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# A FTIR and Raman study of spontaneous reactions occurring at the $\text{LiNi}_y\text{Co}_{(1-y)}\text{O}_2$ electrode/non-aqueous electrolyte interface

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## Abstract

Spontaneous reactions occurring at the surface of  $\text{LiNi}_y\text{Co}_{(1-y)}\text{O}_2$ -based electrodes during contact with non-aqueous organic electrolytes have been investigated by FTIR and Raman spectroscopy. It is found that several types of compounds and/or functional groups are formed on the electrode surface and that these compounds appear to be dependent on the type of electrolyte used. Thus, for a  $\text{LiClO}_4$ -propylene carbonate (PC) electrolyte, the main reaction is formation of Li-carbonate, whereas in the case of  $\text{LiPF}_6$ -ethylene carbonate/dimethyl carbonate (EC/DMC) electrolyte formation of P-, O- and F-containing compounds dominate. Spectroscopic data also show a variation of the  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  crystalline structure during storage in an electrolyte which probably is due to a spontaneous deintercalation of the Li ions. An analysis of the newly formed species is presented and possible reaction mechanisms are discussed. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium polymer battery; Passivating layer; Solid electrolyte interface (SEI); Raman; FTIR

## 1. Introduction

Lithium batteries have a great potential for numerous energy-related applications varying from microbatteries for portable electronics to power sources for electric vehicles [1,2]. To optimise battery performances, such as cycling ability, long life, chemical and physical stability, etc., various electrolyte compositions and electrode materials have been tested. However, along with the improvement of different battery components, one must also take into account the compatibility between the components themselves. It has been found that the electrode–electrolyte interfacial behaviour determines to a large extent, the performance of the whole battery assembly [3].

In late 1960s, Dey and Sullivan [4] proposed that a layer of  $\text{Li}_2\text{CO}_3$  forms on the lithium electrode surface during storage or cycling in non-aqueous organic electrolytes. They also suggested that this layer conducts lithium cations and protects the metal from further chemical reactions [4]. Later, the formation of passivating surface films have been observed by many other researchers for various electrode materials [5–14]. The passivating layer (or, as commonly

named, the solid electrolyte interface, SEI) plays a key role in the electrochemical processes occurring during battery operation. At one hand, SEI prevents the electrode material from the continuous reaction with the electrolyte components thus assuring shelf life, but on the other, it affects the Li intercalation and deintercalation process, thus, decreasing the cycling efficiency of the battery [3]. Therefore, the understanding of the reactions and processes occurring at the electrode–electrolyte interface becomes extremely important for achieving battery optimisation.

The mechanism of SEI formation and the physical and chemical properties of the passivation layers formed at the electrode surface have been the object of intensive study for many different battery systems, carried out with various techniques [3–14]. It is now generally accepted that a SEI may appear just after the contact with an electrolyte, i.e. by a spontaneous chemical reaction, only in the case of alkali and alkali-earth metal electrodes, due to their extremely high reactivity [3,5]; while for all the other commonly used electrode materials, the formation of the passivating layer has always be assumed to be the result of an electrochemical decomposition of the electrolyte components.

It has appeared to us of interest to investigate whether this is effectively the case also for high-voltage electrode materials, such as the  $\text{LiMO}_2$  ( $M = \text{Co}, \text{Ni-Co}$ ) lithium ion positives. In this first work, we report results obtained with

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the family of the  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  cathodes, i.e. the most promising cathodes presently exploited for rechargeable lithium ion batteries [15,16]. The investigation was carried out by storing the  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  samples in different electrolytes (with no applied potential) and then examining by Raman spectroscopy and IR diffuse reflectance techniques the state of their surface.

