

# The use of polarized light in the infrared reflectance spectroscopic investigation of the lithium–organic electrolyte interface

S. Barusseau<sup>a</sup>, B. Beden<sup>a,\*</sup>, M. Broussely<sup>b</sup>, F. Pertont<sup>b</sup>

<sup>a</sup> Université de Poitiers, Laboratoire de Chimie 1, 'Electrochimie et Interactions' URA CNRS DO350, 40 avenue du Recteur Pineau, 86022 Poitiers, France

<sup>b</sup> SAFT, rue G. Leclanché, BP 1039, 86060 Poitiers, France

## Abstract

Surface films formed on lithium were investigated using in situ reflectance infrared spectroscopy. Experiments were carried out using sophisticated techniques like EMIRS (electro-modulated infrared reflectance spectroscopy) or SNIFTIRS (subtractively normalized interfacial Fourier-transform infrared spectroscopy). Spectra were recorded with both p- and s-polarized light to distinguish the surface species belonging to the passive layer from those in solution. The solutions used included LiAsF<sub>6</sub> in mixtures of propylene carbonate, ethylene carbonate and dimethoxyethane (1:1:3). The main components detected at the surface films were lithium alkyl carbonates (ROCO<sub>2</sub>Li) and lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>), this in agreement with previous work by Aurbach and co-workers. Besides, spectra reveal the presence of other types of species whose nature has been discussed.

**Keywords:** Infrared reflectance spectroscopy; Lithium electrodes; Organic electrolytes

## 1. Introduction

Lithium batteries are among the best candidates for high energy density batteries. However, one major obstacle to the development of rechargeable lithium batteries, is that lithium is so reactive with organic electrolyte solutions that insoluble and soluble products are formed by chemical reactions at the lithium electrode–electrolyte interface. Actually, these side reactions, which are thought to be the cause of lower cycleability, also explain the relative stability of the lithium interface due to the formation of a passive film on the surface. Thus, the in situ identification of these surface species is important for understanding the behaviour of lithium battery systems. However, as this information can not be detected by pure electrochemical techniques, there is a need for using coupled techniques, among which infrared (IR) reflectance spectroscopies are probably the most appropriate.

After the pioneer work of Bewick et al. [1,2], different in situ IR reflectance spectroscopic techniques have been developed during the last decade [3,4]. They allow different approaches to elucidate the solid–electrolyte interface, and aim at identifying the composition of

surface species as well as the nature of solution species accumulated in the vicinity of the electrode. The interest of using IR spectroscopy to identify in situ the nature of degradation products and the composition of the passive layer formed at a lithium electrode in contact with organic electrolytes has been well illustrated a few years ago by Aurbach and co-workers [5–7], who used Fourier-transform infrared spectroscopy (FT-IR) as well as a variant of subtractively normalized interfacial Fourier-transform infrared spectroscopy (SNIFTIRS) [8,9].

The SNIFTIRS technique, originally developed by Pons et al. [10,11] consists in collecting short successive series of interferograms at each of the two potentials limits,  $E_1$  and  $E_2$ , until the desired signal-to-noise ratio is obtained (an average of 100 scans is generally sufficient to extract signals of  $10^{-3}$  absorbance unit amplitude) [12,13]. If  $R_1$  and  $R_2$  are the surface reflectivities measured at  $E_1$  and  $E_2$ , it is easy to calculate the relative change of reflectivity,  $\Delta R/R$ , by:

$$\frac{\Delta R}{R} \cong \frac{R_2 - R_1}{R_1} = \frac{R_2}{R_1} - 1 \quad (1)$$

As noted by Greenler [14],  $\Delta R/R$  is equivalent to the absolute change of absorbance,  $\Delta A$ :

\* Corresponding author.

$$\Delta A \cong -\Delta R/R \quad (2)$$

By comparing spectra recorded separately with p- and s-polarized lights (i.e., p, parallel, and s, perpendicular to the incidence plane, respectively) it is possible to distinguish the surface species from the solutions species. At high incidence angles, the solution species, due to their random orientation, absorb the light in the two polarization states. Conversely, the surface species, due to the application of the so-called 'surface selection rule', absorb the p-polarized light (provided that the dipole moment oscillates in the normal to the surface) but not the s-polarized light which is inactive by cancellation of the s-polarized electric field vectors upon reflection.

