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Nano-CoF $_3$ prepared by direct fluorination with F $_2$ gas: Application as electrode material in Li-ion battery

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ABSTRACT

Nano-CoF₃ powders were synthesized by direct fluorination at various temperatures (up to 300 °C) of cobalt nanoparticles and their electrochemical features in lithium battery were investigated. The structure and composition of the raw and fluorinated materials are explored by SEM/TEM, HRTEM, XRD and XPS experiments. The influence of the fluorination temperature on the crystallite size has been evidenced by XRD. It is shown that such fluorination process allows the direct synthesis of nano-CoF₃, at T_{F2} = 100 °C. The XPS investigation of mixtures of CoF₃ and acetylene black has shown that, when handled in very dry atmospheres, CoF₃-based samples can be used to prepare electrodes for Li-ion batteries in safe conditions. The electrochemical reaction of nano-CoF₃ powders vs. lithium metal studied in organic medium involves a conversion process as described in the case of cobalt oxide. Successive impedance measurements were carried out at different discharge states to follow the modifications occurring at the electrode/electrolyte interface during the discharge step. The evolution of the reversible capacity retention of Li⁺ vs. time capacity of the powdered materials as well as the cycle life of the battery were investigated as a function of the fluorination temperature used for the preparation of the cobalt fluoride nanopowders. The best electrochemical performances were obtained with nano-CoF₃ powders prepared at fluorination temperature of 100 °C, for which a reversible capacity of about 390 mAh/g is obtained after subsequent cycles.

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1. Introduction

The demand of clean and performing energy storage devices is growing up and requires much attention for the development of electrochemical systems such as Li-ion batteries. Among available electrode materials to be used in such devices, main interest has been focused on transition metal-based compounds. Indeed, owing to the presence of empty channels or layers in the lattice, these materials are able to insert/extract reversibly Li⁺ ions without any detrimental structural changes. Therefore, the improvement of the electrochemical battery performances could imply the development of new classes of electrode materials able to incorporate three electrons per 3*d*-metal, thus delivering higher energy density, and exhibiting longer cycle life in addition to moderate cost.

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For a long time, minor attention has been devoted to metal fluorides due to their poor electronic conductivity. However, iron fluoro-compounds are of interest for batteries because of their low cost and low toxicity. In addition, conversion reactions are involved during the reduction of metal fluorides, enabling full utilization of all the redox potentials of the host metal [1-8]: indeed, the metal fluoride can be reduced fully to the metallic state according to the reversible following reaction: $xLi^+ + xe^- + MF_x \leftrightarrow xLiF + M$. This conversion reaction is characterized by full reduction of the metal leading to the stabilization of nano-sized M/LiF domains, i.e. the stabilization of metallic nano-metal embedded in a lithiated matrix. This reaction is generally reversible due to the nanoscale nature of the resulting composite. Moreover, MF₃ such as FeF₃ support also intercalation, forming Li_xMF₃ compounds, as also demonstrated for TiF₃, FeF₃ and VF₃ [2,5,9]. It results a two-step mechanism involving at first an one-electron intercalation reaction (Reaction (1)) followed by a two-electrons conversion reaction (Reaction (2)) according to:

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(1)

(2)

$$M^{3+}F_3 + Li^+ + e^- \rightarrow LiM^{2+}F_3$$

and

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 $LiM^{2+}F_3 + 2Li^+ + 2e^- \rightarrow 3LiF + M^0$

The nature of the LiF/metal nano-composite may induce a high reversibility of the conversion reaction, giving rise to large reversible capacities. Indeed, the theoretical specific capacity of positive electrode is significantly enhanced from ~280 mAh/g for layered intercalation compounds to more than 700 mAh/g for metal di- or tri-fluorides. Thus, MF_2 and MF_3 compounds (with M = Bi, Ti, V, Fe, Mn, Ni . . .) have been already studied as positive electrode materials [2–5,9,10]. For instance, Amatucci et al. [1] reported that metal fluorides such as iron and bismuth fluorides can be considered as suitable candidates for electrode materials for rechargeable lithium batteries [1,8,10]. Recently, oxyfluoride and hydroxyfluoride were considered as new candidates in such rechargeable batteries [11–13].

Here, we focus our attention on the properties of nano-sized cobalt trifluoride. Few articles have been devoted to the use of CoF₃ as negative electrode [14]. The lack of reports may be due to the instability of this metal fluoride in the presence of air that limits its further development. CoF₃ decomposes upon contact with water to give HF, CoF₂ and O₂. In addition, as other metal fluorides, an enhancement of its electrical conductivity, σ_{e} , is requested for applications. Among the possible routes to increase the electric contact between particles, ball milling technique using various carbonaceous products (graphite, black carbon, etc.) is one of the most popular. This would lead to the formation of CoF₃/C composites [15] such as for FeF₃. However, CoF₃ is a strong fluorinating agent and high energy arising from ball milling performed in presence of CoF3 and carbon could lead to the decomposition of CoF_3 into $CoF_2 + F_2$, with formation of insulating CF_x phases. Therefore, severe precautions should be taken to perform such surface modification of CoF₃ powder by this technique.

In spite of these limitations and because we perfectly know how to handle all kinds of fluorinated species, we focused our attention to the study the electrochemical behaviour in Li-ion battery of nano- CoF_3 prepared from direct fluorination of cobalt nanoparticles at different temperatures using F_2 gas. It is well established that the use of nano-sized particles greatly improves the electrochemical activity, such as for other metal fluorides. Optimizing the synthesis conditions in order to achieve nano-sized crystallites of CoF_3 will thus constitute one important issue of this study. In the second part, the reactivity of CoF_3 in different atmospheres will be checked in the presence of acetylene black, a material used during the fabrication process of lithium battery electrodes.

