

# Reactivity of lithium battery electrode materials toward non-aqueous electrolytes: spontaneous reactions at the electrode–electrolyte interface investigated by FTIR

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## Abstract

Spontaneous reactions occurring at the surface of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  and  $\text{LiMn}_2\text{O}_4$ -based electrodes during the storage in organic non-aqueous electrolytes have been investigated by diffuse reflectance FTIR technique. It is found that both materials spontaneously form different inorganic and organic compounds on their surface when in contact with electrolyte solutions. The nature of these self-acting reactions is moreover found to be similar to that of the processes occurring during electrochemical cycling of the electrodes. Reaction mechanisms and the final products depend on both electrode surface chemistry and the nature of electrolyte used. It appears that the spontaneous reactions are initiated by lithium deintercalation from the electrode active material. The influence of different factors, e.g. degree of lithiation of the active material, roughness of the electrode surface and temperature on the reaction rate is discussed. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Interfacial reactions; Infrared spectroscopy; Lithium batteries; Insertion cathodes

## 1. Introduction

The existence of chemical reactions at the electrode–electrolyte interface in lithium batteries (LB), leading to decomposition of electrolyte components is known since late 1960s [1]. Later, it was suggested that the products of these reactions create a film on the surface of lithium metal [2] and graphite [3] electrodes. This surface film, often called a “passivating layer” or a “solid electrolyte interphase” (SEI), was found to play an important role in the electrochemical processes occurring during LB cycling and has, therefore, attracted great scientific interest. Since pioneering work [2,3], the mechanisms of formation, the composition and the different characteristics of passivating layer were intensively studied by various techniques, and the amount of relevant publications is continuously growing [4–16].

The SEI formation is usually believed to take place only at the negative electrodes, such as metallic lithium or graphite compounds, whereas interfacial effects on the positive

electrodes have rarely been discussed. Only recently [17,18], the formation of passivation film (or even more exactly — appearance of new surface species) has been detected for the positive electrodes based on  $\text{LiNiO}_2$  and  $\text{LiMn}_2\text{O}_4$ . It is also generally accepted that only in the case of alkali-metal electrodes (due to their extremely high reactivity) a SEI may appear just at contact with an electrolyte, without applied potential [4,5]. For all other commonly used electrode materials, formation of the passivating layer is believed to start upon cycling, and no signs of reduction of the electrolyte or electrode material solely due to the contact between them are usually observed. In our recent study [19], however, we found that new compounds and/or functional groups appear on the surface of  $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ -based electrode during storage in non-aqueous organic electrolytes even without an applied potential. Moreover, the type of these new compounds depends on the electrolyte used, and it was, therefore, suggested that the spontaneous reactions at the electrode surface occurs due to decomposition of the electrolyte components caused by chemical reactions between electrode active material and electrolyte.

In this work, we report the results of an extended spectroscopic investigation of the behavior of several typical

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electrode materials in contact with organic non-aqueous electrolytes. Different battery electrodes were stored in various electrolyte solutions over times varying from 2 to 6 weeks and thereafter examined by IR diffuse reflectance spectroscopy. In order to further discuss the mechanisms of the spontaneous surface reactions, the influence of different parameters, such as degree of lithiation of active material, specific surface area, etc. were also investigated.

## 2. Experimental

### 2.1. Materials and samples preparation

The  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  and  $\text{LiMn}_2\text{O}_4$  cathodic material powders were obtained from Merck. The electrodic membranes were prepared using poly(vinylidene fluoride-co-hexafluoropropylene) PVdF-HFP, Solvay or poly(ethylene-co-propylene-co-5-methyl-2-norbornene), EPDM-70, Aldrich as binder and Super P (M.M.M. Carbon Belgium) as carbon. The weight ratio of the components was (93–95) wt.% active material, (3–5) wt.% carbon, 2 wt.% binder.

After dissolving PVdF-HFP in 1-methyl-2-pyrrolidinone (Aldrich) or EPDM in toluene (Carlo Erba), the carbon powder Super P and the active material powder were added, carefully mixing until a viscous dispersion were obtained. This slurry was then cast on an aluminum foil and spread evenly on it using the doctor blade procedure. After a slow solvent evaporation, flexible and mechanically stable membranes were obtained.

Two commercially available non-aqueous 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) (LP30) and (ii) 1 M solution of  $\text{LiClO}_4$  in propylene carbonate (PC) (ZV1005). Both electrolytes were used without further purification.

### 2.2. Sample treatment

The pristine electrode samples were first carefully dried in vacuum at elevated temperature ( $10^{-7}$  bar at 80–90°C, 24 h), then placed in sealed cans with electrolytes and kept there between 15 and 40 days. After storage, the samples were thoroughly cleaned in the corresponding solvent (PC or 1:1 EC/DMC, respectively) with following drying in vacuum at room temperature (24 h,  $10^{-7}$  bar). All handling was performed inside a glove box under dry argon gas atmosphere ( $\text{H}_2\text{O}$  and  $\text{O}_2$  content less than 1 ppm).

