



HAL
open science

Synthesis of “ $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ ” materials by different routes: Is there fluorine substitution for oxygen?

Laurence Croguennec, Jessica Bains, Michel Ménétrier, A. Flambard, Emilie Bekaert, C. Jordy, Ph. Biensan, Claude Delmas

► To cite this version:

Laurence Croguennec, Jessica Bains, Michel Ménétrier, A. Flambard, Emilie Bekaert, et al.. Synthesis of “ $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ ” materials by different routes: Is there fluorine substitution for oxygen?. *Journal of the Electrochemistry*, 2009, 156 (5), pp.A349-A355. 10.1149/1.3080659 . hal-00364482

HAL Id: hal-00364482

<https://hal.science/hal-00364482>

Submitted on 18 Mar 2009

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Synthesis of " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ " materials by different routes: is there fluorine substitution for oxygen?

L. Croguennec^{1,2,*}, J. Bains^{1,2}, M. Ménétrier^{1,2}, A. Flambard^{1,2},
E. Bekaert^{1,2}, C. Jordy³, Ph. Biensan³ and C. Delmas^{1,2}

¹ *CNRS, Institut de Chimie de la Matière Condensée de Bordeaux*

87 av. Schweitzer, PESSAC, F-33608, France

² *Université de Bordeaux, Institut de Chimie de la Matière Condensée de*

Bordeaux, ENSCPB, PESSAC, F-33608, France

³ *SAFT, Direction de la Recherche,*

111-113 Bld Alfred Daney, Bordeaux, F-33074, France

KEYWORDS: Lithium-ion battery; positive electrode material; layered oxide; $\text{Li}(\text{Ni},\text{Mn},\text{Co})\text{O}_2$; fluorine substitution; coating; X-ray diffraction; NMR spectroscopy; solid state electrochemistry

ABSTRACT:

A one-step synthesis method was used, with LiF or NiF₂ as fluorine precursor, to prepare " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ " materials. ⁷Li and ¹⁹F MAS NMR analyses revealed the presence of fluorine as LiF at the surface of the $\text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$ particles, rejecting the formation of fluorine-substituted $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ materials. These results allowed also highlighting that change in cell parameters with increasing fluorine content is not by itself a proof for effective fluorine substitution for oxygen in layered oxides, and that heterogeneity in the transition metal and fluoride ions distribution at the crystallites' scale can be at the origin of these modifications.

That LiF was shown to be present as small particles in some grain boundaries, but not as a continuous layer covering the particles surface. Improved cycling stability was observed for these LiF-"coated" materials, showing that effective fluorine substitution for oxygen is not required for an improvement of these layered oxides cyclability: a surface modification can be sufficient and can have also a huge impact.

* Corresponding author (L. Croguennec) Tel.: +33-5-4000-2647 (or 2234), fax:
+33-5-4000-2761

E-mail address: laurence.croguennec@icmcb-bordeaux.cnrs.fr

Introduction

Recently, the layered transition metal oxide $\text{Li}_{1+x}(\text{Ni}_y\text{Mn}_y\text{Co}_{1-2y})_{1-x}\text{O}_2$ has attracted much attention due to its large capacity, good cyclability and large thermal stability at high voltage in the highly deintercalated state [1-6]. These systems consist of $\text{Ni}^{2+, 3+}$, Mn^{4+} and Co^{3+} ions; Mn^{4+} being electrochemically inactive, it provides significant structural stability during electrochemical cycling (there is no detrimental effect of the Jahn-Teller distortion associated with Mn^{3+}) [2,7-10].

In order to improve the electrochemical performance of these materials, two approaches were developed: (i) ionic substitution to increase the structural stability of the layered oxide [11-14] and (ii) surface modification to decrease its catalytic effect on electrolyte degradation and thus to decrease the impedance during cycling [15]. LiF addition to $\text{Li}_{1+x}(\text{Ni}_y\text{Mn}_y\text{Co}_{1-2y})_{1-x}\text{O}_2$ materials used as positive electrode in lithium batteries was shown to improve their cycling performance and thermal stability in the charged state [16]. But conflicting explanations are proposed in literature to explain the effect of fluorine: most of the authors considered that fluorine substitution for oxygen is effective since changes in cell parameters were for instance observed using X-ray diffraction [17-22], while others assumed [16] or proved using X-ray Photoelectron Spectroscopy analyses [23] that fluorine is only present as an LiF surface layer.

Recently, we showed also using ^7Li and ^{19}F MAS NMR analyses that no fluorine substitution for oxygen occurs in " $\text{Li}_{1+z/2}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{1-z/2}\text{O}_{2-z}\text{F}_z$ " ($0 \leq z \leq 0.2$) formed in two steps ((i) coprecipitation of the layered oxide and (ii) addition of LiF as a solid state reaction), but there is formation of an LiF "coating" (this denomination was not considered to mean that this

constituted a uniform layer on the whole surface of the material, since this was not characterized) [24]. However, several synthesis methods were reported in literature to form these fluorine-substituted layered oxide materials, such as combination of coprecipitation and solid state reactions [18-19, 25-26], solid state reaction only [14, 27], sol-gel synthesis [20, 28] and spray drying process [23]. Although LiF was the main fluorine precursor reported, NH₄F [19, 29], NiF₂ [30] and NaF [31] were also used.

In this paper, we report on one-step solid state reactions to obtain "Li_{1.1}(Ni_{0.425}Mn_{0.425}Co_{0.15})_{0.9}O_{1.8}F_{0.2}" materials, with LiF or NiF₂ as fluorine precursor, that are assumed in literature to lead to the formation of Li_{1+x}(Ni_yMn_yCo_{1-2y})_{1-x}O_{2-z}F_z materials via direct fluorination. We aim at determining if fluorine substitution for oxygen is actual or not in this case, or if only a mixture of a parasitic fluorine-containing compound with Li(Ni_{0.425}Mn_{0.425}Co_{0.15})O₂ is obtained as for the materials synthesized according to a two-step synthesis with fluorine addition only in the second step we recently studied.

