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1 Fluorination of (Mg,Cu,Al,Fe)-based LDHs template for conversion 2 materials usable in all-solid state lithium metal batteries

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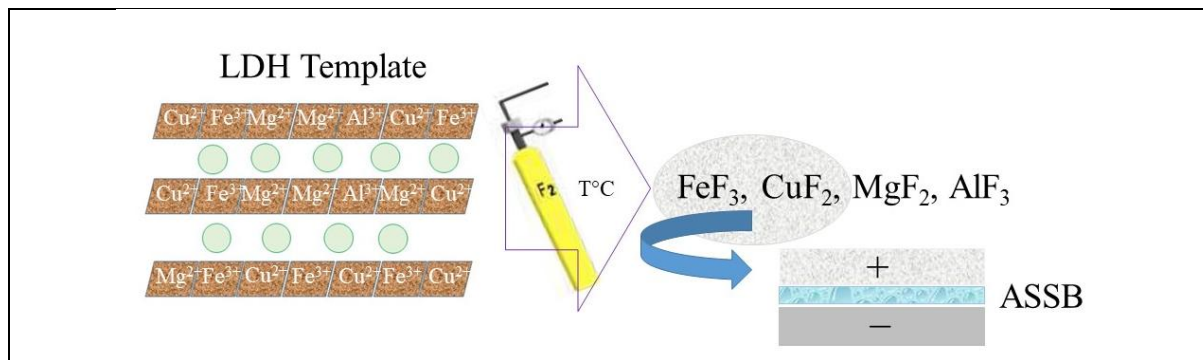
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15 16 GRAPHICAL ABSTRACT



18 19 20 ABSTRACT

21 Iron and copper fluorides are of interest as conversion cathode materials in lithium batteries
22 but they suffer from high hysteresis and low cyclability, respectively. To overcome these
23 limitations and take advantage of the electrochemical properties of each of the fluorides,
24 fluoride mixtures that combine the two redox centers Fe³⁺ and Cu²⁺ are synthesized using
25 Layered Double Hydroxides (LDH) as a 2D multi-metallic template. Hydrotalcite-type phases

26 substituted with Cu^{2+} and Fe^{3+} ions are prepared by coprecipitation then fluorinated with
27 fluorine gas in static mode at temperatures chosen according to their thermal evolution
28 monitored by mass spectrometry. After each fluorination treatment, the materials are
29 characterized by X-ray diffraction and most LDH materials are found stable up to 200°C ,
30 treatment above leads to the formation of fluorides of each of the cations. The initial
31 dispersion of the cations in the LDH sheets nevertheless allows, after fluorination, a
32 composite of fluorides making them totally accessible to the phenomenon of electrochemical
33 conversion shown here in a metallic lithium battery assembly with a Solid Polymer
34 Electrolyte (SPE). In such All-Solid-State Battery (ASSB) configuration often limiting in
35 terms of columbic efficiency, 76 % the first discharge capacity is recovered in charge for an
36 optimized composition (up to 560 mAh.g^{-1}). This good reversibility positions these LDH
37 templates very well for future investigations in the field of electrochemical storage.

38

39 **Keywords:** Layered Double Hydroxide, Solid-Gas Fluorination, Solid-State Lithium Metal
40 Battery

41

42 1. INTRODUCTION

43

44 Transition Metal Fluorides (TMFs) are emerging as promising cathode materials in
45 Lithium batteries (Turcheniuk et al., 2021). Among the TMFs of particular interest, FeF_3 and
46 CuF_2 are extensively studied in the literature (Hua et al. 2021). Indeed, FeF_3 exhibits a
47 theoretical capacity of 712 mAh.g^{-1} at a voltage of 2.74 V vs. Li^+/Li (Eveillard et al., 2020;
48 Guérin et al., 2016; Huang et al., 2019; Shimoda et al., 2020) while CuF_2 displays a
49 theoretical capacity of 528 mAh.g^{-1} at a voltage of 3.55 V vs. Li^+/Li (Hua et al., 2014; Krahl
50 et al., 2018; Omenya et al., 2019; Seo et al., 2017). However, TMFs usually suffer from high
51 voltage hysteresis and low cyclability, both related to the dramatic volume change and deep

52 reduction state involved in the conversion step resulting from the transformation of TMF to
53 LiF and TM (Wu et al., 2020a). Interestingly electrochemical properties for both FeF₃ and
54 CuF₂ are enhanced in ternary metal fluorides of general formula Cu_yFe_{1-y}F₂ (Omenya et al.,
55 2019; Seo et al., 2017; Wu et al., 2020a; Wang et al., 2015) obtained by mechanochemistry.
56 This underlines the benefit of mixing fluorides together in particular to optimize the battery
57 energy density (depending on both the capacity and the voltage of the working electrodes).
58 This also prompts us to step further in the level of mixing between fluorides to combine in
59 one material high voltage provided by Cu²⁺ ions and high capacity provided by Fe³⁺ ions.
60 Indeed, the synthesis of such TMFs including both copper and iron cations is really topical to
61 meet the high energy requirements.

62 In this sense, a Multi-Metallic Template Fluorination MMTF is presented here to prepare
63 similar materials. This synthesis procedure is carried out by solid-gas fluorination using
64 gaseous F₂ reacting with Multi-Metallic Templates MMT of interest. It allows working
65 without water and the formation of a subsequent hydrated phase. This method of synthesis is
66 uncommon, as conventional fluorination methods use a fluorinating solution such as fluorytic
67 sol-gel method with usually trifluoroacetic acid (Erhard and Noack, 2015). In a previous
68 study, fluorination of a 3-dimensional (3D) MMTF, namely Copper-based Prussian Blue
69 Analogue (CuPBA), led either to a fluorinated multi-metallic structure phase at low
70 fluorination temperatures or a CuF₂/FeF₃ two-phase mixture at higher temperatures, all with
71 interesting electrochemical properties compared to a similar composition obtained by
72 mechano-chemistry (Eveillard et al., 2022). After fluorination of the template at 350°C, a first
73 discharge of 878 mAh.g⁻¹ and 59% reversibility in subsequent charge was obtained in
74 comparison with 620 mAh.g⁻¹ and 68% reversibility for the ball milling reference sample of
75 similar CuF₂/FeF₃ composition. Another article reports the formation of multi-metallic
76 pyrochlore fluorides by gaseous fluorination of multi-metallic ammonium fluoride precursors

77 (Lemoine et al., 2021). The oxidation is found to proceed through a topotactic mechanism;
78 however, the obtained materials show poor electrochemical properties. Among the MMTs of
79 interest, Metal Organic Frameworks (MOFs) exhibit a tunable multi-cation forming large
80 open structure that should facilitate fluorine diffusion (Glowniak et al., 2021; Liu et al., 2020;
81 Sun et al., 2019; Xia et al., 2016). The preliminary synthesis of fluorinated organic linkers
82 enables the formation of various fluorinated MOF structures (Chen et al., 2013; Pachfule et
83 al., 2011; Pachfule et al., 2016) whereas the calcination of a non-fluorinated MOF template
84 exposed to a fluorinating agent promotes the formation of analogous metal fluorides with
85 interesting electrochemical features (Liu et al., 2020; Wu et al., 2021; Zhang et al., 2019).
86 However, the large quantity of organic linkers in MOFs hinders their use as solid-gas
87 fluorination precursors, since it may lead to the formation of insulating carbon fluoride CF_x
88 and/or highly toxic gaseous by-products.