In order to examine whether the degree of lithiation of the active material influences the surface layer formation, a chemical delithiation of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  was performed. The initial powder was treated during 2 h (at room temperature) with 1:20 v/v solution of 36% HCl in water. Such treatment has earlier been reported [20] to remove about 70% of the Li ions from the material.

### 2.3. FTIR measurements

All infrared measurements were carried out in a diffuse reflectance (DR) mode since this technique is known to be highly suitable for non-destructive testing of thin surface layers [8,12,19]. The typical probe area in the present DR-FTIR experiments had a diameter of 5–7 mm, and the observed spectrum, therefore, provides an information about the state of sample surface on a macroscopic level. It is also important to stress that no direct mechanical influence on a sample surface (e.g. scraping, mechanical cleaning or pressing with covering windows) was performed during the experimental procedure, thus, warranting that the obtained spectra reflect only the changes due to the reactions at the electrode surface. The spectra were recorded with a Bruker IFS-66v FTIR spectrometer (with vacuumated sample compartment) equipped with a liquid nitrogen cooled MCT detector and a standard diffuse reflectance unit (Graseby Specac). The spectral resolution was set to  $2\text{ cm}^{-1}$  and all spectra were collected as an average of at least 150 scans.

## 3. Results and discussion

The products of spontaneous interfacial reactions observed for different electrode–electrolyte combinations are summarized in Table 1. The detailed description of the infrared spectra along with identification of the surface species appearing upon electrode storage is presented below.

### 3.1. $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -based electrodes

In a recent work [19], we showed that  $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ -based electrodes demonstrate an active behavior in contact with typical battery electrolytes. For completeness, the main results of that study are redrawn in Fig. 1. It is clearly seen that the new bands appearing in the infrared spectra of electrolyte stored samples show a gradual increase with storage time and depends on the electrolyte used. Thus, when the electrodes were stored in the  $\text{LiClO}_4$ -PC solution, new spectral features arise that can be assigned to the lithium carbonate ( $\text{Li}_2\text{CO}_3$ ), different (Cl–O)-containing species and  $\text{ROCO}_2\text{Li}$  compounds, whereas the main reaction products in the case of  $\text{LiPF}_6$ -EC/DMC solution can be ascribed to (P–O)- and (P–F)-containing species as well as  $\text{Li}_x\text{PO}_y\text{F}_z$  compounds and LiF [8,10–13,21]. Such assignment indicates that the dominating type of spontaneous surface reactions is the decomposition of electrolyte components — a situation also observed during electrochemical cycling. We note, however, that the reaction rate of the spontaneous processes is essentially lower than that of electrochemically initiated ones and that the range of final products is smaller. In addition, we find no significant differences in the interfacial behavior of the electrodes with variation of amount of active material (within 90–95 wt.%) and variation of active material composition (Ni:Co ratio

Table 1  
Products of spontaneous interfacial reactions<sup>a</sup>

LiNi <sub>0.8</sub> Co <sub>0.2</sub> O <sub>2</sub> <sup>b</sup>	LiMn <sub>2</sub> O <sub>4</sub> (room temperature)	LiMn <sub>2</sub> O <sub>4</sub> (60°C) <sup>c</sup>
1 M LiPF <sub>6</sub> in EC/DMC (1:1)		
Li <sub>2</sub> CO <sub>3</sub> (separate groups)	–	
P–O and P–F c.c. <sup>d</sup>	P–O and P–F c.c.	Stronger (+) solvent polymerization
Li <sub>x</sub> PO <sub>y</sub> F <sub>z</sub> , LiF	Li <sub>x</sub> PO <sub>y</sub> F <sub>z</sub> (wide variety), LiF	
Solvent fragments	Solvent fragment Polymerized solvent OH groups	Stronger (+) formation of OH species and H <sub>2</sub> O
1 M LiClO <sub>4</sub> in PC		
Li <sub>2</sub> CO <sub>3</sub> (bulk compound)	–	No changes
Cl–O c.c.	Cl–O c.c.	
ROCO <sub>2</sub> Li	–	
PC fragments (O–C–O)	PC fragments (O–C–O) Polymerized solvent	

<sup>a</sup> General assignment performed on the basis of literature reports [8–18,21]. Storage time 25–40 days.

<sup>b</sup> The same compounds have been observed for LiNi<sub>0.75</sub>Co<sub>0.25</sub>O<sub>2</sub> and LiNi<sub>y</sub>Fe<sub>1–y</sub>O<sub>2</sub> (y = 0.7, 0.8, 0.9) based samples.

<sup>c</sup> In comparison with room temperature storage.

<sup>d</sup> c.c.: containing compounds.

0.75:0.25 and 0.8:0.2 in [19] and in the present study, respectively).

