports on the studies of both Li and Ni electrodes in propylene carbonate (PC) solutions containing various Li salts. Impedance spectroscopy and, to a limited extent, surface sensitive Fourier-transform infrared spectroscopy were used. The impedance spectra were modelled by equivalent analogs of resistance–capacitance (RC) circuits in series which is in line with the expected multilayer structure of the Li–solution interphase formed in PC solutions. The calculated  $C$  and  $R$  values of the various time constants separated by the modelling and related simulation enable the thickness and resistivity of the various films formed to be estimated and their changes upon storage, salt concentration and contamination level to be followed. It was found that the Li salt used has a remarkable impact on the interfacial properties of Li electrodes in these solutions. The comparative study of the surface films formed on Ni electrodes at low potentials in these solutions enabled a better understanding of the ageing process of the surface films formed on Li.

*Keywords:* Electrodes; Nickel; Lithium; Propylene carbonate; Impedance spectroscopy

### 1. Introduction

It is generally accepted that the electrochemical behaviour of Li electrodes in the battery electrolyte solutions is controlled by the interphase which is always formed on the active metal in solutions [1]. Thus, the electrode processes include  $\text{Li}^+$  diffusion in solution phase, migration of Li ions in the surface films, and charge transfer. In addition, solution species are reduced by electron injection, probably through the interphase, and the products precipitate on the surface as insoluble Li salts. Thus, Li dissolution and deposition are always accompanied by structural changes of the surface films through which they occur.

Impedance spectroscopy is an ideal tool for the study of the electronic properties of the Li–solution interface since it reflects all the above processes, and indeed was extensively applied to these systems Refs. [2] and [3] are typical examples.) Nyquist plots obtained from impedance measurements of Li electrodes in organic polar aprotic electrolyte systems are usually flat semi-circles that may be coupled with ‘Warburg’-type elements (straight lines) at low frequencies. It is clear

that such spectra are a result of the coupling of several time constants which may be difficult to separate. There are several different equivalent circuit analogs that can be fitted to each single impedance spectrum measured from Li electrodes in solutions. In recent work [4–6] we attempted to extract the significance of impedance spectra obtained from Li in several important electrolyte systems in relation to the physical and chemical structure of the Li–solution interphase (which controls the electrochemical behaviour of these systems). It had the following advantages over previous studies: (i) the Li surfaces were prepared in situ, fresh in solutions [4]; (ii) the separation of time constants and modelling was performed using very good software based on the work of McDonald [7] (Zsim-Scribner) and (iii) the surface chemistry of the Li electrodes was intensively investigated and determined in the same electrolyte solutions studied in the present work (in the same laboratory) using in situ and ex situ Fourier-transform infrared spectroscopy (FT-IR). Thus, the impedance spectroscopic data could be correlated and understood in light of the previously determined surface chemistry.

Li electrodes were intensively studied in propylene carbonate (PC) and ethereal solutions (e.g., tetrahy-

drofuran (THF), 2-methyltetrahydrofuran (2MeTHF), 1,3-dioxolane). The impact of the Li salt used and the presence of additives such as  $H_2O$ ,  $CO_2$ ,  $O_2$  and species such as methylfuran (MF) or propylene glycol on the interfacial properties was studied [4,5]. The salts used included  $LiAsF_6$ ,  $LiClO_4$ ,  $LiBF_4$ ,  $LiPF_6$ ,  $LiSO_3CF_3$  and  $LiN(SO_2CF_3)_2$ .

In addition, the impedance spectroscopy of Ni electrodes polarized to low potentials in PC [4,5] and ethereal solutions was also studied. It was previously found that non-active metal electrodes, when polarized to low potentials in Li salt solutions of esters, ethers and alkyl carbonates, are covered with surface films of similar structure to those of Li electrodes in the same solutions [8]. The advantage of such a study is that the surface films on non-active metals may be formed at a different degree of selectivity by applying different potentials, and thus the influence of contaminants on the structure of the surface films may be better understood.

In this manuscript we demonstrate the use of impedance spectroscopic measurements of both Li and Ni electrodes in a single study as a tool for the study of ageing processes of the surface films formed on Li electrodes in Li battery electrolyte solutions. A few critical measurements of the Li-surface chemistry in solution using FT-IR are also reported. While the experimental work involved a variety of solvent systems, the present paper concentrates on results obtained with PC solutions of various important Li salts.

