



ACADÉMIE  
DES SCIENCES  
INSTITUT DE FRANCE

# *Comptes Rendus*

---

## *Chimie*

Alexandre Terry, Guillaume Duval, Samuel Mathiot, Jean-Marc Grenèche, Ralf Weisbarth, Edouard Boivin, Vincent Maisonneuve, Annie Hémon-Ribaud, Nikolay Kornienko, Amandine Guiet and Jérôme Lhoste

**Impact of  $\text{Co}^{2+}$  substitution by  $\text{Fe}^{2+}$  on the thermal behavior of a hydrated fluoride, precursor of a mixed iron-based oxyfluoride with reduced cobalt content as efficient OER electrocatalyst**

Volume 28 (2025), p. 289-300

Online since: 21 March 2025

<https://doi.org/10.5802/crchim.371>



This article is licensed under the  
CREATIVE COMMONS ATTRIBUTION 4.0 INTERNATIONAL LICENSE.  
<http://creativecommons.org/licenses/by/4.0/>



*The Comptes Rendus. Chimie are a member of the  
Mersenne Center for open scientific publishing*  
[www.centre-mersenne.org](http://www.centre-mersenne.org) — e-ISSN : 1878-1543

## Research article

# Impact of $\text{Co}^{2+}$ substitution by $\text{Fe}^{2+}$ on the thermal behavior of a hydrated fluoride, precursor of a mixed iron-based oxyfluoride with reduced cobalt content as efficient OER electrocatalyst

Alexandre Terry<sup>\*,a,b</sup>, Guillaume Duval<sup>\*,a</sup>, Samuel Mathiot<sup>a</sup>, Jean-Marc Grenèche<sup>\*,a</sup>,  
Ralf Weisbarth<sup>b</sup>, Edouard Boivin<sup>\*,a</sup>, Vincent Maisonneuve<sup>\*,a</sup>,  
Annie Hémon-Ribaud<sup>\*,a</sup>, Nikolay Kornienko<sup>\*,b</sup>, Amandine Guiet<sup>\*,\*,a</sup> and  
Jérôme Lhoste<sup>\*,\*,a</sup>

<sup>a</sup> Institut des Molécules et Matériaux du Mans, UMR 6283 CNRS, Le Mans Université,  
Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France

<sup>b</sup> Institute of Inorganic Chemistry, University of Bonn, Gerhard-Domagk-Str. 1, 53121  
Bonn, Germany

E-mails: [amandine.guiet@univ-lemans.fr](mailto:amandine.guiet@univ-lemans.fr) (A. Guiet), [jerome.lhoste@univ-lemans.fr](mailto:jerome.lhoste@univ-lemans.fr)  
(J. Lhoste)

**Abstract.** In a sustainable development objective, it is necessary to consider both the performance and the preciousness of metals for the development of new catalysts. In this way, this work aims to reduce the amount of cobalt in the mixed Co-Fe oxyfluoride  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{0.5}\text{F}_{1.5}$ , obtained from the thermal degradation of the hydrated fluoride precursor  $\text{CoFeF}_5(\text{H}_2\text{O})_7$ , while maintaining its electrocatalytic performance as an electrocatalyst for the Oxygen Evolution Reaction (OER) in alkaline media. To achieve this, the proposed strategy consists in substituting the  $\text{Co}^{2+}$  ions by  $\text{Fe}^{2+}$  ions in  $\text{CoFeF}_5(\text{H}_2\text{O})_7$ , chosen for its earth abundance, leading to the solid solution  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  obtained by co-precipitation. This series of hydrated precursors was then subjected to a thermal treatment in ambient air in order to obtain the corresponding solid solution of the oxyfluorides  $\text{Co}_{(1-x)/2}\text{Fe}_{(1+x)/2}\text{O}_{(1+x)/2}\text{F}_{(3-x)/2}$ . Structural and thermal analyses confirm a  $\text{Co}^{2+}/\text{Fe}^{2+}$  substitution in hydrated fluoride precursors, while those of calcined samples indicate a complex thermal decomposition leading to Co-Fe oxyfluorides. The OER electrocatalytic performance of these oxyfluorinated materials shows that it is possible to reduce the amount of cobalt by up to 20% without affecting the overall OER activity, namely an overpotential of 320 mV at  $10 \text{ mA}\cdot\text{cm}^{-2}$  and a mass activity of  $112 \text{ A}\cdot\text{g}^{-1}$  at 1.55 V vs. RHE, with high stability.

**Keywords.** Oxyfluoride, Solid solution, Coprecipitation, Thermal treatment, Electrocatalysis, OER.

**Funding.** French National Research Agency (ANR OPIFCAT, ANR-20-CE08-0026), Fondation Banque Populaire d'Entreprise de l'Ouest, NSERC (Discovery Grant RGPIN-2019-05927), International Emerging Action IEA, FRQNT Samuel de Champlain program (award 293526).

Manuscript received 30 August 2024, revised 30 October 2024, accepted 9 December 2024.

\*Corresponding authors

## 1. Introduction

In order to meet the growing demand for energy, it is essential to promote renewable means of production and transformation. Hydrogen is a promising candidate that can be sustainably produced from water [1] via a green electricity-driven water splitting reaction [2,3] and used as an energy vector [4,5]. Unfortunately, the cost competitiveness of these systems suffers in part from low energy efficiency due to the high overpotential required to initiate the Oxygen Evolution Reaction (OER), that oxidizes water to oxygen [6,7]. Reducing the overpotential requires the use of an electrocatalyst to lower the energy barrier associated with the formation of reaction intermediates [8–10]. Noble metal catalysts such as RuO<sub>2</sub> and IrO<sub>2</sub> are the reference materials as OER electrocatalysts but the scarcity of these metals and their prohibitive cost make large-scale industrialization impossible in the future.

In this way, the scientific community has focused on the development of 3d-metal-based catalysts and this research has highlighted some iron-based materials as the best OER catalysts in alkaline electrolytes reported in the literature, such as Ni–Co–Fe layered double hydroxides (LDH) [11–13]. Although the role of iron in the OER mechanism is not yet clear, its presence seems essential to further improve the electrochemical performance [14–16].

While many works in the literature focus on the determination of the best cationic composition, which seems to lean towards the Co/Ni/Fe association [17], few studies are devoted on the modification of the anionic part, which is nevertheless of interest [18,19]. Fluorine, the most electronegative element in the periodic table, is of particular interest to modulate the electronic structure of neighboring metals thanks to its strong inductive effect. As a result, the metal active site is electron-depleted and easily hydroxylated in highly alkaline electrolytes [20], which is the first step of the OER mechanism [9,21]. The first transition-metal fluoride reported in the literature as an OER catalyst in alkaline media is a nanostructured mixed Co–Ni–F material, which exhibits a low overpotential of 300 mV at 10 mA·cm<sup>−2</sup>, outperforming the reference material IrO<sub>2</sub> [22]. Pei *et al.* reported the fluorination of Fe–Co Prussian blue analog nanocubes, which resulted into 3D porous Fe–Co–F nanocubes reaching an

overpotential of 250 mV at 10 mA·cm<sup>−2</sup> with a Tafel slope of 39 mV·dec<sup>−1</sup> [23]. Subsequently, Pei *et al.* fluorinated NiFe-LDH to further enhance its OER activity [24]. This study shows that a suitable fluorination temperature changes the initial morphology of NiFe-LDH and leads to the formation of fluorides, resulting in an excellent OER activity with an overpotential of 225 mV for a Co-free material, close to the best performance obtained with trimetallic NiCoFe-LDH.

