



# NMR evidence of LiF coating rather than fluorine substitution in $\text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$

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## ABSTRACT

A series of “ $\text{Li}_{1+z/2}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{1-z/2}\text{O}_{2-zF_z}$ ” materials was prepared by a coprecipitation route and their structure was characterized using X-ray diffraction (XRD), as well as  $^7\text{Li}$  and  $^{19}\text{F}$  Magic Angle Spinning (MAS) NMR spectroscopy. Two hypotheses were considered: (i) formation of layered oxyfluoride materials and (ii) formation of a mixture between the layered material and LiF. Structural parameters were refined by the Rietveld method, using XRD diffraction data. The refinement results did not allow us to choose between these two hypotheses: no significant change in crystallinity and structural parameters was observed irrespective of the fluorine ratio.  $^7\text{Li}$  and  $^{19}\text{F}$  MAS NMR analyses showed signals with isotropic positions characteristic of LiF, but envelopes characteristic of very strong dipolar interactions with the electron spins of the material, demonstrating that LiF was not incorporated into the layered oxide structure but was instead present as a coating.

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## 1. Introduction

Currently,  $\text{LiCoO}_2$  is the most widely used positive electrode material in commercial lithium-ion batteries. However, because of its high cost and limited cyclability and chemical stability at high voltage, various partial substitutions for Ni in  $\text{LiNiO}_2$  were investigated [1–7]. Recently,  $\text{Li}_{1+x}(\text{Ni}_y\text{Mn}_y\text{Co}_{1-2y})_{1-x}\text{O}_2$  systems have been suggested to be the most promising alternative to  $\text{LiCoO}_2$  [8–12]. These systems consist of  $\text{Ni}^{2+}$ ,  $^{3+}$ ,  $\text{Mn}^{4+}$  and  $\text{Co}^{3+}$  ions.  $\text{Mn}^{4+}$  is electrochemically inactive so that it provides significant structural stability during electrochemical cycling (no detrimental effect of the Jahn–Teller distortion associated with  $\text{Mn}^{3+}$ ), while  $\text{Ni}^{2+}$  and  $\text{Co}^{3+}$  are electroactive through  $\text{Ni}^{2+/3+/4+}$  and  $\text{Co}^{3+/4+}$  redox couples [9,13,14]. The electrochemical performance of the  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$  system was found to be highly dependent on the current density and cut-off voltage, with a rather fast reversible capacity fading when cycling is, for instance, performed in a large potential window [15]. In order to improve the electrochemical performance, two approaches were developed: (i) ionic substitution to increase the structural stability of the layered oxide [16–19] and (ii) surface modification to stabilize

the layered oxide surface through an impedance decrease [20]. The LiF addition to  $\text{Li}_{1+x}(\text{Ni}_y\text{Mn}_y\text{Co}_{1-2y})_{1-x}\text{O}_2$  materials was shown to improve their cycling performance and thermal stability [21]. But conflicting explanations are proposed in the literature: 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 (XRD) [22–25], while others recently showed by XPS analyses that fluorine exists as an LiF surface layer [26].

In this paper, we report attempts for the synthesis of “ $\text{Li}_{1+z/2}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{1-z/2}\text{O}_{2-zF_z}$ ” materials by the coprecipitation route. Their structural properties have been studied by XRD and NMR spectroscopy. The aim of this paper was to determine whether fluoride ions are actually incorporated within the layered lattice.