89 To overcome this issue while retaining the benefit of an accessible open structure as well as to
90 generalize the MMTF concept, Layered Double Hydroxides are considered here as templates.
91 Indeed, these versatile compounds are known to present a lamellar structure and a chemical
92 composition tunable by a simple synthesis using pH-regulated metal ion coprecipitation,
93 making them interesting for innovative applications and industrial transfer (Taviot-Guého et
94 al., 2018). These compounds have the general formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2] \cdot A_{x/n}^{n-} \cdot m\text{H}_2\text{O}$ with
95 M^{2+} and M^{3+} divalent and trivalent cations, respectively, and interlayer anions A that
96 compensate the excess of charge of the positive layers. In order to compare the templates
97 between each other as much as possible and in particular between the 3D PBA (Eveillard et
98 al., 2022) and the 2D LDH, the cation composition is selected to form similar ratios between
99 CuF_2 and FeF_3 fluorides.

100 Such cationic LDH compositions have already been explored in literature, either with only the
101 couple $\text{Cu}^{2+}/\text{Fe}^{3+}$ in the cationic sheets (Nejati et al., 2013; Wang et al., 2021; Zubair et al.,

102 2021) or mixed with other cations like Zn^{2+} (Lu et al., 2016), Co^{2+} (Lu et al., 2019), Ni^{2+}
103 (Wang et al. 2018), Mg^{2+} (Zhang et al., 2022) or Mg^{2+}/Al^{3+} (Carja et al., 2001; de Melo et al.,
104 2021; Guo et al., 2012). Among these types of Cu/Fe compositions identified, particular
105 attention is given here to Mg/Al/Cu/Fe cationic compositions. The MMTF applied to the LDH
106 compositions is expected to form a composite of fluorides including domains of MgF_2 , AlF_3 ,
107 CuF_2 and FeF_3 . Additionally, TMFs are known to be reactive towards organic electrolytes,
108 especially CuF_2 used in this study (Celik-Kucuk et Abe, 2021). Solid electrolytes are
109 preferred since the end goal is to obtain an All-Solid-State Battery (ASSB) that is safer when
110 embedded in autonomous energy stockage systems such as those needed in space
111 applications. In that sense, the solid polymer electrolyte (SPE) PEO/LiTFSI (Poly Ethylene
112 Oxide impregnated with Lithium bis(trifluoromethanesulfonyl)imide) is used, since it is
113 known to be efficient with FeF_2 as reported by Huang et al. (Huang et al., 2019). However, a
114 special attention should be paid since recent article reports that PEO might not be suitable for
115 electrode materials containing copper fluoride (Omenya et al., 2019).

116 Beforehand, the thermal transformations of synthesized LDH materials are monitored using
117 thermogravimetric measurements coupled with evolved gas analysis by mass spectrometry
118 (MS TGA). Fluorination temperatures of interest are selected as a function of the major
119 thermal events. Structural changes occurring after fluorination are characterized by X-ray
120 diffraction (XRD). The local structural change reported in supporting information is followed
121 as a function of fluorination temperature, reporting the near-edge structure at the two
122 transition metal absorption K edges.

123 An All-Solid-State Battery (ASSB) set-up using PEO/LiTFSI as the Solid Polymer
124 Electrolyte (SPE) is used to explore the electrochemical mechanism of the fluorinated
125 composite materials. Cyclic voltammetry with a scan rate of $20 \mu V.s^{-1}$ is used to scrutinize the
126 insertion and conversion mechanisms over a wide-open potential window (50 mV to 4.1 V vs.

127 Li⁺/Li). The shape of the CVs is compared between fluorinated LDH after fluorination at 200
128 and 350°C. Finally, the voltage as a function of the capacity of each candidate is recorded in
129 galvanostatic mode.

130

131 2. MATERIALS AND METHODS

132 3.1. Material synthesis and fluorination

133 For the synthesis of LDH of general theoretical composition (Mg, Cu)²⁺(Fe,
134 Al)³⁺Cl(OH)₆·nH₂O, hydrated metal chlorides and sodium hydroxide were used as supplied
135 by Aldrich, without further purification. The hydroxalite-like materials were prepared via
136 coprecipitation method. Experimentally, 100 mL of a solution of each CuCl₂, MgCl₂, AlCl₃
137 and FeCl₃ hydrated salt (0.01 mol.L⁻¹) was prepared. Three different solutions of cationic mix
138 Cu²⁺/Mg²⁺/Al³⁺/Fe³⁺ (1.5/1.5/0.5/1) (1.5/1/0.25/1) (1.5/0.5/0/1) were considered for the
139 preparation of three different theoretical (M²⁺/M³⁺ = 2:1) LDH cationic sheet compositions
140 (Cu_{1.5}Mg_{1.5})²⁺(Al_{0.5}Fe₁)³⁺; (Cu_{1.5}Mg₁)²⁺(Al_{0.25}Fe₁)³⁺; (Cu_{1.5} Mg_{0.5})²⁺(Fe₁)³⁺. Solutions of the
141 reactants were added to the reactor with peristaltic pumps at a constant flow of 2.0 mL.min⁻¹
142 for 3 h under a nitrogen atmosphere, to avoid the carbonate contamination from air. The pH
143 was kept constant at different values (7.5, 8.5, 9.5 and 10.5 ± 0.1) through the addition of a
144 sodium hydroxide solution (0.1 mol.L⁻¹) by an automated regulation system. After a 3 h
145 aging, the slurries were centrifuged and finally washed several times with distilled water.
146 After drying, the products were recovered as fine powders and characterized. Only the
147 (Cu_{1.5}Mg_{0.5})²⁺(Fe₁)³⁺ chlorinated LDH product synthesized at pH = 10.5 (theoretical
148 composition [(Cu_{0.5}Mg_{0.17})²⁺(Fe_{0.33})³⁺(OH)₂] Cl_{0.33} · xH₂O) was then used as a fluorination
149 precursor.

150 A dedicated equipment consisting of a passivated cylindrical nickel reactor of approximately
151 50 cm in length and 1 L in volume was used for solid gas fluorination using special care. Pure

152 molecular gaseous fluorine from Solvay Fluor (purity 98-99 % v/v with HF max. 0.5 % v/v
153 and other gases, mainly O₂/N₂ at about 0.5 % v/v) was used for all experiments. A 20 cm long
154 sample holder coated by passivated nickel was loaded with two hundred milligrams of a
155 finely grounded powder recovered after LDH synthesis. The reactor was first degassed at RT
156 by flushing gaseous nitrogen for 1h to remove any moisture and oxygen presences and placed
157 under primary vacuum. To ensure heating, the reactor tube was lined by a horizontal tube
158 furnace, ensuring a homogeneous temperature zone of approximately 10 cm at the centre of
159 the reactor. The furnace was then heated at a 5°C.min⁻¹ rate until the desired fluorination
160 temperature was reached (in between RT and 350 °C). Fluorine was injected at 40 mL.min⁻¹
161 up to 1 bar and maintained during 3 hours in the closed reactor in a static mode. After reaction
162 and when the temperature was below 100 °C in the reactor, nitrogen was injected to remove
163 all the fluorine gas. The powders were then stored under argon in a glove box to avoid
164 degradation by air.

165 **3.2. Structural characterization**

166 A Panalytical X-Pert Pro diffractometer equipped with a Cu K α 1 source diffracted beam
167 monochromator and a linear X'celerator detector and using a home-made sample holder
168 closed to under static inert argon was used to collect X-ray diffraction (XRD) data. Recording
169 conditions were with a counting time of 108 seconds associated with an angle step size 2 θ of
170 0.0167° in 10-80° range. Profex software was used for patterns matching (Doebelin et al.,
171 2015).