2. Experimental section

Raw cobalt nanoparticles were obtained from an original electrochemical route described elsewhere [16–18]. Briefly, the electrochemical process consisted in the anodic dissolution of a Co metal bar giving rise to metal ions (Co^{2+}) in aqueous solution at pH > 6 in order to avoid the reduction of protons; the homogeneous medium was composed of sodium citrate or ammonium citrate, Co^{2+} ions being dissolved as complexes. Due to their close time constants, Co^{2+} ions were reduced on a liquid mercury cathode producing metal nanoparticles directly dispersed in mercury. The obtained material is a magnetic and conducting fluid that can be considered as a source of metal nanoparticles since the metal can be recovered by using a liquid–liquid extraction. The magnetic nanoparticles were extracted using a mixture of surfactant in an organic solvent. To succeed, magnetic mercury and solvent

(surfactant in cyclohexane) were mixed by mechanical stirring for four days. The surfactant used was trioctylphosphineoxide. A black magnetic precipitate was obtained in the organic solution, which was washed several times with acetone and alcohol and then dried. Finally, the powders were heat-treated at 250 °C under vacuum to remove traces of mercury.

The fluorination of pristine Co nanoparticles was performed at temperatures ranging from 100 to 300 °C under 1 atm of elemental fluorine (purity: 99.4–99.7%) in a nickel reactor. A decomposition of nano-CoF₃ occurs at higher temperatures giving rise to the presence of CoF₂. The composition of the fluorinated samples was determined by coupling elemental analysis and X-ray diffraction (XRD) measurements. The latter were performed with a Rigaku Ultima III X-Ray diffractometer with a CuK α radiation $(\lambda_1 = 1.540598 \text{ Å})$. Global Rietveld profile refinement was made to perform a fine analysis of the structure and to determine the average particle size of CoF₃ from the broadening of the Bragg peaks (Scherrer formula) with respect to the instrumental one. The experimental contribution of the diffractometer to the line broadening was established using XRD patterns of standard LaB₆ powder. The peak profiles were fitted using the pseudo-Voigt function of Thompson-Cox-Hastings which allows refining separately the angular dependence of both Lorentzian (HL) and Gaussian (HG) components of FWHM (full width at half maximum). High resolution Transmission electron micrographs were obtained with a Jeol JEM 100 CX II transmission electron microscope equipped with a Jeol high resolution scanning attachment (STEM-SEM ASID 4D). Scanning electron microscopy images were obtained with a Jeol JEM 100 CX II scanning electron microscope equipped with a Jeol high resolution scanning attachment (SEM-FEG). Finally, HRTEM images were collected with JEOL JEM 2011. Surface characterizations were done by XPS measurements using a ThermoFisher Scientific K-ALPHA spectrometer under ultrahigh vacuum conditions. The radiation was an monochromatized Al source (1486.6 eV). All spectra were referenced to C1 s located at binding energy (BE) of 284.8 eV. Surveys were recorded at 200 eV pass energy and high resolution spectra C1s, O1s, F1s and Co2p at 40 eV pass energy, then fitted with an AVANTAGE processing program provided by ThermoFisher. The fluorinated samples were stored in a dry box until they were very rapidly transferred into the XPS chamber.

The stability of the active CoF_3 obtained after fluorination was tested in order to ensure the process of the preparation of an electrode, in same conditions as used in Li-ion batteries. The purpose was to check the stability of CoF_3 vs. a humid atmosphere and also vs. divided carbon which was mixed to the active component in order to enhance the electrode electrical conductivity. The fluoride powders were mixed thoroughly with various amounts of acetylene black (AB) in a dry box containing only a few ppm O_2 , H_2O . The composite material was as follows: 80% CoF_3 , 20% AB. No binder such as PVDF was added, in order to have a clear XPS answer on both C1 s and F1 s spectra, and also because this material is reactive vs. CoF_3 . Afterwards, the mixture was investigated by XPS, either in dry conditions, or after being left for two days in the laboratory's atmosphere.

The electrochemical lithium insertion/deinsertion reaction was studied in 1 mol/L LiPF₆-EC:DMC (1:1) solution (LP30, Merck) at room temperature in a glove box (water content < 10 ppm) under argon atmosphere. The working electrode was composed of 90% of the active material, 5w% of acetylene black and 5w% of PVFD as binder. The counter and reference electrodes were metallic lithium foils. All potential values were referred to this Li⁰/Li⁺ reference henceforth. The galvanostatic charge-discharge curves were performed using a potentiostat/galvanostat impedancemeter (VMP3 Bio-Logic) in the potential range 0.02–4.0 V at various current densities.

3. Results

3.1. Analysis of the starting raw material: Co-based nanoparticles

The morphology of Co nanoparticles prepared by electrochemical route was characterized by SEM and TEM. The SEM image (Fig. 1a) reveals the formation of guasi-spherical aggregated particles. TEM image presented in Fig. 1b shows the polydispersity of the metal with a mean diameter of the order of 10 nm for cobalt nanoparticles. XRD pattern of non-fluorinated cobalt nanoparticles (Fig. 2) evidences the presence of strong diffraction lines of Co_3O_4 (ICDD 00-009-0418) as the main component, while CoO(OH) (JCPDS 01-073-1213); Co(OH)2 (ICDD 00-030-0443), and Co (ICDD 01-089-7373) can also be detected as constituents. It is assumed that the core of the metallic Co particles is thus covered by a surface layer constituted by spinel Co₃O₄ and oxy-hydroxide CoO (OH), whereas hydroxide $Co(OH)_2$ may also be present. Thus, it is suggested that after liquid-liquid extraction the cobalt nanoparticles were oxidized, due to their high reactivity vs. oxidation in air.

