The use of in situ Fourier-transform infrared spectroscopy for the study of surface phenomena on electrodes in selected lithium battery electrolyte solutions

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Abstract

This paper presents some examples of surface studies of noble metals and Li electrodes in Li battery electrolyte solutions using in situ FT-IR spectroscopic techniques. These examples include the study of a mixture of solvents, the role of the reduction of salt in the build-up of surface films on the electrodes and the impact of contaminants such as traces of oxgen and water. The techniques included multiple and single internal reflectance modes and external reflectance (SNIFTIRS-type) mode. The following conclusions were drawn from this study: (i) salts containing the $-SO_2CF_3$ group are much more reactive on Li than $LiAsF_6$. Their reduction dominates the surface chemistry developed on Li in ethereal solutions; (ii) water reduction on Li in wet 1,3-dioxolane solution may not form stable LiOH films due to the further reaction of the hydroxy group with the solvent; (iii) in spite of its low solubility, oxygen dissolved in propylene carbonate and tetrahydrofuran solutions has some impact on the surface chemistry developed on Li in these solutions (probably due to Li_2O formation). © 1997 Elsevier Science S.A.

Keywords. Lithium batteries; Electrolytes; Surface phenomena

1. Introduction

During the past two decades a great deal of effort has been expended worldwide in identifying surface films formed on Li, and other active metals, in polar aprotic systems. X-ray photospectroscopy (XPS) [1], Auger electron spectroscopy (AES) [2] and secondary ion mass spectroscopy (SIMS) [3] were first used for the study of surface films formed on Li. However, these methods, while highly surface sensitive, could not provide specific information on the chemical identification of the surface species. The application of surface sensitive Fourier-transform infrared (FT-IR) spectroscopy using the ex situ external reflectance mode provided more specific information. Extensive studies in the past decade using this technique, as well as energy dispersive analysis of X-rays (EDAX), enabled rigorous chemical identification of the species formed on Li [4–6], noble metal electrodes [7,8] at low potentials and Li–carbon intercalation electrodes [9] in a variety of Li battery solvent systems.

The major consequences of these studies can be summarized as follows.

Alkyl carbonates are reduced on Li to $ROCO_2Li$ species, ethers are reduced to alkoxy species (ROLi) and esters are reduced to carboxylates (RCOOLi). In addition to the above components, the surface films in the various systems include salt reduction products (Li halides such as LiCl, LiF, depending on the salt used) and species such as Li_2O, Li_3N, LiOH and Li_2CO_3 resulting from the reaction of Li with the atmospheric contaminants O_2, N_2, H_2O and CO_2, respectively, present in the dry rooms, glove box atmospheres or, unavoidably, in non-aqueous solutions.

The above work still leaves many questions unanswered since it was not possible to eliminate the impact of the atmospheric contaminants to which both lithium and the surface species formed on it are highly sensitive. In spite of the extensive work carried out, the role of salt reduction, water, CO_2 or O_2 reduction, as well as the influence of solvent mixtures on the surface chemistry of Li, or carbon and noble metals at low potentials in solutions, still remains unclear.

As a result, there have been attempts to develop in situ spectroelectrochemical methods for the study of Li in polar aprotic solvents. In situ X-ray diffraction (XRD) analysis [10] and Raman spectroscopy were also used [11,12]. We developed three different in situ spectroelectrochemical

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methods based on surface sensitive FT-IR [13,14], one of which is based on external reflectance mode — thin layer cell configuration — while the other two methods are based on internal reflectance modes.

In this paper we report new important data regarding the application of in situ FT-IR spectroscopy for the study of the surface chemistry of Li and non-active metals in several important Li battery electrolyte systems. The examples described include the impact of the salt used, the level of contaminants and the surface films developed in solvent mixtures.

2. Experimental

All preparations of solutions and spectroelectrochemical cells, as well as FT-IR measurements and data analyses, are described in details in Refs. [4,13–15]. Fig. 1 presents schematically the various ex situ and in situ techniques that have been applied for FT-IR studies of Li and noble metal electrodes in the solutions of interest.

3. Results and discussion

3.1. The use of internal reflectance mode and its application for the study of DME and PC mixtures

The use of internal reflectance mode (ATR) may be an excellent tool for in situ FT-IR studies of electrode surfaces, as in this technique the IR beam comes from the back of the electrode (see Fig. 1) and hits the surface before it is absorbed by solution species. Thereby the masking effect of the solutions absorbance may be minimal [16,17]. In order to obtain the multiple internal reflectance the electrode has to be a thin metal film deposited on an IR transparent crystal of a high refractive index. Possible materials are germanium, silicon, ZnSe and KRS-5 (refractive index of 4, 3.4, 2.4 and 2.37, respectively). All of these materials were found to be highly reactive with solution species at low potentials when immersed in polar aprotic solvents containing Li salts. Their reactions destroy their polished surface and in many cases the internal reflectivity is thus lost. Although the crystals, which are covered with the working electrode (a 200 Å film of non-active metal), are not supposed to be in contact with the solutions in the electrochemical experiments, it is almost impossible to prevent contact between the crystal and solutions. Consequently, only one out of 10 such experiments actually succeeds and as a result this operation becomes very expensive.