The electro-modulated infrared reflectance spectroscopy (EMIRS) technique makes use of a conventional grating spectrometer. It is based on the interaction of a p-polarized IR beam with a metallic surface whose potential is modulated at a given frequency generally close to 13 Hz [3,4]. The synchronic analysis of the resultant IR signal permits to reject the information due to solutions species.  $\Delta R/R$  and  $R$  are recorded in separated experiments.  $\Delta R$  is the modulated reflectivity (when the potential is modulated) and  $R$  the reflectivity.  $\Delta R$  and  $R$  are then divided, the spectra are therefore displayed as  $\Delta R/R = f(\nu)$ .

In this work, we compare EMIRS and SNIFTIRS in light of investigations carried out at the lithium-organic electrolyte interface. The solvents used are propylene carbonate (PC), ethylene carbonate (EC) and dimethoxyethane (DME). Emphasis is given to the separation between species belonging to the passive layer and species in solution.

## 2. Experimental

All solvents and salt purifications were operated in a glove box by the SAFT company. In the SNIFTIRS cell, the substrate for the working electrode was a small bar of Ni (5 mm diameter) embedded in a syringe piston. An Li wire and an Li ring served as reference and counter electrodes, respectively. The electrolyte was 1.5 M  $\text{LiAsF}_6/\text{PC-EC-DME}$  (1:1:3). The optical window was a KBr disc. The Li working electrode was prepared by depositing Li metal on Ni at  $i=0.07 \text{ mA/cm}^2$  during 30 min. The IR beam was p-polarized or s-polarized according to the experiments. All the FT-IR measurements were performed using a BRUKER IFS 66v spectrometer. In the SNIFTIRS program, 128 interferograms were alternatively collected fifty times.

The cell for EMIRS was of the same thin-layer type, except that the working electrode was a disc of Ni glued at the extremity of a syringe piston. The Li electrode was prepared by depositing Li on Ni at  $i=$

$1 \text{ mA/cm}^2$  during 15 min. Spectra were recorded using an HI-TEK EMIRS III spectrometer coupled with a phase-sensitive detector and a signal averager.

## 3. Results and discussion

Fig. 1 shows examples of SNIFTIR spectra obtained with an Li electrode modulated between  $-50$  and  $+50 \text{ mV}$  versus  $\text{Li}^+/\text{Li}$  in the p- and s-IR polarization states, respectively; p- and s-spectra differ by some marked bands around  $840\text{--}975 \text{ cm}^{-1}$ ,  $1060\text{--}1250 \text{ cm}^{-1}$ ,  $1350\text{--}1500 \text{ cm}^{-1}$  and  $1750\text{--}1850 \text{ cm}^{-1}$ . Peaks seen in p-polarized, and not in s-polarized states, correspond to surface species which are formed on or incorporated in the passive layer. Weak bands also appear in the region associated with the C-H stretching modes ( $2800\text{--}3050 \text{ cm}^{-1}$ ). Those bands are rather identical to the bands belonging to the reference spectra of the solvent mixture (i.e. 1.5 M  $\text{LiAsF}_6/\text{PC-EC-DME}$  (1:1:3)). They will not be discussed further. A few bands are seen in the s-spectra and not in the p-spectra (e.g.,  $971 \text{ cm}^{-1}$  or  $1107 \text{ cm}^{-1}$ ). They definitely belong to the solution species.

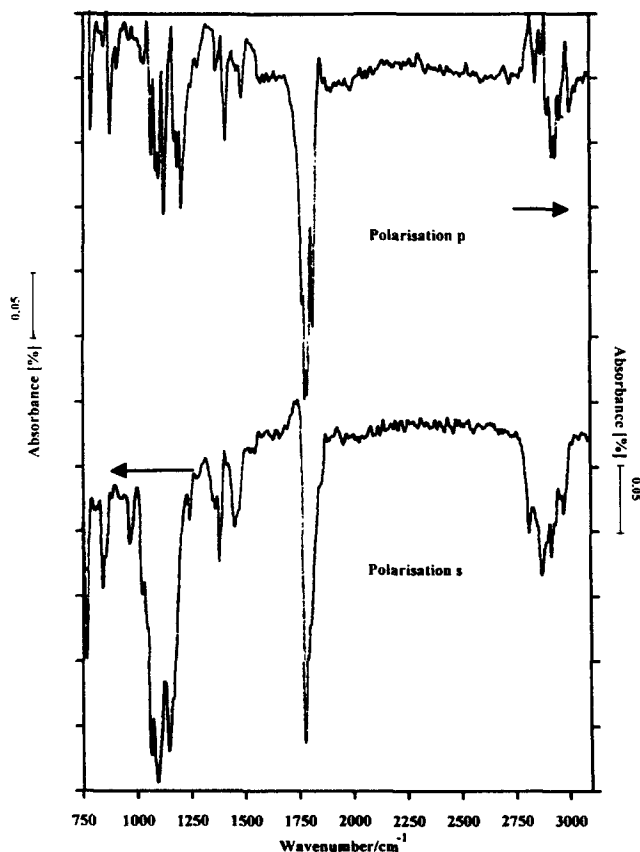


Fig. 1. SNIFTIR spectra of the Li electrode (p- and s-polarisation of the infrared beam, respectively) in  $\text{PC-EC-DME}$  (1:1:3) +  $\text{LiAsF}_6$  electrolyte.