## 2. Experimental

The source and purification of the various solvents and salts used is reported elsewhere [4]. Li electrodes were prepared fresh in solutions and were measured in three-electrode cells of parallel plate configuration as described in Ref. [4]. Ni electrodes were also treated in similar cells of parallel plate configuration (Li reference and counter electrodes) [5]. The surface films on Ni surfaces were prepared by potential steps using PAR potentiostat Model 173. Impedance spectra were measured using the Schlumberger FRA Model 1255 and electrochemical interface Model 1286 driven by the Zplot software (Scribner) with a 286 computer. The frequency range was from 100 KHz to 0.01 Hz and the a.c. amplitude was usually 5 mV around open-circuit voltage (OCV). Equivalent circuit analogs were fitted by the Zsim software (Scribner) using a PC Model 486.

FT-IR measurements of Li electrodes were performed as described in Ref. [9]. In brief, the surfaces were prepared in situ, fresh in solutions and measured ex situ, protected with KBr windows after different periods of storage in solutions.

## 3. Results and discussion

Figs. 1 and 2 show typical Nyquist plots obtained from Ni and Li electrodes treated in  $LiClO_4$  and  $LiPF_6$  solutions, respectively, in PC. The Nyquist plots obtained from Ni electrode are in general semicircular in the high to medium frequencies coupled with a mildly curved line at the low frequency. In a typical experiment, a spectrum was measured at OCV, after which the electrode was polarized to 0.2 V (versus  $Li/Li^+$ ), the surface film was built up and then another spectrum was

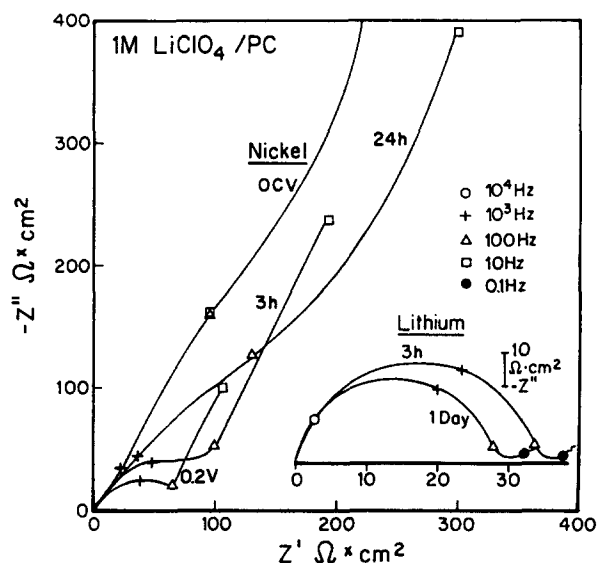


Fig. 1. Nyquist plots obtained from Ni and Li electrodes (as marked) treated in 1 M  $LiClO_4$ -PC solutions. Li electrodes were stored in solutions, storage time is indicated. Li electrodes were measured at OCV (0 V vs.  $Li/Li^+$ ). Ni electrodes were measured at OCV ( $\approx 3$  V vs.  $Li/Li^+$ ), then after film formation at 0.2 V ( $Li/Li^+$ ) and then at open-circuit potential after different periods.

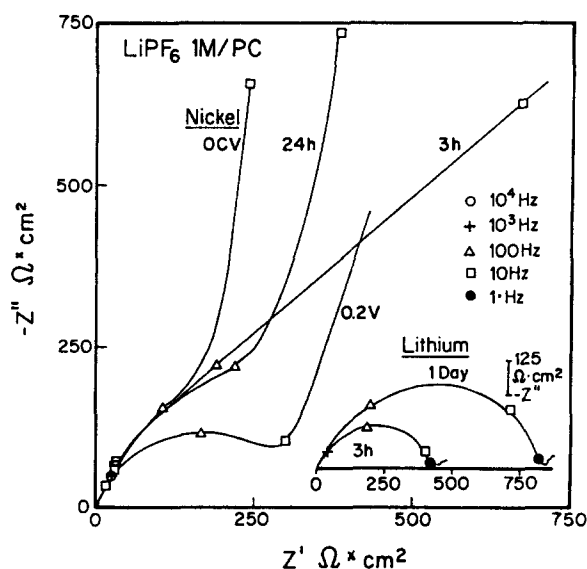


Fig. 2. Nyquist plots obtained from Li and Ni electrodes treated in 1 M  $LiPF_6$ -PC solutions (same as Fig. 1).

measured. The electrodes were then stored at OCV, followed by serial impedance spectroscopic measurements at OCV. The changes in the spectra are spectacular and reflect the formation of surface films at low potentials and their gradual dissolution afterwards (the Nyquist plots become similar to those obtained before polarization). The spectra obtained from Li relate to experiments in which Li surfaces were prepared fresh in solutions followed by measurements after different storage periods.

