Contribution of X-ray Photoelectron Spectroscopy to the Study of the Electrochemical Reactivity of CoO toward Lithium

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The positive attributes of X-ray photoelectron spectroscopy to the field of battery research is illustrated through the study of reaction mechanisms involved during the electrochemical reduction/oxidation of a metal oxide (MO) electrode vs Li. Through the acquisition and interpretation of various (Co 2p, Li 1s, O 1s, and C 1s) XPS spectra during the charge and discharge of a CoO/Li battery, we could confirm the reversibility of the CoO → Co conversion reaction process involving the reversible formation/decomposition of CoO and Li_2O together with the reversible growth of an organic layer. More importantly, such measurements suggested that the organic polymer could contain, among others, oligomer chains of poly(ethylene oxide) $(CH_2CH_2O)_n$.

Introduction

Rechargeable Li-ion batteries are the key component of today's portable electronics and are also standing as serious candidates over Ni−MeH batteries for the next generation of hybrid electric vehicles. This growing worldwide need is very demanding on scientists who are constantly asked to elaborate/design better electrodes. Research trends for positive electrodes have been aimed at optimizing the layered $LiNi_{1-x-y}M_xM'_yO_2$ oxides, or the olivine $LiFePO_4$ structure through cationic substitution and carbon nanopainting. Regarding negative electrodes, intense activities are devoted to the search for a better alternative to the well-functioning carbon electrode presently used in commercial cells. Present approaches are parted between improving existing materials or searching for new ones on the basis of classical insertion/deinsertion or Li−alloying reactions, or more recently by exploiting reversible conversion reactions.

Studying conversion reactions through an arsenal of characterization techniques involving in situ X-ray powder diffraction, transmission electron microscopy, electron diffraction, and so forth,[1,2] some of us have shown that the reduction mechanism of CoO by Li entails the formation of Co nanograins dispersed into a lithia (Li_2O) matrix according to the following reversible reaction: $CoO + 2Li + 2e^- \rightarrow Co + Li_2O$, together with the growth of an electrochemically active organic coating at the surface of the particles. Trying to grasp more insight into this process, we embarked into a study of the CoO electrodes by means of X-ray photoelectron spectroscopy (XPS). XPS is a powerful tool for investigating electronic transfer processes and for identifying the local environments of the atoms, and therefore enabling surface analysis of electrode materials. XPS is a very surface-sensitive technique (ca. 5-nm-depth analysis) and is therefore appropriate to study the electronic processes of lithium intercalation in thin film electrodes[3,4] but also at the surface of bulk materials. It is therefore a powerful tool to study the formation of the solid electrolyte interphase (SEI) at the surface of the electrode. The SEI layer, which contains various organic and inorganic electrolyte reduction/decomposition products, is a well-known phenomenon and is supposed to protect the electrode from side reactions and to allow a stable lithium insertion/deinsertion process.[5,6] In this paper, we analyze by XPS the first cycle of discharge/charge of cobalt oxide after reaction with lithium in a CoO/liquid electrolyte/Li metal electrochemical cell, and we discuss the reduction/oxidation mechanisms as well as the formation of the solid electrolyte interphase (SEI).

Experimental Section

For this study, two types of electrodes were prepared from the same commercial CoO powder batch (Union Miniere) having particles sizes of 0.1 μm, a specific surface area of 1.4 m^2/g, and a purity of 99%. One set of electrodes was obtained

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by dispersing CoO in NMP solvent (*N*-methylpyrrolidinone), so as to obtain a viscous paste placed onto a stainless steel disk, and dried at 80 °C. The other one was simply obtained by sintering 0.5-mm-thick pellets made out of CoO powders. To facilitate XPS interpretations, neither of the investigated samples contained carbon additives or PVDF−HFP (poly-(vinilidene fluoride-*co*-hexafluoropropylene)) binders. Electrochemical measurements were carried out in standard 2035-size coin cells. The cells, using either a dried disk or a sintered pellet as the positive electrode, Li metal as the negative electrode, and electrolyte-saturated Whatman borosilicate glass fiber sheet as the separator, were assembled in an argon drybox and tested using a Mac Pile cycling/data recording system (Biologic S.A., Claix, France) operating in galvanostatic mode. The cells were cycled at 20 °C over the 0.02−3 V voltage range at a C/5 rate (C being defined as 1 Li in 1h). If not otherwise specified, the electrolyte used was a 1 M $LiPF_6$ in 1:1 weight ratio of dimethyl carbonate (DMC) and ethylene carbonate (EC).