To confirm this assumption, surface XPS measurements were performed. Table 1 summarizes the elemental analysis of all investigated samples. Note that 2.5% Hg was found at the surface in the starting nano-Co particles due to the presence of the mercury electrode in the electrochemical cell (see "Experimentals" above). High-resolution Co 2p spectra show a spin-orbit splitting into $2p_{3/2}$ and $2p_{1/2}$ components at ~789.0 eV range and 795.0-810.0 eV range, respectively. As expected, the intensity ratio of the Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks is close to 2. These components contain qualitatively the same chemical information [19–21]. Therefore, only the envelope relative to Co $2p_{3/2}$ peak was fitted (including satellites) and discussed hereafter. Individual fitted parameters, i.e.



Fig. 1. (a) SEM and (b) TEM images of raw cobalt nanoparticles.



Fig. 2. XRD pattern of raw Co-based nanoparticles.

Quantification of XPS spectra (atomic%, Scofield library).

	С	0	Со	F
Nano-Co	28.5	53.0	16.0	-
Nano-Co F100	36.3	24.5	13.0	26.2
CoF ₃ -F300	42.2	9.8	11.5	36.5
CoF ₃ -F300-AB-dry	61.3	6.9	7.6	24.2
CoF ₃ -F300-AB-air	58.2	10.7	8.3	22.8

binding energy (BE), as well as the relative contribution of each component (Ii%) to the total area of the Co $2p_{3/2}$ peak are calculated for the different groups in Tables 2a and 2b.

Concerning the starting nano-Co sample, the XPS Co $2p_{3/2}$ spectrum (Fig. 3a) can be fitted into several asymmetrical

Table 2a

Table 1

XPS data of pristine Co nanoparticles – Binding energies BE (eV), and relative amounts of the different components I_i (%). in Co2p_{3/2} and O1s spectra.

	BE (eV)	I _i (%)	Assignment
Co 2p _{3/2}	780.0 781.3 788.3 790.2 791.4	74.5 25.5	Co3O4 CoO(OH) satellites
O 1s	529.9 531.2 532.4 533.9	38.3 42.8 15.6 3.3	Co ₃ O ₄ CoO(OH) + O = C O-C H ₂ O

Table 2b

XPS data of cobalt nanoparticles fluorinated at 100 and 300 °C under F₂ atmosphere. [BE (eV), and relative amounts of the different components I_i (%) of Co $2p_{3/2}$ F1 s and O1 s spectra].

	Nano-Co F100		CoF ₃ -F300			
	BE(eV)	I _i (%)	Assignment	BE (eV)	I _i (%)	Assignment
Co 2p _{3/2}	780.8	15.9	Co ₃ O ₄ , CoO(OH)	-	-	-
,	781.8	55.1	$Co-O_xF_{y+}Co-O_yF_x$	782.6	51.1	Co-O _v F _x
	784.6	29.0	Co-F _z	784.6	48.9	Co-F _z
	788.3		Satellites	788.8		satellites
	790.9			793.2		
F 1s	684.5	92.8	F _z -Co	684.9	93.6	F _z -Co
	686.6	7.2	F-C	687.2	6.4	F-C
0 1s	530.0	11.7	Co_3O_4	531.2	9.8	CoO(OH),
	531.5	57.9		532.3	36.9	O=C
	533.1	30.4	CoO(OH), O=C	533.6	53.3	Co-O _x F _y , O-C
			Co-O _x F _y , O-C, Co-			Co-O _y F _x

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Fig. 3. Fitted Co2p_{3/2}, O1s, F1 s and C1 s XPS spectra of (a) nano-Co and (b) nano-Co F100 samples.



Fig. 4. Experimental X-ray diffraction powder patterns (red curve); Rietveld-refined profile (blue curve), and difference curve (green curve) of Co-nanoparticles fluorinated at (a) 100 and (b) 300 °C under pure F₂ (p = 1 bar), during 3 days. Vertical bars are the positions of the Bragg reflections. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

components located at 780.0, 781.3, 788.3, 790.2 and 791.4 eV. The first two components are assigned to the elastic peaks, whereas the three last are satellites peaks. The main contribution at 780.0 eV corresponds to Co₃O₄, which is consistent with the presence of a satellite on the higher BE side of the main 2p component (higher than 10.2 eV) [20–24]. The second component at 781.3 eV could be due to either Co hydroxide or oxide-hydroxide, i.e. Co(OH)₂ or CoO (OH). As no satellite is found at 786.3 eV corresponding to the fingerprint signature of the hydroxide, the component at 781.3 eV can be therefore assigned to Co oxide-hydroxide, as reported in [20]. It can be noted that the area of the two main components represents 68.6 and 23.5% of the total area of the $Co2p_{3/2}$ envelope (Table 2a), respectively. The O1 s XPS spectrum is decomposed into four peaks (Fig. 3a). The two main peaks observed at 529.9 and 531.2 eV are due to the oxygen from Co₃O₄, oxy-hydroxyl groups and O=C pollution, respectively [20,23,26,27], whereas the peaks at 532.4 and 533.9 eV could be attributed to the pollution of O-C and water, respectively [25]. The presence of O=C and O-C groups is also revealed by the 286–289 eV shoulder in the C1 s spectrum (Fig. 3a). Such results account for the coverage of the raw cobalt nanoparticles with a layer of Co oxide and oxide-hydroxide, as shown previously on Co-based nano-particles exposed to oxidative atmospheres [22].

To summarize, XPS measurements performed on pristine Cobased nanoparticles evidence that these particles are fully covered by layers of cobalt oxide and oxide-hydroxide. Let us consider now the effect of the fluorination on these nano-particles.