It should be stressed that the mechanism of formation of Li carbonate compound on the cathode surface during the storage in LiClO<sub>4</sub>–PC electrolyte is not clearly understood. For a moment, we do not have any consistent explanation for this phenomenon. The observed effect, however, cannot be related to the presence of carbon additive in the composite electrode. At first, no Li<sub>2</sub>CO<sub>3</sub> formation was observed in the case of lithium manganese-based samples (see below),

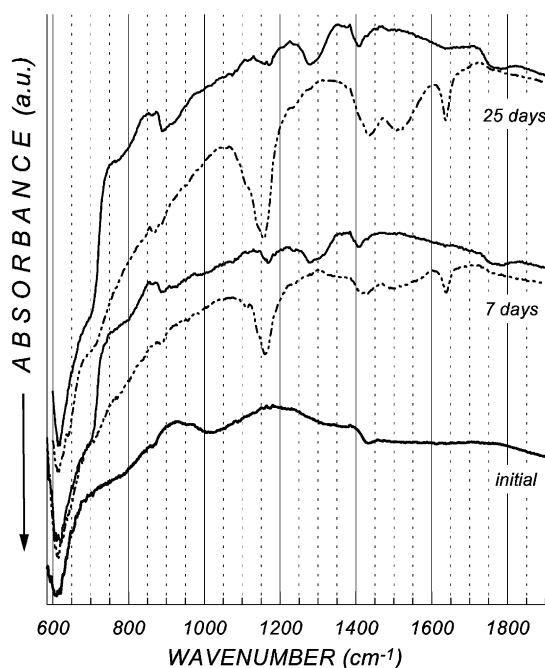


Fig. 1. (Redrawn from [19]) DR–FTIR spectra of LiNi<sub>0.75</sub>Co<sub>0.25</sub>O<sub>2</sub>-based electrode before and after storage in electrolyte: (—) 1 M LiPF<sub>6</sub> in EC/DMC; (---) 1 M LiClO<sub>4</sub> in PC.

although the amount of carbon additive was practically the same. Secondly, and most importantly, under the same storage conditions, no traces of Li carbonate appeared on the surface of membranes consisting of 90 wt.% of carbon (spectra not shown). Therefore, it becomes clear that Li<sub>2</sub>CO<sub>3</sub> is the product of chemical reaction(s) between LiNi<sub>y</sub>C<sub>1–y</sub>O<sub>2</sub> compound and LiClO<sub>4</sub>–PC solution, but the nature of those reactions should be further investigated.

Aside from the surface modification, a variation of LiNi<sub>0.75</sub>Co<sub>0.25</sub>O<sub>2</sub> crystalline structure were also observed in both infrared and Raman spectra [19], in particular, as an appearance of a high-frequency shoulder at 700 cm<sup>–1</sup> near the characteristic band of MO<sub>6</sub> (M = Ni, Co) vibration at 615 cm<sup>–1</sup> (see Fig. 1). Because of this observation, we suggested earlier [19] that, when no electrical potential is applied, the main “driving force” providing free electrons and lithium cations to initiate the interface reactions, is a spontaneous deintercalation of Li ions from the active material.

### 3.2. LiMn<sub>2</sub>O<sub>4</sub>-based electrodes

LiMn<sub>2</sub>O<sub>4</sub> is another insertion compound for positive electrodes in lithium batteries. Its cubic spinel structure contains a crosslinked channels allowing easy 3D diffusion of Li<sup>+</sup> ions [22–24] and reversible lithium deinsertion from the material at potentials about +3 or +4 V versus Li/Li<sup>+</sup>. However, this material has a quite different surface chemistry in comparison with the LiNi<sub>y</sub>Co<sub>1–y</sub>O<sub>2</sub> family and a lower activity toward electrolyte solutions during battery cycling [18]. Fig. 2 shows DR–FTIR spectra of LiMn<sub>2</sub>O<sub>4</sub>-based electrodes after storage in electrolytes. It is seen that, like in the case of LiNi<sub>x</sub>Co<sub>1–x</sub>O<sub>2</sub>-based samples, the amount of surface compounds gradually increases with storage time, and the content of SEI depends on the type of electrolyte. When storing in a LiClO<sub>4</sub>–PC solution the main spectral