XPS measurements were carried out with a Surface Science Instrument spectrometer (model 301) using a focused monochromatized Al Kα radiation ($h\nu = 1486.6$ eV). The residual pressure inside the analysis chamber was ca. 5×10^{-7} Pa. The spectrometer was calibrated by using the photoemission lines of Au (Au $4f_{7/2} = 83.9$ eV with respect to the Fermi level) and Cu (Cu $2p_{3/2} = 932.5$ eV). For the Au $4f_{7/2}$ line the full width at half-maximum (fwhm) was 0.86 eV under the recording conditions. The peaks were recorded with constant pass energy of 50 eV. The diameter of the irradiated area of the sample was 600 μm. Charging effects were minimized with a low-energy (5 eV) electron flood gun in conjunction with a transmitting fine mesh proximity screen. The binding energy scale was calibrated from the carbon contamination using the C 1s peak at 285.0 eV. The XPS signals were analyzed using a nonlinear Shirley-type background,[7] and the fitting peaks of the experimental curves were calculated using a combination of Gaussian (80%) and Lorentzian (20%) distributions. Peaks assignments were made with respect to reference compounds, namely, CoO powder, metallic cobalt, Li_2O, LiOH, $LiPF_6$, Li_2CO_3, and LiF.

Studied samples were opened in an argon drybox, washed with acetonitrile to remove the electrolyte, and dried prior to being packed into a hermetically sealed aluminum plastic bag for transportation. To prevent any sample exposure to moisture/air on the analysis site, the XPS spectrometer was directly connected through a transfer chamber to a nitrogen drybox so that the “CoO” electrode sample could be easily removed from the plastic bag within the drybox and placed on the XPS sample holder without any contamination. Depth analysis and composition depth profiles were obtained by etching with argon ion sputtering (4 kV, leading to an etching rate between 5 and 50 Å·min^{-1}). Sintered pellets have a weak mechanical solidity after reaction in an electrochemical cell, which however allows scraping their surface with a scalpel blade under ultrahigh vacuum (about 10^{-8} Pa) to analyze them more in depth.

Results and Discussions

1. Study of the Reduction of CoO by Lithium. Figure 1 shows the first cycle of discharge/charge of a cell built with CoO powder as positive electrode material and metallic Li as the negative electrode.

Five samples were chosen for XPS study of the first cycle of discharge/charge: (i) starting cobalt oxide CoO, (ii) after insertion of 1 Li per mole ($x = 1$), (iii) after total discharge at 0.02 V, (iv) after charge at 1.8 V, and (v) after charge at 3.0 V. To make sure that the results of the starting CoO could be compared to those of other samples, it was first soaked in the same electrolyte and then washed in the same conditions as other samples.

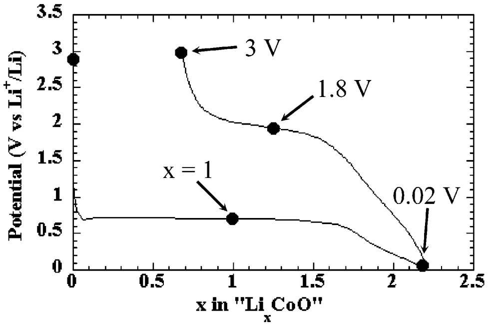

Figure 1. Voltage−composition profile of the first cycle of a CoO/Li cell between 0.02 and 3 V at a C/5 rate (1 lithium in 5 h) with the dots denoting the samples studied by X-ray photoelectron spectroscopy.

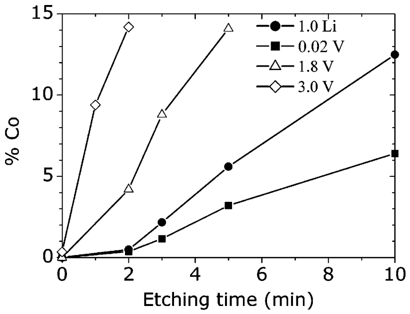

Figure 2. Atomic percent of cobalt observed at the surface as a function of the etching time for (a) discharge at $x = 1$ Li, (b) discharge at 0.02 V, (c) charge at 1.8 V, and (d) charge at 3.0 V.