For comparison Fig. 2 shows spectra recorded with a p-polarized light using the EMIRS and SNIFTIRS techniques. Fig. 3 gives two EMIRS spectra obtained with an Li electrode modulated with a square signal within the limits  $-50$  and  $+50$  mV versus  $\text{Li}^+/\text{Li}$  (Fig. 3(a)), or  $-60$  and  $+60$  mV versus  $\text{Li}^+/\text{Li}$  (Fig. 3(b)). With EMIRS, the wavenumber range is limited because of materials, grating and filters restrictions. Within the common range investigated with the two techniques, and owing to the fact that EMIRS bands have derivative like shapes, strong similarities are obvious. However, it is interesting that the relative intensities differ for certain bands but not for others. For instance, the bands near  $1460\text{--}1482\text{ cm}^{-1}$  are much stronger in EMIRS whereas the  $1405\text{ cm}^{-1}$  band is almost the same. Similarly, the  $1819\text{ cm}^{-1}$  band is strongly emphasised in EMIRS while the  $1793\text{ cm}^{-1}$  band is hardly seen. This change in intensities is important as EMIRS is the best technique for distinguishing the surface from the bulk species. As a consequence, the species having bands at  $1460\text{--}1482\text{ cm}^{-1}$  and near  $1820\text{ cm}^{-1}$  can be said to belong unambiguously to the surface passive film.

A complication which arises with the lithium interface is that it reacts with the electrolyte during the time-scale of the spectral acquisition. Thus, in the thin-layer

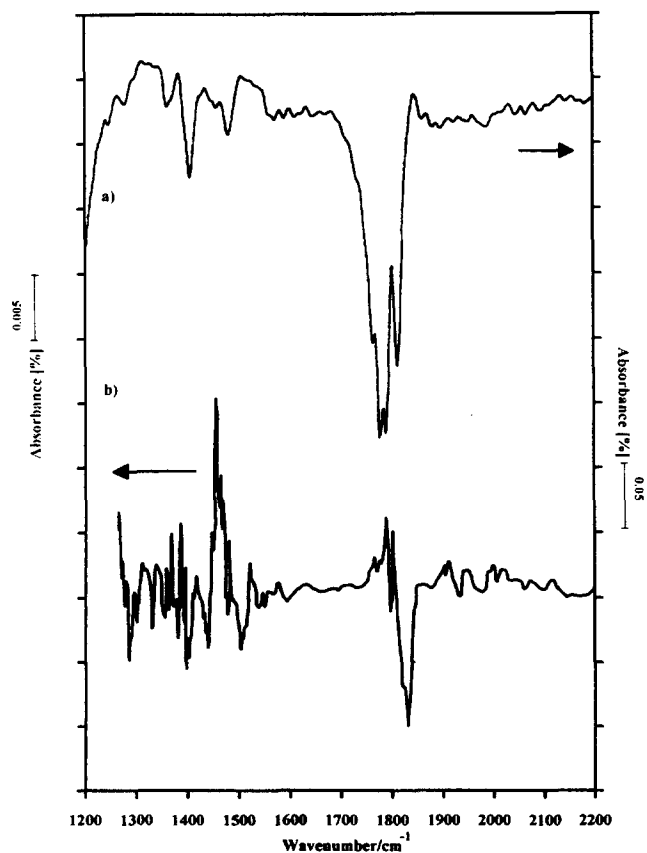


Fig. 2. (a) Spectrum recorded with SNIFTIRS. (b) Spectrum recorded with EMIRS. Same electrolyte as in Fig. 1.

