Hollow porous FeF$_3$·0.33H$_2$O microspheres by AlPO$_4$ coating as a cathode material of Na-ion batteries

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ABSTRACT

As the cathode material of Na-ion batteries based on conversion reaction, the iron-based fluorides have attracted ever-increasing attentions. Nevertheless, its poor electronic conductivity and side reactions usually lead to sluggish reaction kinetics and rapid capacity decay during cycling process, and thus limiting its practical application. Herein, a hollow porous FeF$_3$·0.33H$_2$O microsphere is successfully prepared via a solvothermal route and further modified with AlPO$_4$. The results show that appropriate modification treatment can satisfactorily decrease charge-transfer resistance and enhance sodium diffusion rate. Compared with the pristine FeF$_3$·0.33H$_2$O, 4 wt.% AlPO$_4$-coated sample shows a noticeable initial discharge capacity of 290 mAh g^{-1} in the range of 1.2–4.0 V, outstanding cycling stability (211 mAh g^{-1} after 80 cycles) and excellent rate capability (167 mAh g^{-1} at 2.0 C). The excellent electrochemical properties can be ascribed to the distinctively hierarchical mesoporous hollow structure of FeF$_3$·0.33H$_2$O, which facilitates electrolyte permeation and rapid ionic as well as electronic transmission. Besides, the multifunctional AlPO$_4$ modification layer can improve the electronic conductivity, suppress the surface side reaction and buffer the volume changes during cycling processes, thus boosting the enhancement of the electrochemical performance. Therefore, this study offers a new strategy for improving and modifying the electrochemical performances of cathode materials for sodium-ion batteries.

1. Introduction

Energy production and storage technology is increasingly concerned by all over the world. As the large-scale application of lithium-ion batteries (LIBs) in many fields, a number of defects (such as its lack of resources, high cost and safety problem, etc.) are gradually revealed, which thus prompts the exploration for sustainable alternatives to satisfy demands of energy storage [1,2]. Na-ion batteries (NIBs) have remerged as an ideal candidate for large-scale energy storage systems (ESSs), because of its low cost and natural abundance as well as the similar storage mechanism to LIBs [3,4]. However, since ion radius (0.102 nm) of Na$^+$ is 34% larger than that (0.076 nm) of Li$^+$, and the ionization potential of Na is higher than that of Li, resulting in a lower energy and power density for NIBs [5] Therefore, for the practical application of NIBs, exploring the new cathode materials with much higher capacity and power density as well as excellent electrochemical performance to meet the requirement of energy storage devices is urgently needed. In contrast to intercalation cathode materials like layered oxides, polyanionic compounds, pyrophosphates, and so on, the transition metal fluorides based on multi-electron conversion reactions

have attracted more and more interest owing to its great specific capacity and energy density [6–12]. Among all metal fluorides, iron-based fluorides are the most competitive and attractive alternatives owing to its high theoretical specific capacity, relatively bargain price and low toxicity [13–17].

Serving as a polymorph of iron-based fluoride, open framework FeF$_3$·0.33H$_2$O possesses unique tunnel structure, which is greatly beneficial for improving Na$^+$ storage performance and enhancing Na$^+$ transport kinetics [18]. Nevertheless, in terms of practical application of iron-based fluoride as NIBs cathode material, it has been restricted due to its sluggish kinetics and low electronic conductivity resulted from the high ionicity of Fe-F bonds [19]. In addition, another limitation that affects the cycle and rate property of FeF$_3$·0.33H$_2$O is large volume change during cycling process stemmed from the conversion reaction [20]. To overcome above obstacles, various efforts have been made, such as controlling the size of particles to shorten the transmission pathways of electrons and ions [21–28], doping with other metal cation (Co^{3+}, Cr^{3+} or Ti^{4+}) to decrease band gap [29–31], and mixing with conductive carbon-based materials (conductive carbon, acetylene black, graphene or carbon nanotubes) to increase electronic

conductivity [32–38]. Although the electrochemical performance of the material, to a certain extent, has been improved by the above strategies, there are still plenty of shortcomings. For instance, since the carbon-based material as part of the cathode is electrochemically inert in NIBs, it will reduce the energy density of NIBs [39]. And doping with other metal cation still does not effectively restrict large volume changes. While another potential method to overcome the above barriers is the surface modification with ultrathin coating layer like MoS_2 [40], V_2O_5 [41], and TiO_2 [42], which is an effective approach to enhance the electrochemical performance of materials. Lately, Cho et al. [43] has reported that, in contrast to other surface modification materials, coating with $AlPO_4$ can remarkably enhance the cycling performance of material through suppressing the structural changes and surface erosion.