All the samples showed the presence of an organic/inorganic layer at the surface (the nature of this layer will be discussed later). As the analysis depth of the XPS technique is about 5 nm, this layer was thick enough to make the cobalt atoms unobservable, except for the starting CoO, or to a lesser extent for the sample charged at 3.0 V. An argon ion etching was thus used, first to determine the composition depth profile of the samples and second to uncover the particles hidden by the SEI. Figure 2 shows the atomic percent of cobalt measured at the surface as a function of the etching time. We can see that, to observe more than 5% of cobalt atoms at the surface, the necessary etching time increases during the first discharge, 5 min after reaction with 1 Li and 10 min after discharge at 0.02 V, and decreases during the charge, 3 min after charge at 1.8 V and 1 min after charge at 3.0 V. We can conclude from these results that the thickness of the surface layer increases during the discharge and decreases during the charge. Taking into account our argon ion sputtering conditions, an etching time of 5−10 min indicates a depth of about a hundred angstroms for this layer. This is in good agreement with our previous results of transmission electron microscopy that showed the presence of an 80-Å layer at the surface of the particles at $x = 1$ Li during discharge.[2]

To study the reduction/oxidation processes of cobalt during insertion/de-insertion of lithium, the etching times of these samples were chosen so that equivalent cobalt contents could be observed for each (6−9%). Figure 3 shows the Co 2p XPS core spectra obtained for these samples. Only the Co $2p_{3/2}$ contribution is discussed here.

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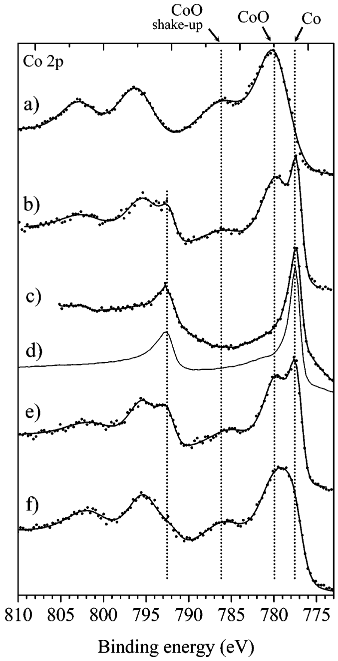

Figure 3. Co 2p XPS spectra of: (a) starting CoO powder, (b) discharged at $x = 1$ Li, (c) discharged at 0.02 V, (d) metallic cobalt foil as a comparison, (e) charged at 1.8 V, and (f) charged at 3.0 V.

For the starting CoO, the 2p$_{3/2}$ peak observed at 780.2 eV can be assigned to Co(II) coordinated to oxygen atoms, while the second peak at 786.1 eV can be attributed to a satellite peak. These values are in good agreement with the literature,[8−10] and the presence of the satellite (shake-up) has been interpreted by the occurrence of a ligand-to-metal charge transfer during the photoemission process, resulting in a 3d^8 configuration in the final state instead of 3d^7 in the initial state.[11,12] It is worth noting that this satellite strongly depends on the chemical state, and an intense satellite peak at ca. 6 eV above the principal line is characteristic of Co(II) in an oxygen environment.[13−15] It is very intense for CoO (ca. 30% of the total Co 2p$_{3/2}$ signal) while it is much smaller for Co$_3$O$_4$, where Co(II) accounts only for one-third of the whole. The presence of this satellite can therefore be used as a signature of the CoO phase in the samples.

After reaction with 1 Li (sample b), the same components can be observed, and an additional narrow peak at 777.8 eV appears, which can be clearly assigned to metallic cobalt. After discharge down to 0.02 V and reaction with 2.2 Li (sample c), both CoO components have disappeared, and the spectrum consists of a unique peak of metallic cobalt. The asymmetric line shape observed is typical of metal core peaks,[12] and the Co 2p spectrum of a metallic cobalt foil has been plotted as a comparison (sample d). This evolution reveals a two-phase mechanism during discharge in an electrochemical cell: both CoO and metallic cobalt coexist, but the amount of CoO decreases while that of metallic cobalt increases during reaction with lithium. It is worth noting at this stage that etching tests have been made on CoO up to 40 min to make sure that no metallic cobalt can be induced by argon ion sputtering (preferential etching effect) in our working conditions. The metallic cobalt observed in Figure 3 is thus induced only by reaction with lithium and not by preferential etching. Moreover, the same results have been obtained with sintered pellets scraped with a scalpel blade under ultrahigh vacuum, for which no argon ion etching has been used.