Nevertheless, we succeeded in some of these experiments which were directed to the study of propylene carbonate–dimethyl carbonate (PC–DME) mixtures using the ATR mode (Fig. 1) with a thin Pt electrode on a ZnSe paralleloid crystal. The results are presented in Fig. 2 which shows the FT-IR spectra obtained in situ from three different experi-
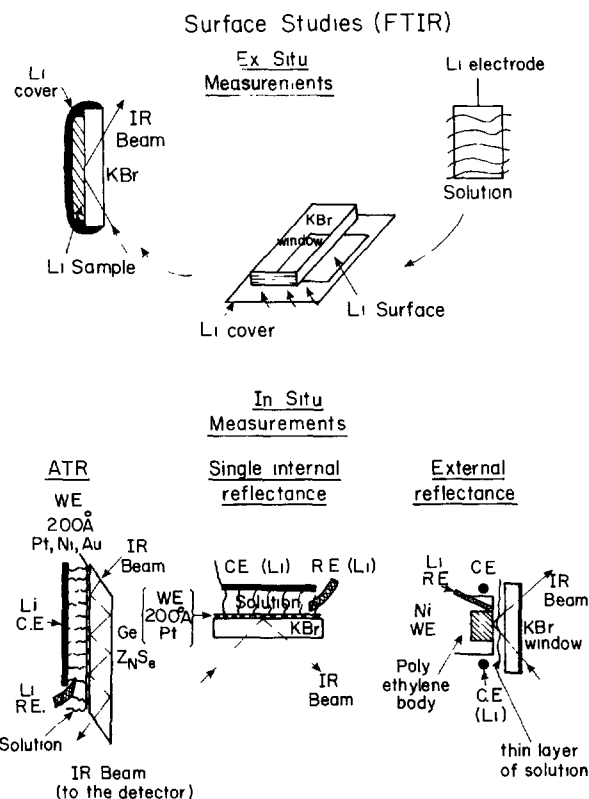

Fig. 1. Schematic view of the ex situ and in situ techniques for the study of Li electrodes using FT-IR spectroscopy (see Refs. [4,5,13,14]).

ments. Spectra (a), (c) and (e) were measured at open-circuit voltage (OCV) (3–2.5 V versus Li/Li^+) and show the typical solution spectra (mostly solvent peaks) of DME/0.5 M $LiAsF_6$, PC/0.5 M $LiAsF_6$ and PC–DME (1:1)/0.5 M $LiClO_4$, respectively. Spectra (b), (d) and (f) were measured in situ after the electrodes were polarized to 0.3 V (Li/Li^+) and the currents decayed to low steady values. The final spectra were obtained by subtracting the OCV spectra from those measured at a low potential As is known from previous ex situ studies of Li or noble metals polarized to low potentials in these solutions at 0.3 V (Li/Li^+), both solvents are reduced to insoluble products which formed on the electrode surface films similar to those formed on Li [7]. PC is reduced to $ROCO_2Li$ species [4,7] while DME is reduced to ROLi [7] (CH_3OLi was identified [18]). However, it was not at all clear what happens in mixtures of these two solvents (which are often used in Li batteries [19]). It was interesting to find out whether reduction of PC (which is supposed to be the more reactive solvent) in the solvent mixtures dominates the surface film formation or whether the ether reduction also influences the electrodes' surface chemistry. Previous studies of these systems by ex situ FT-IR spectroscopy could not be conclusive because ROLi compounds when formed by DME reduction may readily react with traces CO_2 in the glove box or the spectrometer atmosphere to form $ROCO_2Li$ species which may have IR spectra similar to those of the PC reduction products.

Fig. 2. FT-IR spectra measured in situ using the ATR mode (Pt on ZnSe crystal working electrode): (a) DME/0.5 M LiAsF$_6$, a solution spectrum measured at OCV (~2.5–2 8 V vs. Li/Li$^+$); (b) spectrum measured after the electrode was polarized to 0.3 V vs. Li/Li$^+$, the solution OCV spectrum was subtracted; (c) same as (a) PC/0 5 M LiAsF$_6$ solution. (d) same as (b) PC/0 5 M LiAsF$_6$ solution. (e) same as (a) and (c) DME–PC(1:1)/ 0.5 M LiClO$_4$ solution, and (f) same as (b) and (d) DME–PC(1 1)/ 0.5 M LiClO$_4$ solution

Spectrum 2(b) resembles the LiOCH$_3$ spectrum [18] and thus confirms the previous finding that DME reduction of these active surfaces produces Li methoxide as the major product [7,18]. Spectrum 2(d) has several typical peaks of the major PC reduction product — ROCO$_2$Li [4] (e.g. 1650–1640, 1330–1300 cm^{-1} C=O peaks and 2835–2950 cm^{-1} C–H peaks). Spectrum 2(f) seems to be a mixture of spectra 2(b) and 2(d) and indicating that in spite of the expected differences in reactivity, reduction of both solvents contributes to the surface film formation on the electrodes. This conclusion may help in the understanding of the behavior of Li electrodes upon cycling in these mixtures compared with the single solvent solutions [20]. However, discussion of this is beyond the scope of this paper.