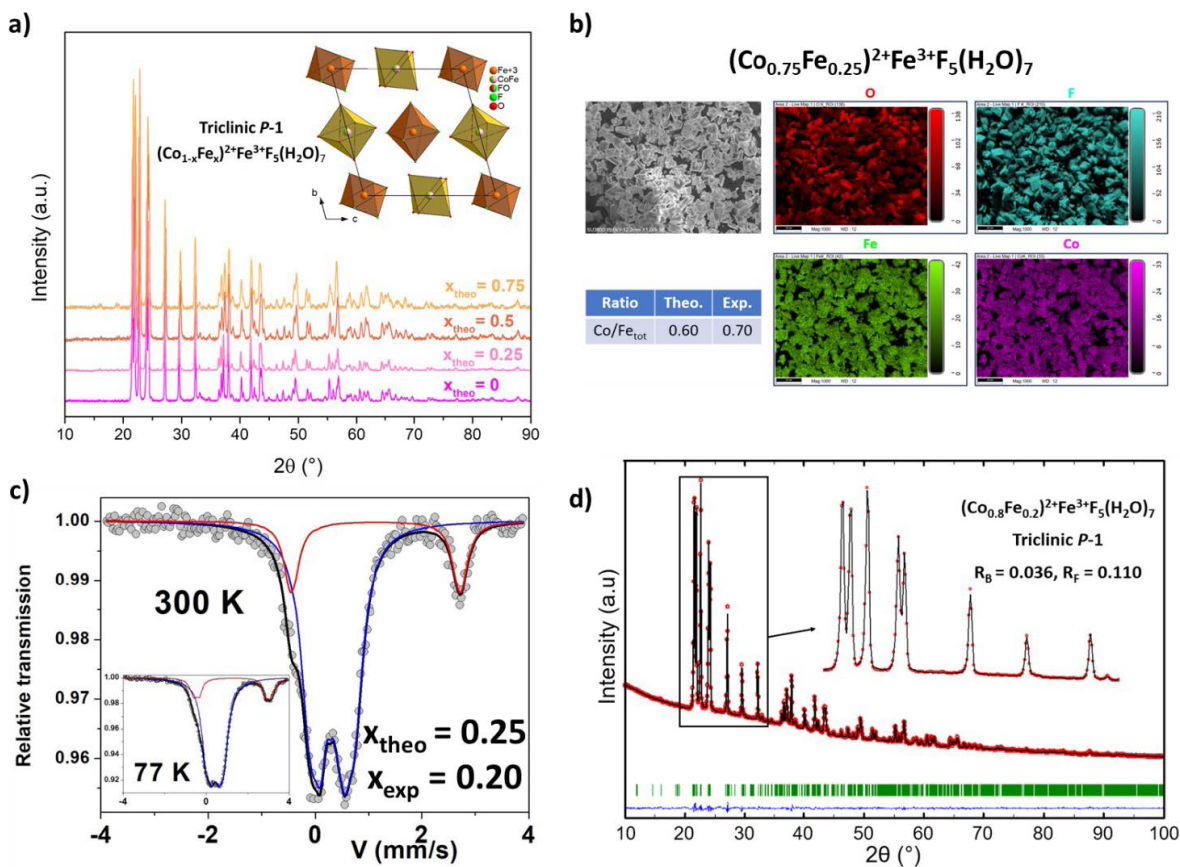
In the same direction, some studies aim to combine oxygen and fluorine anions in 3d-materials and conclude that fluorine incorporation into transition metal oxides improves OER performance [25–27]. Recently, a mixed Co/Fe oxyfluoride with the formulation Co<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>0.5</sub>F<sub>1.5</sub> has been synthesized and further patented by us [28]. This material, synthesized by thermal decomposition of the hydrated fluoride CoFeF<sub>5</sub>(H<sub>2</sub>O)<sub>7</sub>, exhibits excellent OER performance and long-time stability in highly alkaline media [29]. Substitution of the Co<sup>2+</sup> ions by Ni<sup>2+</sup> resulted in better OER performance and stability, with an optimum for the Co<sub>0.25</sub>Ni<sub>0.25</sub>Fe<sub>0.5</sub>O<sub>0.5</sub>F<sub>1.5</sub> composition [30].

In a sustainable framework, this work presents the reduction of Co<sup>2+</sup> amount in Co<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>0.5</sub>F<sub>1.5</sub> by substitution with Fe<sup>2+</sup> following the same method as before [30]. Different (Co<sub>1−*x*</sub>Fe<sub>*x*</sub>)<sup>2+</sup>FeF<sub>5</sub>(H<sub>2</sub>O)<sub>7</sub> compositions (0 ≤ *x*<sub>theo</sub> ≤ 0.75) have been synthesized and structurally characterized. The thermal behavior of these materials is studied by High Temperature X-ray Diffraction (HT-XRD) and Thermogravimetric Analysis (TGA) to understand the decomposition mechanism leading to Fe-enriched oxyfluorides. The phases obtained from the calcination of (Co<sub>1−*x*</sub>Fe<sub>*x*</sub>)<sup>2+</sup>FeF<sub>5</sub>(H<sub>2</sub>O)<sub>7</sub> were tested as catalysts for OER to evaluate the cationic Co<sup>2+</sup>/Fe<sup>2+</sup> substitution on the electrocatalytic performance.

## 2. Results and discussion

### 2.1. Synthesis and characterization of (Co<sub>1−*x*</sub>Fe<sub>*x*</sub>)<sup>2+</sup>Fe<sup>3+</sup>F<sub>5</sub>(H<sub>2</sub>O)<sub>7</sub> (0 ≤ *x*<sub>theo</sub> ≤ 0.75) precursors

Iron-rich hydrated fluorides (Co<sub>1−*x*</sub>Fe<sub>*x*</sub>)<sup>2+</sup>Fe<sup>3+</sup>F<sub>5</sub>(H<sub>2</sub>O)<sub>7</sub> with theoretical compositions *x*<sub>theo</sub> = 0, 0.25, 0.5 and 0.75 have been synthesized by coprecipitation with aqueous hydrofluoric acid (HF) as fluorinating agent. The substitution of Co<sup>2+</sup> ions



**Figure 1.** (a)  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  PXRD diagrams with the corresponding [100] projection of the structure, (b) SEM images of the microcrystalline powder of  $(\text{Co}_{0.75}\text{Fe}_{0.25})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  and elemental mapping of each metal belonging to the hydrated fluoride phase, (c)  $^{57}\text{Fe}$  Mössbauer spectra at 300 K and 77 K of  $(\text{Co}_{0.75}\text{Fe}_{0.25})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$ , (d) Rietveld refinement of  $(\text{Co}_{0.8}\text{Fe}_{0.2})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  structure.

by  $\text{Fe}^{2+}$  is possible only by preventing the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ; it is achieved by dissolving  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  salts together in HF and  $\text{Fe}^{2+}$  salt separately in methanol. The obtained polycrystalline powders, which turn yellow depending on the  $\text{Fe}^{2+}$  amount (Figure S1), were first analyzed by powder X-ray diffraction (PXRD). PXRD diagrams of the  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  series show that the structures are isostructural with the reference  $(\text{Co}^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7, x = 0)$ , and indexed in the triclinic  $P-1$  space group (Figure 1a). Their crystalline structure consists of isolated  $[\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})]^{2-}$  (brown) and  $[(\text{Co}/\text{Fe})^{2+}(\text{H}_2\text{O})_6]^{2+}$  octahedra (beige) (Figure 1a, inset). As the radii of the  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  ions are close, 0.742 Å and 0.781 Å, respectively [31], only a subtle shift of X-ray peaks is observed.

EDX-coupled SEM confirms the crystallinity of particles with sizes in the range of tens of micrometers, together with a homogeneous distribution of 3d cations (Figures S2–S5), as illustrated in Figure 1b, corresponding to the composition  $(\text{Co}_{0.75}\text{Fe}_{0.25})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$ . The experimental values of the  $n(\text{Co}/\text{Fe}_{\text{tot}})$  ratio are consistent with the substitution of  $\text{Co}^{2+}$  ions by  $\text{Fe}^{2+}$  ions in the triclinic phase  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$ . However, the experimental  $n(\text{Co}/\text{Fe}_{\text{tot}})$  ratio for compositions containing  $\text{Fe}^{2+}$  is systematically higher than the theoretical ones, indicating a lower  $\text{Fe}^{2+}$  content, in contrast to  $\text{Fe}^{2+}$ -free  $\text{Co}^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  where the value fits perfectly. Thus, despite the precautions taken during synthesis, a small amount of  $\text{Fe}^{2+}$  is probably oxidized to  $\text{Fe}^{3+}$  in solution.