After charge at 1.8 V (sample e), both components of CoO including a strong shake-up peak reappear, and the peak of metallic cobalt is still present so that the spectrum is very similar to that obtained after reaction with 1 Li during discharge. After charge at 3.0 V (sample f), the spectrum is very similar to that of the starting CoO. The only difference is the persistence of a small metallic cobalt component, which is more easily observable on the 2p$_{1/2}$ spectrum by a small shoulder at 792.4 eV. This highlights the rather good reversibility of the reduction/oxidation process of CoO by lithium since most of the metallic cobalt formed at the discharge is oxidized into CoO during charge. The spotted tiny amount of nonreacted Co on charge can be estimated at 10% of the whole cobalt, which represents a loss of about 0.2 Li, and certainly contributes to the irreversible capacity noted during the first discharge/charge cycle of CoO/Li cells (see Figure 1).

Concerning the analysis of the O 1s core peaks, great precautions must be taken. For this study, only sintered pellets scraped under ultrahigh vacuum have given good results. Indeed, despite all the precautions taken to preserve and to handle samples in an inert atmosphere, it is very difficult to avoid formation of a small amount of LiOH at the very surface of so reactive samples because of water molecules always present, even in very small quantity ($<$0.5 ppm). Now, the argon ion sputtering used to analyze samples in depth induces a transformation of LiOH in Li$_2$O, which distorts the results. To evidence this phenomenon, we have recorded O 1s and Li 1s spectra of pure LiOH powder before and after 5 min of ion etching. The corresponding O 1s spectra are shown in Figure 4. For the starting LiOH sample, we can see one peak at 531.2 eV. After 5 min of etching, we observe an additional peak at 528.5 eV, which is clearly assigned to Li$_2$O.[16] Analysis of the Li 1s spectra confirmed this observation with apparition, in addition to the peak at 54.8 eV due to LiOH, of a shoulder at 54.0 eV due to Li$_2$O. This experiment shows the need to be extremely cautious when using ion gun etching, and in our opinion, this etching technique should not be used to study the formation of Li$_2$O species in electrode materials of lithium-ion batteries.

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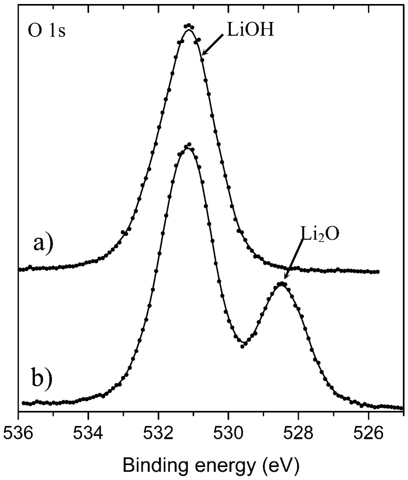

Figure 4. O 1s XPS spectra of (a) pure LiOH powder and (b) the same sample after 5 min of argon ion etching.

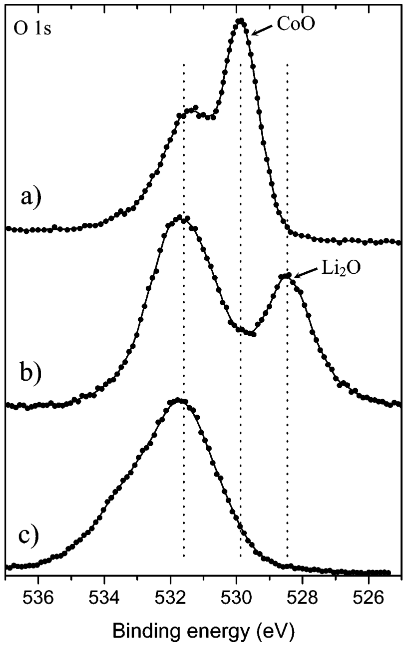

Figure 5. O 1s XPS spectra of (a) starting CoO powder, (b) discharged at 0.02 V, and (c) charged at 3.0 V.

