



# An ionic-liquid-assisted approach to synthesize a reduced graphene oxide loading iron-based fluoride as a cathode material for sodium-ion batteries



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## ABSTRACT

A reduced graphene oxide loading iron-based fluoride (abbreviated as  $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}/\text{rGO}$ ) as a cathode material for sodium ion batteries (SIBs) has been successfully prepared by an ionic-liquid-assisted route. The morphology, structure, physicochemical properties and electrochemical performance are characterized by X-ray powder diffraction (XRD), Rietveld refinement of XRD pattern, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electrochemical tests. The XRD result shows that the crystal structure of the as-prepared sample can be indexed to the cubic  $\text{Fd-}3\text{m}$  space group and the lattice parameter is as follow:  $a = 1.04029 \text{ nm}$  and  $V = 1.12581 \text{ nm}^3$ . Moreover, the SEM and TEM images reveal that the as-prepared rGO has a rough wavy structure and flexural paper-like morphology, and numerous  $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}$  particles are firmly adhered on the surface of the rGO to form a uniform  $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}/\text{rGO}$  composite. Electrochemical tests show that the initial discharge capacity of  $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}/\text{rGO}$  sample is  $248.7 \text{ mAh g}^{-1}$  and the corresponding charging capacity up to  $229.7 \text{ mAh g}^{-1}$  at a rate of  $20 \text{ mA g}^{-1}$ . Especially, the  $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}/\text{rGO}$  possesses good cycling stability, and it can deliver a discharge capacity of  $164.2 \text{ mAh g}^{-1}$  at the 100th cycle. Besides, the rate capability tests show that a stable high capacity of  $186.0 \text{ mAh g}^{-1}$  can be resumed when the current rate returns to  $20 \text{ mA g}^{-1}$  after 20 cycles.

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## 1. Introduction

Energy conversion and storage have become key issues concerning our welfare in daily life [1]. Because of provoking energy and environmental issues, along with the growing human population, the global energy consumption has been accelerating at an alarming rate [2]. Recently, Li ion batteries (LIBs) attract a lot of attention in energy storage as the largest energy density and output voltage of all rechargeable battery technologies in use. But fears of lithium shortage and increased price, an alternative that can compete with LIBs technology on the global market is inevitably needed. Sodium, which is nontoxic and inexpensive and is also the next lighter and smaller alkali metal element other than lithium, has a redox potential suitable for battery applications (0.3 V vs Li), and importantly, is an abundant element, with a similar

electrochemistry to that of lithium in LIBs [3,4]. Hence it is valuable to study high-performance electrode materials with the capability to store and deliver energy for SIBs. Furthermore, many researchers are going to take the cathode material for SIBs as the disquisitive focus.

At the present time, some transition metal compounds based on conversion or insertion reactions have already been extensively studied as cathode materials for SIBs and LIBs, such as metal oxides ( $\text{Li}/\text{Na}_x\text{CoO}_2$  [5,6],  $\text{Na}_{0.66}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$  [7]), polyanion compounds ( $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  [8,9]), and especially metal fluorides ( $\text{FeF}_3$  [10]). Iron-based fluorides have become a researched hotspot because of their high operating voltages and high theoretical capacity, as well as a variety of stoichiometries which lead to a versatility of structures and physicochemical properties. For instance,  $\text{ReO}_3$ -type  $\text{FeF}_3$  [11], pyrochlore  $\text{FeF}_3 \cdot 0.5\text{H}_2\text{O}$  [12], HTB- $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$  [13], rutile structure  $\text{FeF}_2$  [14], pyrochlore-like  $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}$  [15,16], cubic  $\text{Fe}_{1.9}\text{F}_{4.75} \cdot 0.95\text{H}_2\text{O}$  [17] and so on. However, fluorides suffer from the drawback of poor reaction kinetics because of their low electronic conductivities resulting from the ionic nature of metal-