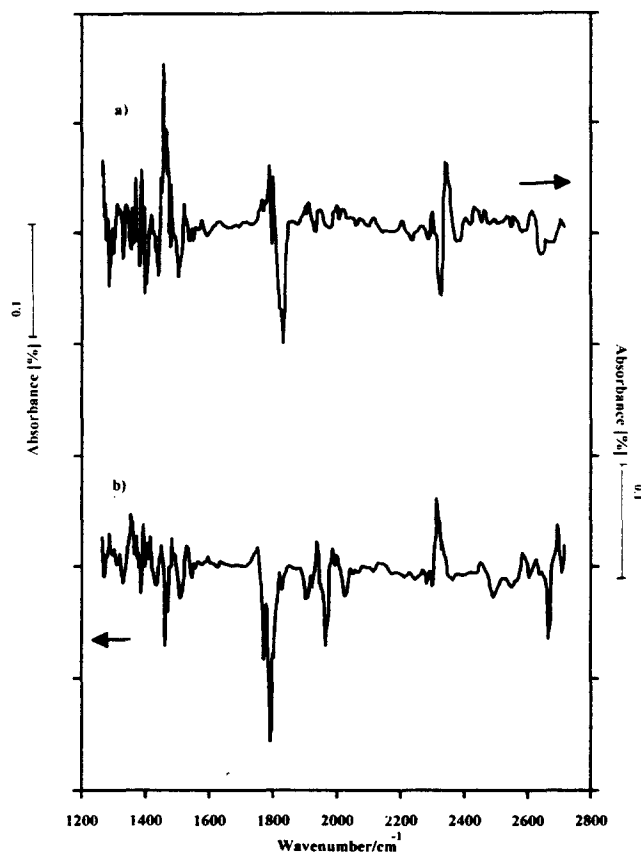


Fig. 3. EMIRS spectrum of Li electrode modulated at  $f=13.5$  Hz between  $-50$  and  $+50$  mV vs.  $\text{Li}^+/\text{Li}$ . (b) EMIRS spectrum of Li electrode modulated at  $f=13.5$  Hz between  $-60$  and  $+60$  mV vs.  $\text{Li}^+/\text{Li}$ . Same electrolyte as in Fig. 1.

configuration, the solution bands, which should be cancelled by spectral subtraction, may actually not be because of thickness variations. So, before any band assignment attempts, it is necessary to point out all bands which may belong to solution species, such as those measured in the  $R$  spectra (Fig. 4).

Table 1 lists all bands and intensities for p- and s-spectra and bulk species. The only bands which occur in p-polarized spectra and not in bulk (or having a much stronger intensity) can be used for non-ambiguous assignments of species belonging to the passive layer (they are underlined with double lines in the Table). Species belonging to s-spectra only can be assigned to reaction products in solution (underlined with simple lines).

### 3.1. Band assignment

From the four normal modes of planar carbonate species noted  $\nu_1$  to  $\nu_4$  [15], three of them fall into the range investigated. With reference to literature, the two bands at  $866\text{ cm}^{-1}$  and  $1061\text{ cm}^{-1}$  can be assigned to the  $\nu_2$  and  $\nu_1$  modes of  $\text{CO}_3^{2-}$ , respectively.  $\nu_1$  should be IR inactive because of its high symmetry, but becomes

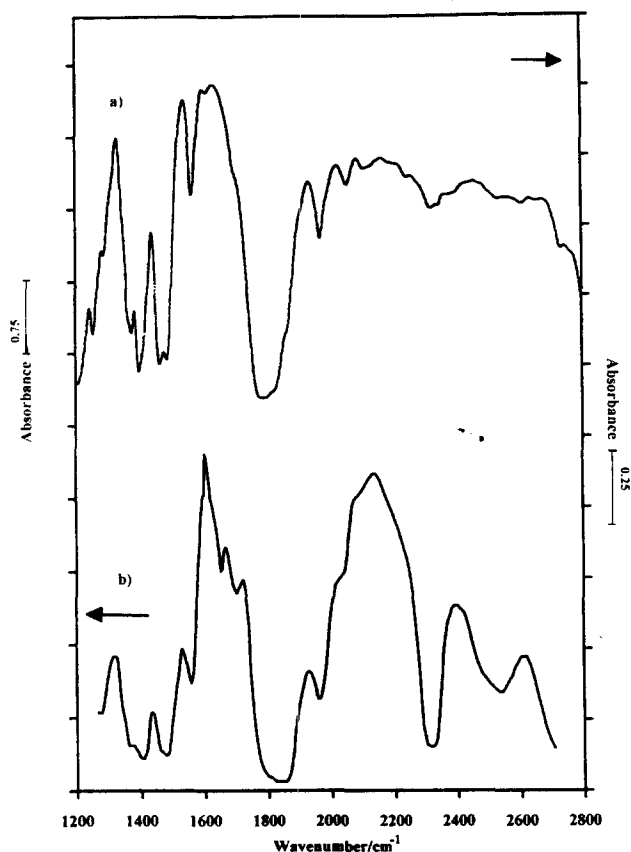


Fig. 4. Reflectivities of the Li surface in PC:EC:DME (1:1:3) + LiAsF<sub>6</sub> electrolyte: (a) *R* measured with SNIFTIRS, and (b) *R* measured with EMIRS.

