



# Cobalt-doped pyrochlore-structured iron fluoride as a highly stable cathode material for lithium-ion batteries



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## ABSTRACT

In the search of high-performance cathodes for next-generation Li-ion batteries (LIBs), iron fluorides are among the most promising materials because of their extremely high theoretical capacity. This study reports on the synthesis, structural and electrochemical characterizations of cobalt doped iron fluoride hydrate as a high-performance cathode material for LIBs. A simple non-aqueous precipitation method is used to synthesize cobalt doped iron fluoride ( $\text{Fe}_{0.9}\text{Co}_{0.1}\text{F}_3 \cdot 0.5\text{H}_2\text{O}$ ) while its structural and electrochemical properties are also evaluated. The thermogravimetric analysis reveals that the structure of the as-prepared material remains stable up to 243 °C. The structure was then found to collapse beyond this temperature due to the removal of water contents from the crystal structure. The material delivers a high discharge capacity of 227  $\text{mAh g}^{-1}$  at 0.1C in the potential range of 1.8–4.5 V versus  $\text{Li/Li}^+$ . The electrode retains a high reversible capacity of 150  $\text{mAh g}^{-1}$  at a rate of 0.1C after 200 cycles, indicating high reversibility and stability of the material. The electrode also shows a superior rate capability of up to 10C, showing its potential use as a cathode material for LIBs.

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## 1. Introduction

Li-ion batteries (LIBs) are the most common electrical energy storage devices being used in the electronics industry for applications, such as cell phones and laptops. But, current LIBs do not meet the growing demand of new application areas. There is need to develop high-performance batteries to meet the increasing demand of energy storage for electrical vehicles and grid storage. One of the key challenges in developing large-scale batteries is to obtain high-performance cathodes with readily available materials [1]. Polyanion-frameworks such as  $\text{LiMnPO}_4$ ,  $\text{LiCoPO}_4$ , and  $\text{LiNiPO}_4$  as cathode materials in LIBs have been found to suffer from limited capacities and poor cyclability due to their structural instabilities [2–5]. Attempts have been made to implement other promising cathode materials, such as lithium-containing layered materials ( $\text{LiNiO}_2$ ,  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , etc) and spinel ( $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ , etc) based compounds [6,7]. These materials also suffer from either structural or chemical instability, resulting in poor cyclability [7]. To meet the requirement of all

electric vehicles and large-scale energy storage devices, alternative cathodes with improved capacity and low-cost material are urgently required.

Metal fluorides have received much attention as cathode materials for LIBs because of their positive attributes such as high working potential, high theoretical capacities, low cost and low toxicity [8–10]. Among them,  $\text{FeF}_3$  exhibits promising electrochemical performance with a large theoretical capacity of 237  $\text{mAh g}^{-1}$  (with one  $\text{Li}^+$  insertion/extraction), a value higher than the  $\text{LiFePO}_4$  (170  $\text{mAh g}^{-1}$ ) and the high ionicity of metal-fluorine bond that induces an operating voltage of  $\sim 3\text{V}$  [9,11]. Moreover, a much larger theoretical capacity ( $\sim 712\text{mAh g}^{-1}$  corresponding to three  $\text{Li}^+$  insertion/extraction) is achievable from  $\text{FeF}_3$  when a conversion reaction is involved [11]. But, the main drawback of  $\text{FeF}_3$  as a cathode material is its intrinsically low electronic conductivity due to the high ionic nature of metal-fluorine bonding, which leads to the low experimental capacity and fast capacity deterioration [12,13]. In order to address this limitation, various strategies have been proposed, such as nano-size synthesis of  $\text{FeF}_3$  and its composite structures with carbonaceous materials such as carbon nanotubes [14], graphene [15], and ordered mesoporous carbon [16]. But, such procedures usually require a controlled particle growth during synthesis, high

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temperature or pressure, toxic reagents (e.g. HF), and a substantial amount of carbon additives [17]. This has prompted researchers to explore other possibilities for improving the electronic conductivity of FeF<sub>3</sub> based cathodes. One such attempt that has received recent attention is the cation doping of FeF<sub>3</sub> lattice [18–20]. Among the various metals, Co stands out as a promising candidate for effective doping due to the comparable ionic radii of Co with Fe. The replacement of Fe by Co (~10%) may lead to a little variation in the lattice parameters but the original crystal structure remains unchanged [19,20].