However, the above-mentioned problems with this method led us to abandon it and to concentrate ourselves on the single internal mode (SIR) [13–15] (Fig. 1) or external reflectance mode (SNIFTIRS-like [21]) that use the non-reactive KBr on NaCl windows.

3.2. Studies of salt reactivity using SIR

The application of in situ FT-IR spectroscopy for a comparative study of the reactivity of Li salts towards lithium is demonstrated for solutions of 1,3-dioxolane (DN). As already reported, DN is reduced on Li to alkoxides of the CH$_3$CH$_2$OCH$_2$OLi type as well as to poly(DN) with –OLi edge groups (products of a polymerization of DN through a nucleophilic mechanism [22]). Occasionally, depending on the electrode used, DN reduction in the presence of Li salt may also produce Li formate (HCO$_2$Li). LiAsF$_6$ is reduced to LiF- and Li$_x$AsF$_y$-type species [4–9,14]. Fig. 3 presents FT-IR spectra measured in situ (SIR mode, Fig. 1) from a Pt electrode polarized to low potentials in DN/1 M LiAsF$_6$ solutions (each spectrum was obtained finally by subtraction of the OCV spectrum). Spectra 3(a) and (b) were measured at 1 and 0 V (versus Li/Li$^+$), respectively, soon after the current decayed to a low steady value (a few μA/cm^2, about 10 min after the potential was applied). Spectrum 3(c) was measured at 0 V about 30 min after the current reached its low steady value and spectrum 3(d) was measured at 0 V after deposition of about 1 C/cm^2 of Li at −0.2 V (versus Li/Li$^+$). These spectra are indeed typical of Li alkoxides [7,13–15,18] and also have the typical, expected As–F (Li$_x$AsF$_y$) peaks around 700 cm^{-1}. The lower the potential and the longer it was applied, the more pronounced are the alkoxy and As–F peaks (Fig. 3) due to a further reduction of the solvent, the salt and the precipitation of the products on the electrode surface. It is interesting to note that the spectra obtained from electrodes containing bulk Li deposits are not too different from the spectra measured at 0 V (versus Li/ Li$^+$) before Li bulk deposition. (Only Li UPD (ultra potential deposition) and Li–Pt alloying may occur above 0 V in addition to the surface film formation [7]).

Fig. 4 shows three FT-IR spectra measured from Pt electrodes (SIR mode, Fig. 1) polarized to 0 V (versus Li/Li$^+$) in 1,3-dioxolane solutions containing 1 M Li salts. The lower spectrum (4(a)) relates to the LiAsF$_6$ solution, and reflects mostly solvent reduction (and some LiAsF$_6$ reduction to Li$_x$AsF$_x$ as discussed above. Spectra 4(b) and (c) relate to LiN(SO$_2$CF$_3$)$_2$ (imide) and LiC(SO$_2$CF$_3$)$_3$ (methide) solutions and are much richer in peaks than spectrum 3(a). The peaks around 900–1000 cm^{-1} (v_{S-O}), 1100–1150 cm^{-1} (v_{S-O}) and 1200–1170 cm^{-1} (v_{C-F}) appearing in both spectra are characteristic for possible S, O, C and F containing reduction products of the –SO$_2$–CF$_3$ group, as already discussed [23].

Hence, from these measurements it is clear that these two salts are more reactive on Li electrodes than LiAsF$_6$ and their reduction dominates the electrodes' surface chemistry.