Experimental

Materials of "Li_{1.1}(Ni_{0.425}Mn_{0.425}Co_{0.15})_{0.9}O_{1.8}F_{0.2}" composition were prepared using two different methods. The first synthesis method was a usual solid state reaction between transition metal oxides, lithium carbonate (99 % Alfa Aesar) and lithium fluoride (99.9 % Prolabo), used as fluorine precursor. NiO and MnO₂ were obtained from the decomposition of Ni(NO₃)₂·6H₂O and Mn(NO₃)₂·4H₂O at 450°C during 15 h, whereas Co₃O₄ was obtained from the decomposition of CoCO₃ at 400°C during 12 h in oxygen atmosphere. These oxide materials are highly reactive because of their small particle sizes

(~ 150 nm and ~30 nm for NiO/MnO₂ and Co₃O₄, respectively) and large specific area. A ~ 10 g mixture of Li₂CO₃, LiF, NiO, MnO₂ and Co₃O₄ was prepared with molar ratio 0.45 / 0.2 / 0.3825 / 0.3825 / 0.045, mixed for 1 h in a Turbula[®] shaker-mixer and milled three times during 30 min. in a planetary mill using 7 agate balls (Ø 13 mm) in an agate jar (45 mm in diameter and 50 cm³ in volume). This mixture was finally calcinated two times in a gold crucible at 900°C and one time at 950°C for 24 h in an oxygen atmosphere with intermediate grindings. The second synthesis method was very similar to the first one, but with NiF₂ (99 % Aldrich) as precursor for fluorine. The following molar mixture was prepared: 0.55 Li₂CO₃ / 0.1 NiF₂ / 0.2825 NiO / 0.3825 MnO₂ / 0.045 Co₃O₄, and then calcinated three times in a gold crucible at 950°C for 24 h in an oxygen atmosphere with intermediate grindings.

Powder X-ray diffraction (XRD) analyses were performed using a Siemens D5000 diffractometer equipped with a graphite diffracted beam monochromator and Cu K α radiation. The diffraction patterns were collected in the 5 - 120° (2 θ) range using steps of 0.02° (2 θ) with a constant counting time of 8 s and analysed using the Fullprof program and the Le Bail method (refinement of the background, profile and cell parameters only). The profile was described using a pseudo-Voigt function.

In order to confirm the chemical composition of the various samples, lithium and transition metal ions were titrated using ICP measurements (using a Thermo Iris Intrepid II XP spectrometer). Fluorine and transition metal ions were also titrated using electron microprobe (CAMECA SX 100 spectrometer). Powders were pressed into pellets (13 mm in diameter) and metallized by gold – palladium plasma deposition. The analysis area was (15 x 15) μm^2 with 1 μm depth, the accuracy being around 1-2 at.%. Finally, the average oxidation state

of the transition metal ions was determined by iodometric titration. The samples were dissolved in a concentrated acidic solution with an excess of KI and the produced iodide I_3^- ions were titrated with a $Na_2S_2O_3$ solution.

Materials were characterized by 7Li and ^{19}F MAS NMR at 116.6 and 282.4 MHz respectively, using an Avance 300 MHz Bruker spectrometer and a (90 – τ – 180) Echo-MAS sequence. The 7Li and ^{19}F chemical shifts were externally referenced to LiCl (1M) and $CFCl_3$ at 0.0 ppm, respectively.

High Resolution Scanning Electronic Microscopy (SEM) analysis of the samples was performed using a Hitachi S-4500 microscope. Powders were metallized by palladium plasma deposition.

Electrochemical characterizations were performed in lithium cells containing lithium foil as the negative and reference electrodes. The positive electrode was a (88: 10: 2) wt. % mixture between " $Li_{1.1}(Ni_{0.425}Mn_{0.425}Co_{0.15})_{0.9}O_{1.8}F_{0.2}$ " materials, carbon black / graphite (1: 1) and polytetrafluorethylene as a binder. The electrolyte solution was $LiPF_6$ (1M) in a mixture of PC: EC: DMC (1: 1: 3). Cells were assembled in an argon-filled dry box and cycled at room temperature in galvanostatic mode at a constant C/20 rate (corresponding to a theoretical exchange of one electron per formula during a charge or a discharge of 20 h).

Results and discussion

The X-ray diffraction patterns of the " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ " materials obtained using solid state reactions, with LiF or NiF_2 as fluorine precursor, are compared in **Fig. 1** to that of " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop" obtained as described in [24] by combination of coprecipitation and solid state reactions and using LiF as fluorine precursor. α - NaFeO_2 type layered phases were obtained with all the diffraction peaks indexed in the R-3m space group. For the two new materials, neither LiF nor NiF_2 were detected by XRD analyses whereas a secondary (minor) layered phase could be detected (highlighted by arrows in **Fig. 1**). In comparison, for the " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop" reported earlier, no extra peaks associated to LiF or to any secondary phase were observed by XRD. The samples obtained by solid state reactions thus appear more heterogeneous than that obtained by combination of coprecipitation and solid state reactions. Let us also recall that, for the " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop" material, LiF was in fact detected by ^7Li and ^{19}F MAS NMR to be present as a thin deposit on the particle surface of $\text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$.

The chemical composition of the three samples was analyzed combining elemental and redox titrations, as well as electron microprobe analyses. As reported in **Tab. 1**, the experimental average composition of the powders was found to be in really good agreement with the nominal compositions. The larger discrepancy observed for fluorine could come from an overlapping in Energy Dispersive X-ray spectrometry (EDX) analyses between peaks characteristic in energy of F, Au (coming from metallization) and Co, and not only from an

actual fluorine loss during the thermal treatment at high temperature. Redox titration showed as expected for the three materials an average oxidation state (oxid. state) close to 3 for the transition metal ions. As shown in **Fig. 2** with the results of the electron microprobe analyses, the transition metal ions distribution is homogeneous in " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop" whereas that of fluorine appears significantly more heterogeneous. Electron microprobe analyses revealed also that the transition metal and fluorine ions are heterogeneously distributed in the two new samples obtained by solid state reactions: as shown in **Fig. 2b-c**, a manganese-rich phase (bright areas) is formed next to the main layered oxide phase. All these results, and especially the heterogeneous distribution of fluorine as in " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop", thus suggest the formation of an $\text{LiF} / \text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$ mixture rather than effective fluorine substitution for oxygen in the two new $\text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$ materials as well.