For this reason, O 1s and Li 1s spectra of samples discharged or charged in an electrochemical cell were recorded with sintered pellets scraped under ultrahigh vacuum. The O 1s spectra are shown in Figure 5. The starting CoO (sample a) presents a peak at 529.9 eV, characteristic of O^{2-} anions in the crystalline network, and a second peak at 531.6 eV due to weakly absorbed species at the surface, but also to oxygen anions of CoO in the neighborhood of the surface, which have a particular coordination.[9] After discharge down to 0.02 V (sample b), an additional peak appears at 528.5 eV, showing the formation of Li_2O. The broad peak at 531.7 eV can be attributed to many species containing oxygen, particularly reduction products of the solvent like Li_2CO_3 or alkyl carbonate species $ROCO_2Li$, but also to other compounds of the organic layer formed at the surface of the particles. These results are in good agreement with a mechanism of formation of cobalt nanograins dispersed in a Li_2O matrix. After charge at 3.0 V (sample c), the spectrum consists of a very broad peak at 531.7 eV with a shoulder at 533.6 eV. A precise assignment of the latter is not possible here, and many organic or inorganic species can contribute to this signal. But this spectrum shows that Li_2O disappears after charge at 3.0 V. The restitution of CoO cannot be observed on this spectrum because CoO particles are hidden by the SEI. The O 1s signal of CoO is therefore much smaller than the O 1s signals coming from species of the SEI. This can be explained by the etching technique chosen for these samples: manual scraping under ultrahigh vacuum results in a clean surface free from oxygen or water contamination, but the CoO or Co particles still may be covered by a thin organic/inorganic layer when it is present at the surface of the particles deep inside the sample. The Li 1s spectra of the same samples are shown in Figure 6. After full discharge (sample b), the spectrum is slightly disturbed by the presence of the unresolved Co 3p peak of metallic cobalt at 58−59 eV, which is more intense than Li 1s peaks because of its high relative sensitivity factor. This spectrum although shows clearly two Li 1s peaks. The first at 54.0 eV corresponds to Li_2O. The second at 55.7 eV can be assigned to several species. Since no fluorine could be detected, it corresponds to Li_2CO_3 and/or to alkyl carbonate species. After charge at 3.0 V (sample c), the spectrum is also disturbed by the Co 3p signal of CoO; nevertheless, we can observe a single broad Li 1s peak centered at 55.6 eV, implying the disappearance of Li_2O as expected from previous TEM microscopy data.

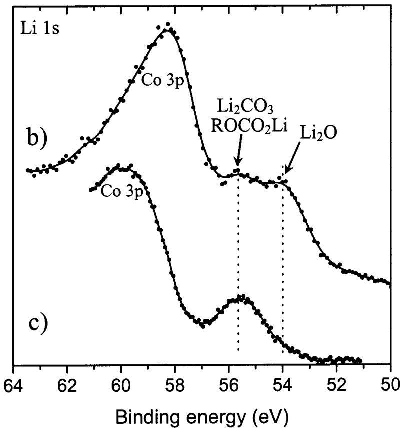

Figure 6. Li 1s−Co 3p XPS spectra of (b) CoO discharged at 0.02 V and (c) charged at 3.0 V.

As a conclusion, this analysis based on the study of Co 2p, O 1s, and Li 1s XPS spectra allows us to confirm the following mechanism: $CoO + 2Li \leftrightarrow Co + Li_2O$, and its reversibility during charge. This reversibility can be explained by the high electrochemical reactivity of nanosized cobalt particles, which makes possible the formation/decomposition process of Li_2O.[1]

2. Study of the SEI. Another approach consists of studying the samples without any ion etching to analyze the nature of the organic/inorganic layer formed at the surface of the particles. First of all, we detected very few degradation products of the $LiPF_6$ salt in this layer. Indeed, in all the samples, before or after ion gun etching, a very small amount of fluorine (<1%) could be detected. A peak at 685.0−685.2 eV typical of LiF characterized it. No peak due to $LiPF_6$ or Li_xPF_y could be evidenced in our samples, confirming the efficiency of our washing process, although it is commonly observed by XPS and other techniques in electrode ma-