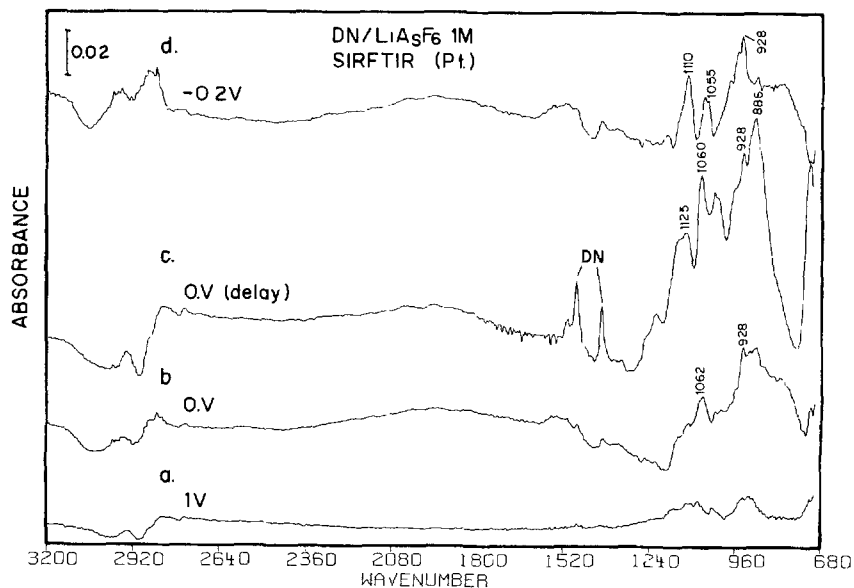This type of study is a typical example in which in situ measurements are highly advantageous over ex situ ones. In

Fig. 3. FT-IR spectra measured from a Pt electrode in DN/1 M LiAsF₆ solution stabilized with 1000 ppm of TBA (tributylamine) using the SIR mode (single internal reflectance, see Fig. 1). The solution OCV spectrum was subtracted. (a). (b) Spectra measured at 1 and 0 V (vs Li/Li⁺) soon after the current measured reached a steady low value. (c) Same as (b) after 30 min of storage at 0 V. (d) The electrode was measured at 0.V (Li/Li⁺) after Li was deposited (≈ 1 C/cm², −0.2 V).

the latter case, residual salt has to be washed out from the samples before measuring. Several possible reduction products of salts containing the –SO₂CF₃ group may have IR spectra similar to the pristine material. Hence, one can never know if all the peaks obtained in spectra measured ex situ belong to products or to residual salt which could not be properly washed out. This ambiguity is, of course, avoided when measuring the electrode surface in situ.

3.3. The role of contaminants

3.3.1. Water in 1,3-dioxolane solutions

The voltammetric behavior of wet (up to 1000 ppm of H₂O) Li salt solutions of esters, ethers and alkyl carbonates with noble metal electrodes is characterized by pronounced cathodic currents in the 1.5–0.5 V (versus Li/Li⁺) range due to water reduction to LiOH [7,8]. However, after a certain passage of current in this range the electrodes become passivated due to LiOH–Li₂O precipitation and thereby steady-state cyclic voltammograms of the above wet solutions with noble metal electrodes such as gold, platinum, silver, etc., become quite similar to those of dry solutions [7,8]. As already reported [24], 1,3-dioxolane solutions are an exception as no electrode passivation is observed in a voltammetric study of noble metal electrodes in wet DN solutions. FT-IR studies (ex situ external reflectance modes) of electrodes, after being treated in these solutions, were not conclusive [24].

Fig. 5 presents spectra measured in situ using the external reflectance mode (SNIFTIRS-type, Fig. 1) from Ni electrodes polarized to 0 V (versus Li/Li⁺) in dry and wet (800 ppm H₂O) LiAsF₆ 1 M DN solutions (stabilized with 1000 ppm of tributyl amine). In this method the IR beam passes

through the thin layer of the solution twice and as a result substraction of the OCV–solution spectrum (required in order to obtain the electrode's surface spectrum) may eliminate information in spectral regions in which the solution also absorbs IR light. Hence, the 1300–850 cm⁻¹ region in the spectra of Fig. 5 in which the solvent DN has its strongest IR peaks cannot be used for the surface studies of these systems. Nevertheless, the spectra of Fig. 5 provide some valuable information, as outlined below.

Spectra 5(a) and (b) which relate to the dry solutions have the typical peaks of Li formate at 1620 and 1380 cm⁻¹ [22] as well as some ROLi peaks and the 700 cm⁻¹ As–F (Li₃AsFᵥ) peak. These spectra differ from those of Figs. 3 and 4 because the electrode is different (Li formate is formed in this case) and the subtraction of the OCV spectrum omits the pronounced Li alkoxy peaks in the 1300–850 cm⁻¹ range (which are visible in Figs. 3 and 4).

As shown in Fig. 5(c), the spectrum measured soon after polarizing the electrode to 0 V in the wet solution also has pronounced peaks, part of which can be attributed to Li formate (1620, 1365 cm⁻¹ [22]). The 700 cm⁻¹ As–F is absent and a pronounced peak at 780 cm⁻¹ is attributed to the As–O (e.g. As₂O₃ [14]) appears. Spectrum 5(d) measured after the electrode was held at 0 V for 1 h in the wet solution has only the 780 cm⁻¹ peak and a pronounced broad peak around 1650–1590 cm⁻¹ being attributed to hydrating water. It should be emphasized that spectra 5(c) and (d) have no LiOH peaks (e.g. the typical 3665 cm⁻¹ ν_{OH} sharp peak is absent).