active in the surface passive layer, as a result of bonding effects. The  $\nu_3$  mode is lowered at  $1406\text{ cm}^{-1}$  and possibly splitted with occurrence of a second component at  $1482\text{ cm}^{-1}$  (superimposed with solution bands) when Li<sub>2</sub>CO<sub>3</sub> precipitates. It is that latter band which is seen by Aurbach and co-workers [5–7].

Numerous bands of the p-spectrum can be related to ROCO<sub>2</sub><sup>-</sup> species, again in agreement with Aurbach et al. [9]: the bands at  $832\text{ cm}^{-1}$  ( $\delta_{\text{as}}\text{ OCOO}^-$ ),  $900\text{ cm}^{-1}$  ( $\delta\text{CH}_2$ ),  $1097$ ,  $1167$  and  $1203\text{ cm}^{-1}$  ( $\nu\text{C-O}$ ),  $1458\text{ cm}^{-1}$  ( $\delta\text{CH}_3$ ),  $1558$  and  $1575\text{ cm}^{-1}$  ( $\nu\text{COO}^-$ ). As no bands are detected in the  $1630\text{--}1650\text{ cm}^{-1}$  or  $1350\text{--}1377\text{ cm}^{-1}$  range (which would be related to  $\nu_{\text{as}}$  and  $\nu_{\text{s}}\text{C=O}$ , respectively) it may indicate that the species are ionised as ROCOO<sup>-</sup> in the superficial layer. It may be also that, if precipitated as ROCOOLi, they cannot be detected by the surface-sensitive spectroscopic technique used in this work.

The EMIRS spectra confirm the importance of Li<sub>2</sub>CO<sub>3</sub> species through the strong derivative band centred at around  $1475\text{ cm}^{-1}$  (extrema at  $1460$  and  $1505\text{ cm}^{-1}$ ), with a companion band at  $1405\text{ cm}^{-1}$ . Strong bands at  $1796$  and  $1820\text{ cm}^{-1}$ , seen both in the p- and s-spectra, have not received any assignment yet. Although the strong solution bands may cause interference in

Table 1  
SNIFTIRS bands, in  $\text{cm}^{-1}$ , and relative intensities for the lithium interface in PC-EC-DME electrolyte

p-Spectrum	S-spectrum	Bulk
781 m	774 m	776 m
<u>832 vw</u>		
<u>866 m</u>	845 m	843 w
<u>900 w</u>	861 w	866 w
<u>953 w</u>		
1027 w	971 w	968 w
<u>1061 m</u>	1030 m	1023 m
1082 m		
<u>1097 m</u>	1079 S	1074 VS
	1107 VS	
1122 S		1118 VS
	1160 S	1159 S
<u>1167 m</u>		
1184 m	1184 S	1188 S
<u>1203 S</u>		
1248 w	1250 vw	1248 m
1277 w	1280 vw	1278 vw
1357 vw	1357 vw	1355 w
1366 vw	1366 w	1366 w
	1391 m	1389 m
<u>1406 m</u>		
1458 vw	1461 w	1456 m
1482 w	1482 w	1480 w
1558 vw	1556 vw	1560 vw
1575 vw		
1769 S		
1781 VS		1778 VS
<u>1796 VS</u>	<u>1793 VS</u>	
		1810 VS
<u>1820 S</u>	1822 m	
	<u>1866 w</u>	
	1966 vw	1963 vw

that region, these bands, if true, could be due to aliphatic peroxides which normally absorb strongly at  $1780\text{--}1800$  and  $1810\text{--}1820\text{ cm}^{-1}$ . This, of course, requires further verification. Similarly, the occurrence of ketals, or acetals, R<sub>2</sub>C(OC)<sub>2</sub> has to be considered.

#### 4. Conclusions

The present results demonstrate the interest of using polarised light for SNIFTIRS and EMIRS measurements of surface films formed on active electrodes in Li-battery solutions. In particular, EMIRS spectra are reported for the first time. We confirm that the species formed in the surface passive layer of Li, in PC-EC-DME electrolyte, are essentially lithium alkyl carbonates (ROCO<sub>2</sub>Li) and lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>).

However, contribution of other species, like peroxides or ketals, could be inferred from polarized spectra as well.

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