



# A graphene loading heterogeneous hydrated forms iron based fluoride nanocomposite as novel and high-capacity cathode material for lithium/sodium ion batteries



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## HIGHLIGHTS

- A sol–gel route is used to synthesize  $\text{FeF}_3 \cdot x\text{H}_2\text{O}$ /graphene cathode material.
- The  $\text{FeF}_3 \cdot x\text{H}_2\text{O}$  was consisted of heterogeneous hydrated iron fluorides.
- The  $\text{FeF}_3 \cdot x\text{H}_2\text{O}$ /graphene forms special morphology and mesoporous structure.
- The  $\text{FeF}_3 \cdot x\text{H}_2\text{O}$ /graphene electrode has been researched for LIB and NIB.

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## ABSTRACT

A graphene loading heterogeneous hydrated forms iron based fluoride (abbreviated as  $\text{FeF}_3 \cdot x\text{H}_2\text{O}/\text{G}$ ) nanocomposite is successfully designed and synthesized for the first time by a sol–gel method. It found that the  $\text{FeF}_3 \cdot x\text{H}_2\text{O}$  nanoparticles distribute randomly on the surface of the graphene, stacking together to form a nanocomposite with high specific surface and abundant mesoporous structure. The  $\text{FeF}_3 \cdot x\text{H}_2\text{O}$  was consisted of  $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{FeF}_{2.5} \cdot 0.5\text{H}_2\text{O}$  with pyrochlore phase structure and  $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$  with hexagonal-tungsten-bronze-type structure (HTB). The  $\text{FeF}_3 \cdot x\text{H}_2\text{O}/\text{G}$  was used as cathode materials of rechargeable lithium/sodium batteries, respectively. It has been found that it can deliver a large reversible capacity exceeding  $200 \text{ mAh g}^{-1}$  and excellent cyclic performance with a residual capacity of  $183 \text{ mAh g}^{-1}$  after 100 cycles at 0.2C and  $149 \text{ mAh g}^{-1}$  after 200 cycles at 1C, especially, an outstanding rate performance exceeding  $130 \text{ mAh g}^{-1}$  at 5C in the voltage range of 1.5–4.5 V for Li-ion batteries. Moreover, when  $\text{FeF}_3 \cdot x\text{H}_2\text{O}/\text{G}$  is used as cathode material of Na-ion batteries, it exhibits also a high reversible capacity of  $101 \text{ mAh g}^{-1}$  after 30 cycles in the voltage range of 1.0–4.0 V at 0.1C. Therefore,  $\text{FeF}_3 \cdot x\text{H}_2\text{O}/\text{G}$  will be a promising cathode material for high-performance lithium/sodium ion batteries.

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## 1. Introduction

With the rapid development of energy consumption equipments, such as rapidly miniaturizing electronics, large-scale mobile devices, especially electric vehicles and hybrid electric vehicles, the investigation of Li-ion batteries (LIB) with high storage capacity and excellent rate performance is imperative. Although typically intercalation materials ( $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiFePO}_4$ ) ensure good reversibility, they have intrinsic limitations in terms of capacity,

which is set by the number of available lithium sites. A general consensus has been formed that such limitation handicaps the device in terms of energy density, so that breakthroughs in performance need to develop a novel concept in materials research.

A reversion conversion reaction seems to provide a significant breakthrough choice to achieve a larger specific capacity by utilizing all possible redox during the charge/discharge process in transition metal compounds rather than 0.5–1.0 electrons transfer for conventional intercalation compounds. Specially, reversible conversion reactions have provided a rich playground for Li-ion battery technologies with potential to improve specific/rate capacity and achieve high resistance to lithium metal plating [1,2]. Furthermore, in contrast to the intercalation materials, the

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mechanism based on conversion reactions between alkali metals and electrode materials does not primarily rely on the size of alkali cations, offering a promising strategy toward high-capacity electrodes for not only LIB but also Na-ion batteries (NIB) [3,4]. Therefore, continuous research has been focused on designing new cathode materials based on reversible conversion reactions with high capacity, good performance, high safety and low cost. In fact, some transition metal compounds based on conversion reactions had already been reported as cathode and anode materials for LIB and NIB [5–7]. Among the various transition metal compounds, most conversion compounds were used as anodes due to their relatively low operating potentials vs Li/Li<sup>+</sup> (or Na/Na<sup>+</sup>) [8–10], except for metal fluorides such as FeF<sub>3</sub> and FeF<sub>2</sub>, which have been found to exhibit sufficiently high reaction potentials and therefore are suitable for use as cathode [3,11–22].