A comparison of the cell parameters (a_{hex} , c_{hex} and volume) determined for " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - ss LiF" and " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - ss NiF₂" with those already reported for $\text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$ in " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop" is given in **Tab. 2**. Considering the major phases, the cell parameters were found larger than those determined for $\text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$ in " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop". These results are in very good agreement with changes in lattice parameters reported in literature for layered $\text{Li}(\text{Ni},\text{Mn},\text{Co})\text{O}_2$ materials as a function of their fluorine content and taken as a proof for effective substitution [14,17,19, 26-27, 30]. On the contrary, we

observed earlier no changes in structural parameters for a series of coprecipitated materials which were finally shown to be non-successfully substituted [24]. Note that for the two materials obtained by solid state reactions, the secondary phases detected, which are manganese-rich after electron microprobe analyses, have smaller a_{hex} and larger c_{hex} cell parameters than the major phase. In our opinion, changes in cell parameters with increasing fluorine content are not by themselves proofs for effective fluorine substitution for oxygen in these layered oxide materials, especially because careful analyses using combination of X-ray diffraction and electron microprobe have shown heterogeneity in the transition metal and fluoride ions distribution at the crystallites' scale. Indeed, changes in composition (Li/M and Ni/Mn/Co ratios) due to this heterogeneity for these layered oxides would induce also cell parameters modifications. At this step, the question remains thus open: is there really any fluorine substitution for oxygen in these compounds?

As reported previously for the sample " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop" [24], MAS NMR spectroscopy analyses allow discriminating between presence of fluorine in a paramagnetic layered oxide material (large shift expected for the NMR signal due to transfer of electron spin density from the transition metals to fluorine) and presence of fluorine in a diamagnetic material such as LiF (small shift expected). As shown in **Fig. 3** and **Fig. 4**, for the two materials obtained by solid state reaction the ^7Li and ^{19}F NMR spectra reveal LiF signals separated into narrow spinning sidebands (-1.4 ppm in ^7Li resonance and -204 ppm in ^{19}F resonance), similar in relative magnitude and in shape to those of " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop". The chemical shifts of these ^7Li and ^{19}F NMR signals show that fluorine is not successfully substituted for oxygen

in $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - ss LiF" and $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - ss NiF₂" but present as LiF; their shape shows that this LiF is present - as it was shown previously for $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop" - as a thin deposit at the surface of the layered oxide with a similar thickness for the three samples; finally, their magnitude shows that the amount of LiF is similar for the three samples in good agreement with similar nominal fluorine amount. In addition to the LiF signal, the very broad signal in **Fig. 3** (not separated into spinning sidebands) corresponds to Li in the layered oxide material; its width (~ 600 ppm) results from dipolar interactions with the electron spins of nickel and manganese and its (Fermi contact) shift around 250 ppm is due to the transfer of some electron spin density from the transition metals to lithium. An other signal, with its isotropic position at ~ 410 ppm, separated into spinning side bands and negligible in relative magnitude, corresponds most probably to Li in the secondary manganese-rich layered material detected by XRD and confirms the heterogeneous cation distribution. In ¹⁹F resonance, **Fig. 4** also shows, as discussed previously for $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop" in reference [24], a broad signal from the probe that contains PTFE in non-spinning parts. These ⁷Li and ¹⁹F NMR spectra therefore allow us to conclude that fluorine was not incorporated into these layered oxide materials synthesized by solid state reaction using either LiF or NiF₂ as fluorine precursor, despite changes in structural parameters with increasing fluorine content. Fluorine is again present as a thin deposit of LiF, not detected by XRD. The feature in the NMR spectra that allows us to conclude for the immediate proximity of LiF from the surface of the layered oxide is the striking difference in the line shape (spinning sidebands envelope) for the ⁷Li and ¹⁹F signals in the LiF standard compared to

those in the materials. Indeed, for both nuclei, the larger global width (number of spinning sidebands) for the " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ " samples than for the LiF standard indicates that LiF is very close to the electronic spins of the layered oxide, which lead to a through space dipolar interaction and to a broadening of the NMR signals.

Combination of X-ray diffraction, chemical analyses and ^7Li and ^{19}F MAS NMR spectroscopy has thus revealed that fluorine substitution for oxygen does not occur in " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ " samples, despite the use of different synthesis methods or fluorine precursors assumed in literature to lead to the formation of $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_{2-z}\text{F}_z$ materials. Nevertheless, it was found interesting to characterize the morphology and electrochemical performances of these materials proven to be LiF-"coated" and not fluorine substituted, and to compare these results with those reported in literature for materials announced to be $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_{2-z}\text{F}_z$.

The Scanning Electron Microscopy micrographs obtained for the three samples are given in **Fig. 5**. The primary particles of the two materials " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ " synthesized by solid state reaction are as expected larger in size (more than 700 nm in diameter) and distributed more heterogeneously in comparison with those observed for " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop" (~ 300 nm in diameter), indeed they were obtained after longer thermal treatments at higher temperature. The micrographs show the presence of small particles or "sheets" (assumed to be LiF as confirmed by analyses using Auger electron spectroscopy under etching – not shown here) in the grain boundaries. LiF would thus be present in some grain boundaries, as small particles of 30 nm in diameter for " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop", as "sheets" of 30 nm in thickness

for " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - ss LiF" and as formless grains of 15 to 50 nm in diameter for " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - ss NiF₂". Altogether, although LiF appears not to be in the form of a uniform film at the surface of the materials, the proximity with the material can be considered as similar in all cases. Since this distribution of distances governs the global lineshape of the Li and F MAS NMR spectra, this leads to similar lineshapes for the three compounds.

Fig. 6 gives changes in voltage versus capacity during the first 10 galvanostatic charge / discharge cycles performed between 2 and 4.5 V (vs. Li⁺/Li) at C/20 rate in lithium cells using LiF-"coated" samples as positive electrode materials, in comparison with that obtained for the bare Li(Ni_{0.425}Mn_{0.425}Co_{0.15})O₂ material. Since we have demonstrated, especially by NMR analyses, that –irrespective of the synthesis method used - LiF-"coated" layered oxide materials were obtained, the active mass was corrected from its LiF content for the electrochemical tests. The reversible capacity obtained in first discharge is rather good for the four samples, but significantly larger for the bare sample (175 mAh.g⁻¹ vs. 150 to 160 mAh.g⁻¹ for the LiF-"coated" samples). Larger irreversible capacity is also observed for the LiF-"coated" materials (30 - 50 mAh.g⁻¹) compared to that obtained for the bare material (16 mAh.g⁻¹). The polarization measured between charge and discharge curves is also significantly more important for " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ – ss NiF₂" (250 mV vs. 180 mV for the others). Nevertheless, the LiF-"coated" samples show better stability of their capacity during cycling in non-optimized laboratory lithium cells, with less than 6 % of capacity loss after 10 cycles,

whereas the bare $\text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$ material loses more than 13 % of its capacity after 10 cycles between 2 and 4.5 V (vs. Li^+/Li).