## 2. Experimental

The  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  electrode membranes were prepared with two different techniques commonly in use in one of our laboratories, i.e. by the “sray” and “doctor blade” methods. In the first case, the membrane samples consisting of polyvinyl chloride (PVC) (binder, 5 w/o), Super P (electronic conductor, 5 w/o) and  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  (active material, 90 w/o), were obtained by thoroughly mixing the three components in tetrahydrofuran and spraying the resulting slurry onto a 10  $\mu\text{m}$  aluminium foil. In the second case, the membrane samples consisted of polyethylene-co-propylene-co-5-methyl-2-norbornene, EPDM (binder, 2 w/o), Super P (electronic conductor, 5 w/o) and  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  (active material, 93 w/o). The polymer powder component was dissolved in toluene and the solution was added to the mixture of the other two components. The so-obtained slurry was carefully mixed and finally spread onto a 10  $\mu\text{m}$  aluminium foil, allowing the solvent to evaporate out at room temperature. Two members of the  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  family have been tested, namely the  $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$  and the  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  compounds.

To investigate the occurrence of spontaneous reactions and layer formation at the electrode membrane surface during its contact with an electrolyte, the following procedure was carried out. The electrode membrane samples were first dried in vacuum ( $10^{-7}$  bar) at 80–90°C for 24 h, and then placed under argon atmosphere in sealed cans containing the selected electrolytes and stored there for length of times varying from 3 to 25 days. Two different, commercially-available, non-aqueous organic electrolytes (both Merck battery grade) have been used in this study, namely, (i) 1 M solution of  $\text{LiPF}_6$  in 1:1 mixture of ethylene carbonate and dimethyl carbonate (EC/DMC) and (ii) 1 M solution of  $\text{LiClO}_4$  in propylene carbonate (PC). After storage, the samples were thoroughly cleaned in the corresponding solvent and dried in vacuum at room temperature ( $10^{-7}$  bar, 24 h). All handling was performed inside a glove box under dry argon gas atmosphere.

The samples were then transferred to the evacuated test compartment of the FTIR spectrometer. The time that the samples were exposed to atmosphere during this transferring operation never exceeded 30 s. To check whether this operation could have lead to any contamination we have carefully controlled the state of the samples' surface, both for the starting and for the electrolyte-treated samples. No changes were detected even after three weeks of exposure.

Infrared measurements were carried out in a diffuse reflectance mode, which allows to register the signal scattered directly by the surface of the sample. The spectra were recorded with a Bruker IFS 66v FTIR-spectrometer equipped with a standard diffuse reflectance unit (Graseby Specac). The spectral resolution was set to  $2\text{ cm}^{-1}$  and all spectra are here reported as average of 100 scans.

The Raman spectra were recorded with a Dilor–Labram monochromator equipped with a Raman confocal microscope (Olympus BX-40), 1800 lines/mm holographic grating and a Peltier cooled CCD detector (spectral resolution is about  $1.5\text{ cm}^{-1}$ ). About 7 mW of the 638 nm line of a He–Ne laser was used as an excitation source. To prevent the contact with the atmosphere during the measurements, the samples were sealed between two optical glasses. Each spectrum presented in this work is an average of at least 10 scans of 5 min each.

## 3. Results

Fig. 1 shows the optical  $100\times$  image (A) of a  $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ -based electrode membrane and the corresponding Raman spectra (B, C and D) recorded before and after storage in the organic electrolytes. Fig. 1A reveals that on the surface of the sample one can clearly visualise two regions: a bright and dark one. Fig. 1B shows that the Raman spectra taken from these regions are essentially different and can be readily recognised as related to the  $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$  crystal (bright region) [17] and to the disordered carbon compound (dark region) [18]. It may also be seen that the shape of the  $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$  characteristic band in the region  $300\text{--}600\text{ cm}^{-1}$  slightly varies passing from spot to spot on the sample surface (see inset in Fig. 1B). Such a variation may be due to minor differences in the crystal lattice parameters of this polycrystalline material [17,19,20]. Finally, Fig. 1B and C demonstrate that the spectra of the samples stored in electrolytes are remarkably different from that of the pristine samples. Indeed, the spectral profiles are essentially changed, although in some cases, the spectral features remain unaltered. It should be stressed that the variation of the Raman spectra is absolutely random. In fact, we could not rule out any ordered behaviour even after 100 experimental spectra, run on 7–8 different spots of 14 different samples stored in different electrolytes for different lengths of time. An essential change of the spectrum could be observed after 3 days of storage, while unchanged spectral bandshapes were found in the samples stored for 15 days. Such a situation suggests that the processes responsible for the alteration of the crystal structure are rather spontaneous and are not directly dependent on the storage time or on the type of the storing electrolyte.