The data in both Figs. demonstrate that both Li and Ni behave differently in these two salt solutions. The films formed on Ni in  $\text{LiPF}_6$  dissolve very quickly (compared with the behaviour in  $\text{LiClO}_4$  solutions). The surface films formed on Li in  $\text{LiPF}_6$  solutions are also less stable than in  $\text{LiClO}_4$  solutions as reflected by the remarkable change of the interfacial resistance upon storage (the diameter of the semicircles in the Fig.).

The behaviour with  $\text{LiAsF}_6$  or  $\text{LiBr}$  solutions is similar to that of  $\text{LiClO}_4$ , while the behaviour of both types of electrodes in  $\text{LiBF}_4$  or  $\text{LiSO}_3\text{CF}_3$  solutions is quite similar to that of  $\text{LiPF}_6$  solutions. The presence of water,  $\text{O}_2$  and  $\text{CO}_2$  in solutions affects the behaviour presented in Figs. 1 and 2. Their presence in solutions stabilizes the interphase formed on Ni (as reflected by the relative stability of the impedance spectra upon storage at OCV). The presence of  $\text{CO}_2$  reduces the interfacial resistance of Li electrodes in these solutions.  $\text{CO}_2$  may be formed instantly in PC solutions by their storage over neutral  $\text{Al}_2\text{O}_3$  which partially decomposes the solvent to  $\text{CO}_2$  and derivatives of propylene glycol [10]. The effect of the Li salts used on the interfacial resistance of Li electrodes in PC solutions is demonstrated in Fig. 3. This Fig. displays the interfacial resistance of Li electrodes prepared fresh in various 0.25 M Li salt solutions as a function of storage time. These results are further proof of the involvement of salt reduction processes in the build-up of the Li–solution interphase and, hence, in determining the interfacial properties of these systems. Increasing the salt concentrations drastically changes the picture of Fig. 3. For instance, the Li-interfacial resistance in  $\text{LiPF}_6$  or  $\text{LiBF}_4$  solutions in PC is one order of magnitude higher than that measured in  $\text{LiAsF}_6$  or  $\text{LiClO}_4$  solutions. Thus, the various Li salts tested in this work can be divided into two groups in relation to their influence on the interfacial properties of Li in PC solutions:  $\text{LiBr}$ ,  $\text{LiClO}_4$  and  $\text{LiAsF}_6$  which can be categorized as relatively non-reactive salts, and the others, including  $\text{LiSO}_3\text{CF}_3$ , Li amide,  $\text{LiBF}_4$  and  $\text{LiPF}_6$ , which seem to be highly reactive with the Li surfaces at high concentration ( $> 0.5$  M). The impedance spectra (as well as properties such as the interfacial resistance calculated from them) obtained from Li electrodes stored in solutions of salts of the first group change only slightly or moderately

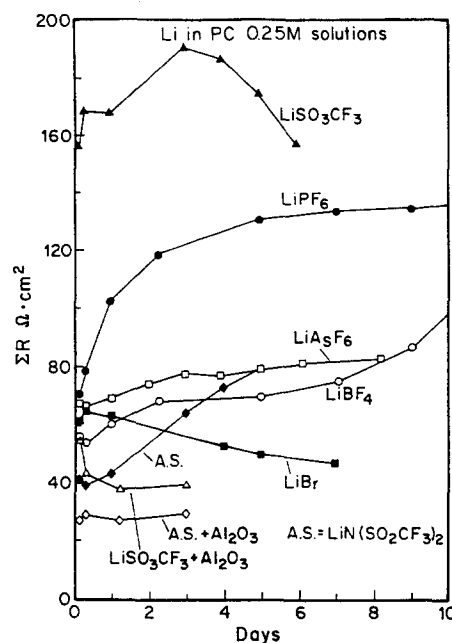


Fig. 3. The interfacial resistance of Li electrodes in various 0.25 M Li salt solutions in PC upon storage (calculated from the diameters of the semicircles of the Nyquist plots).

upon storage. In contrast, the changes in the impedance spectra of Li electrodes stored in solutions of salts of the second group (high reactivity) is very pronounced.

It is interesting to see that the impedance spectroscopic studies show that the surface films formed on Ni at low potentials in solutions of the 'non-reactive' salts (group 1) are much more stable than those formed in solutions of the 'reactive' salts (group 2). This is reflected by the changes in the impedance spectra when the electrodes are held at OCV after surface-film formation at low potentials. The above difference in reactivity of the various salts towards Li is also confirmed by surface spectroscopic studies of Li in these solutions using FT-IR spectroscopy and elemental analysis by X-ray dispersion [6]. Fig. 4 shows a typical example. Fig. 4(a) was obtained from a Li electrode stored in 1 M  $\text{LiPF}_6$ -PC solution for 3 h. This spectrum is typical of the major PC reduction product on Li which is  $\text{ROCO}_2\text{Li}$  species. (Peak assignments appear in the Figure and are based on previous work [9,10].)