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fluorine bonding, making it more difficult to develop these materials as cathodes for both LIBs and SIBs [18,19]. To further improve the electrochemical properties of the iron-based fluoride, various endeavors have been made. Wang's group synthesized prelithiated  $\text{FeF}_3$  with extremely small size of Fe and LiF nanoparticles (both  $\sim 6$  nm) homogeneously embedded in the carbon matrix using a facile and scalable in situ strategy, which showed a high initial discharge capacity of  $230 \text{ mAh g}^{-1}$  at  $0.1 \text{ A g}^{-1}$  and an outstanding rate capability of  $128 \text{ mAh g}^{-1}$  at  $4 \text{ A g}^{-1}$  [20]. Song et al. reported a porous honeycomb-like iron fluoride hybrid composite comprising iron fluoride nanocrystals ( $\sim 1\text{--}4$  nm) encapsulated in separate carbon nests. As cathode materials for LIBs, the hybrid electrode delivers a large capacity nearly  $500 \text{ mAh g}^{-1}$  at  $20 \text{ mA g}^{-1}$  [21]. And our group prepared  $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{ACMB}$  (active carbon microbead) as cathode materials for LIBs [22]. Whereas comparing with polymerization coating or CNTs or ACMB, graphene has become a desired conductive building unit for hybridizing iron-based fluoride due to its extraordinary properties like electrical and thermal conductivity and mechanical property [23]. Kim et al. reported  $\text{FeF}_3$  microspheres/r-GO composites as an electrode material for LIBs, which shows improved discharge capacity and cycling stability. For example, the composites delivered an initial discharge capacity of  $196 \text{ mAh g}^{-1}$  at a rate of  $0.1 \text{ C}$  in the range of  $2.0\text{--}4.5 \text{ V}$  with  $0.28\%$  fading per cycle during 50 cycles [24]. And our group recently obtained a graphene loading heterogeneous hydrated forms iron-based fluoride nanocomposite via a modified sol–gel method for LIBs and SIBs [25]. But SIBs have higher requirements for the material structure since the radius of  $\text{Na}^+$  is larger than that of  $\text{Li}^+$ . It needs especially open channels with optimal width for ion insertion and robust structures to achieve the high specific capacity. However, Okada and co-workers attempted to apply  $\text{FeF}_3$  and  $\text{FeF}_3/\text{C}$  composites in SIBs, but the results are disappointing because of its dense structure [26]. Subsequently, Li's group reported a open-framework pyrochlore phase  $\text{FeF}_3 \cdot 0.5\text{H}_2\text{O}$ , which had a much large cell volume ( $\sim 1.13 \text{ nm}^3$ ) and interconnected 3D ion channels, a more favorable cation insertion capacity can be achieved especially for the larger radius  $\text{Na}^+$  [12]. Recently, Chung et al. prepared  $\text{FeF}_3 \cdot 0.5\text{H}_2\text{O}$ -rGO as a high-capacity cathode material for SIBs. The material delivers a substantially enhanced discharge capacity of  $266 \text{ mAh g}^{-1}$  at  $0.05 \text{ C}$  and a stable cycle performance with a higher than  $86\%$  capacity retention after 100 cycles [19].

Based on the above discussion, it is well know that the graphene-modified iron-based fluoride will have a great prospect as a high-capacity cathode material for SIBs, especially the iron fluoride graphene composite with open-framework pyrochlore phase. However, the pyrochlore-like phase iron-based fluoride  $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}$  is rarely reported as an electrode material of SIBs or LIBs. Kuang's group once systematically studied formation and properties of iron-based magnetic "superhalogens". They discovered that  $\text{Fe}_2\text{F}_5$  was the only case where the neutral and anionic clusters had a similar structure, and in a series of transition metal iron-based fluorides  $\text{Fe}_2\text{F}_n$  ( $n = 1\text{--}7$ ), when  $n = 5$ , the transformation from two-dimensional (2D) to three-dimensional (3D) structures can be observed [15]. In addition, for the pyrochlore-like phase  $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}$ , the trace water existed in the structure is good to stabilize structure and expand channel without the cost of a decrease in ion channel dimensionality. Thus, it is benefit for the  $\text{Na}^+$  rapid and reversible insertion/extraction to obtain high-capacity.