**Table 1.** Theoretical and experimental  $n(\text{Fe}^{2+}/\text{Fe}^{3+})$  and  $n(\text{Co}^{2+}/\text{Fe}_{\text{tot}})$  ratios determined by  $^{57}\text{Fe}$  Mössbauer spectrometry (Möss.) and EDX-coupled SEM analysis (EDX). The value of  $x$  in  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  were adjusted in accordance to these results ( $x_{\text{exp}}$ ).

| $x_{\text{theo}}$ | Theoretical                                      |                                                          | Experimental                                |                                                     |                                                   |                  |
|-------------------|--------------------------------------------------|----------------------------------------------------------|---------------------------------------------|-----------------------------------------------------|---------------------------------------------------|------------------|
|                   | $n(\text{Fe}^{2+}/\text{Fe}^{3+})_{\text{theo}}$ | $n(\text{Co}^{2+}/\text{Fe}_{\text{tot}})_{\text{theo}}$ | $n(\text{Fe}^{2+}/\text{Fe}^{3+})$<br>Möss. | $n(\text{Co}^{2+}/\text{Fe}_{\text{tot}})$<br>Möss. | $n(\text{Co}^{2+}/\text{Fe}_{\text{tot}})$<br>EDX | $x_{\text{exp}}$ |
| 0                 | 0                                                | 1                                                        | 0                                           | 1                                                   | 1                                                 | 0                |
| 0.25              | 0.25                                             | 0.60                                                     | 0.20                                        | 0.67                                                | 0.70                                              | 0.20             |
| 0.5               | 0.50                                             | 0.33                                                     | 0.45                                        | 0.38                                                | 0.43                                              | 0.45             |
| 0.75              | 0.75                                             | 0.14                                                     | 0.72                                        | 0.16                                                | 0.17                                              | 0.72             |

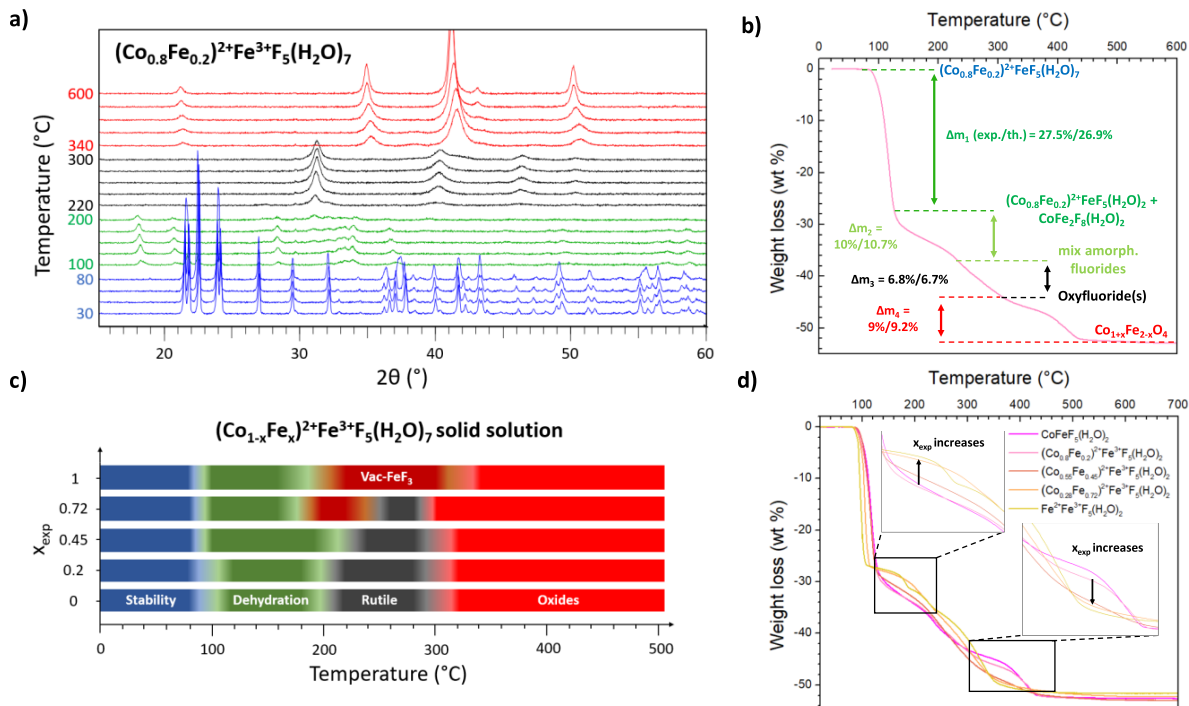
$^{57}\text{Fe}$  Mössbauer experiments were then performed to gain insight into the iron environment and on its valence state. All Mössbauer spectra of the  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  series were collected at 300 K, while one was obtained at 77 K (Figure S6), shown here in Figure 1c for a theoretical value of  $x_{\text{theo}} = 0.25$ . At 300 K they consist of a quadrupolar structure resulting from two different doublets, which can be unambiguously attributed to the presence of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  species, except for the composition  $x_{\text{exp}} = 0$  where the quadrupolar doublet is attributed to  $\text{Fe}^{3+}$  species only. Different fitting models with 2, 3 and 4 quadrupolar components were considered. The table in Figure S6 shows the mean refined values of the hyperfine parameters: the isomer shift and quadrupolar splitting values are quite independent of the cationic composition, but their respective absorption regions are strongly dependent on the cationic composition. It is important to note that these values are the same at 77 K, suggesting that the Lamb–Mössbauer factors are similar for the two Fe species. In addition, the values of isomer shift suggest that the  $\text{Fe}^{3+}$  ions are on average located in octahedral  $\text{FeF}_5\text{O}$  units, while the  $\text{Fe}^{2+}$  ions are located in octahedral  $\text{FeO}_6$  units. The  $^{57}\text{Fe}$  Mössbauer data exploitation allowed quantifying the proportion of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  cations, and then, identifying the real formulations. The latter are in agreement with the  $\text{Co}/\text{Fe}_{\text{tot}}$  ratios determined by EDX-SEM (Table 1), revealing an incomplete substitution of  $\text{Co}^{2+}$  by  $\text{Fe}^{2+}$ . In the following, the experimental values of  $x$  are used (i.e.,  $x_{\text{exp}}$  in  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$ ).

The PXRD diagrams of the  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  series were refined by the Rietveld method (Figure S7), as shown for the  $(\text{Co}_{0.8}\text{Fe}_{0.2})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  series in Figure 1d. The details of the structure

refinement are summarized in Table S1, and atomic coordinates (except for hydrogen atoms, which were not refined) together with interatomic distances are gathered in Tables S2–S9. The  $\text{Co}^{2+}/\text{Fe}^{2+}$  occupancy ratios in the 1e and 1f Wyckoff positions were fixed considering  $x_{\text{exp}}$  and assuming a statistical distribution on both sites. Good reliability factors confirmed the crystalline purity for all samples. The substitution of  $\text{Co}^{2+}$  ions by  $\text{Fe}^{2+}$  in the whole composition range ( $0 \leq x_{\text{exp}} \leq 0.72$ ) is confirmed by the linear increase of the unit cell volume as a function of the Fe content (Figure S8).

## 2.2. Thermal behavior of $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$ precursors

The structural evolution of  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  precursors ( $0 \leq x_{\text{exp}} \leq 1$ ) was studied as a function of the temperature by HT-XRD and TGA under ambient air from room temperature to 600 °C (Figures S9 and S10). First, hydrated precursors are stable up to 80–100 °C for all compositions, as exemplified by  $(\text{Co}_{0.8}\text{Fe}_{0.2})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  in Figure 2a (in blue). Above 100 °C, the weight losses are consistent with the departure of five water molecules, leading to mixtures of  $\text{MFeF}_5(\text{H}_2\text{O})_2$  and  $\text{MFe}_2\text{F}_8(\text{H}_2\text{O})_2$  with  $\text{M} = \text{Co}^{2+}/\text{Fe}^{2+}$  (Figure 2b and Figure S11). For  $(\text{Co}_{0.8}\text{Fe}_{0.2})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$ , an additional loss of two water molecules is then observed due to progressive thermal degradation of  $\text{MFeF}_5(\text{H}_2\text{O})_2$  and  $\text{MFe}_2\text{F}_8(\text{H}_2\text{O})_2$  ( $\Delta m_2$  (exp./th.): 10.7%; 10%) leading to quasi amorphous fluorides. After complete dehydration, oxyfluorinated phases with a rutile-type structure appear, resulting from the hydrolysis of amorphous phases ( $\Delta m_3$  (exp./th.): 6.7%; 6.8%) with air humidity (220 °C–300 °C, in black), as shown in



**Figure 2.** (a) Evolution of the X-ray diffractograms of  $(\text{Co}_{0.8}\text{Fe}_{0.2})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  with temperature under ambient air. (b) TGA analyses of  $(\text{Co}_{0.8}\text{Fe}_{0.2})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  performed under ambient air. (c) Temperature range of stability domains determined by HT-XRD for  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$ . (d) Corresponding TGA analyses performed under ambient air.