## 2. Experimental

A series of materials with nominal “ $\text{Li}_{1+z/2}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{1-z/2}\text{O}_{2-zF_z}$ ” ( $z = 0, 0.1, 0.2$ ) compositions was prepared following the solid-state syntheses reported by Kim et al. [22,23] using LiF as the fluorine precursor. The first step of the synthesis consisted in the formation of  $\text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$  using the coprecipitation route and then in the addition of LiF aiming the

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target stoichiometry  $\text{Li}_{1+z/2}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{1-z/2}\text{O}_{2-z}\text{F}_z$ . A mixed (1 M) aqueous solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98% Prolabo),  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (98% Prolabo) and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $\geq 98\%$  Fluka), prepared with the 42.5/42.5/15 Ni/Mn/Co molar ratio, was added dropwise into a basic solution ( $\text{LiOH}$  1 M (98% Alfa Aesar)/ $\text{NH}_4\text{OH}$  3 M (28% Prolabo)) under magnetic stirring. The nominal Li/M ratio was adjusted to 1.02 to compensate for lithium loss due to the high temperature of the synthesis ( $M$  being for transition metal ions). A green–brown mixed hydroxide precipitated. Water was evaporated at  $80^\circ\text{C}$  under primary vacuum using a rotavapor device. The resulting precipitate was dried overnight in an oven at  $105^\circ\text{C}$ ; then it was heated in air in a tubular furnace up to  $500^\circ\text{C}$  for 5 h to decompose nitrates and finally calcinated in air at  $900^\circ\text{C}$  for 12 h (heating and cooling rates:  $2^\circ\text{C}/\text{min}$ ). As described just after, the  $\text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$  phase was characterized in detail by XRD and an ICP titration before being used as a precursor for the synthesis of the fluorinated phases. The second step consisted of mixing in an agate mortar the prepared  $\text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2$  powder with LiF powder (99.9% Prolabo) according to the chemical equation:  $1-z/2 \text{Li}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})\text{O}_2 + z \text{LiF} \rightarrow \text{Li}_{1+z/2}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{1-z/2}\text{O}_{2-z}\text{F}_z$  ( $z = 0, 0.1, 0.2$ ). The resulting mixture was heated in a gold crucible in air at  $875^\circ\text{C}$  for 5 h (heating and cooling rates:  $2^\circ\text{C}/\text{min}$ ) and finally ground in an agate mortar. According to these expected chemical formulae  $\text{Li}_{1+z/2}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{1-z/2}\text{O}_{2-z}\text{F}_z$ , irrespective of the  $z$  value, the average oxidation state of the transition metal ions is expected to remain equal to 3. Indeed, the only fluorine substitution for oxygen would theoretically lead to the reduction of  $M$  according to  $(1\text{O}^{2-} + 1\text{M}^{3+} \equiv 1\text{F}^- + 1\text{M}^{2+})$ . Nevertheless, in  $\text{Li}_{1+z/2}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{1-z/2}\text{O}_{2-z}\text{F}_z$  the presence of extra-lithium ions—that would be theoretically compensated by the oxidation of  $M$  ions ( $3\text{M}^{3+} \equiv 1\text{Li}^+ + 2\text{M}^{4+}$ )—leads in fact to charge compensation without any modification of the transition metal ion oxidation state (as  $\frac{1}{2}\text{M}^{3+} + 1\text{O}^{2-} \equiv \frac{1}{2}\text{Li}^+ + 1\text{F}^-$ ).

The average oxidation state of the transition metal ions was determined by iodometric titration with  $\text{Na}_2\text{S}_2\text{O}_3$ . Lithium and transition metal ions were titrated using ICP measurements (Thermo Iris Interpid II XP). Synthesized powders were solubilized in an acidic solution. Fluorine and transition metal ions were titrated using an electron microprobe (CAMECA SX 100). Powders were pressed into  $\varnothing 13\text{ mm}$  pellets and metallized by gold–palladium plasma.

Powder XRD analyses were performed using a Siemens D5000 diffractometer and  $\text{CuK}\alpha$  radiation. The diffraction patterns were recorded in the  $10\text{--}80^\circ$  ( $2\theta$ ) range using  $0.02^\circ$  ( $2\theta$ ) step of a 2 s duration for routine characterization. For structural study using the Rietveld method, data were collected in the  $5\text{--}120^\circ$  ( $2\theta$ ) range with steps of  $0.02^\circ$  ( $2\theta$ ) and a constant counting time of 8 s.