Fig. 4(a) is typical of spectra obtained from Li electrodes stored in PC solutions of all the above Li salts for a short period of time. However, as shown in Fig. 4(b), after prolonged storage in  $\text{LiPF}_6$ -PC solutions (days), the spectra measured from Li surfaces are remarkably different from that of Fig. 4(a), although the two electrodes of Fig. 4 were identically prepared and measured.

Fig. 4(b) does not have the pronounced  $\text{ROCO}_2\text{Li}$  peaks as shown in Fig. 4(a). Its most pronounced peak is around  $1060$  to  $1020$   $\text{cm}^{-1}$ . For comparison, an infrared spectrum of  $\text{Li}_3\text{PO}_4$  (KBr pellet) is also shown

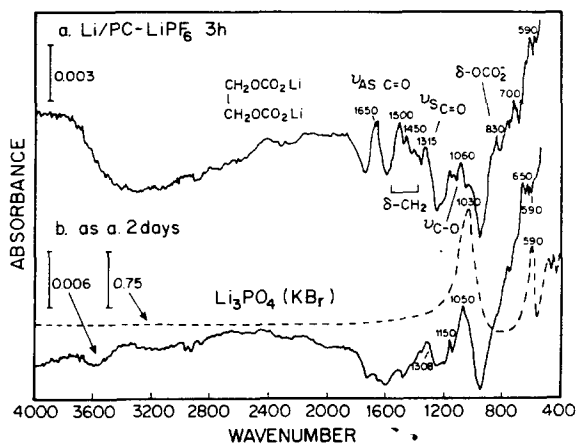


Fig. 4. FT-IR spectra obtained from Li electrodes (ex situ, external reflectance mode, protected with KBr plates) prepared fresh in PC-LiPF<sub>6</sub> solution and stored for different periods: (a) 3 h; (b) 2 days, and (---) a spectrum of Li<sub>3</sub>PO<sub>4</sub> pelletized with KBr (transmittance) for comparison.

in Fig. 4 (dashed line), and it has its pronounced peak around 1030 cm<sup>-1</sup> (νP-O). Thus, it is quite possible that the pronounced peak around 1050 cm<sup>-1</sup> in Fig. 4(b) relates to species with P-O bonds. As already shown [9], when the salts are 'non-active' ones, such as LiAsF<sub>6</sub> or LiClO<sub>4</sub>, the major ageing process of the surface films formed initially on Li in their PC solutions (composed mostly of ROCO<sub>2</sub>Li species) is the reaction of the ROCO<sub>2</sub>Li species with trace water to form stable Li<sub>2</sub>CO<sub>3</sub> surface species (in addition to CO<sub>2</sub> and ROH in solution phase).

Similar FT-IR surface studies of Ni electrodes polarized to low potentials in the various Li salt-PC solutions show that when the salts are LiClO<sub>4</sub> or LiAsF<sub>6</sub>, stable ROCO<sub>2</sub>Li surface species are formed on Ni and stay on the surface upon ageing at OCV. While in the case of salts, such as LiBF<sub>4</sub> or LiPF<sub>6</sub>, the ROCO<sub>2</sub>Li species formed initially on Ni at low potentials do not stay stable on the surface upon storage. The above results obtained from the studies of both Ni and Li electrodes provide a complementary picture of the ageing processes of Li electrodes in solutions and can be explained as follows: in the case of salts such as LiBr, LiAsF<sub>6</sub> or LiClO<sub>4</sub>, stable surface films composing ROCO<sub>2</sub>Li are formed on Li or Ni at low potentials in PC solutions. Their major ageing process involves a secondary reaction of these surface species with water to form Li<sub>2</sub>CO<sub>3</sub>. Thus, the interfacial properties of the Li-solution interphase do not change considerably upon storage. In the case of reactive salts such as LiPF<sub>6</sub>, LiBF<sub>4</sub> or LiSO<sub>3</sub>CF<sub>3</sub>, the surface ROCO<sub>2</sub>Li species formed initially on Li or Ni at low potentials do not remain stable on the surface. In the case of Ni they dissolve rapidly, and in the absence of a driving force the electrode returns close to its initial state before film formation. In the case of Li, where a constant

driving force for film formation always exists, there is a gradual substitution of the unstable ROCO<sub>2</sub>Li, initially formed, by salt reduction products which are Li halides, and other salt anion reduction products (e.g., species of the type Li<sub>x</sub>PO<sub>y</sub>F<sub>z</sub> in the case of LiPF<sub>6</sub>). The gradual change in the surface chemistry explains the pronounced increase in the Li-interfacial resistance upon storage shown in Figs. 2 and 3. However, understanding the reasons for the instability of the PC reduction products in solutions of LiPF<sub>6</sub> or LiBF<sub>4</sub> as well as an exact chemical analysis of the surface species formed by salt reduction in these cases is beyond the scope of this work.