3.2. Fluorination procedure of Co-based nanoparticles

The fluorination of cobalt nanoparticles was performed at two temperatures (noted $T_{\rm F}$ henceforth): 100–300 °C. The corresponding XRD patterns for $T_{\rm F}$ = 100 and 300 °C presented in Fig. 4a and b are in total agreement with those of cobalt trifluoride CoF₃ (JCPDS-ICDD file 04-005-4245) [28]. It should be noted that the reaction starts at even moderate temperatures (i.e. $T_{\rm F}$ = 100 °C), because of the high reactivity of F₂ gas vs. cobalt oxide and (oxy)hydroxide. However, the crystallinity of the powder is improved when increasing the temperature to $T_{\rm F}$ = 300 °C (Fig. 4b). CoF₃ possesses a trigonal structure with *R*-3*c* space group symmetry. The fluorination temperature has a great influence on the particles size as evidenced by a narrowing of the XRD peaks with increasing temperatures. Whatever, good refinements were obtained as a

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Table 3

Crystallographic data of CoF3 nanoparticles prepared by treating nano-Co particles at T_F = 100 and 300 $^\circ C.$

<i>T</i> _F (°C)	a (Å)	<i>c</i> (Å)	Average particle size (nm)
100	5.174	13.263	11
300	5.028	13.218	77



Fig. 5. HRTEM image of CoF₃ prepared at $T_F = 100 \degree$ C.

function of the fluorination temperature, at T_F = 100 and 300 °C, as shown in Fig. 4. The average CoF₃ particle size increases with the fluorination temperature from 11 to 77 nm (Table 3) for T_F = 100 and 300 °C, respectively.

HRTEM images obtained on Co nanoparticles fluorinated at 100 °C are shown in Fig. 5. As expected, nanometric particles are still observed after the fluorination procedure. It means that the

morphology of the particles is kept even after fluorination at $T_{\rm F}$ = 100 °C under F₂ gas. Note that the material is partially decomposed under the electron beam during the collection of the TEM images.

XPS investigations were carried out on Co-based nanoparticles fluorinated at 100 °C due to the best conditions yielding fluorinated powders with smallest particle size. The data were compared with those of raw pristine material (Fig. 3). Although CoF₃ is the main phase observed in the XRD pattern, the presence of \sim 25 at.% O is detected at the surface by XPS spectroscopy (Table 1). The Co $2p_{3/2}$ spectrum is presented in Fig. 3b, for which individual binding energy as well as the relative contribution of each component (Ii/%) are given in Table 2b. This spectrum can be decomposed by five asymmetrical peaks situated at 780.8, 781.8, 784.6, 788.3, and 790.9 eV. The first three components are attributed to the elastic peaks, whereas the two last are due to satellite peaks. The peak located at 780.8 eV can be assigned to remaining oxide/oxidehydroxide present at the surface, that is also confirmed by the occurrence of the low BE component at 530 eV in the O1s spectrum (compare O1s spectra in Figs. 3a and 3b). Both contributions around 782 and 784.5 eV are the fingerprints of cobalt in a fluorinated environment. If we refer to the XRD pattern, it is possible to assess that Co is mostly present in its trivalent oxidation state. From quantitative results, the oxygen rate is similar to the fluorine one, which could induce various mixed (F, O) anionic environments around the cobalt at the surface: $Co-O_xF_y$ and $Co-O_vF_x$, in which x is higher than y. This means two Co environments, one oxygen-rich and the other one fluorine-rich. Such assumption is reinforced by the presence in O1 s spectrum of high BE component (Table 2b). The high BE peak at 533.1 eV could be linked also to oxidized carbon species, which is also observed at high BE in the C1 s spectrum (Fig. 3b). The main peak in the F1 s region (Fig. 3b) observed at 684.5 eV (93% of the total area of the F1 s region) is due to mostly fluorinated environment of Co, whereas the minor contribution at 686.6 eV (7% of the total area of



Fig. 6. Fitted Co2p_{3/2}, O1s, F1s and C1s XPS spectra of (a) CoF₃-F300, (b) CoF₃-F300-AB-dry and (c) CoF₃-F300-AB-air samples.

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the F1 s region) might be due to some C—F bonding, as previously observed [29]

3.3. Reactivity of CoF₃-based electrode

Before electrochemical investigation, samples were prepared to test the stability of CoF₃ in different atmospheres during the elaboration process of the electrode. CoF₃ and acetylene black (AB), i.e. 80:20 ratio, were mixed thoroughly in a dry box. A part of the samples was left for several days in these ultra-dry conditions (O₂, $H_2O < 2$ ppm) (CoF₃-AB-dry), whereas another part was brought for a couple of days in a vial under laboratory atmosphere (CoF₃-AB-air). Results of the XPS investigations of the CoF₃-AB mixtures are shown in Fig. 6a–c. CoF₃ powder fluorinated under a stream of elemental fluorine for 12 h at 300 °C is used as a reference (CoF₃-F300).

A comparison of this reference sample with the one obtained after fluorination at $T_{\rm F}$ = 100 °C (nano-Co F100 in Fig. 3) shows that \sim 10 at.% oxygen are only present at the surface, with respect to 25 at.% for Nano-Co F100 and 36.5 at.% F (Table 1). [Note that in Fig. 6a, the fitted O1 s spectrum is represented full scale, despite the small amount of surface oxygen]. The F:Co ratio (at.%) deduced from these XPS analyses is about 3, in good agreement with the chemical composition of CoF₃. The Co2p_{3/2} spectrum is free from the oxide/oxide-hydroxide component at low BE. Deconvolution of this spectrum shows four components appearing at 782.6, 784.6, 788.8 and 793.2 eV. The first two components are the fingerprints of Co in (oxy)fluorinated environment as follows: Co-O_vF_x (x > y) and a more fluorinated environment, $Co-F_{7}$; the latter two components being satellite peaks. From a comparison of these XPS data with those of nano-Co fluorinated at 100 °C (Table 2b), we note a shift to higher BE of 0.8 eV for the main peak position, together with an increase of the 784.6 eV area for CoF₃-F300. These changes correspond to a same trend. The shift from 781.8 to 782.6 eV could be due to a diminution of the number of oxygen ligands around Co in Co(O_F) particles, whereas the increase of the component at 784.6 eV could be assigned to an increase of the number of Co-F bonds after the treatment at $T_{\rm F}$ = 300 °C treatment. We should remark that for both fluorination treatments, the latter (higher) BE is in agreement with that of Co³⁺-F bonds, since Co²⁺-F bonds occur at lower BE of 783.2 eV for CoF₂ [30]. The F1 s spectrum of CoF₃-F300 (Fig. 6a) is similar to that of nano-Co F100 (Fig. 3b). The main peak, observed at 684.9 eV (94% of the total area of the F1 s region) is mostly due to fluorinated environments of cobalt, F_z—Co. Concerning the O1 s spectrum, it could be noted an increase of the component at higher BE: 53.3 vs. 30.4% I_i (%), which corresponds to $\text{Co-O}_{y}F_{x}$ with higher amount of fluorine.