Materials were characterized by  $^7\text{Li}$  and  $^{19}\text{F}$  MAS NMR at 116.6 and 282.4 MHz, respectively, using an Avance 300 MHz Bruker spectrometer and a (90– $\tau$ –180) rotor-synchronized Echo-MAS sequence (30 kHz spinning speed). The  $^7\text{Li}$  and  $^{19}\text{F}$  chemical shifts were externally referenced to  $\text{LiCl}$  (1 M) and  $\text{CFCl}_3$  at 0.0 ppm, respectively.

### 3. Results and discussion

#### 3.1. Structural characterization: XRD analyses

The XRD patterns of “ $\text{Li}_{1+z/2}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{1-z/2}\text{O}_{2-z}\text{F}_z$ ” materials are compared in Fig. 1. Unexpectedly, these three diffraction patterns are very similar irrespective of the fluorine ratio ( $z = 0, 0.1$  and  $0.2$ ). All the diffraction peaks could be indexed in the  $R\bar{3}m$  space group: no extra peaks associated with LiF could be observed. According to XRD, pure  $\alpha$ - $\text{NaFeO}_2$ -type phases are thus obtained. The widths of the diffraction lines are very similar for the three materials. The full widths at half maximum (FWHM) of the (003) and (104) diffraction lines are about  $0.10^\circ$  and  $0.16^\circ$ , respectively, with an intensity ratio  $I_{(003)}/I_{(104)}$  close to 1.06. The splitting of the (018)/(110) doublet is also very similar for the three materials.

The chemical composition of the resulting powders was analyzed by the ICP titration and microprobe. The experimental results were found to be in very good agreement with the nominal compositions (Table 1) and redox titration showed an average oxidation state of the transition metal close to 3; we thus considered the nominal compositions for the refinements of the XRD data by the Rietveld method.

XRD patterns were first analyzed by full pattern matching: only the cell and the profile function parameters were refined. The profile function was described by a pseudo-Voigt and the profile function parameters were found to remain almost constant with increasing fluorine substitution ( $U \sim 0.11$ ,  $V \sim 0.03$  and  $W \sim 0.002$ ).

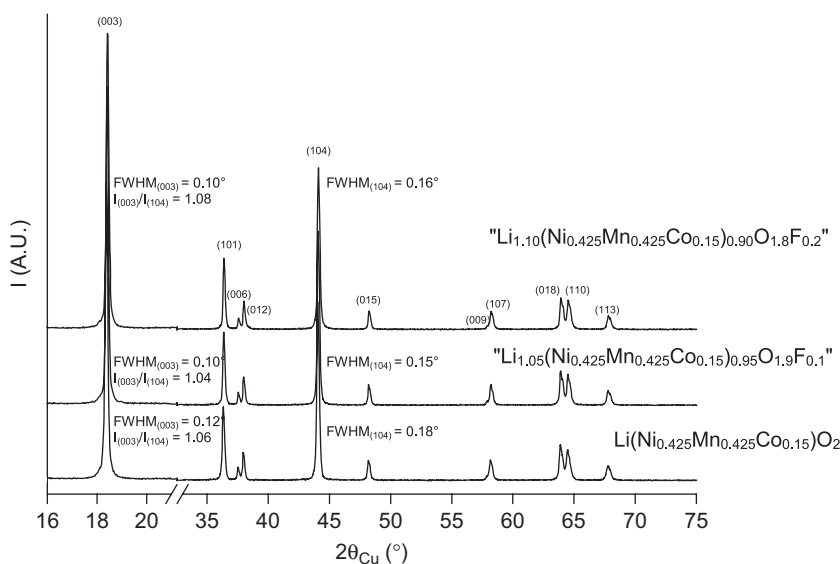


Fig. 1. XRD patterns of the “ $\text{Li}_{1+z/2}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{1-z/2}\text{O}_{2-z}\text{F}_z$ ” samples prepared by coprecipitation.

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