172 Using SOLEIL Synchrotron facilities (France), X-ray absorption spectroscopy (XAS)
173 measurements at both K-edges of copper and iron were performed at 80 K in transmission
174 mode. The ROCK beamline was equipped with a sagittal focusing Si (220) monochromator
175 (Briois et al., 2016). The intensity of the monochromatic X-ray beam was measured by the
176 detectors placed in the ionization chambers. Dispersed with cellulose, the powders were

177 pressed into pellets. Any contact of the fluorinated products with air was avoided by placing
178 the pellet in Kapton. Three successive scans with energy steps of 0.5 eV were performed to
179 ensure reproducibility of the measurements. For each scan, calibration in energy was possible
180 by simultaneously recording absorption measurements of Fe and Cu metal foils. The data
181 were averaged and normalized using ATHENA software (Ravel et al., 2005), and the
182 resulting pseudo radial distributions (PRD) were not corrected for phase shift.

183 A Netzsch STA F3 Jupiter apparatus was used for thermal analyses. Before any
184 measurements, three successive vacuum cycles were applied to clean the sample chamber.
185 Each sample was heated using a temperature slope of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ and a constant flux of 70
186 $\text{ml}\cdot\text{min}^{-1}$ either under He or dry air (80/20 % v/v N_2/O_2). An average of 20 mg of powder was
187 placed in an alumina crucible with a lid in the glove box to avoid contact with air during the
188 transfer to the TG sample chamber. The analysis was processed by mass spectrometry
189 (Netzsch Aeolos Quadro) and the main signals of the evolved gases were shown stacked for
190 qualitative comparison.

191 The different samples were characterized by Scanning Electron Microscopy (ZEISS Supra
192 SEM operating at 3 kV).

193 **3.3. Electrochemical characterization**

194 A cycling temperature of 60°C was used to favour lithium diffusion in the solid electrolyte
195 used. Beforehand, each powder (MF) was mixed for 6 h at 350 rpm in a planetary ball milling
196 with acetylene black (AB) to improve its electron conductivity using a weight ratio MF/AB of
197 50/50. All subsequent steps were performed in an argon-filled glove box. The milled powder
198 MF and AB was mixed with PVDF powder as a binding agent in a weight ratio of 90:10, and
199 the resulting mixture was then dispersed in propylene carbonate to obtain a homogeneous
200 slurry. Wet deposits were syringed onto stainless-steel grids (14 mm diam., 0.2 mm thickness)
201 and subsequently dried at 80°C under vacuum (usually 1.8-2.7 mg of active mass of MF). The

202 resulting cathodes were assembled in a two-electrode coin cell (CR2032) with lithium metal
203 disk (1 mm thick - Aldrich) acting as both negative and reference electrodes, *i.e.* voltage
204 values expressed *vs* Li⁺/Li. A 200 μm-thick PEO-LiTFSI membrane (H-Polymer, NEI
205 Corporation) was placed between the cathode and lithium. Solubilized PEO-LiTFSI powder
206 in 14 wt. % of pure acetonitrile was poured on a PTFE foam leading to an amorphous
207 polymer presenting a glass transition temperature below 0°C associated to an ionic
208 conductivity of about 5.10⁻⁵ S.cm⁻¹ at RT.

209 Electrochemical measurements were carried out on a VMP3 or a BCS Biologic instrument.
210 Relaxation time of no less than 5 h was performed to stabilize the open circuit voltage (OCV).
211 Cyclic voltammetry was performed at 0.02 mV.s⁻¹ in the potential range 50 mV to 4.1 V.
212 Galvanostatic experiments were carried out in the potential range 1-4.1 V with a C/50 and
213 C/250 per mA.g⁻¹ of active mass current density for discharge/charge, respectively.

214

215 3. RESULTS AND DISCUSSION

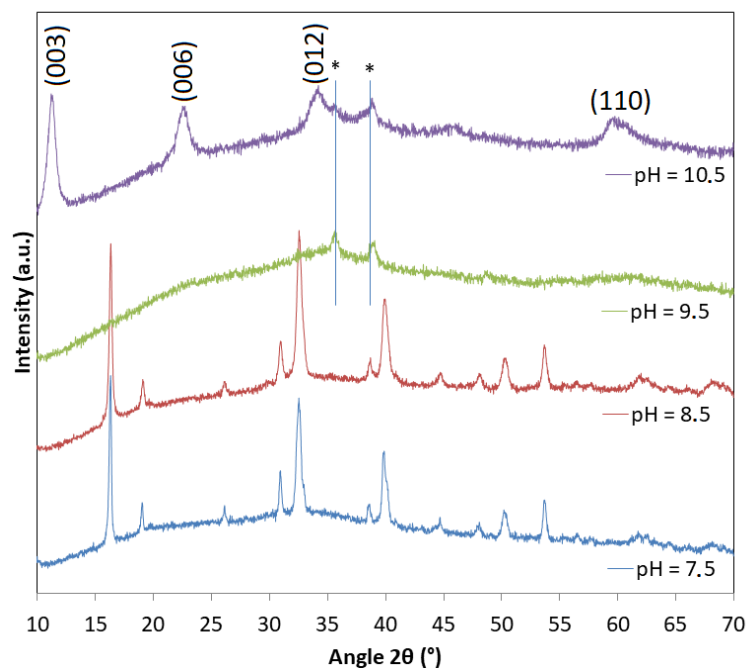
216 3.1. Optimization of the synthesis

217 A range of materials considering multiple substitution in the variable composition (Cu,
218 Mg)₂(Fe, Al) was studied: XRD results of three types of LDH with different cationic sheet
219 compositions are presented in Fig. S1. As the overarching target is here on the composition
220 adopting the less non-electrochemical cation and keeping the ratio of Cu/Fe of 3/2 similar to
221 PBA, the LDH of theoretical composition (Cu_{0.5}Mg_{0.17})²⁺(Fe_{0.33})³⁺(OH)₂(Cl)_{0.33} . xH₂O is
222 retained in the following. A chloride LDH form is here preferred since the reaction of chlorine
223 with fluorine is expected to be total without any by-product.

224 Figure 1 shows the effect of the pH value applied constant during the coprecipitation. At pH
225 of 7.5 and 8.5, a paratacamite phase is formed. Indeed, all the diffraction peaks are assigned to
226 this phase (ICSD 64956). Paratacamite is a mineral of composition Cu₂(OH)₃Cl that is found

227 to crystallize in space group $R3$ (Fleet, 1975). Jahn-Teller cation Cu^{2+} is well-known to
228 destabilize the edge-sharing LDH sheets when in too much quantity converting LDH either to
229 botallackite-type structure (Jiménez-López et al., 1993; Leroux et al., 2002) or to two-
230 dimensional $\text{Cu}_2(\text{OH})_3\text{X}$ paratacamite as observed here for $\text{X} = \text{Cl}$ (Fujita et al., 1997).
231 Increasing pH to 9.5 results in the formation of CuO (monoclinic with $C2/c$ space group)
232 while at 10.5, a LDH phase is dominant with a very small amount of CuO. The presence of
233 the observed phase domains agrees with recent literature covering the structural changes as a
234 function of pH values between 7 and 13 (Jang et al., 2021): below $\text{pH} = 8$, malachite of
235 composition $\text{Cu}_2\text{CO}_3(\text{OH})_2$ is formed, while in our case it is paratacamite due to the presence
236 of chlorine anion. At pH of 8 to 9, a mixture of malachite and LDH is then observed, a pure
237 LDH phase is observed at $\text{pH} = 10$, it is $\text{pH} = 10.5$ in our case with the presence of small
238 quantity of CuO. Increasing the pH up to 12 leads to the presence of CuO only (Jang et al.,
239 2021).