our previous studies on the thermal decomposition of  $\text{CoFeF}_5(\text{H}_2\text{O})_2$  [29] and  $\text{CoFe}_2\text{F}_8(\text{H}_2\text{O})_2$  [27]. It is important to note that in the  $\text{CoFe}_2\text{F}_8(\text{H}_2\text{O})_2$  study, the oxyfluoride phase was considered to be amorphous. However, a closer inspection of the thermal decomposition of  $\text{CoFe}_2\text{F}_8(\text{H}_2\text{O})_2$  reveals a poorly crystallized rutile oxyfluoride with unit cell parameters close to the rutile oxyfluoride obtained from  $\text{CoFeF}_5(\text{H}_2\text{O})_2$ , as the XRD peak positions are similar (Figure S12). For  $\text{Fe}^{2+}$ -rich compositions ( $x_{\text{exp}} = 0.72$  and 1),  $\text{FeF}_3$ -type oxyfluorides with anionic vacancies (referred to as  $\text{vac-FeF}_3$  in this work) are observed on HT-XRD diagrams, in the temperature range 190–240 °C and 210–310 °C, respectively (Figure S9 and Figure 2c), identified as  $\text{FeF}_{2.5}\text{O}_{0.25}\square_{0.25}$  and  $\text{FeF}_{2.66}\text{O}_{0.17}\square_{0.17}$ , which have been identified as the result of the thermal treatment of  $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$  and  $\text{Fe}_3\text{F}_8(\text{H}_2\text{O})_2$ , respectively [32]. For all compositions, spinel-type  $\text{M}^{2+}\text{M}_2^{3+}\text{O}_4$  and/or  $\alpha\text{-Fe}_2\text{O}_3$  oxides (for  $x_{\text{exp}} \geq 0.45$ ) are observed at temperatures above 300 °C (Figure S13), resulting from the

slow hydrolysis of oxyfluorinated rutile phases and  $\text{vac-FeF}_3$  phases, respectively.

The HT-XRD results, summarized for all the compositions in Figure 2c, show that the temperature range for obtaining pure oxyfluoride(s) with rutile structure (in black) shrinks as the amount of  $\text{Fe}^{2+}$  increases, until it disappears completely for  $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_7$  ( $x_{\text{exp}} = 1$ ). This trend indicates that  $\text{Co}^{2+}$  is required to produce the rutile oxyfluorinated phase. In order to better understand the differences between the thermal behavior of the  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{FeF}_5(\text{H}_2\text{O})_7$  compounds, the PXRD diagrams at 120 °C where  $\text{MFeF}_5(\text{H}_2\text{O})_2$  and  $\text{MFe}_2\text{F}_8(\text{H}_2\text{O})_2$  phases are produced from the thermal degradation of the initial precursors, have been studied. The data obtained from Rietveld refinements through two hypotheses (Figures S14–16 and Tables S10–12) showed that  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  is decomposed into  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_2$  and  $\text{Co}^{2+}\text{Fe}_2\text{F}_8(\text{H}_2\text{O})_2$ , and additionally to  $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$  and  $\text{Fe}_3\text{F}_8(\text{H}_2\text{O})_2$  for

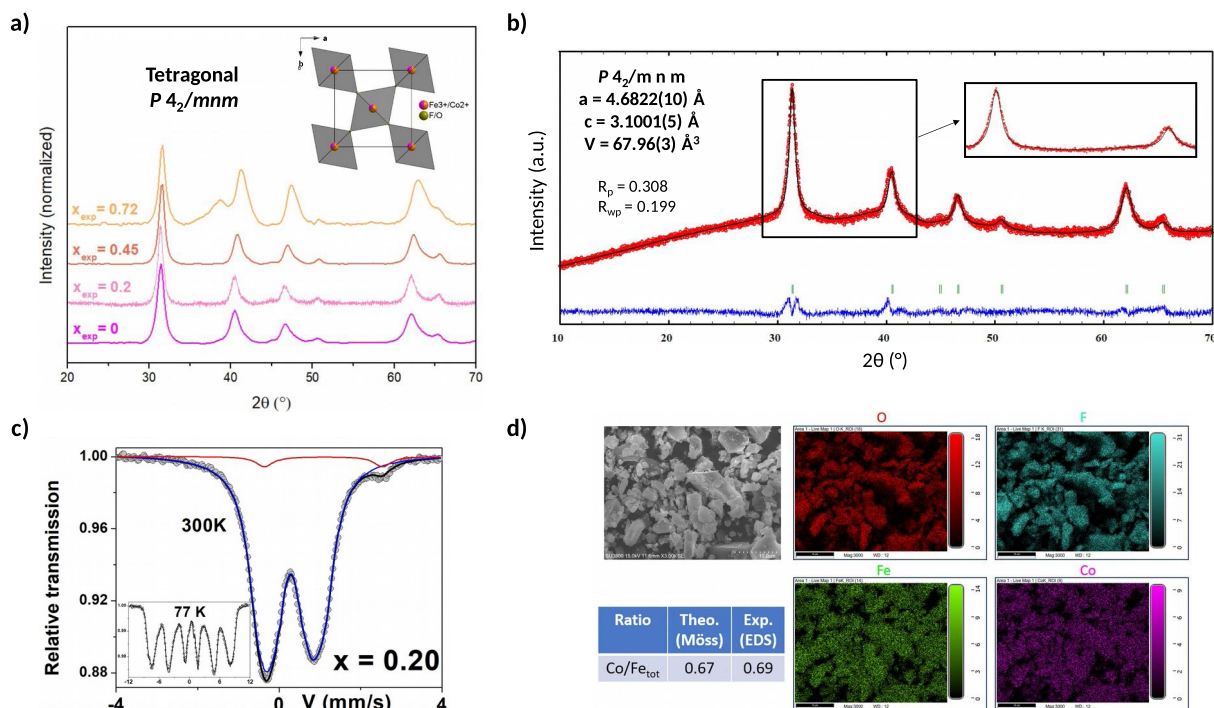
$x_{\text{exp}} \geq 0.45$ . In fact, the linear increase in unit cell volume of the  $\text{M}^{2+}\text{FeF}_5(\text{H}_2\text{O})_2$ -type phase as a function of  $x_{\text{exp}}$  indicates the existence of a solid solution for  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_2$  while the invariant volume for the  $\text{M}^{2+}\text{Fe}_2\text{F}_8(\text{H}_2\text{O})_2$ -type phase proves that the  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}_2\text{F}_8(\text{H}_2\text{O})_2$  solid solution does not seem to exist (Figure S16). The formation of pure Fe phases,  $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$  and  $\text{Fe}_3\text{F}_8(\text{H}_2\text{O})_2$ , manifested by the presence of  $\alpha\text{-Fe}_2\text{O}_3$  on PXRD up to 600 °C for  $x_{\text{exp}} \geq 0.45$  compositions, could be explained by the mass balance. Indeed, for all  $0 \leq x_{\text{exp}} \leq 0.72$  compositions, a spinel-type phase indexed as  $\text{CoFe}_2\text{O}_4$  is observed at 600 °C, with a ratio  $n(\text{Fe})/n(\text{Co})$  equal to 2. For  $x_{\text{exp}} \geq 0.45$  compositions, the ratio  $n(\text{Fe})/n(\text{Co})$  is superior to 2 and consequently, an iron-based oxide is required to achieve the mass balance, which is  $\alpha\text{-Fe}_2\text{O}_3$ , as observed in Figure S13. On the other hand, for  $x_{\text{exp}} \leq 0.2$  compositions, only spinel-type  $\text{CoFe}_2\text{O}_4$  is identified although  $n(\text{Fe})/n(\text{Co}) < 2$  so a Co-rich material is needed to equilibrate the mass balance. In our previous work on  $\text{CoFeF}_5(\text{H}_2\text{O})_7$ , the PXRD pattern at 600 °C was identified as a mixture of  $\text{CoFe}_2\text{O}_4$  and  $\text{CoO}$  [29,30], but as shown in Figure S17, it's more likely to be a mixture of two spinel-type oxides with the formulations  $\text{Co}^{2+}(\text{Co}_{0.24}\text{Fe}_{1.76})^{3+}\text{O}_4$  and  $\text{Co}^{2+}(\text{Co}_{1.17}\text{Fe}_{0.83})^{3+}\text{O}_4$ . These formulations were calculated according to their unit cell volumes determined by Le Bail refinements, 583.1 and 549.2 Å<sup>3</sup>, respectively, and used in the formula extracted from Vegard's law for the solid solution  $\text{Co}^{2+}(\text{Co}_{2-x}\text{Fe}_x)^{3+}\text{O}_4$  (Figure S18). The formula  $\text{Co}^{2+}(\text{Co}_{0.24}\text{Fe}_{1.76})^{3+}\text{O}_4$  and  $\text{Co}^{2+}(\text{Co}_{1.17}\text{Fe}_{0.83})^{3+}\text{O}_4$  indicate a partial oxidation of  $\text{Co}^{2+}$  to  $\text{Co}^{3+}$ , which has already been observed in the literature for the thermal treatment of  $\text{CoF}_2$  under similar thermal treatment conditions [33]. By plotting the respective spinel volume as a function of  $x_{\text{exp}}$  obtained by Le Bail refinements for the different compositions (Figure S19), a gradual increase in unit cell volume is observed, indicating a progressive increase in the amount of Fe in the spinel up to a limit dictated by  $\text{CoFe}_2\text{O}_4$ . Finally, the reason for the appearance of  $\text{CoFe}_2\text{F}_8(\text{H}_2\text{O})_2$  and  $\text{Fe}_3\text{F}_8(\text{H}_2\text{O})_2$  phases is probably related to a partial oxidation of  $\text{Fe}^{2+}$  ions under such thermal decomposition conditions (high temperature, ambient air), leading to  $\text{Fe}^{3+}$ -rich phases, which is not obviously observed for  $\text{Fe}^{2+}$ -free  $\text{Co}^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  (Figure S11).