In addition, from Fig. 1, there are no signs of the formation of new compounds on the sample surface. However, the thickness of surface layers is expected to be quite small, i.e. of the order of 10–25 Å while the probe dimension in this

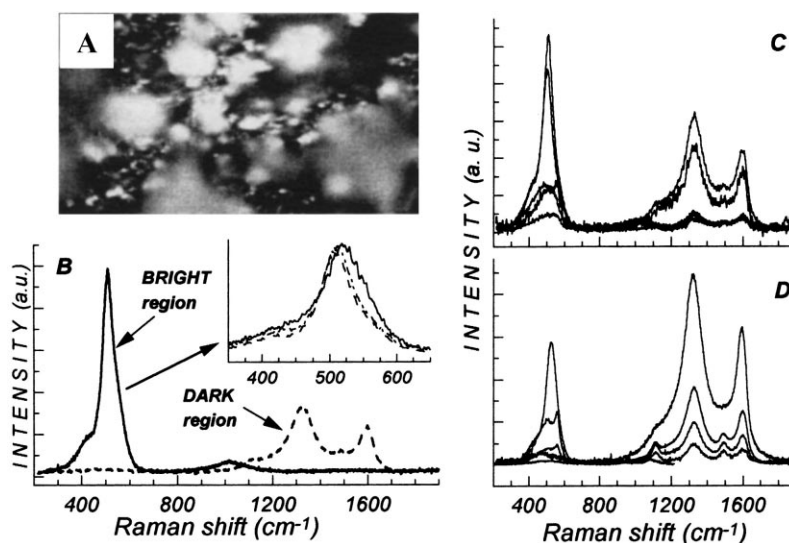


Fig. 1. Optical image (A) and Raman spectra (B, C, D) of  $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ -based electrode: B — initial (before storage); C, D — after 7–15 days of storage in different electrolytes.

micro-Raman experiments is of the order of several micrometers (both in diameter and depth). Under such conditions, the Raman technique is rather not enough insensitive to detect changes at the sample surface. In this respect, a more efficient technique for surface layer characterisation appears to be the diffuse reflectance. Fig. 2 compares IR diffuse reflectance spectra of the samples before and after storage in electrolytes. Indeed, significant spectral transformations are here clearly resolved (see also Table 1 which lists the exact frequency position of the observed IR bands). The spectrum of the initial sample reveals the strong broad band centred at  $615\text{ cm}^{-1}$ , which is assigned to the  $\text{MO}_6$  vibration in the  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  crystals [21,22]. There are also two minor features around  $870$  and  $1410\text{ cm}^{-1}$ , corresponding to the  $\nu_2$

and  $\nu_3$  vibrations of  $\text{CO}_3^-$  anions, respectively [23–25], which can be residual traces of the  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  synthesis materials [16]. The spectra of the samples stored in electrolyte clearly reveal new bands, which growth in intensity with time (compare the spectra marked as “7 days” and “25 days”). These new spectral features are different for samples stored in different electrolytes, suggesting that the new compounds or/and functional groups formed on the electrode surface depend on the electrolyte composition. In addition, in the spectra of the electrolyte-stored samples, we also observe the appearance of a high-frequency shoulder near the band of the  $\text{MO}_6$  vibration at  $615\text{ cm}^{-1}$  that, in accordance with [21], may be explained as a variation of the crystalline structure of the material. Such a spectral