240 For the LDH phase, the first three diffraction peaks are attributed to the harmonic contribution
241 (00ℓ) of the layered structure, and the corresponding basal spacing of 7.8 nm agrees well with
242 the formation of a chloride LDH phase (Constantino et Pinnavaia, 1995). The broad
243 contribution observed at around $2\theta = 60^\circ$ comes from the overlap between two diffraction
244 peaks (110) and (113). Usually the position of (110) informs on the intra-layer order and its
245 value is related to the combination of cation edge-sharing octahedral sites. However, it is
246 difficult here to apply this relation because of the excessive width of peak. The exact
247 quantification of the CuO small impurity is also difficult to establish from any XRD pattern
248 refinement for the aforementioned reason.



249
 250 **Fig. 1.** XRD patterns of the targeted LDH composition $(\text{Cu}_{0.5}\text{Mg}_{0.17})^{2+}(\text{Fe}_{0.33})^{3+}(\text{OH})_2(\text{Cl})_{0.33}$.
 251 $x\text{H}_2\text{O}$. The value of pH for the coprecipitation is indicated. One note that the experimental
 252 composition deviates from the initial cation input. * are the two most intense diffraction peaks
 253 for CuO at $2\theta = 35.6^\circ$ (111) and 38.8° (022).

254

255 3.2. Chemical analyses

256

257 The sample prepared at pH of 10.5 is analysed by ICP AES as well as by TG coupled MS.

258 From the chemical analyses, the input ratio of Fe/Cu/Mg of 33/50/17 is found to deviate to

259 31.4/30.3/38.3 (Supporting), thus indicating that a part of the cations Cu^{2+} has not precipitated

260 to form the LDH phase of pyroaurite type. This can be explained by the fact that high pH

261 value is usually not adapted to stabilize Cu^{2+} in LDH, but is more prone to form cupric

262 hydroxide or cupric oxide. For the lower content of Fe^{3+} cations compared to its initial input,

263 it is unexpected. The initial ratio is Fe/Mg of 2 and Cu/Mg of 3 with M^{2+}/M^{3+} of 2, while it is

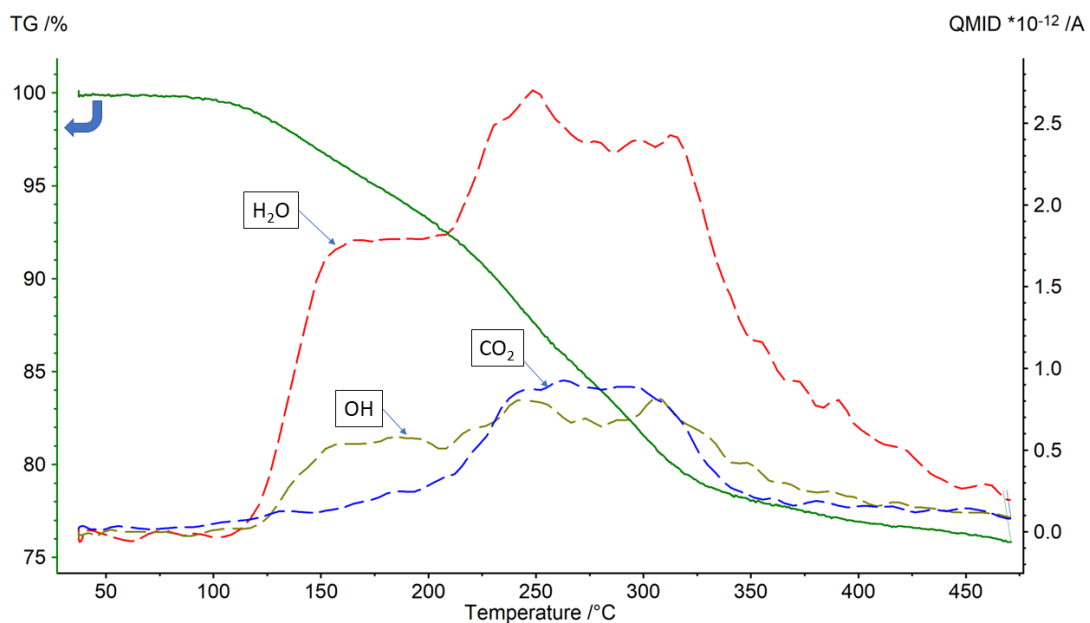
264 found for both Fe/Mg and Cu/Mg of less than 1 but keeping the ratio M^{2+}/M^{3+} of 2.

265 Such chemical deviation from the initial input is usually observed (when chemical analyses
266 were performed) on various Cu-containing LDH phases such as Cu, Zn, Al hydrotalcite-like
267 materials (Behrens et al., 2010). It is usually explained by the fact that the edge-sharing layout
268 between $\text{Cu}(\text{OH})_6$ with other $\text{M}(\text{OH})_6$ octahedra inside the sheets is strongly restrained by
269 elongation and compression due to Jahn-Teller distortion of the cations Cu^{2+} , thus forming
270 other phases or else remaining in solution when the Cu phases, *i.e.* paratacamite at $\text{pH} < 9$ or
271 CuO at $\text{pH} > 11$, are not stable. In other chemical compositions, it leads to a change of
272 structure as for $(\text{Mg}_{4-x}\text{Cu}_x)\text{Al}_2\text{OH}_{12}\text{CO}_3, n\text{H}_2\text{O}$ where the space group is modified from
273 rhombohedral to monoclinic when increasing the copper content (Intissar et al., 2015), or a
274 change in the local structure as for Cu, Zn, Al where the incorporation of Cu^{2+} induces the
275 presence of AlO_4 species (Wu et al., 2020b) to compensate the constraints imposed by the
276 Jahn–Teller effect of copper. Concerning the lower content in Fe^{3+} cations, it may be due to
277 the presence of Cu^{2+} cations since the pyroaurite type phase is known to be formed at this pH
278 value or a little higher (Hansen and Koch, 1995; Rozov et al., 2010). This deviation in the
279 chemical composition will need further investigation by varying copper substitution to
280 establish a suitable solid solution $(\text{Cu,Mg})\text{Fe}$ LDH-type phases.

281 TG-coupled MS analysis is carried out for the sample (see Fig. 2). To complete this analysis,
282 XRD was performed on residues obtained after heating under vacuum at 150°C , 200°C and
283 350°C (denominated afterwards as LDH V150, LDH V200 and LDH V350 respectively): the
284 resulting diffractograms are presented in Fig. S2. In between RT and 215°C , the
285 transformation step is attributed to the dehydration of the product but also to a partial
286 dehydroxylation as observed by the intensity of H_2O and OH signals. The loss of mass is
287 therefore both associated to the degree of hydration of the product but also to an
288 amorphization of the LDH structure as shown in the associated X-ray diffractogram after
289 heating to 150°C in vacuum (see Fig. S2). This amorphization is related to a destabilization of

290 the interlamellar space and a reduction of the average crystallite size. Nevertheless, the
291 presence of peaks corresponding to the (003), (006), (012) and (110) diffraction peaks of the
292 pristine LDH structure indicates that the template LDH structure is at least partially
293 maintained after this heat treatment. With increasing fluorination temperature, the interlayer
294 distance increases as shown by the (003) shift for LDH V200, and counter-intuitively, it
295 corresponds to an increase in the interlayer distance due most probably to reorganization
296 during the dehydration process.