These first electrochemical results suggest thus that presence of LiF would improve the stability of the capacity during cycling – as also reported in literature for materials announced to be $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_{2-z}\text{F}_z$ materials - and that the modification of the composition and structure of the active material is thus not essential to have this impact on its electrochemical performances in lithium cells. In fact, as already reported for instance for metal-oxide coated materials [15], although SEM micrographs have shown discontinuous small particles or platelets on grain boundaries, the modification of its surface by the presence of LiF probably modifies locally the composition of the material/electrolyte interface and can also be beneficial to a better cyclability during cycling, for instance through a minimization of the electrolyte degradation at its surface. From a general point of view, changes in the interface nature could also affect thermal stability of the positive electrode in the charged state. This will be discussed in the case of the LiF-"coated" materials in a forthcoming paper [32].

Conclusion

" $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ " materials were prepared with LiF or NiF_2 as fluorine precursors using a one-step solid state method. These synthesis methods were reported in literature to lead to the formation of fluorine-substituted layered oxides. In fact, ^7Li and ^{19}F MAS NMR analyses revealed the presence of fluorine as a thin LiF deposit at the surface of the $\text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$ particles and thus showed that fluorine-substituted $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ materials were not obtained (like for

materials obtained with a two-step coprecipitation and solid state synthesis reported earlier [24]). Changes in cell parameters with increasing fluorine content were observed for these samples obtained by solid state reaction: combining X-ray diffraction, chemical and NMR analyses it was possible to discriminate between actual fluorine substitution for oxygen and heterogeneity in the transition metal ions distribution, this latter being at the origin of those changes in cell parameters. This LiF coating was shown to be present as small particles or "sheets" in some grain boundaries (30 nm in diameter or in thickness, respectively): interestingly, although different synthesis methods and fluorine precursors were used, the proximity of LiF with the paramagnetic material can thus be considered as similar in all cases, explaining the similar lineshapes of the ^7Li and ^{19}F MAS NMR spectra for the three compounds. LiF is not present as a continuous layer covering the particles surface. Nevertheless, improved cycling stability was observed for these LiF-"coated" materials, at least during a few cycles in the [2 – 4.5 V] potential window at the C/20 rate, showing that surface modification (without substitution and thus bulk modification) can be sufficient to improve the cyclability.

Acknowledgements: the authors thank O. Jan (Saft), C. Denage (ICMCB) and L. Raison (ICMCB) for their technical assistance, Pr A. Lecerf (INSA, Rennes, France) and Dr S. Levasseur (Umicore, Olen, Belgium) for fruitful discussions and Région Aquitaine and Saft for their financial support.

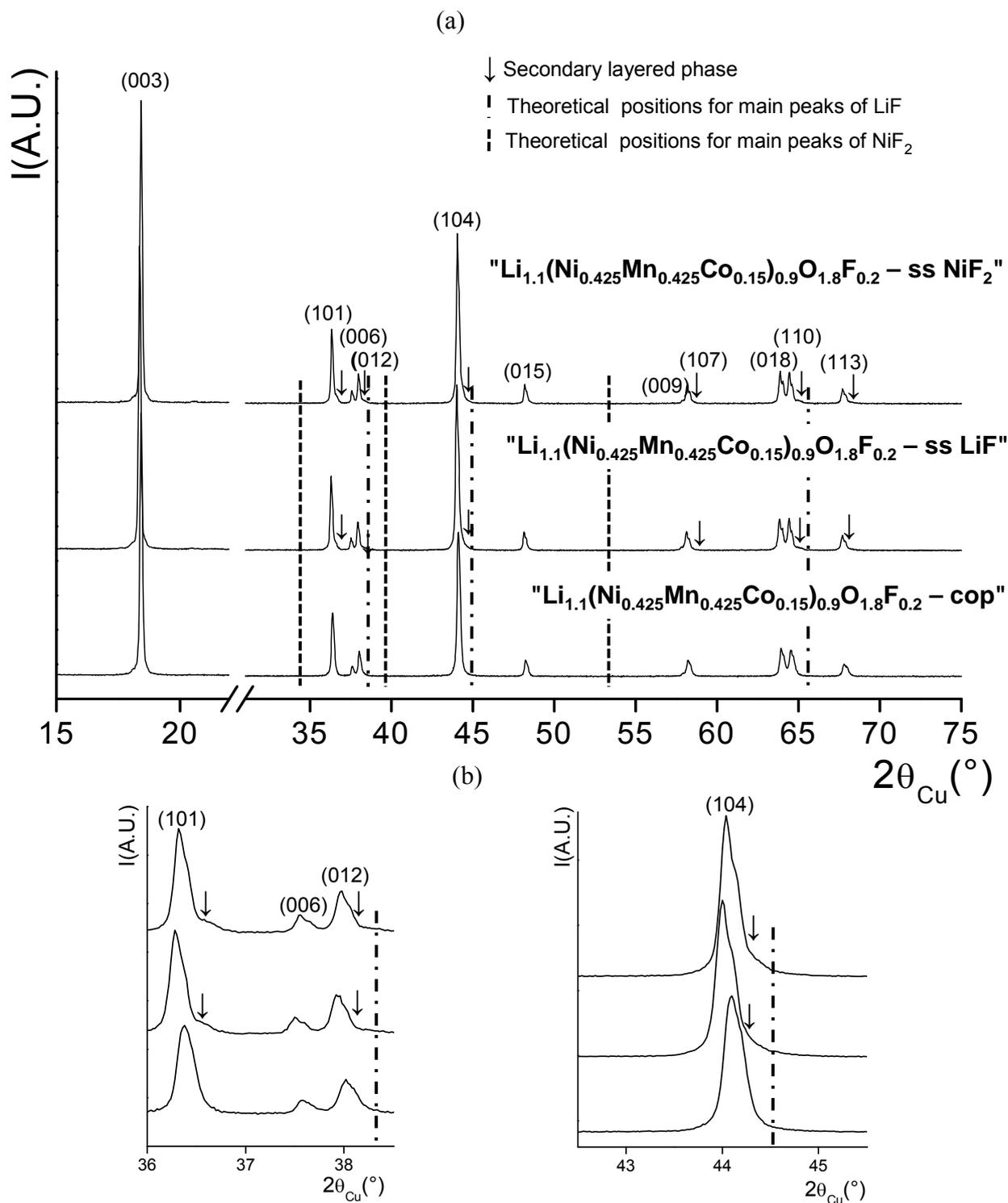


Figure 1: XRD patterns of the "Li_{1.1}(Ni_{0.425}Mn_{0.425}Co_{0.15})_{0.9}O_{1.8}F_{0.2}" samples prepared by combination of coprecipitation and solid state reactions (cop) or solid state reactions only (ss), using LiF or NiF₂ as fluorine precursor (a). Enlargements given in the 36-38.5° and 42.5-45.5° 2θ angular ranges (b).