The comparison of the TGA profiles in Figure 2d shows an evolution of the thermal behavior according to the proportion of  $\text{Fe}^{2+}$  in the initial precursor. First, the thermal behaviors of  $x_{\text{exp}} = 0$  and 0.2 are very similar, which is not surprising since, from the previous results at 120 °C,  $x = 0.2$  is mainly composed of  $\text{M}^{2+}\text{FeF}_5(\text{H}_2\text{O})_2$ . The few changes can be attributed to the contribution of the thermal behavior of  $\text{CoFe}_2\text{F}_8(\text{H}_2\text{O})_2$ , which is quite similar to that of  $\text{CoFeF}_5(\text{H}_2\text{O})_2$ , since it decomposes into a rutile oxyfluoride and then a spinel-type oxide (Figure S20). For the composition  $x_{\text{exp}} = 0.45$  there is a significant change between 300–450 °C which could be attributed to the appearance of pure Fe phases to the detriment of  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_2$ . For  $x_{\text{exp}} = 0.72$ , the thermal behavior is very close to that of pure  $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_7$ , except that a clear distinction between the two successive weight losses associated with the formation of  $\text{FeF}_{2.5}\text{O}_{0.25}\square_{0.25}$  and  $\text{FeF}_{2.66}\text{O}_{0.17}\square_{0.17}$  cannot be made (Figure S10).

### 2.3. Synthesis and characterization of the oxyfluoride(s)

The oxyfluorides with the theoretical formulation  $(\text{Co}_{(1-x)/2})^{2+}(\text{Fe}_{(1+x)/2})^{3+}\text{O}_{(1+x)/2}\text{F}_{(3-x)/2}$  assuming the formation of rutile  $\text{MX}_2$ , were prepared by thermal treatment of the corresponding hydrated fluorides  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$ . For each composition, the selected calcination conditions to obtain the pure rutile oxyfluorides, according to XRD and theoretical weight loss (about 44–45 wt% for all compositions) are summarized in Table S13. More details on the determination of the thermal treatment conditions are given for  $x_{\text{exp}} = 0$  in our previous study [30].

After calcination, all oxyfluorinated phases were indexed in the tetragonal  $P4_2/mnm$  space group (Figure 3a). The PXRD patterns were refined by the Le Bail refinement method (Figures S21–24), as exemplified for the calcined  $(\text{Co}_{0.8}\text{Fe}_{0.2})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  precursor in Figure 3b. According to the evolution of the volume obtained for the different rutile oxyfluorides (Figure S25), it seems that from  $x \geq 0.45$ ,  $\text{Fe}^{3+}$  and O-enriched oxyfluorides are formed, since the volume of the unit cell decreases slightly, in agreement with the radii of  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{O}^{2-}$  and  $\text{F}^-$  (0.742 Å, 0.649 Å, 1.366 Å and 1.300 Å, respectively) [31]. However, the volume of  $x_{\text{exp}} = 0.2$  is equivalent to  $x_{\text{exp}} = 0$ , indicating a similar chemical composition, even though



**Figure 3.** (a) Calcined  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  PXRD diagrams with the corresponding [001] projection of the rutile structure for oxyfluorides, (b) Le Bail refinement of calcined  $(\text{Co}_{0.8}\text{Fe}_{0.2})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$ , (c)  $^{57}\text{Fe}$  Mössbauer spectra at 300 K and 77 K of calcined  $(\text{Co}_{0.8}\text{Fe}_{0.2})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$ , (d) SEM images of the calcined  $(\text{Co}_{0.8}\text{Fe}_{0.2})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  and elemental mapping of each metal.

the substitution was previously demonstrated in the  $(\text{Co}_{0.8}\text{Fe}_{0.2})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_2$  precursor. This clearly shows the complexity of the decomposition mechanism, especially for  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_2$  and  $\text{Co}^{2+}\text{Fe}_2\text{F}_8(\text{H}_2\text{O})_2$  hydrates, which seem to give a similar oxyfluoride for  $x_{\text{exp}} \leq 0.2$ , while the metal ratio is different. For the sample  $x_{\text{exp}} = 0.72$ , an impurity of  $\alpha\text{-Fe}_2\text{O}_3$  is present, which is not surprising given the narrow stability window of the oxyfluoride (Figure 2c). Rietveld refinement of the PXRD pattern shows an  $\alpha\text{-Fe}_2\text{O}_3$  mass fraction close to 60 wt%, but this could be misestimated given the complexity of the refinement (Figure S26).

The Mössbauer spectra obtained at 300 K and 77 K are shown in Figure S27 and exemplified for calcined  $x_{\text{exp}} = 0.2$  in Figure 3c. At 300 K, a significant change from a pure quadrupolar hyperfine structure ( $x_{\text{exp}} \leq 0.45$ ) to a mixed quadrupolar and magnetic structure ( $x_{\text{exp}} = 0.72$ ) is observed, while the Mössbauer spectra at 77 K consist only of a pure magnetic struc-

ture for all compositions. From the XRD analysis, this magnetic structure at 300 K is probably related to the presence of  $\alpha\text{-Fe}_2\text{O}_3$  magnetic impurity. In addition, as shown in Figure S27 ( $x_{\text{exp}} = 0.20$  and  $0.45$ ), two quadrupolar components can be distinguished, which can be clearly attributed to a large contribution of  $\text{Fe}^{3+}$  species on the one hand, and to a very small contribution of  $\text{Fe}^{2+}$  species on the other hand, which cannot be easily detected from the magnetic hyperfine structures due to their complexity. The quadrupolar spectra were described by similar models as described above, while the magnetic spectra were described using a discrete distribution of the hyperfine field linearly correlated with that of the isomer shift to account for the asymmetry of the sextets. The mean refined values are listed in the Table of Figure S27. These results clearly show that calcination leads, on the one hand, to the almost complete disappearance of  $\text{Fe}^{2+}$  ions and, on the other hand, to the appearance of magnetic oxyfluorinated phases containing predominantly  $\text{Fe}^{3+}$  species. It is important

to note that the large decrease in  $\text{Fe}^{2+}$  content is not related to the difficulty of stabilizing  $\text{Fe}^{2+}$  in the rutile-structure oxyfluoride as Brink *et al.* demonstrated that it is possible to solubilize up to 30% of  $\text{FeF}_2$  in rutile  $\text{FeOF}$  [34]. This decrease is more likely related to  $\text{Fe}^{2+}$  oxidation during thermal decomposition, as has been observed after thermal treatment of the mixed-valent iron fluoride hydrates  $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$  and  $\text{Fe}_3\text{F}_8(\text{H}_2\text{O})_2$  [32]. However, the complexity and lack of resolution of the magnetic hyperfine structures at 77 K make it difficult to rule out the presence of  $\alpha\text{-Fe}_2\text{O}_3$  and to estimate its precise content. The comparison of the quadrupolar hyperfine structures at 300 K of the spectra  $x_{\text{exp}} = 0$  and 0.2 shows three components for  $\text{Fe}^{3+}$  species that are significantly different (Figure S28). This result shows that the cationic distribution is modified by increasing the amount of Fe. However, the mean values of the isomer shift are unchanged, suggesting that the mean anionic environment remains similar, which can be roughly estimated to be about 50:50 F:O. Furthermore, the 77 K spectra show a pure magnetic structure with broadened lines: the mean isomer shift values are also similar, while the distributions of the hyperfine fields are consistent with different atomic environments of the  $\text{Fe}^{3+}$  species, as inferred from the 300 K spectra.