Recently, the hydrated version of iron fluoride has been reported with a chemical formula of FeF<sub>3</sub>·0.5H<sub>2</sub>O where water molecules are located at the center of each cage made of FeF<sub>6</sub> octahedra of pyrochlore structure [21]. FeF<sub>3</sub>·0.5H<sub>2</sub>O with a composite of single-walled nanotubes (SWNTs) was reported as a cathode for LIBs where it showed a reversible capacity of ~135 mAh g<sup>-1</sup> and 110 mAh g<sup>-1</sup> [11,22]. A nanocomposite cathode of FeF<sub>3</sub>·0.5H<sub>2</sub>O with reduced graphene oxide (RGO) exhibited a reversible capacity of 171 mAh g<sup>-1</sup> in LIBs [23]. Until now, FeF<sub>3</sub>·0.5H<sub>2</sub>O has been reported as composites with carbonaceous materials with enhanced electrochemical performance.

This paper demonstrates the preparation of Co-doped FeF<sub>3</sub>·0.5H<sub>2</sub>O nanostructures and investigate its electrochemical performance as a LIB cathode material. Cobalt doping was successfully performed via non-aqueous precipitation method and confirmed by X-ray diffraction analysis. Microstructural characterization, chemical analysis, thermal study and electrochemical tests were performed to investigate the properties of synthesized Fe<sub>0.9</sub>Co<sub>0.1</sub>F<sub>3</sub>·0.5H<sub>2</sub>O as a cathode material for LIBs. The synthesized material showed good electrochemical performance with a discharge capacity of 227 mAh g<sup>-1</sup> at a rate of 0.1C and enhanced cyclic stability up to 200 cycles. The rate performance of the material was also tested at higher current densities and the results are herein presented and discussed.

## 2. Experimental

For the synthesis of cobalt doped FeF<sub>3</sub>·0.5H<sub>2</sub>O, ionic liquid, BMIMBF<sub>4</sub> (>98%, Aldrich), was used as co-solvent, soft template, and a fluorine source. Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (99.99%, Aldrich) and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (>98%, Aldrich) were used to provide iron, cobalt respectively, and hydration water for BMIMBF<sub>4</sub> hydrolysis. The material was prepared using non-aqueous precipitation method as reported in the literature [24]. Briefly, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in a stoichiometric ratio (total 1 g) were mixed in 12 g of BMIMBF<sub>4</sub> and magnetically stirred for 12 h at 50 °C to form the precipitates and then transferred into vacuum oven to evaporate the excess water. The resultant product was achieved after centrifugation at 6000 rpm and washed with acetone several times to remove the nitrate impurities and residual ionic liquid. The final material was then dried under vacuum at 80 °C for 20 h.

The structure and crystalline phase of as-prepared Fe<sub>0.9</sub>Co<sub>0.1</sub>F<sub>3</sub>·0.5H<sub>2</sub>O were identified by Rigaku X-ray diffractometer with Cu Kα radiations (λ=1.542 Å). The diffraction pattern was recorded over a 2θ range of 10–80° with a sampling pitch of 0.02°. The surface morphology and microstructural characteristics were examined using field emission electron microscope (FE-SEM, NOVA NanoSEM200, FEI Company) and high-resolution transmission electron microscope (HRTEM, FEI TECNAI G2 20 S-TWIN) equipped with a LaB6 cathode and a GATAN MS794 P CCD camera. The micrographs were obtained at an acceleration voltage of 200 kV. The thermal properties of Co-doped FeF<sub>3</sub>·0.5H<sub>2</sub>O were examined using thermogravimetric analyzer (SDT-Q600, TA Instruments, USA) under a nitrogen atmosphere. The temperature was scanned from room temperature to 700 °C at a constant heating rate of 5 °C per minute. X-ray photoelectron microscopy

(XPS) spectra of the material were acquired with PHI 5000 VersaProbe (ULVAC-PHI) under high vacuum conditions (6.8 × 10<sup>-8</sup> pa), using a monochromatic Al-Kα X-ray source (1486.6 eV). The data was collected from a spot size of 100 μm x 100 μm. The carbon 1s peak (284.6 eV) was used for internal calibration.