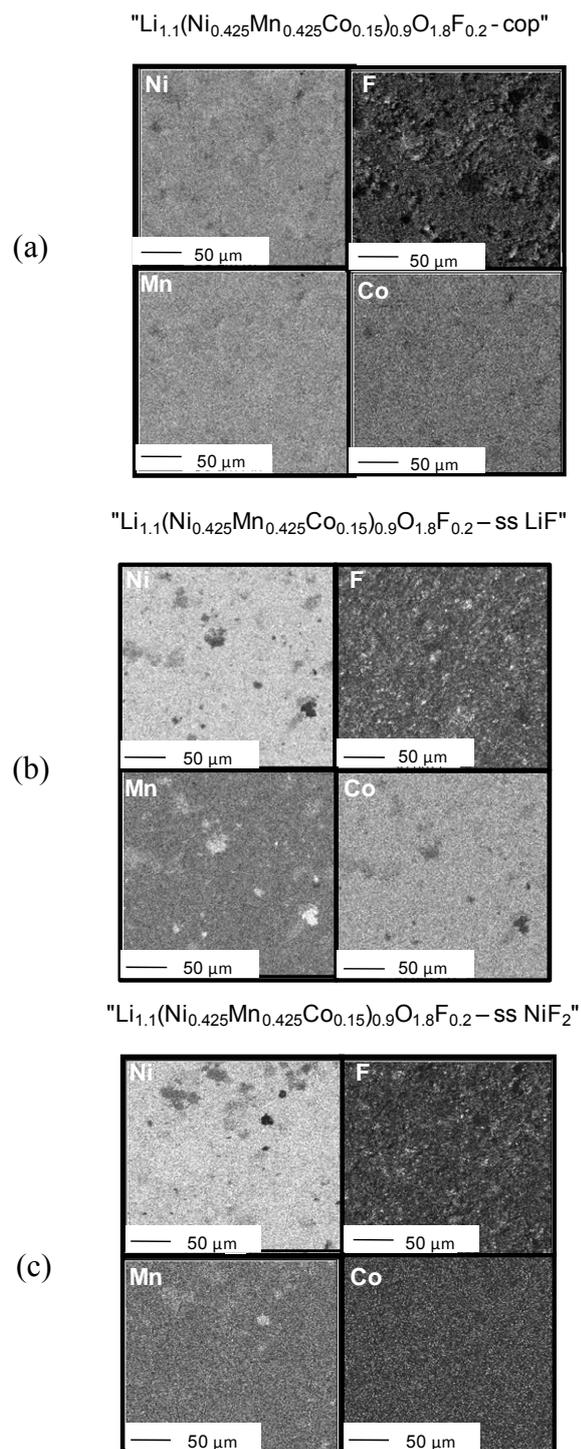


Fig. 2: Electron microprobe analyses of the " $Li_{1.1}(Ni_{0.425}Mn_{0.425}Co_{0.15})_{0.9}O_{1.8}F_{0.2}$ " samples obtained using combination of coprecipitation and solid state reactions (cop) with LiF as fluorine precursor (a), and solid state reactions only (ss) with LiF (b) or NiF₂ (c) as fluorine precursors.

Note that for a given map, the lighter the grey is, the larger the amount of the element.

Furthermore, no quantitative comparison can be done between different maps. Each map is characterized by its own scale in grey levels (concentrations).