When the sample is prepared and kept in very dry conditions CoF₃-F300-AB-dry (Fig. 6b), the Co 2p_{3/2}, O1s, and F1 s XPS spectra are similar with those of pristine CoF₃-F300 sample (surface O content = 7 at.%). However, various modifications are observed for the sample left in ambient atmosphere CoF_3 -F300-AB-air (Fig. 6c), in which the oxygen rate increases to 11 at.%. All Co2p, O1 s and F1 s binding energies are modified, with the re-occurrence of oxidized forms of Co at 780.9 eV and O1 s at 529.9 eV. In addition a shoulder appears in the C1s envelope for higher BE, above 288 eV. These features and the appearance of a strong contribution at 686.7 eV in the F1 s spectrum can be related to the decomposition of CoF₃ in air followed by release of F₂-gas, which immediately reacts with acetylene black to give C-F bonds, similarly to those found in carbon fluorides. It can be noted that in the XPS spectra of electrode samples, the amount of surface oxygen for the sample left in air is higher than the one of sample prepared in dry atmosphere and in both cases the amount of carbon is increased because of the presence of acetylene black.

In conclusion, the above results indicate that during the fabrication of electrodes, a thin film of oxide/oxide-fluoride is likely to be formed. This layer, which acts as an external layer, is assumed to increase the electric conductivity of nano-particles. Finally, one could also state that the interface layer is not homogeneous and composed of nano-domains with Co-O, Co-O-F, etc. bonds. Such surface layer could protect the bulk fluoride particles, avoiding the exfoliation of the lattice as it occurs for example with graphite anode during the discharge process. It induces enhanced electrochemical performances due to the grain boundary contact. When pristine CoF₃ is handled in very dry atmosphere, the CoF₃-based electrodes are assumed to be stable.

3.4. Electrochemical behaviour in Li-ion battery

As observed from XPS experiments, the decomposition of CoF₃ occurs in air followed by the release of F₂-gas. Consequently, the use of CoF₃ as cathode materials in Li-ion battery requests a severe control of the working atmosphere. Indeed, as reported above, conventional battery electrolytes react immediately in contact with CoF₃, leading to partial growth of solid interface film or a second Co-F phase as demonstrated below. In this study, the changes in the structural powders were analyzed by XRD diffraction carried out before and after lithiation. Fig. 7 displays the first discharge profile of a $CoF_3//Li$ cell that displays the states of charge (dots) at which XRD diffractograms were collected (Fig. 8): (a) raw CoF₃ nano-powder prepared by direct fluorination of nano-Co (b) electrode assembled in dry box before testing, (c) electrode discharged at 1.2 V vs. Li and (d) electrode discharged at 0.02 V vs. Li. The XRD diagram of the grid supporting the active material is also shown in (e). The diffractograms (a) and (b) are similar and do not reveal any significant modification of the structure and composition of the electroactive material. XRD patterns exhibit one set of diffraction lines belonging to CoF₃ and peaks at $2\theta = 26.80$, 34.05 and 52.19° corresponding to a small amount of CoF₂. Note that diffraction lines relative to the presence of the additive carbon cannot be observed due to its amorphous nature.

From the XRD patterns of lithiated electrodes at 1.2 and 0.02 V, we clearly observed the disappearance of the Bragg lines of pristine CoF₃, while a broad bump occurring at about $2\theta = 45^{\circ}$ can be attributed to the appearance of metallic Co in good agreement with the 2θ line at 45.92° of α -Co. Further, the electrochemical discharge/charge tests were performed at low current density of ± 5 mA/g for both CoF₃ electrodes prepared at T_F = 100 and 300 °C.



Fig. 7. First discharge curve of a CoF₃//Li cell. Dots are the states of discharge at which XRD diffractograms were collected.

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Fig. 8. XRD patterns of CoF₃-based electrodes: (a) raw CoF₃ nano-powder prepared by direct fluorination of nano-Co with F₂ (nano-Co F100), (b) Electrode assembled in dry box before testing, (c) XRD pattern recorded after discharge to 1.2 V vs. Li, (d) XRD pattern recorded after discharge to 0.02 V vs. Li and (e) stainless steel grid. Dots indicate the diffraction lines of the CoF₂ phase.

The discharge ($Q_{disch.}$) and charge ($Q_{ch.}$) capacity calculated in the potential range 0.02–4 V vs. Li^0/Li^+ , as well as the coulombic efficiency (denoted CE) are reported in Tables 4 and 5.