EDX-SEM analysis revealed the presence and homogeneous distribution of F, O, Co, and Fe within the calcined materials (Figures S29–32) as shown in Figure 3d. The  $\text{Co}/\text{Fe}_{\text{tot}}$  ratio after calcination is still in agreement with the respective precursor composition determined by Mössbauer spectrometry and EDX-SEM. Although a dominant impurity of  $\alpha\text{-Fe}_2\text{O}_3$  is observed by PXRD for the sample  $x_{\text{exp}} = 0.72$ , we are not able to distinguish two clearly separated phases by elemental mapping (Figure S32). This could indicate an intimate mixture of both phases, divided into nanodomains visible only by High Resolution Transmission Electronic Microscopy (HR-TEM), as already observed in our previous study [30]. This is supported by the broadening of the Bragg diffraction peaks observed after thermal treatment (Figure 3a), compared to those of the precursor, indicating small coherent diffraction domains estimated in the range of 10 nm by the Laue–Scherrer relation. High specific surface areas around  $60\text{--}80\text{ m}^2\cdot\text{g}^{-1}$  (Table S13) were obtained with such calcination conditions, as

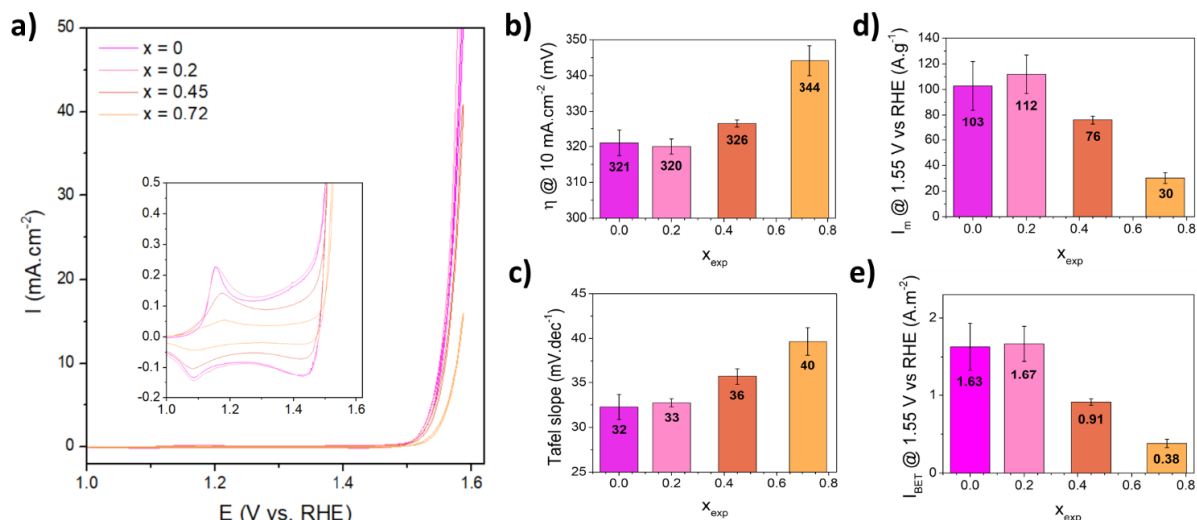
indicated by the grain size reduction before and after calcination (Figure S33).

The molar ratio  $n(\text{Co})/n(\text{Fe})$  in the calcined samples has been verified by ICP-OES (Table S14) and agrees with the formulation previously determined for the initial hydrated precursors. However, for compositions with a higher amount of  $\text{Fe}^{2+}$  (e.g.,  $x = 0.45$  and 0.72), a slight difference between experimental and theoretical is observed. This difference could be explained by an incomplete dissolution of the material, since the experimental  $n(\text{Co})/n(\text{Fe})$  ratio is still in agreement with the theoretical one, or by the presence of amorphous impurities resulting from thermal decomposition of additional  $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$  and  $\text{Fe}_3\text{F}_8(\text{H}_2\text{O})_2$ .

From this analysis, we can first conclude that the structure as well as the chemical composition of the oxyfluoride derived from  $(\text{Co}_{0.8}\text{Fe}_{0.2})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  is similar to that of the oxyfluoride derived from  $\text{Co}^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$ , which is surprising given the difference in the metal ratios and the intermediates involved. Thus, the excess  $\text{Fe}^{3+}$  may be in the form of an amorphous phase not visible by PXRD, or in another Fe enriched oxyfluoride with indistinguishable unit cell parameters arising from  $\text{CoFe}_2\text{F}_8(\text{H}_2\text{O})_2$ . Oxyfluorides prepared from  $(\text{Co}_{0.55}\text{Fe}_{0.45})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  and  $(\text{Co}_{0.28}\text{Fe}_{0.72})^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  are found to be enriched in iron, but not as much as in the initial precursor value, as suggested by the high amount of  $\alpha\text{-Fe}_2\text{O}_3$  impurity observed for calcined  $x_{\text{exp}} = 0.72$ .

#### 2.4. Electrochemical performance for oxygen evolution reaction (OER)

Cyclic voltammetry (CV) in 1M KOH electrolyte was performed to evaluate the performance of the calcined  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  samples as electrocatalysts for OER (Figure 4a). For all compositions, the  $\text{Co}^{2+/3+}$  oxidation peak is clearly visible and varies from 1.16 to 1.18 V vs. RHE depending on  $\text{Fe}^{2+}$  amount. This shift could be explained by a slight modification of the  $\text{Co}^{2+}$  environment in the rutile phase, which is gradually enriched in Fe, and consequently in  $\text{O}^{2-}$  for  $x_{\text{exp}} = 0.45$  and 0.72 samples. Both position and intensity of the  $\text{Co}^{2+/3+}$  oxidation peak are identical between the composition  $x_{\text{exp}} = 0$  and 0.2, the only difference being a slight broadening of the oxidation peak. This could be due to



**Figure 4.** (a) Cyclic voltammetry curves of calcined  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  in 1M KOH, the inset representing a zoom on the redox peaks area. (b) Overpotential at 10 mA·cm<sup>-2</sup> for the different compositions. (c) Tafel slope. (d) Mass activity at 1.55 V vs. RHE. (e) Specific activity at 1.55 V vs. RHE.

the contribution of a second oxyfluoride originating from  $\text{CoFe}_2\text{F}_8(\text{H}_2\text{O})_2$  which, according to the work of Lemoine *et al.*, shows a maximum intensity of  $\text{Co}^{2+}/\text{Co}^{3+}$  oxidation at a slightly higher potential of about 1.20 V vs. RHE [27] instead of 1.16 V vs. RHE for  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{0.5}\text{F}_{1.5}$  ( $x_{\text{exp}} = 0$ ) [30]. For  $x_{\text{exp}} = 0.45$  and 0.72, the intensity of the oxidation peak decreases gradually and proportionally to the amount of  $\text{Co}^{2+}$ , indicating a reduced activity for the main  $\text{Co}^{2+}$  active site. In terms of overpotential (Figure 4b), Tafel slope (Figure 4c), mass activity (Figure 4d), and specific activity (Figure 4e), the calcined  $x_{\text{exp}} = 0$  and 0.2 samples show similar performance, which are the best of the calcined  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{FeF}_5(\text{H}_2\text{O})_7$  series, namely for  $x_{\text{exp}} = 0.2$  an overpotential of 320 mV at 10 mA·cm<sup>-2</sup>, a low Tafel slope of 33 mV·dec<sup>-1</sup>, a mass activity of 112 A·g<sup>-1</sup>, and a specific activity of 1.67 A·m<sup>-2</sup>. This similar activity between calcined  $x_{\text{exp}} = 0$  and 0.2 confirms that both structures and chemical compositions are relatively close, and it does not affect the global OER performance regardless of the presence of an additional phase. On the other hand, the OER activity decreases progressively for calcined  $x_{\text{exp}} = 0.45$  and 0.72, which could be attributed to the increase of less active Fe-enriched oxyfluorinated phases to the detriment of more active Co-phases. Chronopotentiometric measurements were carried out at a current density

of 125 mA·cm<sup>-2</sup> on calcined  $x_{\text{exp}} = 0$  and 0.2 to study the effect of Fe increase on the stability (Figure S34). Both samples are similar and reasonably stable, with only an increase of about 150 mV after 17 days at 125 mA·cm<sup>-2</sup>.