297 Fig. 2 shows that in between 215 and 500 °C, the presence of CO₂ and H₂O release is related
298 to the transformation of LDH into Lamellar Double Oxides (LDO) upon calcination as shown
299 in the literature (Huang et al., 2015). The origin of the CO₂ is a contamination of the LDH
300 powder, often occurring during the successive slurry separations from the supernatant and
301 washing/drying steps, in particular for LDH prepared at high pH value. The relative amount
302 of carbonate anions is calculated from the MS relative intensity and the chemical composition
303 is deduced as Cu_{0.31}Mg_{0.38}Fe_{0.31}(OH)₂(CO₃)_{0.05}Cl_{0.21}·0.45 H₂O. The structural transformation
304 associated within this temperature region is characterized by a strong amorphization of the
305 structure as evidenced from the X-ray diffractograms of the residues obtained after heating
306 under vacuum at 200 (LDH V200) and 350°C (LDH V350) and the absence of peaks
307 associated with the (006) planes of the LDH structure (see Fig. S2). It is interesting to note the
308 presence of a diffraction peak associated with the (003) diffraction peak of the LDH structure
309 around 2θ = 11° in LDH V200 and absent in LDH V350: a partially crystallized LDH phase is
310 thus preserved at 200 °C while it is absent after 350°C. Also, the CuO peaks at 350°C being
311 less intense than the resulting amorphous phase after 350°C confirms the very low amount of
312 this by-product with the LDH phase.

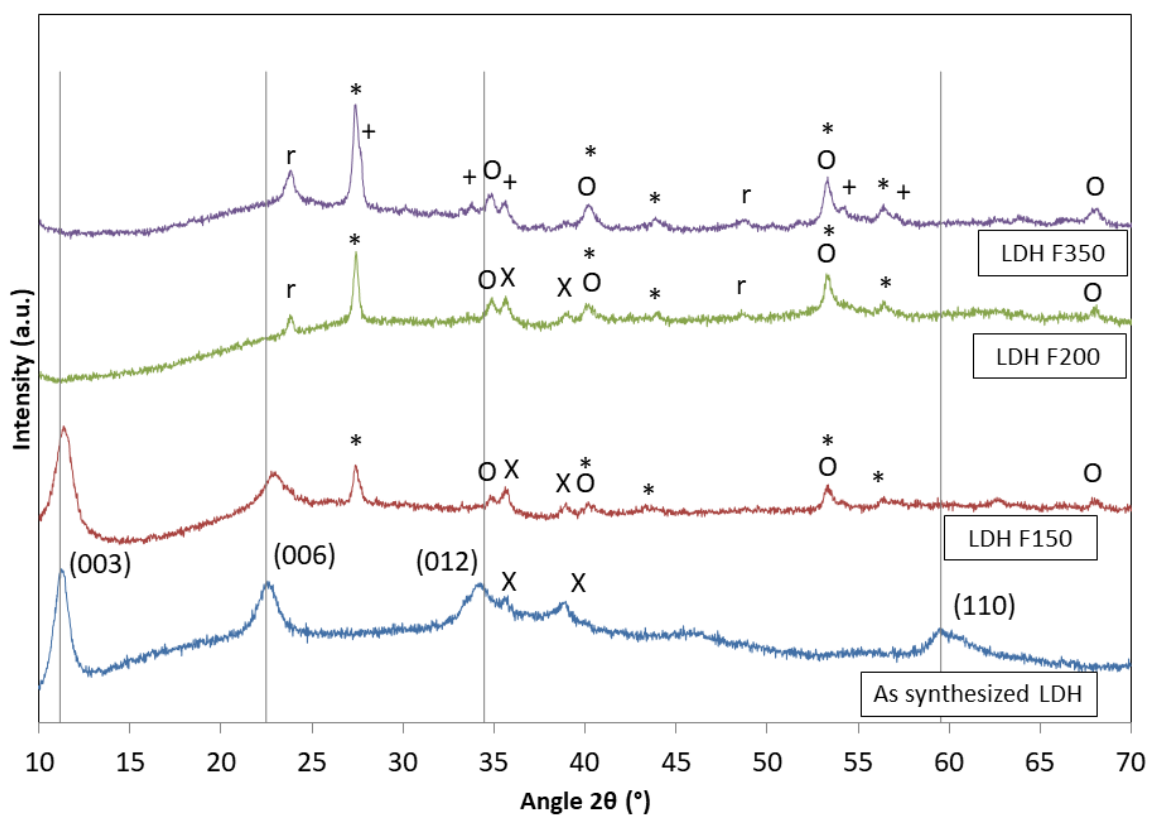


313

314 **Fig. 2.** TG-MS analysis of the sample $\text{Cu}_{0.31}\text{Mg}_{0.38}\text{Fe}_{0.31}(\text{OH})_2(\text{CO}_3)_{0.05}\text{Cl}_{0.21} \cdot 0.45\text{H}_2\text{O}$

315 under Helium (Heating ramp: $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$)

316



317

318 **Fig. 3.** XRD patterns of $\text{Cu}_{0.31}\text{Mg}_{0.38}\text{Fe}_{0.31}(\text{OH})_2(\text{CO}_3)_{0.05}\text{Cl}_{0.21} \cdot 0.45\text{H}_2\text{O}$ as a function of the
319 fluorination temperature and identification of the crystallized phases: x CuO (ICSD#16025);
320 O FeOF (ICSD#2875) ; + CuF_2 (ICSD#71833) ; * MgF_2 (ICSD#394) ; r r- FeF_3
321 (ICSD#41120)

322
323 The structures of LDH fluorination products obtained at different temperatures are first
324 studied by XRD: the as-synthesized LDH was fluorinated at 150°C, 200°C and 350°C
325 (denominated afterwards as LDH F150, LDH F200 and LDH F350 respectively). The thermal
326 treatment under molecular F_2 is known to be efficient in obtaining fluorides at low
327 temperature as 100°C (Louvain et al., 2014). However, in the present results, the layered
328 structure of the pristine LDH remains after fluorination at 150°C. Using static conditions
329 favours substitution of OH^- groups by F^- (Myung et al., 2013). However, the intra-
330 organization is not present anymore (Fig. 3). Indeed, the absence of the diffraction peak (110)
331 at 2θ close to 60° suggests that the intra-sheet organization is strongly disrupted. This is
332 explained by the presence of crystallized phase MgF_2 and FeOF showing that an important
333 quantity of cations constituting LDH sheets is reacting. Most probably their ingress out of the
334 LDH structure creates lacunas and voids, thus cancelling the coherence length in the in-plane.
335 While the fluoride MgF_2 is formed first, it is then followed by r- FeF_3 at 200 °C, LDH
336 structure has totally disappeared while low-crystallized CuO still remains present. Presumably
337 the fluorination temperature of 150°C is not sufficient to convert it to copper fluoride. Indeed,
338 the transformation of CuO into CuF_2 is known to begin at 300°C and is only complete above
339 500°C under pure molecular gaseous fluorine (Haendler et al., 1954). A relatively well-
340 crystallised MgF_2 phase is noted: this compound is the only binary fluoride identified in the
341 product, which suggests that the crystallisation temperature of MgF_2 is lower than that of FeF_3
342 or CuF_2 . Indeed, magnesium fluoride is easily formed at 25°C from HF fluorination of

343 oxygen-based magnesium source (Skapin et al., 2009) whereas rhombohedral iron trifluoride
344 is only obtained above 200°C under pure molecular fluorine (Guérin et al., 2016).

345 FeOF was successfully prepared in literature both by solvothermal reaction (Fan et al., 2015)
346 and wet-chemical method (Zhu et al., 2015) using a FeF₃ precursor. In both cases, the
347 synthesis was performed around 200°C which is consistent with our XRD observations. In the
348 case of LDH fluorination, crystallisation of FeOF could be favoured over FeF₃ at low
349 fluorination temperatures especially at 150°C. Finally, CuO is converted to CuF₂ after
350 treatment at 350°C, as observed with the shoulder at 2θ around 27° and 55°.