Table 1  
Infrared spectra of the  $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ -based samples stored in electrolyte

Frequency position ( $\text{cm}^{-1}$ )		Proposed assignment <sup>a</sup>
LiPF <sub>6</sub> -EC/DMC	LiClO <sub>4</sub> -PC	
615	615	$\text{MO}_6$ vibrations of $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$
700 sh	700 sh	Changes in lattice parameters of $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$
	870	$\nu_2(\text{A}')$ of $\text{Li}_2\text{CO}_3$ (out-of-plane deformation)
890		$\nu(\text{P-O})$ , $\nu(\text{P-F})$
930		$\nu(\text{P-O})$ , $\nu(\text{P-F})$
	1112 sh	$\nu(\text{Cl-O})$
	1155	$\nu(\text{O-C-O})$ of PC
1173		$\text{Li}_x\text{PO}_3\text{F}_z$ , LiF
1285		$\text{Li}_x\text{PO}_3\text{F}_z$ , LiF
1408		$\nu_3(\text{E}')$ of $\text{Li}_2\text{CO}_3$ (asymmetric stretch)
	1435	TO ( $\nu_3(\text{E}')$ of $\text{Li}_2\text{CO}_3$ )
	1516	LO ( $\nu_3(\text{E}')$ of $\text{Li}_2\text{CO}_3$ )
	1637	$\text{ROCO}_2\text{Li}$
1770		$\nu(\text{C=O})$ of solvents

<sup>a</sup> On the basis of [6,8,10–12,17,21–26]; sh: shoulder.

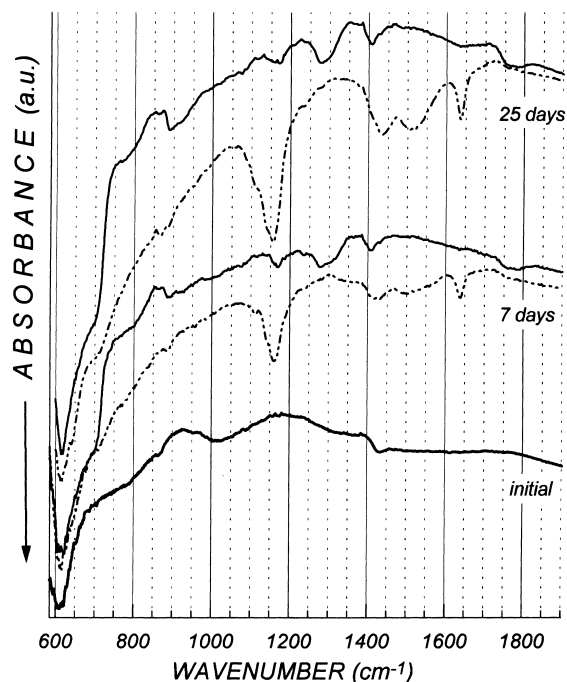


Fig. 2. FTIR diffuse reflectance spectra of  $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ -based electrode before and after storage in electrolyte: (—) 1 M  $\text{LiPF}_6$ -EC/DMC; (— · —) 1 M  $\text{LiClO}_4$ -PC.

behaviour is similar to that observed in Raman experiments where the initial structure of the  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  crystal was altered after storage in electrolyte.

#### 4. Discussion

The above discussed spectroscopic data clearly suggest the occurrence of two simultaneous processes during the storage of a  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$ -based electrode in a non-aqueous organic electrolyte, i.e. (i) the formation of new compounds and/or functional groups on the electrode surface, and (ii) the change of the lattice parameters of  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$ , e.g.  $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$  crystal. The possible mechanisms of these two processes are discussed on the basis of the results presented in this work.