For electrochemical tests, the working electrodes were prepared by mixing Co-doped FeF<sub>3</sub>·0.5H<sub>2</sub>O, carbon black, and polyvinyl difluoride (PVDF) with a weight ratio of 7:2:1 in N-methyl-2-pyrrolidinone and then cast onto a pure Al foil. The electrodes were dried at 80 °C in vacuum for 4 h followed by roll-pressing. CR 2032-type coin cells were fabricated from active electrode material with an average mass loading of 2.2 (±0.2) mg cm<sup>-2</sup> and thickness of 30 μm and a high-purity lithium foil was used as a counter electrode. The electrolyte used was 1 M NaPF<sub>6</sub> in an ethylene carbonate (EC), propylene carbonate (PC) and diethyl carbonate (DEC) with a volume ratio of 1:1:1. Galvanostatic measurements were performed on a battery cycler (Maccor 4000) at room temperature, and the specific capacity of the cathode was calculated on the basis of the total weight of Fe<sub>0.9</sub>Co<sub>0.1</sub>F<sub>3</sub>·0.5H<sub>2</sub>O. Cyclic voltammograms and electrochemical impedance spectroscopy (EIS) analysis were carried out with the coin cells using a Biologic potentiostat/galvanostat Model VMP3 (BioLab, Inc.).

## 3. Results and Discussions

The synthesis of Co-doped FeF<sub>3</sub>·0.5H<sub>2</sub>O was performed using the non-aqueous approach (ionic liquid BMIMBF<sub>4</sub>) which has the advantages of low synthesis temperature, precise control over particle growth, surface morphology, and crystallization of the material. This method generally produces iron fluoride containing hydration water at various proportion, which is necessary for structural stability [13]. The X-ray diffraction pattern of Fe<sub>0.9</sub>Co<sub>0.1</sub>F<sub>3</sub>·0.5H<sub>2</sub>O is shown in Fig. 1. The material exhibited a cubic structure that can be indexed to *Fd3m* space group. All representative diffraction peaks of cubic pyrochlore FeF<sub>3</sub>·0.5H<sub>2</sub>O were evident, consistent with the previous reports [21]. Pyrochlore-type cubic structures usually have large lattice parameter, exhibiting a high volume of the unit cell. Furthermore, a cage-like framework is generated by the corner-sharing of FeF<sub>6</sub> octahedra and the water molecules are located at the center of each cage at zig zag position in the structure. The presence of water molecules expands the volume of the unit cell and a large three-dimensional crystal structure is favorable to the Li<sup>+</sup> insertion/extraction electrochemistry [21]. With Co doping, the crystal structure of FeF<sub>3</sub>·0.5H<sub>2</sub>O remains unchanged. In addition, no impurity signals

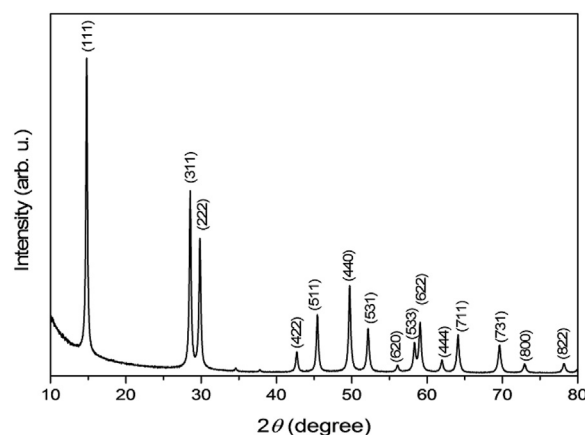


Fig. 1. Powder XRD pattern of Fe<sub>0.9</sub>Co<sub>0.1</sub>F<sub>3</sub>·0.5H<sub>2</sub>O with Cu Kα (λ = 1.5405 Å). All the major diffraction peaks are indexed with *hkl* values.

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