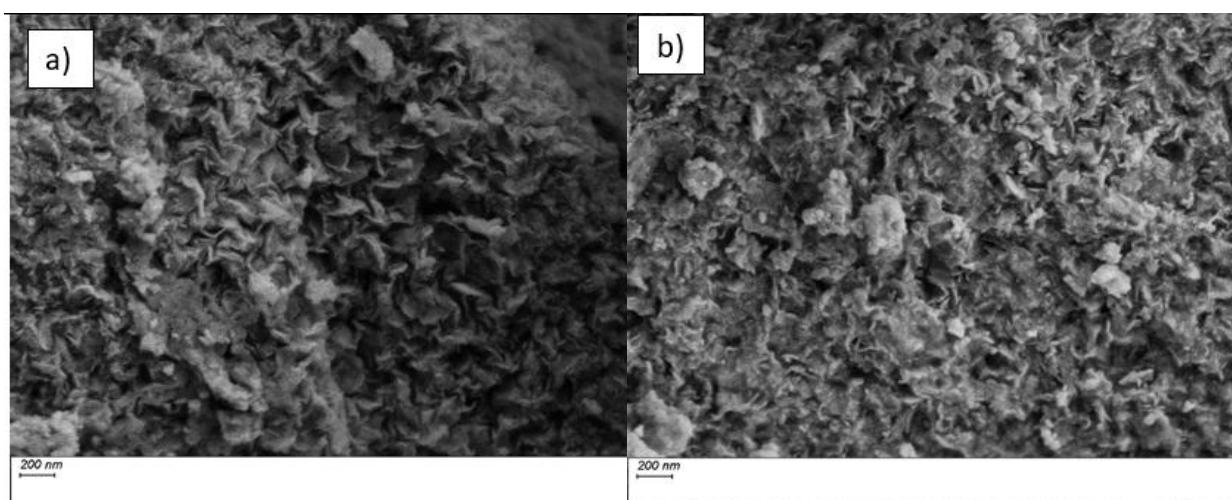
351 The occurrence of the different crystallized phases as a function of the temperature of
352 fluorination agrees with the comparison of the standard enthalpy of formation of the related
353 crystalline phases as follows (at 298,15 K): $\Delta H_f^\circ (\text{MgF}_2) = -1124 \text{ kJ/mol}^{-1}$ (Rudzitis et al.,
354 1964) < $\Delta H_f^\circ (\text{FeF}_3) = -989 \text{ kJ/mol}^{-1}$ (Johnson, 1981) < $\Delta H_f^\circ (\text{CuF}_2) = -540 \text{ kJ/mol}^{-1}$ (Walsh
355 et al., 2012). It helps to understand that – 1) MgF₂ rutile type crystal crystallizes first with the
356 intense diffraction peaks at $2\theta \approx 26^\circ$ and 40° for (110) and (111), respectively, - 2) r-FeF₃
357 crystallizes next to MgF₂, and – 3) CuF₂ crystallizes last at 350°C.

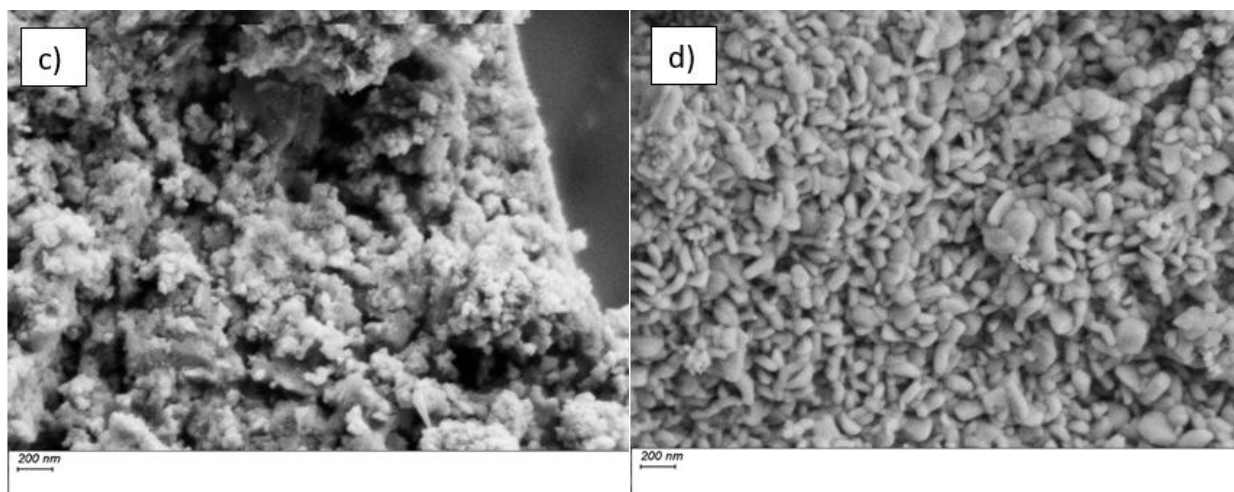
358 To further corroborate the existence of the fluorinated LDH phases, XAS analyses of the
359 fluorinated product, the LDH precursor and reference fluorides recorded at both iron and
360 copper K edges are shown in Fig. S3.

361 From these measurements, the iron and copper environment in the LDH precursor and in
362 LDH F150 are quite similar. Furthermore, the iron environment differs from that of FeF₃,
363 confirming a local iron environment in LDH F150 different from that of a binary fluoride and
364 closer to that present in the non-fluorinated precursor. These observations confirm that
365 fluorination at 150°C is not sufficient to break the LDH structure. The LDH fluorination

366 product obtained at 150°C therefore shows a crystallised LDH phase coexisting with MgF₂
367 phase.

368 To complete these characterizations, the comparison of the thermograms obtained after
369 fluorination at 200°C and 350°C (see Fig. S4) shows a mass loss at 150°C corresponding to
370 the dehydration of the different products (hydration due to their exposure to air before
371 measurements). Apart from this thermal event, all the fluorination products are thermally
372 stable at least up to their fluorination temperature, which confirms the anchoring of fluorine in
373 these fluorination products. According to these analyses, the product obtained after
374 fluorination at 350°C is relatively stable up to 1000°C, its thermogram showing no significant
375 mass loss up to this temperature. On the other hand, the thermogram LDH F200 shows mass
376 losses resembling the non-fluorinated LDH precursor, particularly at 600°C. This may suggest
377 the presence of a LDH phase not only in the fluorinated product at 150°C as confirmed by
378 XRD but also in the fluorinated product at 200°C. Thus, these results indicate that the
379 conversion of the LDH phase to fluoride analogues is not complete at 200 °C which is
380 consistent with the XRD results obtained on the residues after heating in vacuum of the LDH
381 template. However, it is difficult to quantify this phase in the final product.





382 **Fig. 4.** SEM picture of LDH (a) before and after treatment at (b) 150°C, (c) 200°C and (d)
383 350°C under F₂.

384

385 SEM pictures are compared before and after fluorination. The shape of LDH particles before
386 treatment is consistent with a lamellar material and flakes are observed. Such observation is
387 still available for the treatment at 150°C under F₂, thus indicating as stated by XRD that the
388 LDH layered structure is mostly maintained. After treatment at 200°C, the flakes are no
389 longer visible but small geometric shapes are present. At this step, the fluorination appears as
390 having ground the pristine structure. A much more homogeneous morphological distribution
391 appears after 350°C and the particles are oblong worm-shaped not classical of porous 3D-
392 rhombohedral FeF₃ (Guérin et al., 2016) or 3D micrometric dense CuF₂ (Hua et al., 2014).