The electrochemical potentials of the LiF/Co composite have discussed by Zhou et al. [31] and those of cobalt fluoride films by Fu et al. [32]. The theoretical voltage of the reduction of CoF₃ by Li linked by the reaction $Li + CoF_3 \rightarrow LiF + CoF_2$ is 4.85 V, while an open-circuit voltage (OCV) of about 3.5 V was obtained in experimental cell [32]. The electrochemical reaction of CoF₂ with Li was found partially reversible with a potential plateau at 1.1 V for the first discharge that has been attributed to the formation of metallic cobalt. However, it was reported that usual electrolytes such as LiPF₆ in EC-DMC have poor stability with the Co fluoride electrode. High OCV values can be only observed during the first discharge. The potential drops rapidly (Fig. 7) from an OCV of about $3.5\,V$ to ${\sim}1.2\,V$ vs. $\text{Li}^{00}/\text{Li}^{+}$ depending on the current density and then reaches a potential plateau due to the two-phase character of the discharge. These results demonstrate very similar behaviour reported by Zhou et al. [31]. The presence of such low voltage plateau below the theoretical operating potential is attributed to

Table 4 Influence of the fluorination temperature (T_F) on the charge and discharge capacities of CoF₃ prepared under F₂ atmosphere. [Values deduced from the 1st cycle in 1 mol/L LiPF₆-EC:DMC (1:1). CE: coulombic efficiency. Current density: \pm 5 mA/g].

T _F (°C)	Q _{disch.} (mAh/g)	Q _{ch.} (mAh/g)	CE (%)
100	1011	418	41.3
300	992	257	25.9

Table 5

Influence of the current densities on the charge and discharge capacities of CoF₃ prepared at T_F = 100 °C under F₂ atmosphere. [Values deduced from the 1st cycle in 1 mol/L LiPF₆-EC: DMC (1:1). 1=±5 mA/g. CE: coulombic efficiency (in%)].

I (mA/g)	Q _{disch.} (mAh/g)	Q _{ch.} (mAh/g)	CE (%)
5	41011	418	41.3
20	1046	385	36.8
140	824	257	31.1
694	345	101	29.3

the conversion reaction of cobalt fluoride into metal Co nanoparticles embedded into a LiF matrix according to the well-known relation [3,5,33]:

$$\operatorname{CoF}_{x} + x \operatorname{Li}^{+} + x \operatorname{e}^{-} \rightarrow \operatorname{Co} + x \operatorname{LiF}.$$
 (3)

with x = 2 and/or 3.

The structural evolution of CoF₃ electrode studied by XRD (Fig. 8) recorded at potential of \sim 1.2 V (plateau) and at 0.02 V (end of the discharge) ensures the conversion reaction. Note that the observed extra capacity given the length of the plateau should arise from an interfacial interaction of lithium within the Co/LiF matrix [10,26,33] in addition to the formation of a polymer-like solid electrolyte interphase (SEI) film [8]. After the complete reduction (*i.e.* at 0.02 V), the galvanostatic cycles exhibit a continuously decreased/increased profiles without voltage plateau, which is a characteristic of conversion reaction. Also, the detection of the low intensity XRD peaks of metallic cobalt with a bump shape confirms the reversibility of the conversion mechanism.

As mentioned in the introduction, insertion/extraction of Li⁺ in layered materials generally occurs in charge/discharge cycles without any significant structural modifications. Thus, even if the occurring volume expansion is due to the insertion of Li⁺, the original host structure is restored after Li⁺ extraction. However, their ability to insert a large amount of lithium is often limited to about one lithium per mole of electroactive material. In contrast, when the electrode material is composed of transition-based metal fluoride, multiple-electron transfer can occur, and thus the metal fluoride can be fully reduced to metallic state according to the conversion reaction (Eq. (3)). Whatever the metal fluoride, the cell voltage is strongly influenced by an overvoltage as described in Refs. [8,10,34], which results from kinetic barriers. If the overvoltage is large, the voltage variation is significantly influenced by the kinetic terms and the voltage during the experiment reaches the operating oxidation or reduction potential limit. Consequently, during extraction, Li cannot usually be fully extracted from the host lattice as it is claimed in the case of CoF₃. In other words, after the first reduction step, metallic cobalt cannot be converted back to Co^{3+} but to Co^{2+} , thus leading to a progressive suppression of CoF₃ domains as reported before [35,36]. Therefore, after the first cycle, the reaction involved in the electrochemical process is the following:

$$\operatorname{CoF}_2 + 2 e^- + 2 \operatorname{Li}^+ \leftrightarrow \operatorname{Co} + 2 \operatorname{LiF}.$$
(4)

Finally, Maier et al. [10] reported a high overvoltage value of 1.58 V for Li-insertion reaction into CoF₂.



Fig. 9. Galvanostatic charge-discharge curves of nano-CoF₃ (T_F = 100 °C) in 1 mol/L LiPF₆-EC:DMC (1:1). I = ± 5 mA/g.

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Fig. 10. First galvanostatic charge-discharge curves of nano-CoF₃ (T_F = 100 °C) under various current densities.

Fig. 9 shows the galvanostatic charge-discharge curves of nano- CoF_3 ($T_F = 100 \circ C$) in 1 mol/L LiPF₆-EC:DMC (1:1) at current density 5 mA/g. In these experimental conditions, the first charge/ discharge profile does not clearly evidence the presence of a potential plateau but only a shoulder at around 2.4 V vs. Li⁰⁰/Li⁺ (see inset of Fig. 9), which could be related to the insertion/ extraction of Li⁺ into/from the host lattice according to CoF₃+ $xLi^+ + xe^- \rightarrow Li_xCoF_3$ (x < 1). The capacity associated to this reaction is very small, i.e. there is no evidence about the formation of a ternary Li_xCoF₃ compound. However, the origin of the source of cobalt should have a decisive role in the present fluorinated process. An optimization of the electrode preparation should be necessary to improve the knowledge about such a reaction. After the plateau, a continuous voltage drop down to the potential limit (0.02 V vs. Li⁰⁰/Li⁺) has been observed [10,34]. The first charge capacity value is much higher than the theoretical one (694 mAh/g) corresponding to the conversion reaction of CoF₃. For instance, the capacity Q_{disch} = 1011 mAh/g is obtained in the case of a fluorination temperature of 100°C, corresponding to the reaction with about 4.4 Li ions per unit formula. As mentioned above, Li cannot usually be fully extracted during the oxidation step, i.e. after the first reduction step and Co metal cannot be converted back to Co³⁺ but to Co^{2+} [26]. Consequently, the CoF₃ domains disappear after the first charge step and the electrochemical reaction implies CoF₂ according to the reaction Eq. (4). The theoretical capacity related to this reaction is 553 mAh/g.