As already discussed [4–6] the interfacial impedance of both Li and Ni (polarized to low potential) electrodes in PC solutions reflect a multilayer structure of the surface films. These films are formed gradually by a reduction of various types of solution species which precipitate insoluble Li salts under a driving force which decreases as the surface films are built up, and the reduction takes place further and further from the active metal surface. Therefore, the chemical and physical structure (and thus the electronic properties) of the electrode-solution interphase close to the metal side may be different from the outer-solution side of the interphase. It is also generally accepted that the outer part of these interphases are porous. Our results indicate that the inner, compact part of the surface films formed in PC is also multilayer in structure due to the above reasons [5,6]. Therefore, an equivalent circuit analog of 4 to 5 RC circuits in series may be a good electrical model of the interphase formed on Li in these solutions, where each time constant (RC) relates to a different section of the interphase. Consequently, all the spectra obtained were modelled by equivalent analogs of RC circuits in series and the relevant *R* and *C* values were calculated. In the case of Li, 5 RC circuits, one of which also has a 'Warburg'-type element, provided an excellent fit, while in the case of Ni, 4 RC circuits in series were adequate. The physical model of the metal-solution interphase, the relevant equivalent circuit analogs and their relation to the physical model and the spectra obtained are presented in Fig. 5. The validity of the models proposed in this Fig. was discussed and in fact proven in previous papers [4–6]. Note that the sloping line which characterizes the impedance spectra obtained from Ni at low frequencies is not a 'Warburg'-type element, but rather a part of a huge semicircle which relates to a time constant of a high resistance (10<sup>3</sup>–10<sup>4</sup> Ω cm<sup>2</sup>). In cases of the initial spectra (before film formation), the capacitance calculated for this time constant (of the low frequencies) is in the order of 10 to 30 μF/cm<sup>2</sup> which is typical of double-layer capacitances. In the cases of spectra measured after film formation (potential range from 0.2 to 2 V versus Li/Li<sup>+</sup>), the capacitance

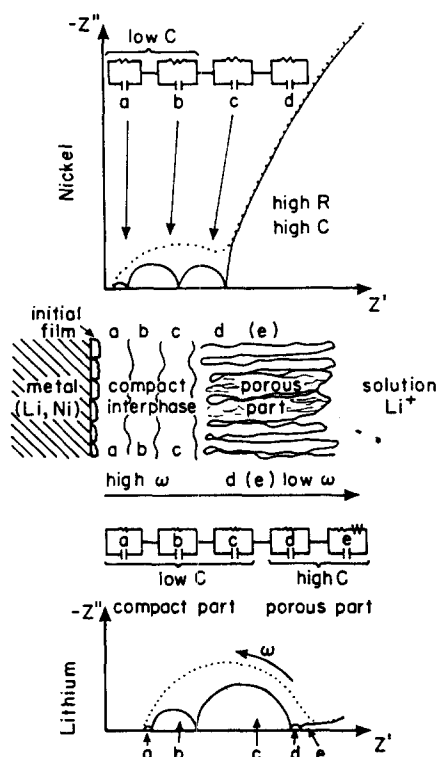


Fig. 5. The physical model of the Li-solution interphase formed both on Li or Ni (low potentials) and the related equivalent circuit analogs fitted to the experimental data obtained, demonstrated with Nyquist plots obtained from Li stored in 1 M LiClO<sub>4</sub> solutions for 7 days and Ni polarized in the same solution to 0.2 V vs. Li/Li<sup>+</sup>.

calculated for the fourth, lower frequencies time constant is in the order of a few hundred  $\mu\text{F}/\text{cm}^2$  which is in line with the formation of a porous interphase. Therefore, the sloping lines which characterize the low frequency domain of the spectra obtained from Ni electrodes (Figs. 1, 2 and 5) are attributed to the film-solution interface and the high  $R$  values calculated are related to the charge-transfer reaction of the solution species. Indeed, the  $R$  value calculated for this time constant decreases considerably as the electrode potential is lower. In the case of Li, since the potential of the measurements is always around 0.V (Li/Li<sup>+</sup>), charge transfer relates only to Li dissolution or deposition and is therefore very low and negligible compared with  $R$  migration of Li<sup>+</sup> through the surface films. Thus, this difference in the major charge-transfer reactions forms the difference between the impedance spectra obtained from Ni and Li as shown in Figs. 1, 2 and 5, although similar surface films are formed in both cases. Three of the capacitances calculated are low ( $0.5$  to  $8 \mu\text{F}/\text{cm}^2$ ) while the others are high ( $10^2$ – $10^3 \mu\text{F}/\text{cm}^2$ ). The low capacitances are assigned as film capacitances of layers which comprise the compact part of the interphase (close to the metal side) from which the thickness and resistivity can be calculated, assuming parallel plate geometry and a roughness factor of unity,