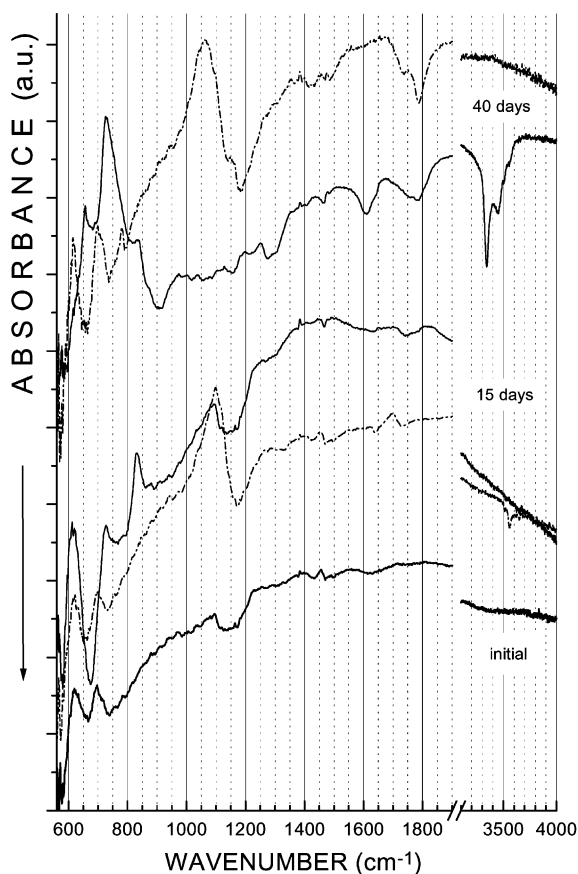


Fig. 2. DR-FTIR spectra of  $\text{LiMn}_2\text{O}_4$ -based electrodes before and after storage in electrolyte: (—) 1 M  $\text{LiPF}_6$  in EC/DMC; (- - -) 1 M  $\text{LiClO}_4$  in PC.

change after 15 days of storage is an appearance of a strong band around  $1160\text{ cm}^{-1}$ , which may be assigned to the fragments of PC molecules ( $\nu_{\text{O-C-O}}$ ) [17]. As storage time increases to 40 days, a new mode around  $1130\text{ cm}^{-1}$ , corresponding to the Cl-O vibrations, appears — this behavior being similar to that observed for  $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$  electrodes (see Fig. 1). However, unlike the latter, the spectra of manganese oxide electrodes show strong bands in the region  $1700\text{--}1850\text{ cm}^{-1}$ , which can be recognized as the signs of polymerized EC solvent [18,25]. It is also interesting to stress that in the case of manganese oxide materials no indications of lithium carbonate formation are present. Indeed, even after 40 days of storage, the DR-FTIR spectra do not show the characteristic  $\text{Li}_2\text{CO}_3$  bands at  $870$  and  $1400\text{--}1600\text{ cm}^{-1}$  (compare with the corresponding spectra in Fig. 1).

When storing in a  $\text{LiPF}_6$ -EC/DMC electrolyte, we note a gradual growth of the spectral bands centered at  $905$  (P-O)- and (P-F)-containing compounds), and  $1150$  and  $1285\text{ cm}^{-1}$  ( $\text{Li}_x\text{PO}_y\text{F}_z$  and LiF). At longer storage time, two other features appear in the spectrum around  $1610$  and  $1780\text{ cm}^{-1}$ . These bands may be attributed to the vibrations of carbonyl groups in the fragmented and polymerized solvent molecules, respectively [17,25]. However, the most

crucial difference between the present case and all considered above, is the appearance of the new spectral bands in the frequency region  $3300\text{--}3500\text{ cm}^{-1}$ . The sharp peak at about  $3320\text{ cm}^{-1}$  has been previously assigned to the crystalline  $\text{LiPF}_6$  compound [18], whereas the mode at  $3450\text{ cm}^{-1}$  may be tentatively ascribed to the OH stretching vibrations. The origin of the hydroxyl groups may be twofold. At first, these species may appear due to residual water, which is always present in electrolyte solutions, causing a hydration of the passivation layer [8,18]. Another way is the H  $\rightarrow$  Li substitution in the  $\text{LiMn}_2\text{O}_4$  due to for example acid delithiation [26], that leads to the formation of stable  $\text{Mn}_2\text{OH}$  groups in the manganese oxide structure. We stress however, that in the present case the latter mechanism is quite doubtful (see below).

The behavior of  $\text{LiMn}_2\text{O}_4$ -based electrodes toward electrolytes dramatically changes when storage is performed at elevated temperature ( $60^\circ\text{C}$ ). It is seen from Fig. 3 that while in the case of  $\text{LiClO}_4$ -PC electrolyte the surface modification shows practically no dependence on temperature (compare corresponding plots in Figs. 2 and 3), the samples kept in  $\text{LiPF}_6$ -EC/DMC behave very different. First of all, the surface of these electrodes was completely covered by a crumbly white shell, which never appeared in all other cases. This shell demonstrated extremely high infrared absorbance, such that it was impossible to record directly DR-FTIR