393

394 **2.3. Electrochemical study**

395 Firstly, the cyclic voltammetry cycle at 0.02 mV.s⁻¹ obtained on each of the three products is
396 presented in Fig. S5. The redox activity of the LDH fluorination products increased with
397 increasing fluorination temperature. This difference in activity cannot be attributed to a
398 change in oxidation state, as XAS and XRD analysis confirmed that the oxidation states are

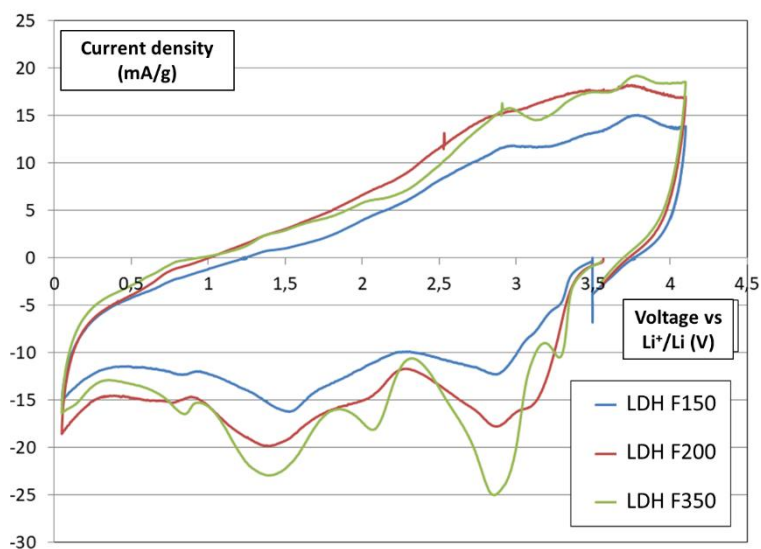
399 kept for Cu^{2+} and Fe^{3+} based on the XAS white line position study for these two transition
400 metals and for Mg^{2+} due to the formation of MgF_2 found by XRD. It can be related to a
401 difference in the electrochemical activity of the stabilized phases in each of the three products.
402 Indeed, according to the characterization of the fluorinated materials, the conversion of the
403 LDH matrix to the analogous fluorides occurs gradually without an intermediate structure. By
404 assuming that the LDH phase formed is less electrochemically active than the fluoride
405 analogues, an improvement in redox activity would be observed as a function of the rate of
406 transformation of the LDH template into fluoride analogues. This hypothesis is based on the
407 difference between the two structures regarding the accessibility to cations and also
408 concomitantly the electronic conduction paths for the reduction of these cations. Indeed,
409 phase total conversion implies the reduction of redox active cations to metal state and the
410 formation of LiF . Following this reasoning, this explains a slightly lower redox activity for
411 LDH F150 due to the proportion of LDH template identified by XRD. Even if the differences
412 in current densities measured between LDH F150 and the other two samples are small
413 because of the slow cycling rate, the redox peaks are more defined with a higher temperature
414 of fluorination of 350°C (Fig. 5). Indeed, a more defined redox peaks after fluorination at
415 350°C compared to that obtained at 200°C is the consequence of the progressive
416 crystallization of the single fluorinated metal phases between these two temperatures but also
417 of the absence of LDH phase in the fluorination product at 350°C as shown by the TGA MS
418 analyses. A better crystallization and the absence of LDH template in LDH F350 lead to a
419 clear separation between the redox domains resulting in an electrochemical mechanism
420 proceeding in distinct electrochemical steps.

421 Finally, it is interesting to note that the general trend observed in the evolution of the
422 electrochemical mechanism of LDH fluorination products as a function of the fluorination
423 temperature is different from that observed for fluorinated CuPBA template (Eveillard et al.,

424 2022). Indeed, in the case of the fluorination of CuPBA, an intermediate structure
425 $[\text{Cu}(\text{H}_2\text{O})_4]_3 \cdot (\text{FeF}_6)_2$ is observed at 200 °C and CuF_2 and FeF_3 crystallize at higher
426 temperatures, while for LDH, the fluorination products (MgF_2 , CuF_2 and r-FeF_3) are observed
427 from 200°C. These observations confirm the existence of fluorination mechanisms different
428 between the two inorganic templates. For CuPBA after fluorination at 200°C, it was found to
429 strongly alter the electrochemical performances. This reduction in redox activity was
430 explained by the high density of redox centers at 200°C, due to a significant rearrangement of
431 the local environment of Cu^{2+} ions at this temperature. The evolution of the redox activity as a
432 function of the fluorination temperature observed for CuPBA was then: CuPBA F200 <
433 CuPBA F140 < CuPBA F350.

434 In the case of LDH, such topochemical reaction of fluorine replacing hydroxide anions into
435 the cationic sheets leads to a progressive structural conversion of the template to fluoride
436 analogues, the rate of fluorination being as a function of temperature. The LDH thermally
437 treated by molecular F_2 phase is less electrochemically active than the simple fluoride phases
438 according to the first voltammetry cycle, the evolution of the redox activity is simply related
439 to the rate of conversion of the LDH template, hence the observed evolution: LDH
440 F150 < LDH F200 < LDH F350.

441 In the following it should be noted that intensity is reported per mass of electroactive material.

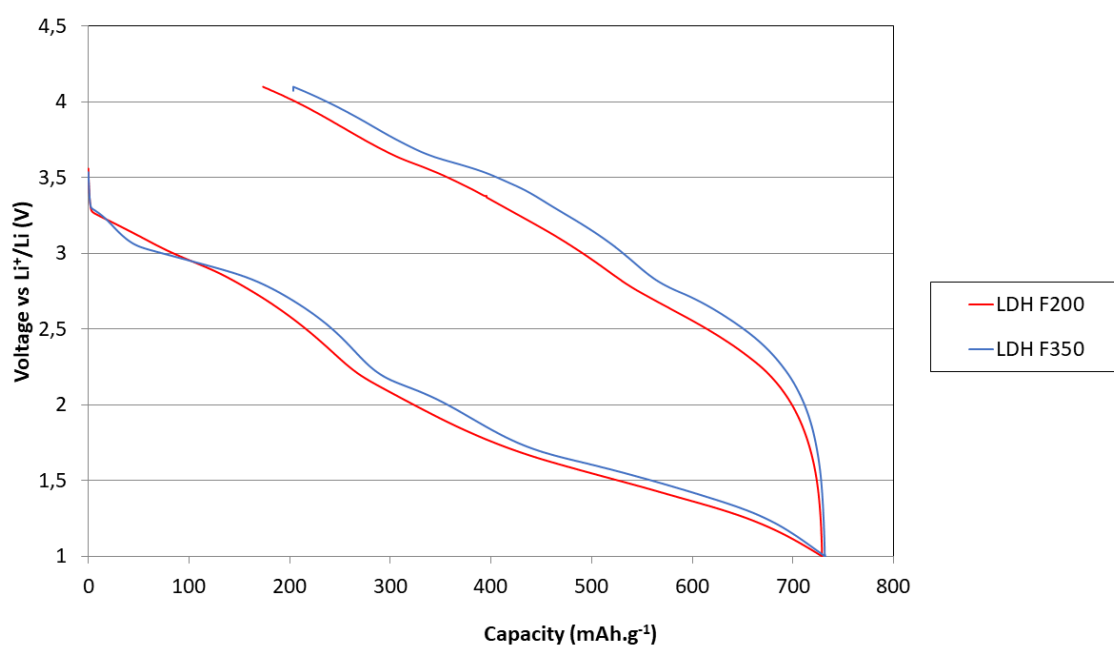


442
 443 **Fig. 5.** Comparison of the first cycle of cyclic voltammetry at $0.02 \text{ mV}\cdot\text{s}^{-1}$ on the LDH
 444 fluorination products at 150, 200 and 350 °C, The current density was determined by dividing
 445 the measured current by the mass of LDH thermally treated by molecular F₂ product
 446 contained in the deposit.