according to the following formulae:

$$d = \epsilon_0 K A / C \quad (1)$$

and,

$$\rho = R A / d \quad (2)$$

where  $d$  is the thickness of the layer,  $\epsilon_0$  the dielectric constant of the vacuum,  $K$  the dielectric constant of the surface species,  $A$  the electrode area,  $\rho$  the resistivity of the surface layer ( $\Omega \text{ cm}$ ),  $C$  and  $R$  the capacitance and resistance calculated for the relevant RC circuit in the equivalent circuit analog fitted to the experimental data. The dielectric constant of the major surface species formed on Li in PC solutions including ROCO<sub>2</sub>Li, Li<sub>2</sub>CO<sub>3</sub> and LiF is  $\sim 5$ . Other possible surface compounds such as LiCl, LiOH, Li<sub>2</sub>O, etc., also have dielectric constants not far from this value. Therefore, the average dielectric constant of the surface films was taken as 5. Fig. 6 shows the results of thickness and resistivity calculations of the layers comprising the compact part of the interphase formed on Li in pure and water-contaminated 1 M LiClO<sub>4</sub>-PC solutions, and 1 M LiPF<sub>6</sub> solution as a function of storage time. These calculations are based on the fitting of 5 RC circuits in series to experimental data obtained from Li electrodes in solutions upon storage. Each layer relates to an RC circuit whose calculated  $C$  value is low enough to be considered as a film capacitance. The various layers are marked (a), (b), (c), (d)... according to their relation to the various time constants from high to

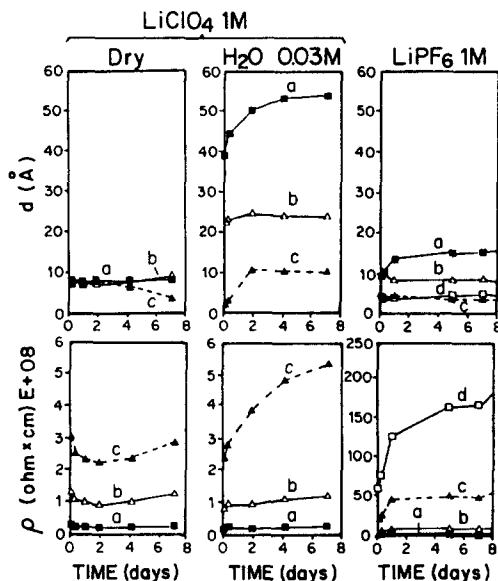


Fig. 6. The thickness and resistivity calculated from the capacitances and resistances (obtained by modelling the spectra with 5 RC circuits in series) of the various layers which comprise the compact part of the interphase formed on Li in PC solutions of LiClO<sub>4</sub> and LiPF<sub>6</sub>, as a function of storage time. The solutions' compositions are indicated: (a), (b), (c), (d) are the identities of these layers according to their sedimentation order on the Li surface; (a) is the closest, etc.

medium frequencies (i.e., layer (a) relates to the highest frequencies, etc., see Fig. 5). In a previous work [4–6] we proved that (a), (b), (c), (d) is also the order of the sedimentation of these layers on the Li surface, i.e. layer (a) is assigned as the closest to the electrode surface, etc. The results presented in Fig. 6 seem to validate our model and our approach and demonstrate its usefulness. The presence of water increases both the resistivity and the thickness of the surface films upon storage. This is to be expected as water diffuses through the surface films and reacts with Li. Note that the layer (c), assigned as the outer part of the compact interphase (and thus close to the solution phase), is indeed the most sensitive to storage and changes in solution composition (resistivity versus storage time). The interphase formed on Li in  $\text{LiPF}_6$  becomes highly resistive upon storage. Thus, the high interfacial resistance measured is due to high resistivity and not because it is thick. These changes in resistivity correlate very well with the instability of the surface films formed initially on Li or on Ni at low potentials as reflected by the impedance spectroscopic studies (Fig. 2) and the spectral studies (Fig. 4) discussed above.