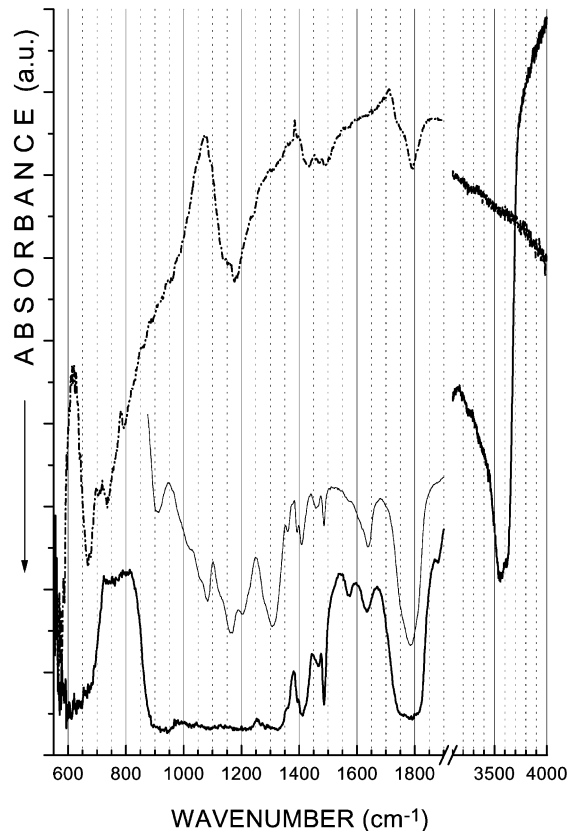
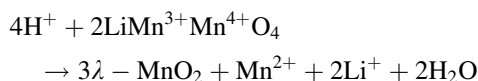


Fig. 3. DR-FTIR spectra of  $\text{LiMn}_2\text{O}_4$ -based electrodes stored 40 days in electrolyte at  $60^\circ\text{C}$ : (—) 1 M  $\text{LiPF}_6$  in EC/DMC; (- - -) 1 M  $\text{LiClO}_4$  in PC.

spectra in the region 800–1900  $\text{cm}^{-1}$ . Therefore, it was necessary to scrape of some material from the sample surface (thin line in Fig. 5). It is seen from the spectrum that this scraping contains a large number of different compounds varying from inorganic kinds ((P–O)-, (P–F)-containing species, LiF and  $\text{Li}_x\text{PO}_y\text{F}_z$ ; 900–1300  $\text{cm}^{-1}$ ) to the polymerized solvents (typical band at about 1800  $\text{cm}^{-1}$ ). In addition, this covering shell contains essential amount of OH groups and possibly water molecules (3450–3700  $\text{cm}^{-1}$ ). We note here that although the shell material practically does not contain manganese oxide, the characteristic features of the OH species are very strong. Therefore, we assume that hydroxyl groups originate from the hydration effects rather than from proton-to-lithium substitution in the crystal structure.

The observed effect of the strong material deterioration can be explained as an acid-induced decomposition of the spinel structure [27,28] in accordance with general formula



caused by the formation in electrolyte solution of HF acid due to reaction between  $\text{LiPF}_6$  salt and contaminant water [8]



It has been also noted in literature [24] that spinel decomposition reaction is greatly accelerated with increasing temperature. In addition, this mechanism explains an increasing amount of water in the reaction products.

### 3.3. Nature and mechanisms of spontaneous reactions: a general consideration

On the basis of all above mentioned, it is reasonable to assume that while the products of spontaneous interfacial reactions depend on the type of electrolyte used, the rate of these reactions will be mostly determined by two factors:

1. The degree of lithiation of the active material.
2. The specific contact area between electrolyte and electrode, or in other words, the roughness of the electrode surface.

In order to check the first statement, a chemically delithiated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  compound was prepared (by treating of initial powder during 2 h in 1:20 v/v solution of 36% HCl in water) resulting in approximately  $\text{Li}_{0.3}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ . Fig. 4 compares the infrared spectra obtained from lithiated and delithiated samples treated under the same conditions, and it is seen that delithiation seriously decreases the reaction rate. Thus, for the delithiated samples stored in  $\text{LiClO}_4$ -PC solution the only observed surface reaction is the formation of Li-carbonate layer (1400–1550  $\text{cm}^{-1}$ ), and no other evidences of electrolyte decomposition can be detected. In the case of  $\text{LiPF}_6$ -EC/DMC electrolyte, all