These spectral studies seem to indicate that LiOH does not precipitate onto the electrode as a stable surface species in these cases. We assume that the OH⁻, which is obviously formed by the H₂O reduction, may react nucleophilically with
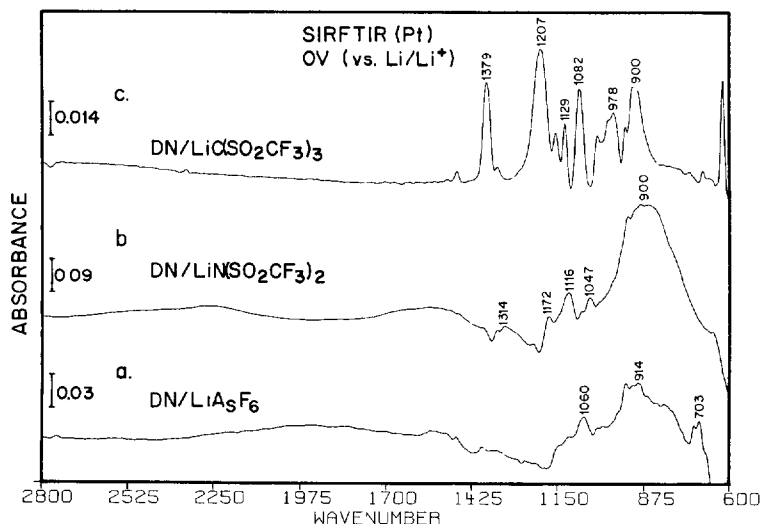
Fig. 4. FT-IR spectra measured in situ from Pt electrodes polarized to 0 V in three 1,3-dioxolane solutions 1 M in salt concentration, stabilized with 1000 ppm of tributylamine. Singe internal reflectance mode. The solution OCV spectrum was subtracted: (a) $LiAsF_6$, (b) $LiN(SO_2CF_3)_2$, and (c) $LiC(SO_2CF_3)_3$.
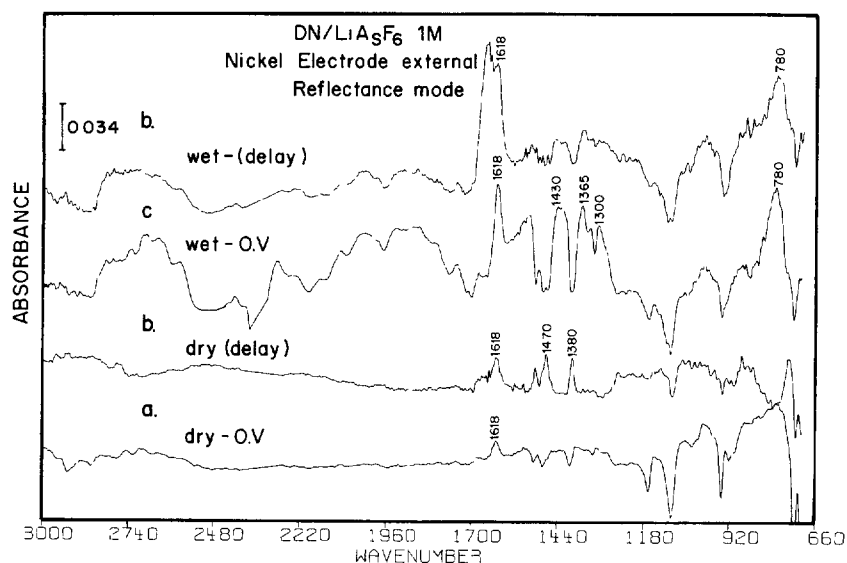

Fig. 5. FT-IR spectra measured in situ from Ni electrodes polarized in DN/1 M $LiAsF_6$/TBA (1000 ppm) solutions using external reflectance (SNIFTIRS-type) mode (a) A dry solution, 0 V (vs. Li/Li^+). The measurement was performed soon after the electrode reached a steady state (low constant current). (b) Same as (a), after 30 min at 0 V. (c) Same as (a) wet solution (800 ppm of H_2O). (d) Same as (b) wet solution.

DN to form soluble alkoxy species of the $OH–CH_2CH_2–OCH_2–O^-Li^+$ type. We assume that the presence of H_2O leads to hydrolysis of the AsF_6^- reduction products such as AsF_3 to arsenic oxide (As_2O_3) and HF, which may either react with the solvent (polymerization to poly(DN) [24]), or on the active electrode's surface to form LiF.

In conclusion, these studies reveal that in wet DN solutions passivating LiOH films are not formed on the electrode surfaces in these conditions. Moreover, the presence of H_2O at the hundreds of ppm level may lead to solubilization of the solvent and salt reduction products by hydrolysis (as is evident by the almost featureless spectrum of Fig. 5(d)).