Fig. 7 shows the thickness and resistivity of the various layers comprising the compact part of the Li–solution interphase after 5 days of storage in LiBr and  $\text{LiPF}_6$  solutions as a function of concentration (calculated as explained above). As already discussed [5,6] it is anticipated that the closer the layer to the Li surface, the thicker and less resistive it should be because it

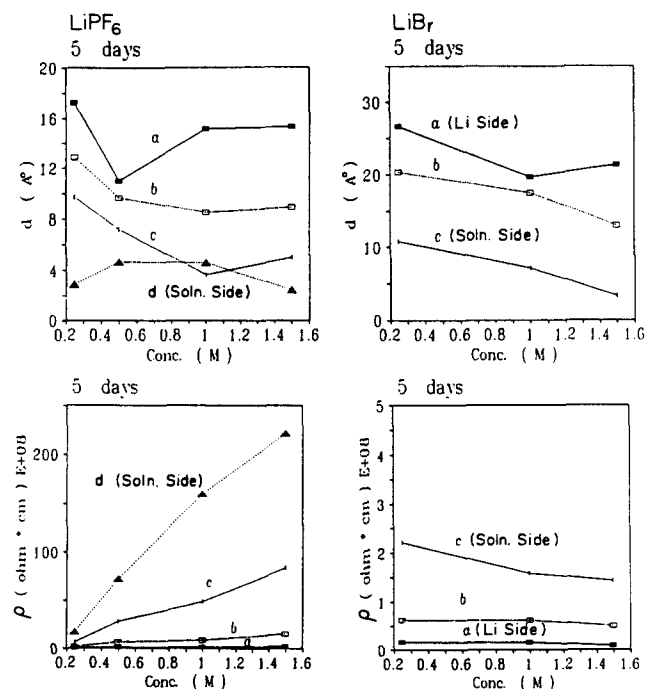


Fig. 7. The thickness and resistivity of the various layers comprising the compact part of the interphase formed on Li in LiBr and  $\text{LiPF}_6$  solutions after 5 days of storage, as a function of salt concentration.

is formed under less-selective conditions (higher driving force of formation which is the electrode–solution potential difference). Indeed, as shown in Fig. 7, layer (a) (lying on the Li surface) is the thickest and the least resistive, while layers (c) or (d) (the outer layers) are the thinnest and the most resistive. Note that the resistivities of layers (c) and/or (d) are the most sensitive to the salt concentration, which is in line with their assignment as the outer part of the surface films. The calculations presented in Fig. 7 demonstrate the difference between ‘reactive’ and ‘non-reactive’ salts in regard to the properties of the Li–solution interphase. In the case of LiBr, the resistivity of the various surface layers depends very slightly on the salt concentration, while when the electrolyte is the reactive  $\text{LiPF}_6$ , its dependence upon the salt concentration is remarkable.

Fig. 8 shows the thickness of the interphase formed on Ni electrodes polarized to 0.5 V ( $\text{Li/Li}^+$ ) in PC– $\text{LiSO}_3\text{CF}_3$  solutions of three salt concentrations as a function of storage time, while the electrodes are held at OCV (after film formation at the low potentials). For a comparison, similar calculations related to Ni electrodes on which surface films were formed at 0.5 V ( $\text{Li/Li}^+$ ) in 1 M  $\text{LiAsF}_6$ –PC solution are also presented in Fig. 8. These results clearly show that the interphase formed on the electrodes in the solutions of the reactive salt ( $\text{LiSO}_3\text{CF}_3$ ) is not stable and dissolves rapidly (decrease in the calculated thickness upon storage). Notice that the thickness of the surface films calculated (Fig. 8) is unrealistically low. This is because the roughness factor for the thickness calculations was taken as 1 (Eq. (1)) while the actual roughness factor is several times higher. However, the relative changes in the thickness are meaningful. As demonstrated in Fig. 8, as the concentration of the reactive salt increases, so the dissolution rate (thickness decrease) increases.

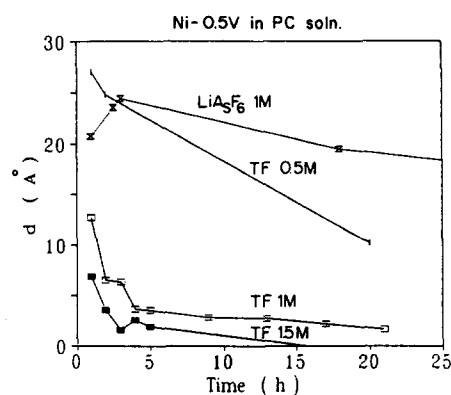


Fig. 8. The thickness of the interphases formed on Ni electrodes in three  $\text{LiSO}_3\text{CF}_3$  solutions (0.5, 1 and 1.5 M in salt concentration) and in a 1 M  $\text{LiAsF}_6$  solution. The surface films were precipitated by polarizing the electrodes to 0.5 V ( $\text{Li/Li}^+$ ) and holding the potential until the current decayed close to zero. The thickness was calculated from the capacitances of the three time constants of the high to medium frequencies (low  $C$  values).