447
 448 The behaviours of LDH F150, LDH F200 and LDH F350 are then studied in more detail in
 449 Fig. 5. For this comparison, it is important to consider the electrochemically active phases
 450 both in the 1 - 4.1 V vs Li⁺/Li potential window and in the extended 0.05 - 4.1 V window. For
 451 the calculation of current density and capacitance for LDH thermally treated by molecular F₂,
 452 assuming a cathode composition ($0.31 \text{ CuF}_2 + 0.38 \text{ MgF}_2 + 0.31 \text{ FeF}_3$) resulting from the total
 453 transformation into analogous fluorides of the metal composition of LDH characterized by
 454 ICP AES (see Table S1). Only the electrochemically active part ($0.31 \text{ CuF}_2 + 0.31 \text{ FeF}_3$) of
 455 the LDH thermally treated by molecular F₂ deposit is considered while 26.3 % of the mass of
 456 the LDH deposit is composed of MgF₂ and is therefore electrochemically inactive both in
 457 cyclic voltammetry and in galvanostatic cycling. The presence of this phase will not be

458 considered in these calculations of current density and capacity. Indeed, MgF_2 phase may be
459 minimized later by different processes, whether in the non-fluorinated LDH precursor by
460 working on the stabilization of the copper within the sheets or in the fluorinated precursor
461 using "selective etching" for example. LDH F150 appears as less efficient than the two others
462 which as a consequence were the only ones to be subsequently measured in galvanostatic
463 mode.

464 The comparison of galvanostatic cycling between LDH F200 and LDH F350 is displayed in
465 Fig.6. These measurements confirm a better definition of the redox steps in LDH F350 than in
466 LDH F200 as already observed on the CV curves. A comparison between the expected
467 theoretical capacity and the experimental capacity of the first discharge is also given in Table
468 I.



469
470 **Fig. 6.** Galvanostatic cycling of LDH F200 and LDH F350 with current densities of 13.6
471 mA.g⁻¹ per active mass ($\text{CuF}_2 + \text{FeF}_3$), 2.7 mA.g⁻¹ in charge.

472

473 **Table 1:** Experimental and theoretical capacity values for the two LDH thermally treated by
 474 molecular F₂ compared to pure FeF₃ and CuF₂ electrochemical behaviors and the predicted
 475 mixture performance.

Sample	LDH F200*	LDH F350*	FeF ₃ **	CuF ₂ **
Q _{exp} (1D) (mAh.g ⁻¹)	731	731	740	560
Q _{exp} (1C) (%)	76	73	67	23
Q _{theo} (1D) (mAh.g ⁻¹)	626	626	712	528

476 Q_{exp}(1D): experimental capacity of the 1st discharge considering the electrochemically active
 477 part of the LDH thermally treated by molecular F₂ (mAh.g⁻¹); Q_{exp}(1C): capacity recovery in
 478 1st charge (%); Q_{theo}(1D): theoretical capacity considering the electrochemically active part of
 479 the LDH thermally treated by molecular F₂; * composition: (0.31 CuF₂ + 0.31 FeF₃ + 0.38
 480 MgF₂), ** see Table S1.

481
 482 The capacity obtained in the first discharge of LDH F200 and LDH F350 is slightly higher
 483 than the theoretical capacity expected for their total conversion as shown in Table 1 and
 484 higher than the value registered for a mixture FeF₃/CuF₂ mechanically ground (Fig. S6). This
 485 suggests a full reduction of the electrode material has taken place, while the excess capacity
 486 being probably due to irreversible reactions as it is already the case for pure FeF₃ and CuF₂
 487 (galvanostatic cycling presented in Fig. S5). The average reaction potential of the two LDH
 488 thermally treated by molecular F₂ is slightly lower than pure CuF₂ and FeF₃. Such observation
 489 may be related to the presence of the insulating and electrochemically inactive MgF₂ phase,
 490 causing an increase in polarization and a lowering of the reaction potentials in discharge. One
 491 should not discard possible irreversibility caused between CuF₂ domains and PEO as well as
 492 the phenomenon of Cu electroplating on Li anode (Omenya et al., 2019). However, the

493 retention of capacity in the first charge is interesting for the two LDH thermally treated by
494 molecular F₂. Up to 10 cycles have been performed whereas the retention of capacity for
495 either FeF₃ or CuF₂ in ASSB fails strongly after few cycles (see Fig. S7 for one and half cycle
496 and Fig. S8 after 10 discharges). The better performance is reached for LDH F350 with a
497 retained capacity of 175 mAh.g⁻¹ at the tenth cycle whereas for LDH F200, it is of about 150
498 mAh.g⁻¹. For this preliminary study such value is interesting and efforts concerning the
499 electrode formulation and its interaction with the polymer electrolyte are further needed.

500

501 4. CONCLUSION

502 Taking advantage of the composition versatility regarding cation substitution in LDH, copper-
503 iron based LDH compositions are selected to minimize the proportion of structuring ions but
504 electrochemically inactive Mg²⁺ and Al³⁺ added to the substituted LDH phases. A LDH phase
505 of theoretical composition [(Cu_{0.5}Mg_{0.17})²⁺(Fe_{0.33})³⁺(OH)₂] Cl_{0.33} . xH₂O is thus prepared by
506 coprecipitation at pH = 10.5. The characterization of the LDH template highlights important
507 chemical deviation from the ideal composition underlining that a part of the cations input
508 (Cu²⁺ and Fe³⁺) remains in solution. The solid state material comprises LDH and a small
509 amount of crystallized CuO, leading to the experimental LDH composition
510 [(Cu_{0.31}Mg_{0.38})²⁺(Fe_{0.31})³⁺(OH)₂]Cl_{0.31} . 0.45H₂O. At 150°C, the formation of a LDH thermally
511 treated by molecular F₂ phase is observed, confirming the possibility of maintaining a multi-
512 metallic template after fluorination by topochemical reaction between hydroxides and fluorine
513 ligands. The LDH phase is still present in small quantities after fluorination at 200°C. The
514 transformation of the LDH phase into fluoride analogues is therefore complete shortly after
515 200°C with the presence of CuF₂, MgF₂ and FeF₃.

516 The study of the electrochemical mechanism highlights an improvement in the capacity
517 retention compared to either FeF₃ or CuF₂, thus taking advantages of both domains while

518 minimizing their side-effect. The role of electrochemically inactive MgF_2 phase should be
519 further scrutinized in future investigations by a solid solution $(\text{Mg,Cu})\text{Fe}$.

520 Overall, the template approach shows the interest of having an intimate cation mixing for
521 electrochemical activity in ASSB as recently reported for Prussian Blue Analogues 3D
522 templates (Eveillard et al., 2022), with a superior behaviour observed with 2D LDH
523 templates. Indeed, while the CuPBAs showed a capacity recovery of first charge of 59%, the
524 LDH thermally treated by molecular F_2 showed a much higher value of redox reversibility of
525 76%.

526

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529

530 **AUTHORS CONTRIBUTIONS**

531

532 **Fabien Eveillard:** synthesis and characterization of the materials and writing-original draft.

533 **Nicolas Batisse:** supervisions; mass spectroscopy calculation; review. **Fabrice Leroux:**

534 conceptualization; supervision; review and editing. **Diane Delbègue;** review and funding

535 acquisition. **Katia Araujo da Silva:** supervision; conceptualization; review and editing. All

536 authors have approved the final version of the manuscript.

537 **CONFLICTS OF INTEREST**

538 The authors declare no conflict of interest.

539

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545

546 **Appendix A**

547 Electronic Supplementary Information available

548

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