3.3.2. Study of oxygen-contaminated solutions

In a previous work it was found that in spite of the low solubility of O_2 in ethers and alkyl carbonates (submillimolar level [25]), its presence in solutions increases Li-cycling efficiency in PC, THF and γ-butyrolactone solutions [26]. Ex situ studies of Li electrodes, after being treated in O_2-containing solutions, indicated the formation of surface Li oxide. However, they could not be one hundred percent conclusive [26].

In the present study we used the above in situ techniques for the study of electrodes in O_2-saturated solutions. Fig. 6 presents FT-IR spectra measured from a Pt electrode in O_2-saturated THF/1 M $LiAsF_6$ solution at 2 V (versus Li/Li^+) and at 0 V (versus Li/Li^+) after Li deposition at −0.2 V (≈ 0.5 C/cm^2) using the SIR mode (OCV spectrum subtracted). While the spectrum measured at the higher potential (spectrum 2(a)) is nearly featureless, the spectrum of the electrode containing Li has the typical peaks belonging to the THF reduction product on Li [7,14] around 1100–1000 cm^{-1} and 890 cm^{-1} and the 700 cm^{-1} peak of the
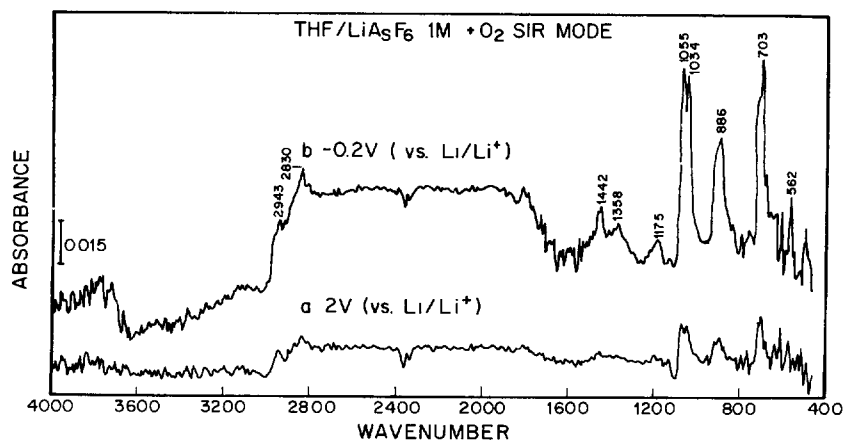
Fig. 6. FT-IR spectra measured in situ from a Pt electrode in O$_2$-saturated THF/1 M LiAsF$_6$ solution, SIR mode. (a) At 2 V (vs Li/Li$^+$). (b) At 0 V (vs Li/Li$^+$) after Li deposition (≈ 0 5 C/cm^2 at −0.2 V vs. Li/Li$^+$).

Li$_x$AsF$_y$ species. The spectra measured in a similar experiment with uncontaminated THF/LiAsF$_6$ solutions were very similar to those of Fig. 6.

Fig. 7 presents FT-IR spectra measured in situ from Ni electrodes using the SNIFTIRS mode (external reflectance) polarized to 1 V and to 0 V (versus Li/Li$^+$) after Li deposition (0.5 C/cm^2 at −0.2 V (versus Li/Li$^+$) in uncontaminated and in O$_2$-saturated THF/1 M LiAsF$_6$ solutions. The spectra related to both solutions are similar and reflect the reduction of THF to ROLi and LiAsF$_6$ to Li$_x$AsF$_y$ on the electrode surfaces at low potentials as explained above and already discussed [7,14,15,26]. However, the intensity of the peaks appearing in the spectra relating to the O$_2$-containing solutions is much higher than those related to the uncontaminated solutions. (The experimental conditions were identical.) In this case it should be noted that subtraction of the solution spectra did not detrimentally affect the quality of the surface spectra and indeed the spectra measured using the

SNIFTIRS or the SIR models are very similar (Figs. 6 and 7). Obtaining similar spectra for the same systems from such different techniques is very important for the validation of the reliability of these techniques.