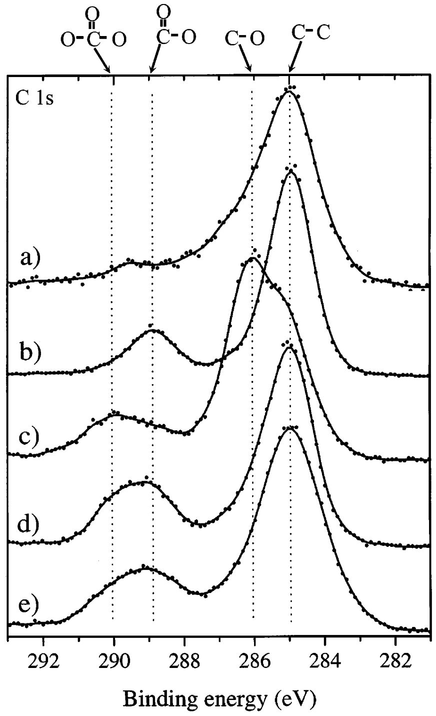

Figure 7. C 1s XPS spectra of (a) starting CoO powder, (b) discharged at $x = 1$ Li, (c) discharged at 0.02 V, (d) charged at 1.8 V, and (e) charged at 3.0 V.

terials after cycling experiments in electrochemical cells with liquid electrolytes containing $LiPF_6$.[5,6] No phosphorus P 2p peak could be detected either. This organic/inorganic layer is therefore mainly made up of carbon, oxygen, and lithium. The Li 1s and O 1s spectra have given very little information on the nature of this layer because a great number of possible species are gathered in a very narrow range of chemical shifts. On the other hand, C 1s XPS core spectra provide some information. Figure 7 shows C 1s spectra of samples without any argon ion etching. The starting CoO, as mentioned before, was soaked in the electrolyte and then rinsed the same way as the other samples. Its spectrum consists of several components. The main component at 285.0 eV can be found in all the spectra and is attributed to contaminating hydrocarbon always present, and to carbon atoms of organic species bound to carbon or hydrogen only. The asymmetry observed at ca. 286−287 eV can be assigned to carbon atoms bound to one oxygen atom (CO-like), while the small component at 289.4 eV corresponds to carbon atoms bound to two oxygen atoms (COO-like). These peaks are due to adsorbed species at the surface. After reaction with 1 lithium (sample b), the spectrum mainly consists of two components. The component observed at 289.0 eV corresponds to COO-like carbons. This peak is not clearly assigned, but the quasi-absence of CO-like carbon component should be the sign of RCOOLi species rather than esters. It is worth noting that, after argon ion etching, this sample showed the presence of Li_2CO_3 and/or alkyl carbonate species. The composition of the SEI is certainly heterogeneous and changes according to the depth. Several mechanisms have been proposed to explain the formation of such species from the solvent, like for example,[17,26]

$$CH_3{-}OCO_2{-}CH_3\ (DMC) + e^- + Li^+ \rightarrow CH_3{-}OCO_2^{\,-}Li^+ + CH_3^{\bullet}$$

$$CH_3{-}OCO_2{-}CH_3\ (DMC) + 2e^- + 2Li^+ \rightarrow Li_2CO_3 + CH_3{-}CH_3$$

$$2(CH_2{-}O)_2CO\ (EC) + 2e^- + 2Li^+ \rightarrow Li^{+\,-}O_2CO{-}CH_2{-}CH_2{-}OCO_2^{\,-}Li^+ + CH_2{=}CH_2$$

We can propose a possible reaction to explain the formation of RCOOLi species due to the presence of radicals, although such hypotheses are difficult to verify:

$$CH_3{-}OCO_2^{\,-}Li^+ + CH_3^{\bullet} \rightarrow CH_3{-}CO_2^{\,-}Li^+ + CH_3O^{\bullet}$$

This mechanism could be explained by the relative stability of $CH_3O^{\bullet}$ radicals as compared to $CH_3^{\bullet}$.[18]

After discharge down to 0.02 V (sample c), the main component is observed at 286.0 eV and corresponds to CO-like carbons. A new component appears at 290.0 eV while a small shoulder is still present at 289.0 eV. As a comparison, C 1s spectra of the same sample and of a sintered pellet discharged and mechanically scraped under vacuum before analysis have been plotted in Figure 8. For the sintered pellet, the amount of organic/inorganic layer at the surface of this sample was still very important after scraping, and the carbon and oxygen atoms assigned to the SEI accounted for about 20% of the whole. We can see in Figure 8 that spectra of both samples are quite similar. The main difference is coming from the intensity of the component at 290.0 eV. This chemical shift is the same as Li_2CO_3. However, the presence of alkyl carbonate species cannot be excluded since their chemical shift may be very similar, and they are commonly detected as reduction products of the solvent during electrochemical cycling.[19−21] We can say that the layer formed at the surface of the particles partially consists of Li_2CO_3 and/or $ROCO_2Li$. The difference in intensity observed for the peak at 290.0 eV between both samples shows a difference of composition in the SEI, the layer being richer in Li_2CO_3 and/or $ROCO_2Li$ in depth than at the very surface. The component at 286.0 eV is too important to be only coming from alkyl carbonate species ($R{-}\underline{\mathbf{C}}H_2{-}OCO_2Li$). Several authors have proposed a mechanism of polymerization induced by decomposition of the solvent,