### 3. Conclusion

In this work, the  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  solid solution with  $0 \leq x_{\text{exp}} \leq 0.72$  is synthesized by a simple coprecipitation inspired by our previous work, as precursors of Co/Fe oxyfluorides as OER catalysts. XRD, EDX-SEM and Mössbauer spectrometry analyses confirmed the  $\text{Co}^{2+}/\text{Fe}^{2+}$  substitution in the heptahydrated precursors, but the quantification of the  $\text{Fe}^{2+}$  amount indicates that it is incomplete, due to a small part of  $\text{Fe}^{2+}$  oxidized to  $\text{Fe}^{3+}$  during the synthesis. A detailed study of the thermal behavior of these hydrates by coupling HT-XRD and TGA analyses revealed for the first time a complex decomposition into a mixture of  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{FeF}_5(\text{H}_2\text{O})_2$  and  $\text{CoFe}_2\text{F}_8(\text{H}_2\text{O})_2$  dihydrates for  $x_{\text{exp}} = 0$  and 0.2, and additionally into  $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$  and  $\text{Fe}_3\text{F}_8(\text{H}_2\text{O})_2$  for  $x_{\text{exp}} = 0.45$  and 0.72. Then, depending on the chemical composition of  $\text{MFeF}_5(\text{H}_2\text{O})_2$  and  $\text{MFe}_2\text{F}_8(\text{H}_2\text{O})_2$  ( $\text{M} = \text{Co}^{2+}$  and/or  $\text{Fe}^{2+}$ ), these materials are decomposed into various mixed Fe/Co or pure amorphous

Fe oxyfluorides. These oxyfluorinated materials, prepared by appropriate thermal treatment in a muffle furnace, were tested for OER in alkaline medium. The results show that it is possible to replace 20% of the cobalt by iron without affecting the electrochemical performance. For higher substitution rates ( $x_{\text{exp}} \geq 0.45$ ), the proportion of  $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$  and  $\text{Fe}_3\text{F}_8(\text{H}_2\text{O})_2$ , giving after thermal decomposition Fe-pure oxyfluorides, is increasing at the detriment of  $\text{CoFeF}_5(\text{H}_2\text{O})_2$  and  $\text{CoFe}_2\text{F}_8(\text{H}_2\text{O})_2$  leading to Co-containing oxyfluorides with higher performance. These results seem to indicate that the best electrochemical performance is obtained for a Co:Fe ratio of 1:1. In order to avoid the formation of pure Fe phases, the synthesis of  $\text{Co}_{(1-x)/2}\text{Fe}_{(1+x)/2}\text{O}_{(1+x)/2}\text{F}_{(3-x)/2}$  oxyfluorides from the alternative hydrate solid solution  $\text{Co}_{1-x}\text{Fe}_x\text{F}_2(\text{H}_2\text{O})_4$ , which does not induce the formation of phases mixing during the thermal decomposition, is in progress. In addition, EXAFS and PDF studies will be performed to understand the local environment of transition metals in these oxyfluorides.

## 4. Experimental section

### 4.1. Synthesis of fluorinated materials

**Chemicals.** The heptahydrate fluorides were synthesized using  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  ( $\geq 98\%$ , Alfa Aesar),  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (99.5%, Acros Organics), and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (98% Alfa Aesar). Hydrofluoric acid solution (HF 48 wt%, Honeywell), methanol (MeOH, 99.8% Honeywell), and absolute ethanol (99.8%, Carlo Erba Reagents) were used as received. **Warning!** HF is a hazardous chemical, toxic by inhalation, contact with skin, and if swallowed. All necessary precautions were taken during our experiments.

#### 4.1.1. Synthesis of $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$ ( $0 \leq x_{\text{theo}} \leq 0.75$ )

$(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  ( $0 \leq x_{\text{theo}} \leq 0.75$ ) precursors were synthesized by coprecipitation at room temperature.  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  are dissolved in 10 mL HF solution (HF<sub>48</sub> wt%) under stirring while  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  is separately dissolved in 1 mL of MeOH. Ongoing study aims to replace HF by solid sources as  $\text{NH}_4\text{F}$  or  $\text{KF}$  for sustainability and security issues. This separate dissolution is necessary because  $\text{Fe}^{2+}$  is easily oxidized to  $\text{Fe}^{3+}$  in HF or

EtOH solutions. After complete dissolution, 15 mL of EtOH is added to the  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  solution and quickly poured into the HF solution containing  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  species, leading to the precipitation of  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$ . Stirring is maintained for 5 min to ensure a complete reaction. The precipitate is filtered, washed several times with EtOH, and dried under ambient conditions. Polycrystalline powders ranging in color from pink to yellow are obtained with good yields and high purity.

#### 4.1.2. Synthesis of $\text{Co}_{(1-x)/2}\text{Fe}_{(1+x)/2}\text{O}_{(1+x)/2}\text{F}_{(3-x)/2}$ ( $0 \leq x_{\text{exp}} \leq 0.72$ )

$\text{Co}_{(1-x)/2}\text{Fe}_{(1+x)/2}\text{O}_{(1+x)/2}\text{F}_{(3-x)/2}$  ( $0 \leq x_{\text{exp}} \leq 0.72$ ) samples were synthesized by calcination under air of 200 mg of the corresponding hydrated fluoride  $(\text{Co}_{1-x}\text{Fe}_x)^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_7$  at various temperatures for a short period of time in a muffle furnace (Nabertherm LT 3/12). The temperature profile is represented in Figure S35 and the calcination conditions in Table S13. The sample was directly placed in the muffle furnace when the targeted temperature was reached and heated for a suitable time. The sample was finally removed and cooled to ambient temperature under ambient air.

### 4.2. Characterization

**X-ray diffraction (XRD).** X-ray diffraction patterns were collected in the range of  $10^\circ \leq 2\theta \leq 120^\circ$  on a PANalytical MPD-PRO diffractometer with a Bragg-Brentano geometry, equipped with a Co  $K\alpha$  source ( $k_{\alpha 1} = 1.78901 \text{ \AA}$ ;  $k_{\alpha 2} = 1.79290 \text{ \AA}$ ) and a linear X'Celerator detector. Rietveld refinements were performed by using the Fullprof program.

#### High-Temperature X-ray diffraction (HT-XRD).

High-Temperature X-ray diffraction (HT-XRD) was performed under ambient air in an Anton Paar XRD 900 high temperature furnace with the diffractometer described above. The samples were heated from 30 to 600 °C at a heating rate of  $3 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ . X-ray diffraction patterns were recorded in the  $[8-80^\circ]$   $2\theta$  range with a scan time of 15 min at 20 °C intervals from room temperature to 400 °C and at 50 °C intervals from 400 to 600 °C.

**Thermogravimetric analyses (TGA).** Thermogravimetric analyses were carried out using a thermoanalyzer SETARAM TGA 92 under ambient air flow at

100 mL/min with a heating rate of  $2\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  from room temperature up to  $600\text{ }^{\circ}\text{C}$ .

**Scanning Electron Microscopy (SEM).** Scanning Electron Microscopy images were obtained thanks to a Hitachi microscope (Hitachi SU3800). The acceleration voltage used is 15 kV. Elemental quantitative microanalyses were performed using an EDAX Energy Dispersive X-ray Octane Elect Super EDS detector.

**$\text{N}_2$  sorption.** The specific surface areas were measured at 77 K using a TriStar II 3020 (Micromeritics). The samples were degassed under secondary vacuum at  $80\text{ }^{\circ}\text{C}$  for 12 h prior to measurement. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method.

**$^{57}\text{Fe}$  Mössbauer spectrometry.** Mössbauer measurements were obtained in transmission geometry with a 925 MBq  $\gamma$ -source of  $^{57}\text{Co}/\text{Rh}$  on a conventional constant acceleration drive. The amount of substance for each sample weighed was calculated to contain 5 mg of Fe per  $\text{cm}^2$ . Spectra were fitted using the MOSFIT program [35] involving quadrupolar and/or magnetic components with Lorentzian lines; the isomer shift values are referred to that of  $\alpha$ -Fe at room temperature. The velocity of the source was calibrated using a  $\alpha$ -Fe foil as a standard at room temperature.