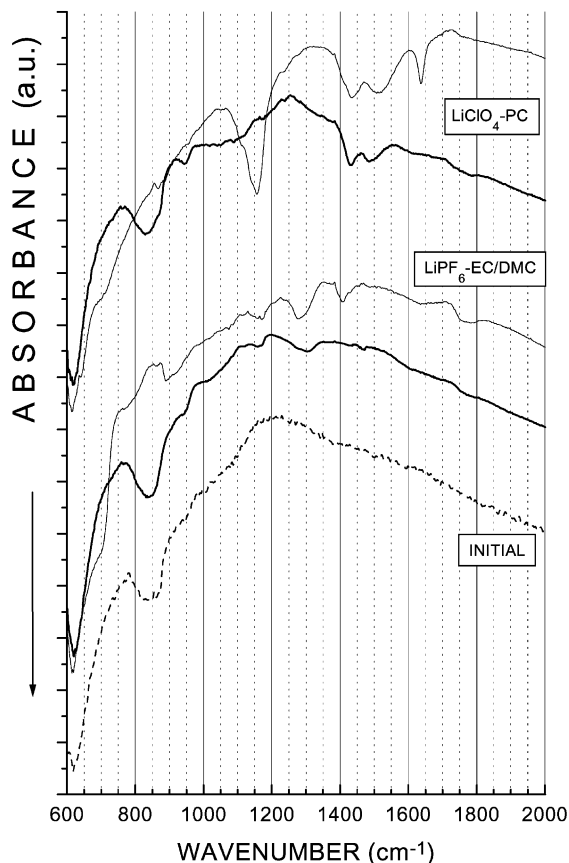


Fig. 4. Comparison of infrared spectra of lithiated  $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ -based electrode (thin line) and acid delithiated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder (thick line) after storage during 25 days in electrolyte. Bottommost spectrum — delithiated powder before storage.

processes are also slowed down, and although the new spectral features are the same to those observed for lithiated sample, their intensity is significantly lower. Such a behavior confirms the supposition that one cause to spontaneous surface reactions is the deintercalation of lithium ions from the electrode.

To investigate the influence of the electrode surface roughness on the reaction rate, two  $\text{LiMn}_2\text{O}_4$ -based cathodes with similar composition but different grain size of the active material were prepared. One sample was made using  $\text{LiMn}_2\text{O}_4$  powder as received from Merck (surface area determined by Brunauer–Emmett–Teller (BET) method to 3  $\text{m}^2/\text{g}$ ). Another sample was made with ball-milled manganese oxide powder (final BET area, 4.5  $\text{m}^2/\text{g}$ ), thus, providing a less rough external surface of the electrode. Both samples were stored in  $\text{LiPF}_6$ -EC/DMC electrolyte under equivalent conditions and then examined by DR-FTIR technique (Fig. 5). It is clearly seen that intensity of the new spectral bands is lower for the electrode with a smooth surface. At the same time, the type of new surface species is practically the same in both cases proving that the variation of specific surface area does not change the general mechanisms of spontaneous reactions.

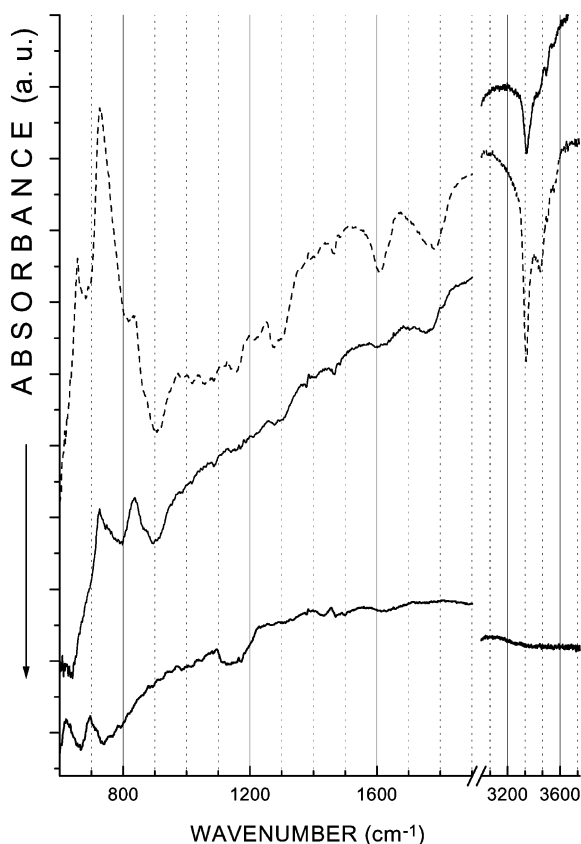


Fig. 5. DR-FTIR spectra of LiMn<sub>2</sub>O<sub>4</sub>-based electrodes with different grain size stored 40 days in 1 M LiPF<sub>6</sub> in EC/DMC. Specific surface area (BET) is 3 m<sup>2</sup>/g (dashed line) and 4.5 m<sup>2</sup>/g (solid line), respectively.

It should be clarified here that seeming inconsistency between the increase of active material surface area after ball-milling and experimentally observed decrease in the electrode activity toward an electrolyte is explained as following. As it was noted above, the DR-FTIR is a surface sensitive technique, i.e. provides information about a thin layer of the sample only. Therefore, obtained spectra depend on the state of the external surface of the sample, which becomes smaller after ball-milling, and do not reflect a general increase of the electrode activity (“bulk” process) due to increase of total surface area of the active material.