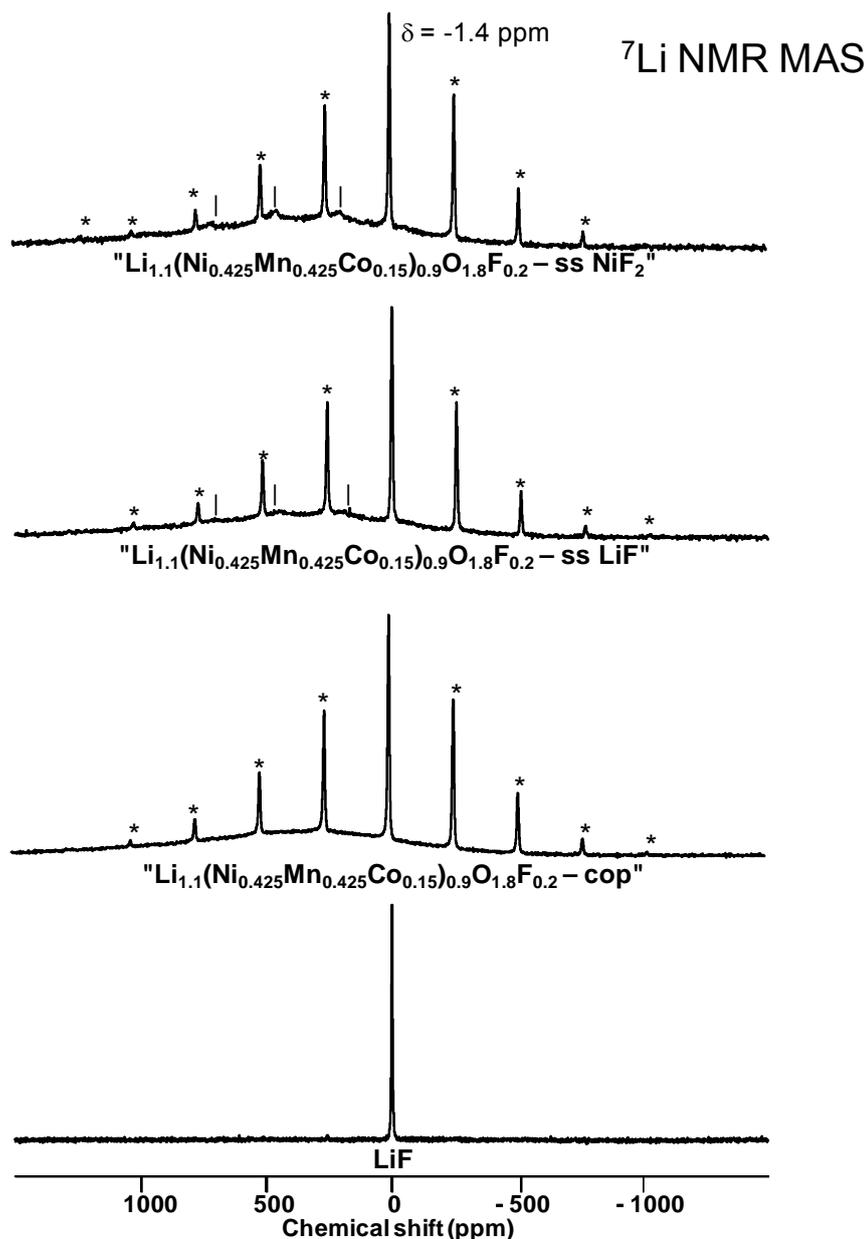


Figure 3: ${}^7\text{Li}$ MAS NMR spectra of " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ " materials synthesized by combination of coprecipitation and solid state reactions (cop) or solid state reactions only (ss) using LiF or NiF_2 as fluorine precursors. The spectra intensity is scaled to the sample mass except for the LiF reference.

(*) Spinning side bands

(l) Secondary layered phase signals

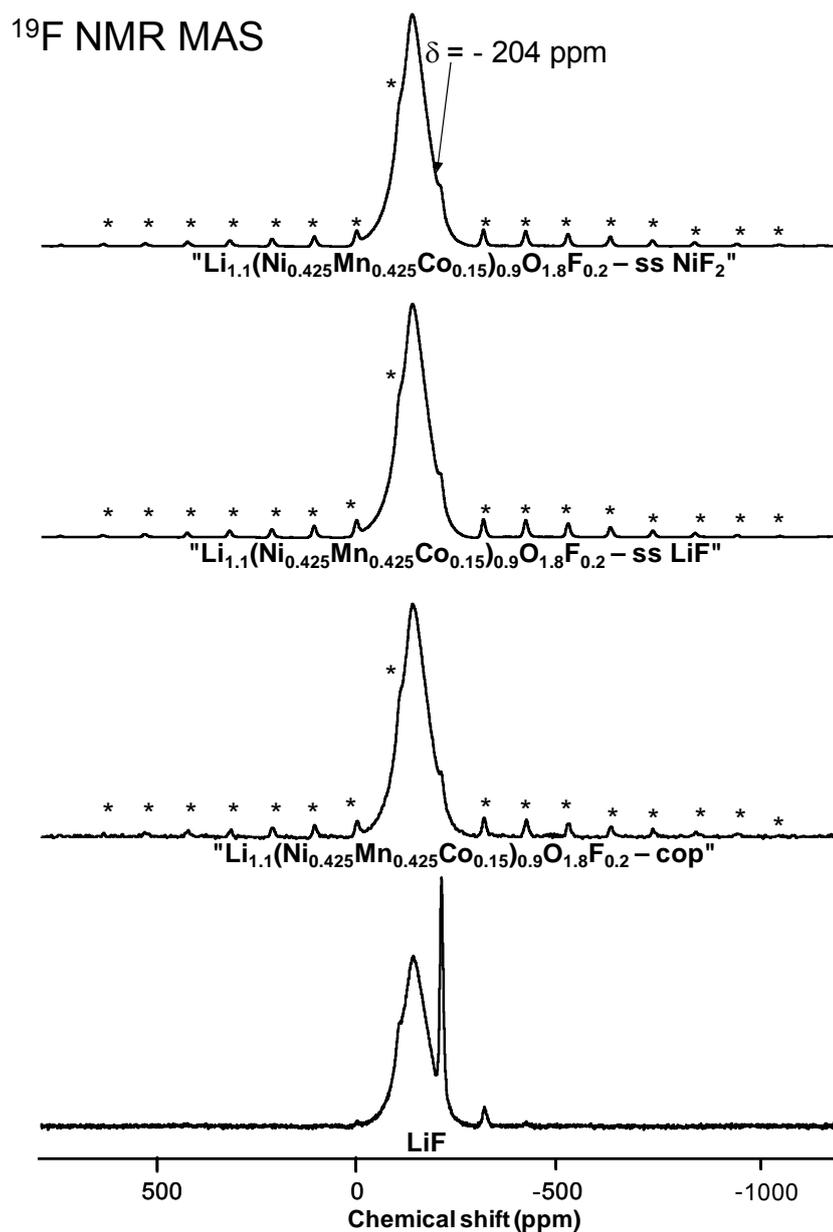


Figure 4: ^{19}F MAS NMR spectra of " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ " materials synthesized by combination of coprecipitation and solid state reactions (cop) or solid state reactions only (ss) using LiF or NiF_2 as fluorine precursors. The spectra intensity is scaled to the sample mass except for the LiF reference.