$AlPO_4$ has the framework structures like zeolites and is used as catalysts or molecular sieves. Owing to lower cost, environmentally friendly as well as excellent electron and ion conductivities, it has also become a popular coating material in the cathode materials of LIBs [44,45]. Furthermore, the strong P-O bond and the high electronegativity of PO_4^{3-} polyanions with Al^{3+} can prevent side reactions by limiting direct contact of electrolyte as well as electrode. Therefore, it has been coated on a variety of cathode materials like BiF_3 [46], $LiCoO_2$ [47], $Li[Li_{0.2}Fe_{0.1}Ni_{0.15}Mn_{0.55}]O_2$ [44], et al. Nevertheless, to the best of our knowledge, it has rarely been reported for coating $AlPO_4$ on the surface of iron fluorides.

Herein, the hollow porous $FeF_3 \cdot 0.33H_2O$ microspheres fabricated through a solvothermal method are further coated with various amounts of $AlPO_4$. The physicochemical and electrochemical performances of all the samples are systematically investigated by XRD, SEM, TEM, EDX, SAED, BET, XPS and electrochemical test. It has been found that 4 wt.% $AlPO_4$ coated $FeF_3 \cdot 0.33H_2O$ exhibits the optimal performance in contrast to other surface modification materials.

2. Experimental section

2.1. Material preparation

All chemicals were directly used without further purification. The hollow porous $FeF_3 \cdot 0.33H_2O$ was synthesized via a solvothermal approach. Firstly, 2.02 g iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, Aldrich) was dissolved in 50 mL ethanol severed as the solvent and agitated for 30 min. Then, 1 mL hydrogen fluoride (HF) (40 wt.%) was dropwise added into the above mixed solution accompanying by agitated stirring. After stirring for 60 min, the mixed solution was transferred to the steel autoclave, and further heated at 120 °C for 10 h. After cooling to room temperature naturally, the product was washed for six times with anhydrous ethanol to remove residual HF, then dried at 80 °C in vacuum atmosphere for 24 h.

To fabricate $AlPO_4$ modified $FeF_3 \cdot 0.33H_2O$ materials, 0.3 g Al(NO_3)$_3 \cdot 9H_2O$ (Aldrich) and 0.1 g (NH_4)$_2$HPO$_4$ (Aldrich) were added respectively to anhydrous ethanol and deionized water under vigorous stirring, until both forming the uniform colorless solution. Then, a desired amount of as-prepared $FeF_3 \cdot 0.33H_2O$ powder was slowly dispersed into Al(NO_3)$_3$ ethanol solution with stirring and followed by an ultrasound process for 30 min. Subsequently, (NH_4)$_2$HPO$_4$ solution was dropwise added into the above mixed solution under vigorous stirring. The weight ratio of $AlPO_4$ and $FeF_3 \cdot 0.33H_2O$ was 2:98. Samples of $FeF_3 \cdot 0.33H_2O$ modified with $AlPO_4$ were synthesized using different ratios of $AlPO_4$:$FeF_3 \cdot 0.33H_2O$ (0, 2, 4 and 6 wt.%). Then, the resulting mixture was obtained by centrifugal separation, then dried in vacuum at 80 °C for 24 h. At last, the obtained product was transferred into a tube furnace to be calcinated in Ar gas at 230 °C in for 5 h and then cooled to obtain the $FeF_3 \cdot 0.33H_2O$/$AlPO_4$ composites. The schematic diagram of the fabrication process for $FeF_3 \cdot 0.33H_2O$/$AlPO_4$ cathode material was displayed in Scheme 1. In addition, the $FeF_3 \cdot 0.33H_2O$ with various $AlPO_4$ coating amounts of 0, 2, 4, and 6 wt.% were marked as

AF-0, AF-2, AF-4, and AF-6, respectively.