The spectra of Fig. 2 and the band assignments given in Table 1 show that several new species can be detected on the electrode surface after storage in electrolyte. At first, one can assume that there are in all cases evidences of a Li-carbonate (or, more exactly, of  $\text{CO}_3^-$  anions) formation. The entity of this carbonate compound, present in small amount in the pristine samples, slightly increases when these are stored in the  $\text{LiPF}_6$ -EC/DMC electrolyte, thus showing that the formation process is quite slow in this case. In contrast, the spectra of the samples stored in the  $\text{LiClO}_4$ -PC electrolyte solution, instead of appearing as a weak single peak at  $1430\text{ cm}^{-1}$ , show a pronounced double-maxima band in the  $1400\text{--}1600\text{ cm}^{-1}$  region. Such an evolution of the spectral profile is quite typical and corresponds to the

splitting of longitude and transverse optical modes (LO and TO, respectively) of the degenerate  $\nu_3(E')$  vibration of the  $\text{CO}_3^-$  anion [23–25]. The appearance of this LO–TO splitting in the IR spectra may only be caused by the strong crystalline field [23,25] that, in turn, unambiguously signals the formation on the sample surface of a bulky polycrystalline layer of the carbonate compound.

Along with the Li-carbonate formation, we also observe the evidences of other compounds and/or functional groups, which are significantly different for samples stored in different electrolytes. In the case of samples stored in the  $\text{LiPF}_6$ -EC/DMC electrolyte solution, the new spectral features are close to those of compounds containing P–O, P–F and Li–F groups, e.g.  $\text{Li}_x\text{PO}_y\text{F}_z$  and LiF. At the same time, the electrodes stored in the  $\text{LiClO}_4$ -PC electrolyte solution show features characteristic of the Cl–O and  $\text{ROCO}_2$  containing species.

Furthermore, for both electrolytes the bands characteristic for fragments of solvent molecules are observed. In the case of  $\text{LiPF}_6$ -EC/DMC-treated samples, the IR spectra contain a band at about  $1770\text{ cm}^{-1}$ , corresponding to the stretching vibrations of the carbonyl groups in EC, PC, and DMC solvents. The spectra of the  $\text{LiClO}_4$ -PC-treated electrodes do not show this band, but rather a very strong peak at  $1155\text{ cm}^{-1}$ , characteristic for the O–C–O stretching vibration of PC ring [26].

It is instructive to note that the observed differences in the composition of the surface layers correlate well with previously published data. The reactivity of different salts and solvents toward lithium metal has thoroughly been investigated by different techniques [6,8–13] and the composition of SEI was reported to accordingly vary from system to system. In particular, Zaban and Aurbah [8] reported that despite practically all salts used in typical electrolytes form  $\text{ROCO}_2\text{Li}$  as a primary product of the electrode–electrolyte reaction, in the case of the of LiBr,  $\text{LiAsF}_6$  and  $\text{LiClO}_4$ , respectively, based solutions, the final product is lithium carbonate whereas for the solutions using  $\text{LiPF}_6$ ,  $\text{LiBF}_4$  and  $\text{LiSO}_3\text{CF}_3$  salts, this is a  $\text{Li}_x\text{PO}_y\text{F}_z$ -type compound. The same authors stressed that these processes are possible only in the presence of a “constant driving force”, such as metallic lithium. In the absence of such force, e.g. in the case of a Ni electrode, the initial unstable  $\text{ROCO}_2\text{Li}$  compounds will rapidly dissolve, thus leaving the state of the electrode surface practically unchanged [8]. Kanamura et al. [9], studying by X-ray photoelectron spectroscopy (XPS) the electrochemical behaviour of the lithium electrode in various salt in PC solutions, have also demonstrated the dependence of the SEI content on the type of the salt. Accordingly, these authors found that in the case of the use of  $\text{LiClO}_4$ , the main compounds formed on the electrode surface were Li-carbonate and LiOH, whereas when  $\text{LiPF}_6$  salt is used, a dense layer of LiF and P-containing compounds was formed. In addition, variations in the SEI composition may also be caused by different solvents. For instance, while EC and PC molecules have rather similar properties,

their action in affecting electrode–electrolyte interfacial processes appears to be quite different [11]. However, this latter aspect was not considered in the present work and it will be to object of future investigations.