(*) Spinning side bands

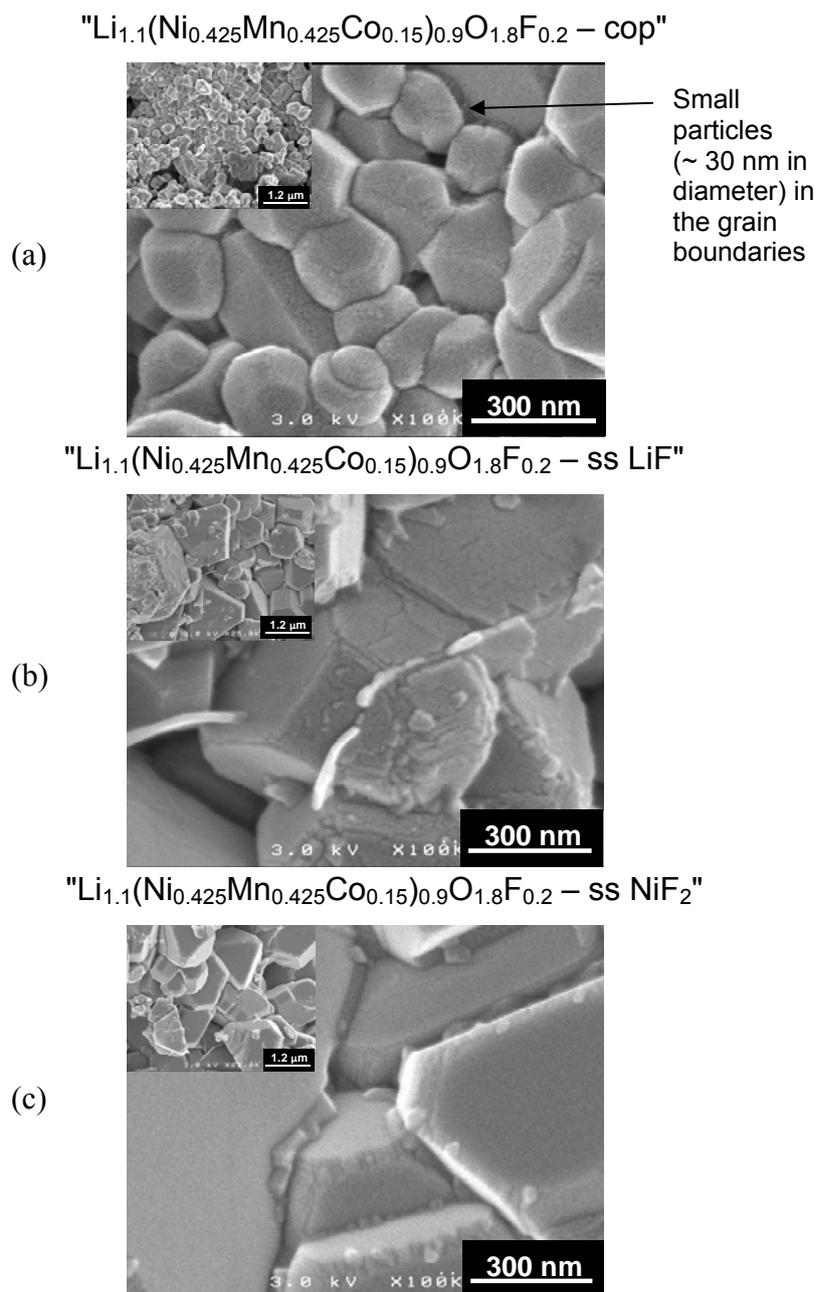


Fig. 5: SEM micrographs of a) " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop" obtained using combination of coprecipitation and solid state reactions with LiF as fluorine precursor, b) " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ – ss LiF" obtained using the solid state method with LiF as fluorine precursor and c) " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - ss NiF₂" obtained using the solid state method with NiF₂ as fluorine precursor.

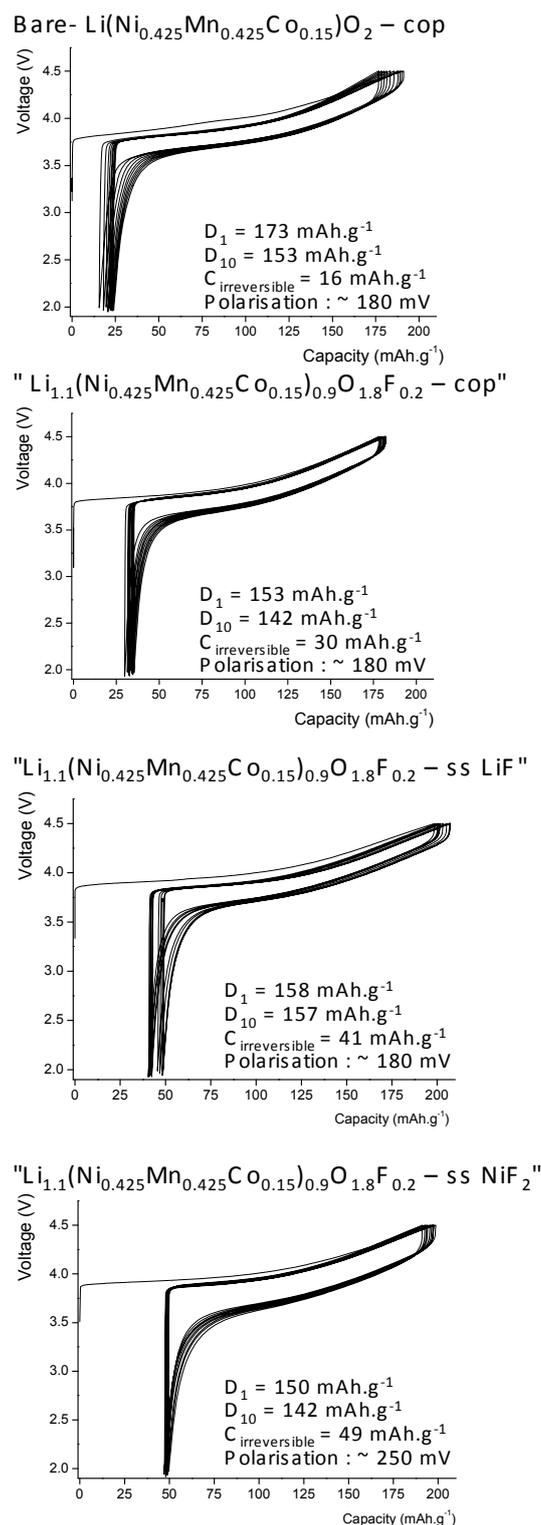


Figure 6: Variation of the cell voltage vs. capacity during the first 10 galvanostatic charge/discharge cycles for lithium cells using " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ " materials as positive electrodes, in comparison with that obtained for the bare $\text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$ material.

As these " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ " materials were shown to be actually mixtures of layered oxides and LiF, the active mass was corrected from its LiF content.

Table 1: Results of the chemical and redox analyses for the samples of target composition " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ "; these results were obtained by iodometric and ICP titrations as well as microprobe analyses.

Material	Oxid. state	ICP analyses ((Li/M) _{th.} = 1.22; (Ni/Mn) _{th.} = 1; (Co/Mn) _{th.} = 0.35)			Microprobe analyses ((F/M) _{th.} = 0.22)
		(Li/M) _{exp.}	(Ni/Mn) _{exp.}	(Co/Mn) _{exp.}	(F/M) _{exp.}
" $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop" <i>i.e.</i> LiF-coated $\text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$	3.02	1.26	1.02	0.35	0.15
" $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - ss LiF"	2.98	1.19	1.01	0.34	0.14
" $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - ss NiF_2 "	2.97	1.16	1.05	0.35	0.14

Table 2: Cell parameters determined for the " $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ " samples by the refinement of their X-ray diffraction data by the Full Pattern Matching method (or Le Bail method).