Fig. 8 presents FT-IR spectra measured in situ from Ni electrodes using the SNIFTIRS mode in similar experiments as those of Fig. 7 in which the electrodes were polarized to 0 V (versus Li/Li$^+$) before and after Li deposition (≈ 0.5 C/cm^2 at −0.2 V) in uncontaminated and O$_2$-saturated PC/ 1 M LiAsF$_6$ solutions. Despite the severe masking effect of the PC solution whose spectrum was subtracted from each of the spectra of Fig. 8, quite meaningful results were obtained because there are several spectral regions of interest in which there is no overlap between the solution and the surface species peaks. The pronounced peaks around 2950–2830 cm^{-1} (v_{C-H} of an open chain product, ROCO$_2$Li), 1660 and 1300 cm^{-2} ($v_{C=O}$, ROCO$_2$Li), 1000 cm^{-1} (v_{C-O}) and 830–800 (δOCO$_2$Li) are typical of the major PC reduction products
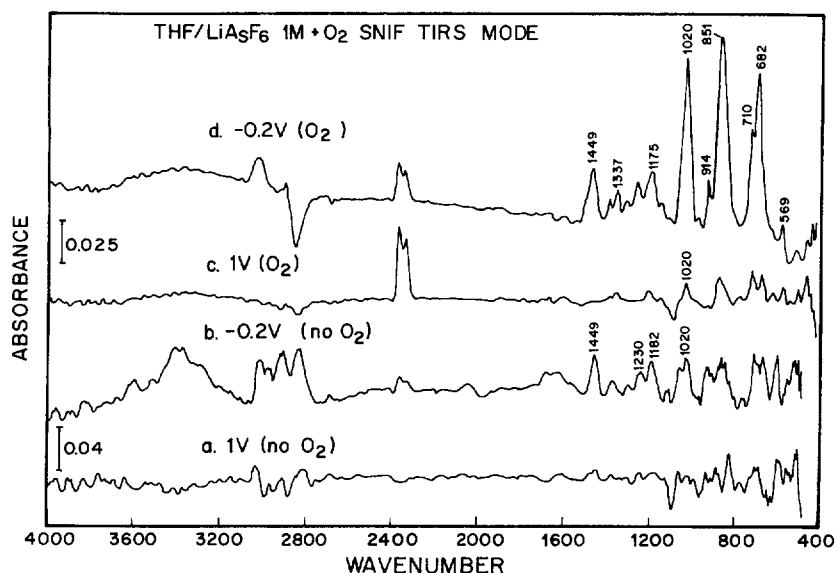

Fig 7. FT-IR spectra measured in situ from Ni electrodes in THF/1 M LiAsF$_6$ solutions using external reflectance (SNIFTIRS) mode. (a) and (b) An O$_2$-free solution. (c) and (d) An O$_2$-saturated solution. (a) and (c) 1 V (vs. Li/Li$^+$). (b) and (d) 0 V (vs. Li/Li$^+$) after Li was deposited at −0 2 V (≈ 0 5 C/cm^2).
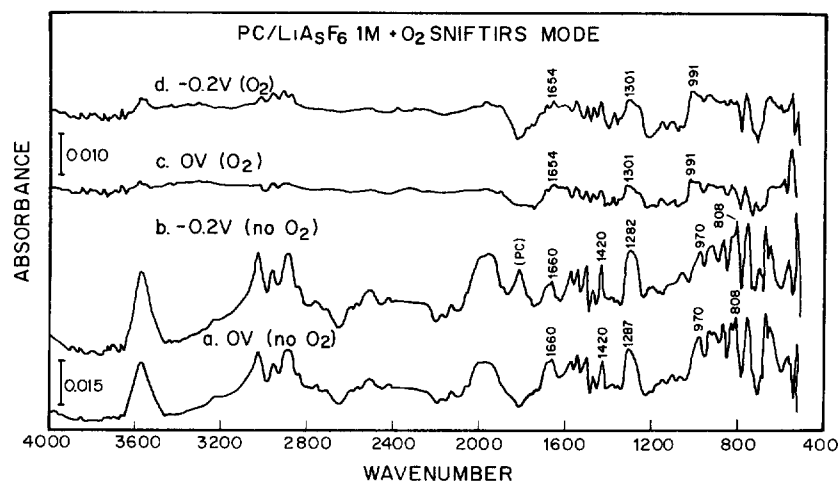
Fig. 8 Same as Fig. 7 PC/1 M LiAsF₆ solutions, (a), (b) and (c), (d) O₂-free and -saturated solutions, respectively (a) and (c) The electrodes were polarized to 0 V (vs. Li/Li⁺) (b) and (d) 0 V (vs. Li/Li⁺) after Li deposition (≈0.5 C/cm² at −0.2 V vs. Li/Li⁺).

on Li (ROCO₂Li, probably CH₃CH(OCO₂Li)CH₂OCO₂Li) as already discussed in previous publications [4,7,13,20,23]. The spectra of Fig. 8 are of the best quality we have ever obtained in in situ FT-IR studies of the surface chemistry developed on these electrodes in PC solutions, and thus they validate our previous identification of ROCO₂Li species as the major PC reduction products on Li (what was recently questioned [27]).

The above studies of both THF and PC solutions indeed showed differences in the spectra measured from electrodes polarized in O₂-saturated or O₂-free solutions. However, these differences were mostly in peak intensity. In the case of THF solutions, the intensity of the spectra measured with O₂-saturated solutions was higher than those measured in O₂-free solutions. For PC solutions the opposite was true. The major reduction product of O₂ on Li should be Li₂O whose major IR absorption is a broad band below 600 cm⁻¹ [5]. Hence, there is no interference between the Li₂O spectrum and any of the spectra of possible surface species formed in the above solutions by solvent or salt reduction.