Herein, considering the advantages of graphene and the characteristics of iron-based fluoride, synthesizing  $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}/\text{rGO}$  by an ionic-liquid-assisted approach is reported in this work. IL 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate (BMMimBF<sub>4</sub>) was not only employed as a green fluoride source instead of the erosive HF, but also served as a dispersant of reduced graphene oxide (rGO). In

addition, graphene oxide (GO) was chosen as the starting materials instead of natural flake graphite to get rGO, thus avoiding additional oxidic treatment. Compared with hydrazine or dimethylhydrazine as reducing agents to reduce GO, we selected a green route, in which the rGO suspension could be quickly obtain by the hydrothermal method in strongly alkaline conditions and then made into paper-like rGO by rotary evaporation instrument [27]. Finally, the uniform loading  $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}/\text{rGO}$  composite can be obtained by in situ crystallization of  $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}$  on the surface of paper-like rGO. Furthermore, the physicochemical and electrochemical properties of the as-prepared paper-like  $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}/\text{rGO}$  sample will be studied in detail.

## 2. Experimental

### 2.1. Synthesis of rGO

GO was derived from the Sixth Element (Changzhou) Materials Technology company. Purified GO was dispersed in distilled water to obtain a yellow-brown suspension (concentration  $1 \text{ mL mg}^{-1}$ ) with the aid of intensive sonication (300 W, 40 KHz, 3 h). Subsequently, 80 mL the yellow-brown exfoliated-GO suspension and 4 g NaOH were loaded into the teflon ware, and then the sealed teflon ware was put into a stainless steel autoclave, which was held at  $160 \text{ }^\circ\text{C}$  for 12 h, followed by cooling at the room temperature to obtain black suspension. Next, the as-prepared rGO sample was washed with a lot of distilled water until the pH to neutral, and then washed with ethanol several times to obtain an alcoholic rGO suspension. Finally, the alcoholic rGO suspension was dried with rotary evaporation instrument to get paper-like rGO and stored for next reaction.

### 2.2. Synthesis of $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}/\text{rGO}$

In a typical synthesis of the  $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}/\text{rGO}$  composite, 9 mg rGO was mixed with 5 g IL 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate (BMMimBF<sub>4</sub>) (Aldrich > 99%) and magnetically stirred for 12 h at  $50 \text{ }^\circ\text{C}$  to achieve a homogeneous dispersion. Subsequently, 0.5 g iron (III) nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was added slowly into the mixed solution, which was agitated again for 12 h at  $50 \text{ }^\circ\text{C}$  to form the black-gray precipitate. Then the precipitate were washed with acetone and centrifuged 5 times at 10,000 rpm to remove residual IL and nitrate impurities, followed by drying under vacuum at  $90 \text{ }^\circ\text{C}$  for 20 h. Besides, the precipitation method for the bared  $\text{Fe}_2\text{F}_5 \cdot \text{H}_2\text{O}$  has been described elsewhere [16].

### 2.3. Characterizations of structure and morphology

Structure and crystallinity of samples were checked by X-ray diffraction on a Rigaku D/MAX-2500 powder diffractometer at 40 kV and 250 mA using a graphite monochromatic and Cu-K $\alpha$  radiation ( $k = 0.15418 \text{ nm}$ ) operated at a scan rate of  $4^\circ\text{min}^{-1}$  in the  $2\theta$  range of  $10^\circ\text{--}80^\circ$ . The morphology was investigated by a JEOL JSM-6610LV scanning electron microscope (SEM). High-resolution transmission electron microscopy (HRTEM) was carried out using a JEOL JEM-2100F transmission electron microscope (TEM) at an acceleration voltage of 200 kV. The weight percentage of carbon in the samples was determined by a C, H, N Analyser model 1106 Carlo Erba Strumentazione.

### 2.4. Electrochemical measurements

The cathode for testing cells was fabricated by mixing the cathode materials, acetylene black, and polyvinylidene fluoride (PVDF) binder with a weight ratio of 80:10:10 in N-methyl

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