For this reason, transition metal fluorides have been considered as a new class of promising cathode materials, which exhibit large theoretical capacities and high discharge voltage due to their highly ionic metal-ligand bonds and small atomic weight. Unlike conventional intercalation reaction, transition metal fluorides, based on reversible conversion reaction, enable the full utilization of redox during the charge/discharge process and thus possess high theoretical specific capacity. A very promising and representative example is iron trifluoride (FeF<sub>3</sub>), which can deliver a high theoretical capacity 712 mAh g<sup>-1</sup> at an average potential of ~2.7 V, enabling a high theoretical energy density of 1950 Wh kg<sup>-1</sup>. However, the high ionicity of FeF<sub>3</sub> combined with large bandgap results in poor electrical conductivity. In addition, LiF or NaF, the product of the conversion reaction, is also highly insulating. Therefore, highly conductive carbon (e.g., graphite, carbon black, activated carbon, and carbon nanotubes) have been used to compensate for the intrinsically poor conductivity. At the same time, size reduction to nanoscale dimension can effectively solve the kinetic problems during the reversible conversion reaction process. Kim and his coworkers reported the new hierarchical nanostructure FeF<sub>3</sub> nanoflowers on Carbon Nanotube (CNT) branches, and found that it can deliver more than 210 mAh g<sup>-1</sup> at a current rate of 20 mA g<sup>-1</sup> [13]. Chu et al. [14,15] reported FeF<sub>3</sub> nanospheres showed a high discharge capacity up to 193 mAh g<sup>-1</sup> in a voltage range of 1.7–4.0 V at a current density of 50 mA g<sup>-1</sup> and a good rate capability of 118 mAh g<sup>-1</sup> at a high current density of 1000 mA g<sup>-1</sup>. Moreover, they also reported that the reduced graphene oxide decorated with FeF<sub>3</sub> nanoparticles can deliver a high discharge capacity of 476 mAh g<sup>-1</sup> at a current density of 50 mA g<sup>-1</sup> in the voltage range 1.0–4.5 V. Furthermore, it is amazing that a wide range of hydrated forms of FeF<sub>3</sub> have been reported to exhibit a fairly high capacity for LIB as well as NIB. Li and his co-workers reported the CNT wiring nanostructured FeF<sub>3</sub>·0.33H<sub>2</sub>O, FeF<sub>2.5</sub>·0.5H<sub>2</sub>O, and FeF<sub>3</sub>·0.5H<sub>2</sub>O synthesized by ionic-liquid-based route, and which exhibited a remarkable improvement of capacity and rate performances as cathode materials for LIB and NIB [1,16,17]. Another carbon-coated iron (III) fluoride with three hydration water (FeF<sub>3</sub>·3H<sub>2</sub>O) prepared by ball-milling with acetylene black was reported as cathode material for LIB in the voltage of 2.0–4.5 V and exhibited an initial discharge capacity of 92.8 mAh g<sup>-1</sup> [19]. Lu et al. also reported dual hydrated iron fluorides phases consisting of Fe<sub>1.9</sub>F<sub>4.75</sub>·0.95H<sub>2</sub>O and FeF<sub>3</sub>·H<sub>2</sub>O have a large reversible capacity exceeding 200 mAh g<sup>-1</sup> and excellent cyclic performance with a residual capacity of 148 mAh g<sup>-1</sup> after 100 cycles are obtained at 0.1C for LIB [22]. Our group have also reported FeF<sub>3</sub>·3H<sub>2</sub>O/C, FeF<sub>3</sub>·0.33H<sub>2</sub>O/C and FeF<sub>3</sub>/C nanocomposites by ball-milling the as-prepared materials with acetylene black as cathode materials for LIB, and found they delivers excellent electrochemical performance in the voltage range of 2.0–4.5 V [18–20].