From the above spectral studies we can conclude that the presence of O₂ in solution does not considerably change the electrode surface chemistry which is mostly dominated by solvent reduction (and a reduction of some AsF₆⁻ as well). However, from the intensity differences shown in Figs. 6 and 7 we assume that O₂ is also reduced on Li when present in solutions and we attribute the above intensity changes observed to the impact of the presence of Li oxide when formed on the reflectivity of these electrodes.

4. Conclusions

The use of in situ FT-IR spectroscopic techniques for the study of Li and noble metal electrodes polarized to low potentials in Li battery electrolyte solutions was again found to be quite important and advantageous over the ex situ investi-

gation. Problems such as contribution of co-solvents, salts and contaminant reduction to the surface chemistry developed on these electrodes could be better addressed when measuring the electrodes in solution and under potential control. In brief, in spite of the difference in reactivity, ether reduction also contributes to the build-up of surface films in ethers and alkyl carbonate mixtures. The salts based on the −SO₂CF₃ group are more reactive on the Li surface than AsF₆⁻ and thus their reduction dominates the surface chemistry developed in ethereal solutions. Water reduction in 1,3-dioxolane solution does not precipitate LiOH surface species, probably due to a further nucleophilic reaction of the hydroxide with the solvent. Finally, the presence of O₂ in THF and PC solutions slightly affects the state of the surface of Li electrodes, probably due to the formation of Li₂O. However, the surface chemistry remains dominated by the solvent reduction.

Acknowledgements

References

[1] K. Kanamura, H. Tamura and Z.I. Takehara, J. Electroanal. Chem., 333 (1992) 127.

[2] V. Schily and J. Heitbaum, Electrochim. Acta, 37 (1992) 731.

[3] G. Nazri and H. Muller, J. Electrochem. Soc., 132 (1985) 2050; 2054.

[4] D. Aurbach, M.L. Daroux, P. Faguy and E.B. Yeager, J. Electrochem. Soc., 134 (1987) 1611.

[5] D. Aurbach, J. Electrochem. Soc., 136 (1989) 1606; 1610.

[6] D. Aurbach and Y. Ein-Ely, Langmuir, 8 (1992) 1845.

[7] D. Aurbach, M.L. Daroux, P. Faguy and E.B. Yeager, J. Electroanal. Chem., 297 (1991) 225.

[8] D. Aurbach, J. Electrochem. Soc., 136 (1989) 906.

[9] D. Aurbach, O. Chusid, Y. Ein-Ely, M. Babai and Y. Carmeli, J. Power Sources, 43 (1993) 47.

[10] G. Nazri and R.H. Muller, *J Electrochem Soc., 132* (1985) 1385

[11] D. Aurbach, M.L Daroux, P Faguy, A. Wilkinson and E.B. Yeager, *Ext. Abstr., Proc. National Meet. The Electrochemical Society, Toronto, Canada, May 1985*, pp. 760–761.

[12] M Odziemkowski, M. Krell and D.E. Irish, *J. Electrochem. Soc., 139* (1992) 3052.

[13] D. Aurbach and O Chusid, *J. Electrochem. Soc., 138* (1991) L6

[14] D. Aurbach and O. Chusid, *J. Electrochem. Soc , 140* (1993) L1

[15] D. Aurbach, O. Chusid, I. Weissman and P Dan, *Electrochim Acta, 41* (1996) 747

[16] F. Adani, M.C. Pham, P.C. Lacaze and J E DuBois, *J Electroanal. Chem., 210* (1986) 295

[17] T. Ichino, B D Chahan and D.A. Scherson, *J. Electrochem. Soc , 138* (1991) L59

[18] D. Aurbach, M L. Daroux, P. Faguy and E.B. Yeager, *J. Electrochem. Soc , 135* (1988) 1863

[19] N. Margalit, in J.P Gabano (ed.), *Lithium Batteries*, Academic Press, New York, 1983, Ch 7.

[20] D. Aurbach and Y. Gofer, *J. Electrochem Soc., 138* (1991) 3529.

[21] J. Foley and S. Pons, *Anal. Chem., 57* (1985) 945A.

[22] Y Gofer, Y. Ein-Eli and D. Aurbach, *Electrochim. Acta, 37* (1992) 1897.

[23] D Aurbach, I. Weissman, A Zaban and O Chusid, *Electrochim. Acta, 39* (1994) 51.

[24] O Youngman, P. Dan and D. Aurbach, *Electrochim. Acta, 35* (1990) 625.

[25] H.A. Frank and P.D Lawson, *Lithium Batteries*, The Electrochemical Society Softbound Proceedings Series, Proc. Vol 81-4, Pennington, NJ. USA, 1981, p. 354.

[26] D. Aurbach, Y Langzam and Y Gofer, *J. Electrochem Soc., 136* (1989) 3198

[27] A.N. Dey, D. Aurbach and Y. Ein-Eli, *J Electrochem. Soc., 142* (1995) 990