### 3.4. Structure of the surface film: SEI and PEI

Along with the question about the composition of the surface layer, a knowledge of its structure is also important. Up to now, there are two models of passivation film proposed in literature. The first one is the “solid electrolyte interphase” (SEI), which is believed to have a simple chemical composition consisting mostly of inorganic compounds [5]. The second model is the “polymer electrolyte interphase” (PEI) appearing as a result of polymerization of organic solvent molecules. Usually this type of surface layer is described [7] as a porous polymeric membrane swollen with a liquid electrolyte. Both models have experimental

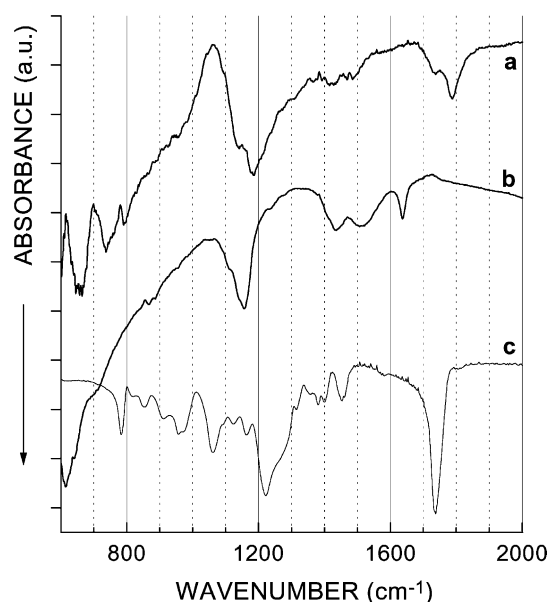


Fig. 6. Comparison of FTIR spectra of the samples stored in LiClO<sub>4</sub>-PC electrolyte and of the solid poly-PC (commercial): a — LiMn<sub>2</sub>O<sub>4</sub>-based; b — LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub>-based; c — PPC. Spectra a and b were recorded by DR-FTIR, whereas spectrum c was obtained by attenuated total reflectance (ATR) technique.

confirmations, and the real passivation film should probably be considered as a combination of these two types [11,13]. We note, however, that unlike the situation emerging at electrochemical cycling, the products of spontaneous surface reactions may be somewhat different.

Fig. 6 compares the infrared spectra of the surfaces of different electrodes stored in PC-based electrolyte with the spectrum of solid poly(propylene carbonate) (PPC), and it is immediately seen that the curves are quite different. Thus, for example, the surface of LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub>-based sample shows no evidences of polymerized solvent [25] — carbonyl stretches at about 1750 cm<sup>-1</sup> — whereas this band is quite strong in the PPC. The spectrum of the manganese oxide-based electrode, however, shows traces of PPC: although less intensive bands of polymerized solvent are not observed in the spectrum of the sample, the features corresponding to the strongest PPC modes (1200–1300 and 1720–1780 cm<sup>-1</sup>) are quite intense. Such behavior is in line with the different electrochemical activity of LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub> toward electrolyte solution, as reported in literature [18].

Considering instead, the samples stored in LiPF<sub>6</sub>-EC/DMC, a polymerization of solvents can be assumed for both types of investigated materials. The surface of LiMn<sub>2</sub>O<sub>4</sub>-based electrode contains clear evidences of solvent polymerization, such as carbonyl group vibration in the region 1700–1800 cm<sup>-1</sup> (see Fig. 2) and, moreover, the intensity of this band becomes essentially stronger when the sample is stored at elevated temperature (Fig. 3). In the case of a LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub>-based electrode (uppermost curve in Fig. 1) the corresponding spectral features are much lower, although weak traces in the region 1730–1800 cm<sup>-1</sup> may

be seen. In addition, the spectral band between 1250–1330  $\text{cm}^{-1}$  which we previously assigned to the  $\text{Li}_x\text{PO}_3\text{F}_z$  and  $\text{LiF}$  compounds may contain the contribution from the polymerized EC molecules as well. Thus, it becomes evident that in some cases spontaneous reactions lead to the polymerization of the solvent on the electrode surface.

### 3.5. Effect of the initial lithium carbonate layer

It has been reported in literature (see, for example [18]) that the surface of pristine  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  and  $\text{LiMn}_2\text{O}_4$  materials is often covered by a thick layer of  $\text{Li}_2\text{CO}_3$ . The origin of this compound in the initial powder is still controversial, but it is generally accepted that it may appear as a result of material synthesis or due to the continuous contact of lithiated oxides with the atmosphere. In all our experiments, the surface of the tested electrodes were however free from lithium carbonate: the  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ -based samples were cleaned before use, while the  $\text{LiMn}_2\text{O}_4$  material did not contain  $\text{Li}_2\text{CO}_3$  initially. Nevertheless, the properties and behavior of lithium carbonate in contact with organic electrolytes seem to be quite important since this compound frequently forms on the electrode surface during battery cycling.