Material	Phases	a_{hex} (Å)	c_{hex} (Å)	V (Å ³)	R_{wp} (%)
" $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - cop" i.e. LiF-coated $\text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$	1 [24]	2.8785(2)	14.281(2)	102.48(2)	13.0
" $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - ss LiF"	1*	2.8823(2)	14.293(1)	102.83(2)	12.9
	2	2.8654(2)	14.319(1)	101.81(2)	
" $\text{Li}_{1.1}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.9}\text{O}_{1.8}\text{F}_{0.2}$ - ss NiF_2 "	1*	2.8836(3)	14.292(3)	102.92(3)	29.7
	2	2.8686(3)	14.322(3)	102.06(3)	

(*) Major phase

References:

- [1] T. Ohzuku, Y. Makimura, *Chem. Letters*, **642** (2001)
- [2] B.J. Hwang, Y.W. Tsai, D. Carlier, G.Ceder, *Chem. Mater.*, **15**, 3676 (2003)
- [3] D. Li, T.Muta, L. Zhang, M. Yoshio, H. Noguchi, *Journal of Power Sources*, **132**, 150 (2004)
- [4] N. Tran, L. Croguennec, C. Labrugère, C. Jordy, P. Biensan and C. Delmas, *J. Electrochemical Soc.*, **153 (2)**, A261 (2006)
- [5] N. Tran, L. Croguennec, C. Jordy, P. Biensan and C. Delmas, *Solid State Ionics*, **176**, 1539 (2005)
- [6] N. Yabuuchi and T. Ohzuku, *Journal of Power Sources*, **119-121**, 171 (2003)
- [7] K.M. Shaju, G.V. Subba Rao, B.VR. Chowdari, *Electrochem. Acta*, **48**, 145 (2002)
- [8] W.S. Yoon, C.P. Grey, M. Balasubramanian, X.Q. Yang, J. McBreen, *Chem. Mater.*, **15**, 3161 (2003)
- [9] A. Deb, U. Bergmann, S.P. Cramer and E.J. Cairns, *J. Appl. Phys.*, **97**, 113523 (2005)
- [10] D.C. Li, T. Muta, L.Q. Zhang, M. Yoshio, H. Noguchi, *Journal of Power Sources*, **132**, 150 (2004)
- [11] S.K. Hu, T.C. Chou, B.J. Hwang and G. Ceder, *Journal of Power Sources*, **160**, 1287 (2006)
- [12] J. Guo, L.F. Jiao, H.T. Yuan, L.Q. Wang, H.X. Li, M. Zhang and Y.M. Wang, *Electrochem. Acta*, **51**, 6275 (2006)
- [13] G.H. Kim, S.T. Myung, H.S. Kim and Y.K. Sun, *Electrochem. Acta*, **51**, 2447 (2006)

- [14] M. Kageyama, D. Li, K. Kobayakawa, Y. Sato and Y-S. Lee, *Journal of Power Sources*, **157**, 494 (2006)
- [15] S.T. Myung, K. Izumi, S. Komaba, H. Yashiro, H.J. Bang, Y.K. Sun and N. Kumagai, *J. Phys. Chem.*, **111**, 4061 (2007)
- [16] S. Jouanneau and J.R. Dahn, *J. Electrochemical Soc.*, **151**, A1749 (2004)
- [17] G.-H. Kim, J.-H. Kim, S.-T. Myung, C. S. Yoon and Y.-K Sun, *Journal of Electrochemical Society*, **152**, A1707 (2005)
- [18] S.T. Myung, G.H. Kim and Y.K. Sun, *Chem. Letters*, **33**, 1388 (2004)
- [19] S.U. Woo, B.C. Park, C.S. Yoon, S.T. Myung, J. Prakash and Y.K. Sun, *J. Electrochemical Soc.*, **154**, A649 (2007)
- [20] S.H. Kang and K. Amine, *Journal of Power Sources*, **146**, 654 (2005)
- [21] G.H. Kim, S.T. Myung, H.J. Bang, J. Prakash and Y.K. Sun, *Electrochemical and Solid State letters*, **7**, A477 (2004)
- [22] G.H. Kim, M.H. Kim, S.T. Myung and Y.K. Sun, *Journal of Power Sources*, **146**, 602 (2005)
- [23] D. Li, Y. Sasaki, K. Kobayabawa, H. Noguchi and Y. Sato, *Electrochemical Acta*, **52**, 643 (2006)
- [24] M. Ménétrier, J. Bains, L. Croguennec, A. Flambard, E. Bekaert, C. Jordy, P. Biensan and C. Delmas, *J. of Solid State Chem.* (2008),
[doi:10.1016/j.jssc.2008.09.002](https://doi.org/10.1016/j.jssc.2008.09.002)
- [25] Y. Kim, J. Eom, M.G. Kim, Y.K. Sun, C.S. Yoon and J. Cho, *J. Electrochemical Soc.*, **154**, A561 (2007)
- [26] H.-S. Shin, S.-H. Park, C. S. Yoon et Y.-K Sun, *Electrochemical and Solid State Letters*, **8** (11), A559 (2005)
- [27] Y.-S. He, L. Pei, X.-Z. Liao and Z.-F. Ma, *Journal of Fluorine Chemistry*, **128**, 139 (2007)

[28] L. Liao, X. Wang, X. Luo, X. Wang, S. Gamboa, P.J. Sebastian, *Journal of Power Sources*, **160**, 657 (2006)

[29] X. He, J. Li, Y. Cai, Y. Wang, J. Ying, C. Jiang and C. Wan, *Solid State Ionics*, **176**, 2571 (2005)

[30] A.R. Naghash et J.Y. Lee, *Electrochimica Acta*, **46** 941-951 (2001)

[31] K.-H. Dai, Y.-T. Xie, Y.-J. Wang, Z.-S. Song and Qilu, *Electrochem. Acta*, **53**, 3257 (2008)

[32] L. Croguennec, J. Bains, C. Jordy, P. Biensan and C. Delmas, in preparation