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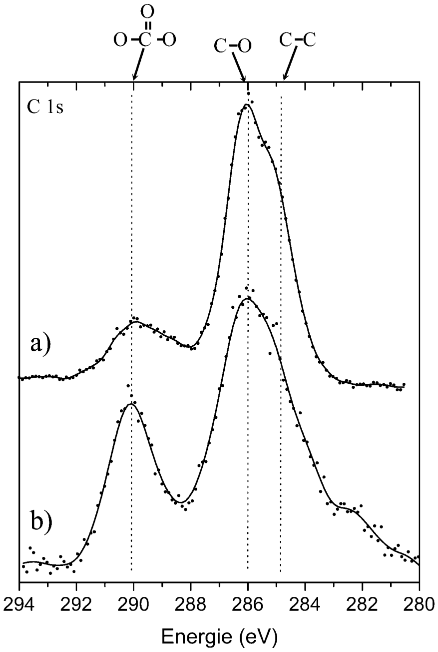

Figure 8. C 1s XPS spectra of CoO samples recorded after discharge at 0.02 V: (a) powder, without ion gun etching and (b) sintered pellet scraped under ultrahigh vacuum with a scalpel blade.

leading to polymer or oligomer chains of poly(ethylene oxide) $(CH_2CH_2O)_n$.[22−24] Our measurements are in good agreement with this hypothesis. A probable mechanism of polymerization results from the decomposition of the solvent to form gaseous CO_2,

$$n(CH_2-O)_2CO\ (EC) \rightarrow (-O-CH_2-CH_2\text{-})_n + nCO_2$$

where small chains of poly(ethylene oxide) can be formed with $-H$, $-CH_3$, or $-C_2H_5$ as ending due to the presence of corresponding radicals during the reduction process.

The small shoulder observed at ca. 282.5 eV can be interpreted by the presence of a small amount of lithium carbide Li_xC since this sample has been discharged at low potential (0.02 V vs Li). This kind of species is commonly observed at the surface of lithium or graphite electrodes.[25,26] Anyway, its contribution is very weak since it represents less than 1% of the whole atomic concentration. Figure 7 shows the C 1s spectra obtained after charge at 1.8 and 3.0 V (samples d and e). These spectra clearly show the disappearance of the intense component at 286 eV, while both peaks at 289 and 290 eV still remain. These results show that organic species corresponding to the peak at 286 eV, probably $(CH_2\text{-}CH_2O)_n$-like polymers or oligomers, disappear during charge while the formation of Li_2CO_3 and/or $ROCO_2Li$, and probably of RCO_2Li, is not reversible.

Parallel investigations allowed us to better characterize the different carbonated solvent-based electrolyte decomposition products and to confirm the formation of the ether oxide-type oligomers from EC/DMC $LiPF_6$ used in the present study. Indeed, the electrolyte (containing decomposition product) was recovered from a separator of the Li/electrolyte/CoO cells after long cycling at 55 °C and then analyzed by means of a soft modern-day technique of electrospray ionization high-resolution mass spectroscopy (ESI-HRMS). The spectrum showed different sets of peaks separated by 44 amu, implying the presence of oligomer species of poly(ethylene oxide)-type $(CH_2CH_2O)_n$ with $n_{max} = 9$.

Conclusion

We reported on the use of X-ray photoelectron spectroscopy as a powerful means to follow the electrochemical reaction mechanism involved during the reduction of CoO by Li. We confirmed the conversion process previously reported with namely the appearance/disappearance of metallic Co concomitant with the formation/decomposition of Li_2O. Moreover, we gave evidence upon reduction by lithium of the growth of both an inorganic and an organic layer with the latter partially vanishing upon cycling. From a careful analysis of the XPS spectra we could deduce that Li_2CO_3 and alkyl carbonates were the main constituents of the inorganic layer, while we identified the presence of poly(ethylene oxide) oligomers within the organic layer.

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