In summary, it appears from the comparison from experimental results and the literature data that the  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$ -based electrodes behave similarly to the lithium metal electrode when in contact with organic electrolytes. However, this is somewhat intriguing since “injection” of free electrons in the electrolyte is required to initiate effective chemical reactions on the electrode surface. The various mechanisms of electrolyte decomposition processes have been widely discussed in [10,11] and it is generally assumed that these processes demand one or two electrons per each solvent molecule or salt anion. In the absence of applied potential, i.e. under open circuit conditions, this requirement is apparently fulfilled in the case of very active alkali or alkali-earth metal electrodes. Indeed, if the electrode material does not provide free electrons (e.g. in the case of Ni metal or carbon), no decomposition reactions occur [7,8]. From the above considerations, one has to conclude that if  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  type electrode materials are active towards electrolyte decomposition, they must provide a sufficient amount of free electrons. This conclusion is confirmed by the Raman results reported in this work. One may first point out that in both Raman and IR spectra of the samples stored in electrolyte, a variation of the spectral profiles characteristic for the  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  crystal vibrations is observed. Similar spectral transformations have been previously observed by other researchers [17,21] and the intensity redistribution and frequency shift of the Raman bands in the region  $400\text{--}600\text{ cm}^{-1}$  have been associated to the specific behaviour of the  $\text{Li}_x\text{Ni}_{(1-y)}\text{Co}_y\text{O}_2$  crystal during the variation of the “ $x$ ” parameter [17]. Similarly, an appearance of the high-frequency component in the band of  $\text{MO}_6$  vibration in the IR spectra (around  $600\text{ cm}^{-1}$ ) has been observed along with an alteration of the Ni/Co content [21]. In general, such a transformation of the band profiles in the vibrational spectra is usually attributed to the change of the interatomic distances [17,21], e.g. caused by compositional variation. This is also confirmed by recent results of X-ray diffraction and absorption studies [19,20,27] showing that the  $a$  and  $c$  parameters of the hexagonal structure of  $\text{Li}_x\text{Ni}_{(1-y)}\text{Co}_y\text{O}_2$  crystal change with both lithium content and Ni:Co ratio. Therefore, we can conclude that the spectral evolution of the stored  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  electrodes observed in this work can be explained by assuming either a change of Li content or/and a variation of the Ni:Co ratio during storage in the electrolyte. The second effect, however, is hardly probable since  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  materials have a high chemical stability. In addition, considering the degree of lithiation, a spontaneous intercalation of Li ions into the  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  crystal structure is also doubtful. Consequently, we assign the observed variation of this structure to a decrease of the lithium content, or in the other words, to a spontaneous lithium deintercalation reaction. This model

supports the proposed electrolyte decomposition, where an efficient “injection” of free electrons from the electrode is needed. Indeed, under no applied potential, these free electrons may only be provided by the assumed spontaneous deintercalation of Li ions from the cathode material.

## 5. Conclusion

The results here reported suggest that the  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$ -based electrode in contact with non-aqueous organic electrolyte solution undergoes an active behaviour which results in the formation of a surface layer. The content of this layer depends significantly on the type of the electrolyte which is placed in contact with the electrode. For  $\text{LiClO}_4\text{--PC}$ -based electrolyte solutions, the main electrode–electrolyte reaction results in the formation of surface Li-carbonate compounds, whereas in the case of  $\text{LiPF}_6\text{--EC/DMC}$  electrolyte solutions, the formation of P-, O- and F-containing compounds predominates. Such type of behaviour, which is similar to that generally found as characteristic of lithium metal electrode, has been rationalised as being caused by lithium deintercalation from the  $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$  crystal.

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