Transition metal fluorides are usually prepared by mechanical

milling, chemical precipitation or ionic-liquid-based route [13–20]. Compared to mechanical milling and the other chemical approaches, sol–gel method exhibits extensive advantages. Firstly, the whole reaction process occurs close to room temperature, while well-defined nanocomposites can be obtained by one-step reaction. Secondly, sol–gel method is a good route to produce nanoscopic metal fluorides, and it can effectively restrict particle growth then nanocomposites can be obtained [23]. Thirdly, the used raw materials are common chemical compound and the cost is very low. Finally but by no means the least, by making use of sol–gel methods, selecting the raw materials and altering the reaction conditions can be easily achieved to manipulate the desired microstructures, morphologies and crystallization degrees. Especially, graphene is used as an effectively mixed conductive network matrix to further improve the electrical conductivity of FeF<sub>3</sub>·xH<sub>2</sub>O and a support for FeF<sub>3</sub>·xH<sub>2</sub>O nanoparticles [15].

Herein, a modified sol–gel route was used to prepare the graphene loading heterogeneous hydrated FeF<sub>3</sub> materials. The synthesis route started with the iron precursor, a nitrate salt. The precursor and graphene are first dissolved or suspended in a solvent, then one-step fluorinated by HF solution to form a sol, further drying to obtain a xerogel. The product xerogel was finally calcined and grinded to fine powders. Besides, the physiochemical and electrochemical properties of the as-prepared FeF<sub>3</sub>·xH<sub>2</sub>O/G sample were studied in detail.

## 2. Experimental

Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (10 mmol, 4.04 g) and 0.06 g conduction type graphene (The Sixth Element Inc) were dissolved or suspended in 50 ml methanol, then 1.5 ml (30 mmol) of 40% HF acid was added with stirring to gain a solution. The obtained FeF<sub>3</sub> sol was aged for 16 h before dried at 60 °C. The product xerogel was further calcined at 150 °C for 3 h in a vacuum drying oven and grinded to fine powders.

The specific surface area and pore structure of the as-prepared material were determined by N<sub>2</sub> adsorption/desorption isotherm at 77 K (JW-BK112). The specific surface areas were calculated by the conventional Brunauer–Emmett–Teller (BET) method. Micropore volumes of the samples were analyzed by Horvath–Kawazoe (HK) theory. Pore volumes and the pore size distribution (PSD) plot were derived from the adsorption branch of the isotherm based on the Barrett–Joyner–Halenda (BJH) model.

X-ray powder diffraction was performed using Rigaku D/MAX-2500/PC equipped with Cu-Kα source (40 kV, 250 mA) to get the crystal structure. The sizes and morphologies of compound particles were characterized by a field emission scanning electron microscope using JEOL JSM-3500N. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken on a JEOL-2100 microscope instrument at an acceleration voltage of 200 kV.

The electrochemical performance of the as-synthesized material was characterized on 2025 type coin cells as a cathode and a lither/sodium disk as anode for Li/Na ion batteries, respectively. The cathodes for Li/Na cells were fabricated by mixing the cathode material, Super carbon (SP), and polyvinylidene fluoride (PVDF) binder with a weight ratio of 80:15:5 in N-methyl pyrrolidinone, which were then pasted on aluminum foil followed by drying under vacuum at 110 °C for 24 h. The testing lithium cells were assembled with the cathodes thus fabricated, metallic lithium anode, Celgard 2300 film separator, and 1 mol L<sup>-1</sup> LiPF<sub>6</sub> in 1:1 ethylene carbonate (EC)/dimethyl carbonate (DMC) electrolyte. While for the testing sodium batteries metallic sodium anode, Glass fiber (GF/D) from Whatman was employed as the separator, and the electrolyte was 1 mol L<sup>-1</sup> NaClO<sub>4</sub> in a solvent of propylene carbonate (PC). The

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