XRD measurements have evidenced that an increase of T_F induces a strong modification of the particles size and has a direct impact on the electrochemical performance of cobalt fluoride in Liion battery, as often pointed out. Here, the highest the particle size (Table 3), the lowest the irreversible capacity deduced at the end of the first cycle, i.e. $Q_{disch} - Q_{ch.}$, and the lowest the reversible capacity ($Q_{ch.}$). Thus, for T_F = 100 and 300 °C, the reversible capacity is 418 and 257 mAh/g, respectively (Table 4), for crystallite size deduced 11 and 77 nm, respectively (see Table 3).

The first discharge-charge profiles obtained with CoF₃ prepared at $T_F = 100 \,^{\circ}$ C are given in Fig. 10 for various current densities. The difference between the first and the subsequent cycle profiles should arise from the occurrence of irreversible structural modifications of the electrode materials during the insertion of Li⁺ ions. An increase in the discharge current causes a decrease in the charge voltages, which means that the values of the potential plateau are strongly dependent on the discharge rates.



Fig. 11. Evolution of the charge and discharge capacities vs. cycle number obtained in 1 mol/L LiPF₆-EC:DMC (1:1) for CoF₃ prepared at 100 and 300 $^{\circ}$ C (current: \pm 5 mA/g).

No significant difference in the average plateau voltage and Q values has been observed for low current density ($\leq 20 \text{ mA/g}$) indicating that the diffusion of lithium ions controls the reaction. This difference is more pronounced for higher rates. Thus, the potential plateau decreases from around 1.5 to 1.0 V vs. Li⁰⁰/Li⁺ at 5 and 140 mA/g due to internal polarization, respectively. The capacities decrease also significantly with increasing current densities (Table 5). Thus, Q_{ch} decreases from 418 to 101 mAh/g and the coulombic efficiency from 41.3 to 29.3%, for increasing current densities from 5 to 694 mA/g, respectively.

The evolution of Q_{ch.} and Q_{disch.} vs. cycle number of in 1 mol/L LiPF₆-EC:DMC (1:1) electrolyte (rate: ± 5 mA/g) for CoF₃ prepared with two different fluorination temperatures is presented in Fig. 11. Reversible and stable capacities are observed after subsequent cycles for the sample prepared at T_F = 100 °C (390 mAh/g), whereas a drastic decay of the discharge capacity is observed for powders prepared at T_F = 300 °C. This behaviour is explained by the particle size, which is the largest for the sample prepared at T_F = 100 °C than for T_F = 300 °C.

Finally, the lithiation conversion mechanism of CoF_3 at the electrode/electrolyte interface was investigated using a galvanostatic intermittent titration method coupled with electrochemical



Fig. 12. OCV and CCV curves recorded after fourteen discharge/charge cycles obtained in 1 mol/L LiPF₆-EC:DMC (1:1) (rate: 5 mA/g) for nano-CoF₃ (nano-Co F100). Impedance measurements were carried out at each point indicated on the curve. Duration of each galvanostatic pulse: 3 h. Rest time before impedance measurement: 15 h. Inset: electric equivalent circuit for the electrode/electrolyte interface.

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Fig. 13. Experimental and fitted impedance spectra obtained at different points of the discharge curve given in Fig. 11: (a) point 1, (b) point 3, (c) point 6, (d) point 12, (e) point 18 and (f) point 22.

impedance spectroscopy (EIS) measurements in the case of sample prepared at $T_{\rm F}$ = 100 °C, which gives rise to the best electrochemical performance. It is the reason why we decided to perform impedance measurements after performing fourteen charge/ discharge cycles, i.e. after reaching a stabilization of the charge/ discharge cycling. EIS data at different points of the discharge curve are illustrated in Fig. 12. To succeed, a constant discharge current is applied to the electrode during a time t to reach a certain discharge state. Then, the current is interrupted and a rest time of several hours is imposed to the system. During this relaxation period, the cell voltage tends to a constant value indicating that the system tends to equilibrium, and after t=4h EIS measurements are performed. Then, a further galvanostatic pulse is applied to the cell and so on. In the present case, a current of 5 mA/g is applied to the electrode for 3 h and the duration of the rest time step is 15 h. Point referenced #6 on the curve presented in Fig. 12 is reached after six successive discharge/rest time sequences. The experiments were done until the potential reached 0.02 V vs. $\text{Li}^{00}/\text{Li}^+$ and gives rise to the variation of the OCV (open circuit voltage) and CCV (closed circuit voltage) curves. EIS spectra recorded at steps of discharge referenced 1, 3, 6, 12, 18 and 22 to follow the influence of the depth of discharge on the spectra are given in Fig. 13a–f, respectively.

Before studying the shape and the evolution of the impedance spectra vs. discharge states, let us consider briefly the evolution of the CCV and OCV curves (Fig. 12). The difference between OCV and CCV was defined as the cell polarization. The polarization is about 0.75 V at the beginning of the discharge. Then, the polarization gradually decreases with the increase in discharge to reach a rather constant value of about 0.25 V after few discharge/rest time sequences. This trend is consistent with the progressive generation of conducting Co nano-clusters during the discharge.