2.2. Material characterizations

Crystal structures of materials were tested over the 2θ range of $10° - 80°$ by Rigaku D/MAX-2500 X-ray diffraction (XRD) techniques with Cu-Kα radiation at a speed of $10°$ min^{-1}. The morphologies of materials were determined via JEOL JSM-6610LV scanning electron microscope (SEM), Quanta FEG250 field emission scanning electron microscopy (FE-SEM) and JEOL JSM-2100F High-resolution transmission electron microscopy (HRTEM). The atomic concentration and elemental mappings of the materials were carried out by using an JEOL Quanta FEG250 energy-dispersive X-ray spectroscope (EDXS). The diffraction patterns were checked by employing the selected area electron diffraction (SAED, JEOL JSM-2100F) mode. The Brunauer–Emmett–Teller (BET) method was utilized to measure the specific surface area and pore size distribution of the samples via N_2 adsorption-desorption employing a BET instrument (Micromeritics TriStar II 3020, USA). The element analyses presenting in composites were investigated using K-Alpha 1063 X-ray photoelectron spectroscopy (XPS) with the Al Kα X-ray source. Before ex situ XRD or TEM test, the cycled electrodes were washed with dimethyl carbonate (DMC) to get rid of the residual sodium salt derived from electrolyte.

2.3. Electrochemical tests

The electrochemical properties of the $FeF_3 \cdot 0.33H_2O$/$AlPO_4$ composites were tested in the CR2025 coin cells using metallic sodium as the counter and reference electrode. Active materials, acetylene black (EC) and polyvinylidene fluoride (PVDF) binder with a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone (NMP), with aluminum foil current collector, were mixed to prepare the working electrodes. Glass microfiber filter from Whatman was utilized as the separator. The electrolyte employed involves a mixed solvent of 1 M $NaClO_4$ in diethyl carbonate (DEC), EC and propylene carbonate (PC) at a volume ratio of 1:1:1. The average loading mass of active material is approximately 1.5 mg cm^{-2}. The cycling performances of the $FeF_3 \cdot 0.33H_2O$/$AlPO_4$ electrodes were measured by charge-discharge tests at different current densities between 1.2 and 4.0 V on Neware battery tester (Shenzhen, China). Electrochemical impedance spectroscopy (EIS) and Cyclic voltammetry (CV) curves were obtained through an electrochemical workstation (VersaSTAT3, Princeton Applied Research). The frequency range of EIS was from 0.01 Hz to 100 kHz with the amplitudes of 5 mV. The CV tests were conducted at a scanning speed of 0.2 mV s^{-1} between 1.2 and 4.0 V. All the tests were measured at room temperature.

3. Results and discussion

Fig. 1a depicts the XRD patterns of $FeF_3 \cdot 0.33H_2O$/$AlPO_4$ composites. It can be clearly seen that all diffraction peaks are indexed to hexagonal tungsten bronze (HTB) structure $FeF_3 \cdot 0.33H_2O$ (PDF No. 76-1262) with a space group of Cmcm, indicating the introduction of $AlPO_4$ and heat treatment at 230 °C will not cause the change of $FeF_3 \cdot 0.33H_2O$ crystal structure. The main peaks of all the samples are sharp, which indicate that the samples are well-crystallized. For the X-ray diffraction patterns of the coated samples, no any diffraction peaks corresponding to $AlPO_4$ have been observed, which is probably because the $AlPO_4$ coating layer on the surface of material is only a thin layer. To understanding the HTB structure $FeF_3 \cdot 0.33H_2O$ with unique tunnel, its crystal structure is shown in Fig. 1b. The FeF_6 octahedral chain is linked by the corner-sharing fluorine atom to form a huge hexagonal tunnel along the [001] direction, which is more beneficial for the transport and storage of Na$^+$, compared with the traditional ReO_3 type FeF_3. The local structures of water molecules in the tunnel act as a stabilizing frame skeleton, which is directly related to the migration path of Na$^+$ as well as insertion sites [48], while conductive $AlPO_4$