**Elemental analysis.** From an initial solution containing iron and cobalt (1000 ppm), standard solutions have been prepared to obtain the concentrations: 0, 0.5, 1, 2, 5, and 10 ppm. The intensity of the signal as a function of the element concentration, obtained for each element (Fe, Co) is reported in (Figure S36). The samples were prepared by digestion of approximately 10 mg of samples dissolved first in 5 wt%  $\text{HNO}_3(\text{aq})$  followed by a dilution with deionized water by a factor of 100 to be in the right range of measurements.

**Electrochemical measurements.** A Biologic SP200 potentiostat and EC-lab software were used. Ag/AgCl reference (4M KCl gel) and carbon rod counter electrodes were employed for the measurements. Custom-built one-compartment glass electrochemical cells were employed, and 1M KOH was used as the electrolyte. Working electrodes were constructed from Toray carbon paper. A catalyst ink

was prepared by sonicating typically 10 mg of the catalyst and 0.1 mg of carbon nanotubes in 1 mL of 2:1 ethanol:water (V:V) with 80  $\mu\text{L}$  of Nafion. The ink was dropped-cast onto the working electrodes and allowed to dry under ambient conditions for 20 min prior to use. Catalyst loadings on the carbon paper were  $0.1\text{ mg}\cdot\text{cm}^{-2}$  and  $1\text{ mg}\cdot\text{cm}^{-2}$  for cyclic voltammetry and chronopotentiometry, respectively. Prior to electrochemical measurements, the impedance between reference and working electrode was recorded in open circuit, and the ohmic drop was subsequently corrected for at 95% with the ZIR function in the EC-lab software.

## Declaration of interests

The authors do not work for, advise, own shares in, or receive funds from any organization that could benefit from this article, and have declared no affiliations other than their research organizations.

## Acknowledgments

The authors attached to IMMM gratefully acknowledge the technical platforms “X-ray Diffusion and Diffraction” and “Electron Microscopy” of IMMM (Le Mans University) as well as the French National Research Agency (ANR OPIFCAT, ANR-20-CE08-0026) and the Fondation Banque Populaire d’Entreprise de l’Ouest for financial support. NK acknowledges NSERC for its Discovery Grant RGPIN-2019-05927, and the International Emerging Action IEA. All authors thank FRQNT Samuel de Champlain program, award 293526.

## Supplementary data

Supporting information for this article is available on the journal’s website under <https://doi.org/10.5802/crchim.371> or from the author.

## References

- [1] J. Turner, G. Sverdrup, M. K. Mann, P. C. Maness, B. Kroposki, M. Ghirardi, R. J. Evans and D. Blake, *Int. J. Energy Res.* **32** (2008), pp. 379–407.
- [2] X. Li, L. Zhao, J. Yu, X. Liu, X. Zhang, H. Liu and W. Zhou, *Nano-Micro Lett.* **12** (2020), pp. 1–29.
- [3] S. Yin Tee, K. Yin Win, W. Siang Teo, et al., *Adv. Sci.* **4** (2017), article no. 1600337.

- [4] Z. Abdin, A. Zafaranloo, A. Rafiee, W. Mérida, W. Lipiński and K. R. Khalilpour, *Renew. Sustain. Energy Rev.* **120** (2020), article no. 109620.
- [5] J. D. Fonseca, M. Camargo, J. M. Commenge, L. Falk and I. D. Gil, *Int. J. Hydrog. Energy* **44** (2019), pp. 9486–9504.
- [6] N. T. Suen, S. F. Hung, Q. Quan, N. Zhang, Y. J. Xu and H. M. Chen, *Chem. Soc. Rev.* **46** (2017), pp. 337–365.
- [7] Y. Gong, J. Yao, P. Wang, Z. Li, H. Zhou and C. Xu, *Chinese J. Chem. Eng.* **43** (2022), pp. 282–296.
- [8] Z. F. Huang, J. Song, S. Dou, X. Li, J. Wang and X. Wang, *Matter* **1** (2019), pp. 1494–1518.
- [9] J. Song, C. Wei, Z. F. Huang, C. Liu, L. Zeng, X. Wang and Z. J. Xu, *Chem. Soc. Rev.* **49** (2020), pp. 2196–2214.
- [10] W. T. Hong, M. Risch, K. A. Stoerzinger, A. Grimaud, J. Suntivich and Y. Shao-Horn, *Energy Environ. Sci.* **8** (2015), pp. 1404–1427.
- [11] F. Song and X. Hu, *Nat. Commun.* **5** (2014), article no. 4477.
- [12] F. Dionigi, Z. Zeng, I. Sinev, et al., *Nat. Commun.* **11** (2020), article no. 2522.
- [13] T. Wang, W. Xu and H. Wang, *Electrochim. Acta* **257** (2017), pp. 118–127.
- [14] H. Jin, S. Mao, G. Zhan, F. Xu, X. Bao and Y. Wang, *J. Mater. Chem. A* **5** (2017), pp. 1078–1084.
- [15] M. Li, Y. Gu, Y. Chang, X. Gu, J. Tian, X. Wu and L. Feng, *Chem. Eng. J.* **425** (2021), article no. 130686.
- [16] Y. Zhang, B. Wang, C. Hu, et al., *Chinese J. Struct. Chem.* **43** (2024), article no. 100243.
- [17] R. Subbaraman, D. Tripkovic, K. C. Chang, et al., *Nat. Mater.* **11** (2012), pp. 550–557.
- [18] J. Xiong, H. Zhong, J. Li, et al., *Appl. Catal. B Environ.* **256** (2019), article no. 117817.
- [19] S. Wan, J. Qi, W. Zhang, et al., *Adv. Mater.* **29** (2017), article no. 1700286.
- [20] M. Li, H. Liu and L. Feng, *Electrochem. Commun.* **122** (2021), article no. 106901.
- [21] Q. Liang, G. Brocks and A. Bieberle-Hütter, *J. Phys. Energy* **3** (2021), article no. 2.
- [22] Y. Xue, Y. Wang, H. Liu, X. Yu, H. Xue and L. Feng, *Chem. Commun.* **54** (2018), pp. 6204–6207.
- [23] C. Pei, H. Chen, B. Dong, X. Yu and L. Feng, *J. Power Sources* **424** (2019), pp. 131–137.
- [24] C. Pei, Y. Gu, Z. Liu, X. Yu and L. Feng, *ChemSusChem* **12** (2019), pp. 3849–3855.
- [25] J. Xie, W. Liu, J. In, et al., *ChemSusChem* **10** (2017), pp. 4465–4471.
- [26] Z. Zhao, H. Chang, R. Wang, et al., *Small Struct.* **2** (2021), article no. 2100069.
- [27] K. Lemoine, J. Lhoste, A. Hémon-Ribaud, N. Heidary, V. Maisonneuve, A. Guet and N. Kornienko, *Chem. Sci.* **10** (2019), pp. 9209–9218.
- [28] J. Lhoste, N. Kornienko, Z. Gohari-Bajestani, V. Maisonneuve, A. Guet, A. Ribaud, R. Moury and C. Galven, Novel oxyfluorides, electrodes containing them and their use for hydrogen production, WO2022234120 (A1), 2022.
- [29] Z. Gohari-Bajestani, X. Wang, A. Guet, et al., *Chem. Catal.* **2** (2022), pp. 1114–1127.
- [30] A. Terry, S. Mathiot, A. Guet, et al., *ACS Appl. Energy Mater.* **7** (2024), pp. 11466–11474.
- [31] F. C. Hawthorne and O. C. Gagné, *Acta Crystallogr. B* **80** (2024), pp. 326–339.
- [32] K. Lemoine, L. Zhang, D. Dambournet, et al., *Chem. Mater.* **31** (2019), pp. 4246–4257.
- [33] K. Huang, Z. Zhao, H. Du, et al., *ACS Sustain. Chem. Eng.* **8** (2020), pp. 6905–6913.
- [34] F. J. Brink, R. L. Withers and L. Norén, *J. Solid State Chem.* **161** (2001), pp. 31–37.
- [35] J. Teillet and F. Varret, *unpublished MOSFIT Program*, Le Mans Université: France.