As shown in Fig. 13 for the first discharge states, the EIS diagrams exhibit a semi-circle at high-frequency range followed by a very large second one. At the beginning of the discharge process,

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Fig. 14. Evolution of R_e, R_{ct}, R_{SEI} and Q_{SEI} (inset) deduced from the fitting of the impedance spectra for different depth of discharge of nano-Co F100 sample (i.e. at different points of the discharge curve given in Fig. 11).

the charge transfer is difficult to observe since the two semi-circles obtained in this frequency domain overlap and the fitting of the experimental curve is therefore more difficult. The contribution of this loop hinders also the Warburg phenomenon at low frequencies. Then, for deeper discharge states, the influence of the charge transfer is reduced and a second semi-circle appears (for example see Fig. 13d); in the same time, an inclined line with a slope of 45° characteristics to Warburg contribution appears in the low frequency region. Due to their close time constants, data cannot be well extracted directly from the experimental curves and a fitting of the experimental curves using the equivalent circuit given in the inset of Fig. 12 is required. The electric equivalent circuit used for the fitting of the experimental diagrams is composed of R_{e} relative to the ionic resistance of the electrolyte resistance in series with an inductance L and with two (R, Q) loops. Note that constant phase elements (CPE), i.e. pseudo-capacitance Q, are used instead of pure capacitance to take into account the non-homogeneous nature of the composite electrode and the electrode/electrolyte interface. The first loop (high frequency region) is composed of the resistance of the SEI layer generated during the discharge process in parallel with its corresponding pseudo-capacitance Q_{SEI}. The second loop (middle frequency range) contains the contribution double layer pseudo-capacitance, Q_{dl}, in parallel with two terms in series: the charge transfer resistance (R_{ct}) and the contribution of Warburg diffusion (W). The latter must be considered for a perfect fitting of the experimental curves even if it is not discussed hereafter. The main data extracted from the fitting of the impedance diagrams are given in Fig. 13.

A very good agreement between the experimental and the fitted curves are obtained (Fig. 13) in the entire frequency range and whatever the discharged states. The evolution of R_{e} , R_{tc} and R_{SEI} vs. the depth of discharge (DOD) is given in Fig. 14 The electrolyte resistance $R_{\rm e}$ does not vary with DOD. The resistance of the SEI slightly decreases from point 1 (284 Ω) to point 9 (195 Ω) and then tends to a rather constant value. This can be interpreted by the stabilization of the SEI layer in terms of thickness and composition during the first steps of the discharge process. Thus, the SEI layer formed during the first discharge step is restored rapidly during the first cycles. The charge transfer resistance drastically decreases indicating that the reaction between lithium ions and electrons at the electrode/electrolyte interface occurs more and more easily with deeper discharge. The formation of Co/LiF nano-composites during the discharge process does not constitute a limitation for the electronic transfer at the interface and in contrast with results obtained for example with FeF_3 [12], the nano-Co formation facilitates the cell reaction by enhancing electronic contact between particles.

Finally, the variation of the pseudo-capacitance of the SEI (denoted Q_{SEI}) is presented in the inset of Fig. 14. Q_{SEI} does not vary significantly in the explored region vs. DOD, indicating a good stability of the SEI layer upon discharge. The variation of Q_{SEI} vs. DOD is in good accordance with the evolution of the associated resistance The R_{SEI} slightly decrease until point 9, before tending to a rather constant value, is interpreted by a small increase of the SEI thickness until this state and after its stabilization.

It should be noted that cobalt oxide and fluoride are conversion materials exhibiting during the discharge process a long plateau which appears in both cases. A simple interpretation of these plateaus could be hazardous since several reactions can be involved as the reactivity vs. CoF_3 , the formation of a passivation layer, etc., but in our case electrochemical analysis, coupled with XRD analysis of samples before discharge, partially discharged and after discharge did not reveal the presence of Co oxide, but only Co fluorides.

To summarize, the study of the electrochemical conversion reaction after subsequent cycles by EIS measurements does not highlight any significant modifications of the electrode materials such as volume change, growth of the SEI layer, mechanical stress, microstructural failures, and so on. The SEI layer is formed during the first steps of the discharge and reaches rapidly a stable state, allowing good electrochemical features and explaining the good cycle life observed with the CoF₃ nano-powders. The decrease of the charge transfer resistance is an indication that the conversion reaction does not give rise to detrimental modifications of the electrode such as volume expansion or formation of isolated areas from the bulk. Indeed, the two last phenomena should lead to the decrease of the electrochemical performances of the battery and generate local heating capable to strongly affect the security of the battery, but this is not evidenced here.

4. Conclusions

Co nanoparticles synthesized in aqueous medium by electrochemical route were fluorinated between 100 and 300 °C by F₂ gas. XPS measurements performed on the raw materials have pointed out the presence of a coverage of the starting Co metal by cobalt oxide and oxide-hydroxide. The nano-size of CoF₃ particles is maintained after fluorination treatments, at least at $T_{F2} = 100$ °C.

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XRD measurements coupled with Rietveld refinements reveal that the average size of the resulting CoF₃ particles depends on the fluorination temperature, the smallest size (11 nm) being obtained for T_{F2} = 100 °C. HRTEM investigations have evidenced well crystallized cobalt fluoride nanoparticles. Mixtures of active CoF₃ material and acetylene black were tested in order to control the preparation process of the electrode, in similar conditions as used in the elaboration of Li-ion batteries. The XPS investigation has shown that, when handled in very dry atmospheres, CoF₃based mixtures are stable vs. traces of humidity and can be used to prepare in good conditions electrodes for Li-ion batteries in safe conditions.

The fluorinated cobalt nanoparticles prepared by fluorination at 100 °C have been tested in 1 mol/L LiPF₆-EC:DMC (1:1) electrolyte as electrode materials in lithium battery. A reversible capacity of 390 mAh/g is obtained after subsequent cycles. Due to poor electronic conductivity properties, CoF_3 powder cannot accept high discharge rate and the maximum one is 1C-rate. Efforts focused on the modification of the surface are in progress to enhance the electrochemical performances.

Finally, one must underline that the mechanism from which the lithium uptake occurs is not straightforward and requires more investigations. The use of CoF_3 is a challenge because of its high reactivity. For example, the presence of shoulders during the charge or the discharge process could be interpreted by the presence of cobalt fluorides with various oxidation degrees.

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