Fig. 7 shows DR–FTIR spectra of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -based electrodes stored in different electrolytes without pre-cleaning, such that the surface of the initial sample is covered by a layer of polycrystalline lithium carbonate (characteristic peaks at 870 and 1420–1500  $\text{cm}^{-1}$ ). In this case the first step of the interfacial reactions will obviously be an interaction between electrolyte solution and  $\text{Li}_2\text{CO}_3$ . Likewise, all electrode–electrolyte reactions discussed above, this reaction appears to be dependent on electrolyte used. Thus, in the case of  $\text{LiClO}_4$ –PC solution the amount of  $\text{Li}_2\text{CO}_3$  on the electrode surface visibly increases with time and, in addition, the weak traces of electrolyte decomposition

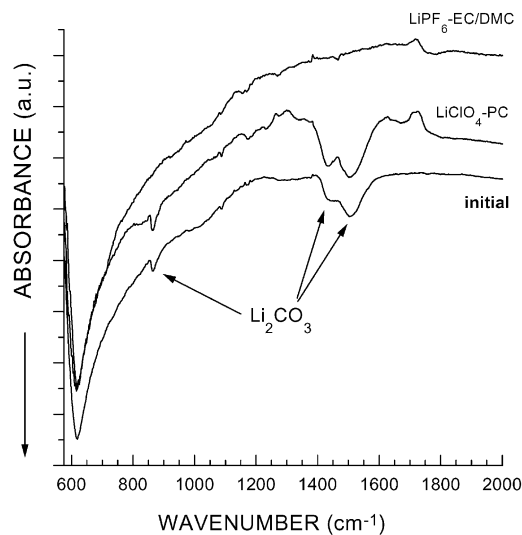


Fig. 7. DR–FTIR spectra of untreated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -based electrode before and after 25 days storage in different electrolytes (as indicated).

appears (around 1200–1300 and 1650  $\text{cm}^{-1}$ ). In contrast, after 25 days of storage in  $\text{LiPF}_6$ –EC/DMC, the surface of the sample shows no longer any signs of lithium carbonate, nor the presence of any other surface compound, demonstrating that the dominating interface process is a dissolution of  $\text{Li}_2\text{CO}_3$  by the electrolyte. The degradation of  $\text{Li}_2\text{CO}_3$  layer during the storage in electrolytes based on different  $\text{Li}[\text{PF}_6, \text{AsF}_6, \text{BF}_4]$  salts, has also been observed by other researchers [18]. The most likely mechanism is, therefore, a formation of HF in the electrolyte solution (see above).

Thus, it appears that, despite the fact that the presence of lithium carbonate layer on the surface of pristine active material is a drawback for the battery performance, it might play a positive role in the case of long-term storage inhibiting other electrode–electrolyte reactions. Indeed, if we compare the spectra of all our samples after 25 days of contact with electrolytes, it is immediately seen that the surface of the initially  $\text{Li}_2\text{CO}_3$ -covered electrodes (Fig. 7) is now clean, whereas initially “clean” materials (Fig. 1) contain more new surface species of both organic and inorganic origin.

It is also important to stress that the observed effect of surface layer dissolution (i.e. disappearance of one compound without formation of another one) suggests that the products of this reaction remain in the electrolyte. Indeed, in a recent study [29], a gas chromatography analysis of the electrolyte solutions after they were used for electrode cycling has been performed. It has been found that these “used” electrolytes contain a wide variety of organic and inorganic compounds not originating from the electrolytes themselves or from the electrode materials. Therefore, it should be taken into account that electrode–electrolyte interfacial reactions lead not only to the modification of the electrode surface but may also result in the soiling of the electrolyte.

## 4. Conclusion

The main result of the present study is the observation of the occurrence of spontaneous electrode–electrolyte reactions for some commonly used lithium ion cathode materials in contact with typical organic non-aqueous electrolytes. In the absence of applied potential, the main type of reactions is the reduction of the solvent molecules and salt anions, the main cause suggested to be a spontaneous lithium deintercalation from the electrode’s active material. The rate and the type of these reactions, however, depend essentially on the individual surface chemistry of the electrode and the type of electrolyte used (see Table 1).

The results of this work show that  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  materials demonstrate a slow rate of spontaneous surface modification, and the main products of the reactions seem to be mostly inorganic, although in the case of  $\text{LiPF}_6$ –EC/PC electrolyte an insignificant solvent polymerization is also possible. In contrast,  $\text{LiMn}_2\text{O}_4$  materials show essentially

higher activity toward electrolyte solutions, and cause intensive polymerization of solvent molecules in both PC and EC/DMC-based solutions. In addition, the storage of  $\text{LiMn}_2\text{O}_4$ -based electrodes at elevated temperatures seems to be quite insecure due to enhanced degradation of the electrode surface.

It also appears that spontaneous interfacial reactions are multi-stage processes. Initially, the interaction occurs only between the electrolyte components and the electrode active material (first stage), while further steps include the same reaction(s), as well as reaction between electrolyte and the products of previous reactions already formed on the electrode surface. From this point of view, the formation of OH groups and water molecules in the passivation layer, which is typical for electrolytes based on salts like  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ , etc. may play an important role in electrode–electrolyte interaction.

The influence of polymer binder, carbon electron conductor as well as small variation of the cathode composition (in the range of practical applications) on the interface reactions is found to be negligible.

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