As already reported [6], the surface films formed on noble metals at low potentials in  $\text{LiSO}_3\text{CF}_3$  solutions are very rich in various salt reduction products which are probably much less stable on the surface than the solvent reduction products in the case of PC. In contrast, when  $\text{LiAsF}_6$  is the salt, the dissolution rate is considerably lower because the interphase formed (mostly  $\text{ROCO}_2\text{Li}$  species) is more stable, as discussed above.

Fig. 9 presents calculations of overall thickness and average resistivity of the interphase formed on Li in four salt solutions (PC) as a function of salt concentration after 3 h and 5 days of storage.

These results demonstrate the influence of the electrolyte chosen on the Li-interfacial properties and the pronounced difference in this respect between 'reactive' and 'non-reactive' salts. They can be summarized as follows:

(i) The interphase formed in the solution of the least-reactive salt (LiBr) or at low salt concentration of any other salt is the thickest. This may be due to the electronic properties of the  $\text{ROCO}_2\text{Li}$  species when precipitated with only a minor interference of any other competing surface reactions. (Since the salt concentration is low its reaction on the surface may be negligible.)

(ii) The resistivity of the interphase formed in  $\text{LiClO}_4$  or LiBr solutions is low and stable upon storage and depends only moderately on the salt concentration.

(iii) In contrast, the resistivity calculated for the surface films formed on Li in the reactive salt ( $\text{LiPF}_6$ ,

$\text{LiSO}_3\text{CF}_3$ ) solutions increases considerably upon storage and depends strongly on the salt concentration.

#### 4. Conclusions

This work demonstrates that impedance spectroscopy is a very useful and sensitive tool for the study of ageing processes of the surface films formed on Li in solutions. The spectra obtained may be modelled with a relatively simple equivalent circuit analog of 4 to 5 RC circuits in series, which is in line with the expected multilayer structure of the Li-solution interphase in PC solutions. Impedance spectroscopic studies of Ni electrodes polarized to low potentials in Li salt solutions also provide useful information on the stability of the surface films formed on the non-active metal at low potentials. These films are very similar in their chemical structure to those formed on Li in the same solutions, and therefore their study sheds light on the more complicated case of the Li electrodes (where a constant driving force for surface-film formation exists).

This work demonstrates the strong impact of the electrolyte used on the Li-interfacial properties in solutions. In this respect, the common Li salts used in Li-battery systems may be divided into two groups: non-reactive salts such as LiBr,  $\text{LiClO}_4$  and  $\text{LiAsF}_6$  and reactive salts including  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiSO}_3\text{CF}_3$  and  $\text{LiN}(\text{SO}_3\text{CF}_3)_2$ . When the non-reactive salts are used, the Li-solution interphase formed is stable, while in the case of the reactive salts the interfacial resistance is high, strongly dependent on the salt concentration and increase upon storage.

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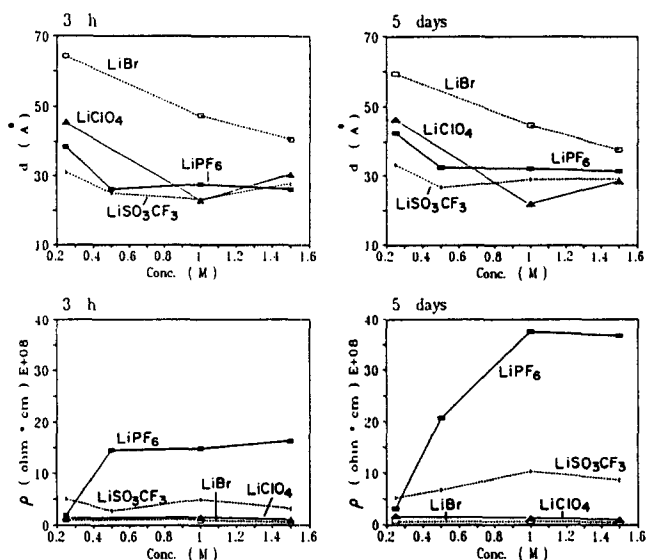


Fig. 9. The overall thickness and the average resistivity of the compact part of the interphase formed on Li in PC solutions of LiBr,  $\text{LiClO}_4$ ,  $\text{LiSO}_3\text{CF}_3$  and  $\text{LiPF}_6$  after 3 h and after 5 days of storage as a function of salt concentration.