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Spherical FeF_3•$0.33H_2O$/MWCNTs nanocomposite with mesoporous structure as cathode material of sodium ion battery

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ABSTRACT

FeF_3•$0.33H_2O$ crystallizes in hexagonal tungsten bronze structure with more opened hexagonal cavities are considered as next generation electrode materials of both lithium ion battery and sodium ion battery. In this paper the mesoporous spherical FeF_3•$0.33H_2O$/MWCNTs nanocomposite was successfully synthesized via a one-step solvothermal approach. Galvanostatic measurement showed that the performances of sodium ion batteries (SIBs) using FeF_3•$0.33H_2O$/MWCNTs as cathode material were highly dependent on the morphology and size of the as-prepared materials. Benefitting from the special mesoporous structure features, FeF_3•$0.33H_2O$/MWCNTs nanocomposite exhibits much better electrochemical performances in terms of initial discharge capacity (350.4 mAh g^{-1}) and cycle performance (123.5 mAh g^{-1} after 50 cycles at 0.1 C range from 1.0 V to 4.0 V) as well as rate capacity (123.8 mAh g^{-1} after 25 cycles back to 0.1 C). The excellent electrochemical performance enhancement can be attributed to the synergistic effect of the mesoporous structure and the MWCNTs conductive network, which can effectively increase the contact area between the active materials and the electrolyte, shorten the Na^+ diffusion pathway, buffer the volume change during cycling/discharge process and improve the structure stability of the FeF_3•$0.33H_2O$/MWCNTs nanocomposite.

1. Introduction

Lithium ion batteries (LIBs) have successfully captured the portable electronic markets over the past decades [1,2]. But fears of exhaustion of limited and unevenly distributed lithium resources, an alternative that can compete with LIBs technology on the global market is inevitably needed [3,4]. Sodium resources are practically inexhaustible and ubiquitous [5]. Furthermore, sodium is the second lightest and smallest alkali metal next to lithium, and has much in common with lithium in physical and chemical properties [6–8]. Given this background, intense interest in the use of sodium ion batteries (SIBs) for energy system has been rekindled [9]. Consequently, it is highly estimable to develop high performance cathode materials with potentially large specific capacity and high rate capability to store and deliver energy for SIBs [10,11].

Although the structural chemistry of the sodium battery system is much more complicated in comparison to the lithium system [12–14], similar to LIBs, various metal oxides (e.g., $NaCoO_2$ [15], $NaFeO_2$ [16], $NaVO_2$ [17], $Na_{0.66}Co_{0.5}Mn_{0.5}O_2$ [18] and $NaFe_{1/2}Mn_{1/2}O_2$ [19]), polyanion compounds (e.g., $NaFePO_4$ [20], $Na_3V_2(PO_4)_3$ [21] and Na_2FePO_4F [22]) and metal fluorides (CoF_2 [23], MnF_2 [24] and FeF_3 [25]) based on conversion or insertion reactions all have been extensively studied as the cathode materials for SIBs. Especially, iron fluoride has attracted great interests as a prospective new class of cathode materials, which exhibit high theoretical capacity (712 mAh g^{-1} for 3 e^- transfer), low cost, abundant sources, low toxicity, and high safety. Among numerous polymorphs of iron fluorides, such as FeF_3, FeF_3•$0.33H_2O$, $FeF_{2.5}$•$0.5H_2O$, FeF_3•$0.5H_2O$ and FeF_3•$3H_2O$, FeF_3•$0.33H_2O$ is of the most attention due to its unique tunnel structure which is greatly beneficial to the Na^+ storage performance [26–29]. Unfortunately, the high electro-negativity of fluorine induces a large band gap, and thus leading to a poor electronic conductivity, a very low actual capacity and fast capacity fading [30].

To overcome the above obstacles, significant efforts have currently been made; the most typical one is the preparation of carbon-metal-fluoride nanocomposites (CMFNCs) as electrode materials. Hybridizing with a conductive additive phase (such as SWNTs, 3DOM, CNHs, rGO and OMC) has been regarded as a promising strategy to enhance the electrochemical performances of

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FeF_3 electrode materials, which can provide a facile electron pathway [31–33]. The decrease in particle size from bulk to nanoscale is another alternative approach to shorten ion/electrode transport distance and enlarge surface area, which facilitate conversion reaction kinetics and improve the electrochemical properties of the iron fluoride [31,34]. In our previous works, the mixed conducting matrix, such as $FeF_3{\cdot}xH_2O$/G [35], $Fe_2F_5{\cdot}H_2O$/G [36] and $Fe_2F_5{\cdot}H_2O$/rGO [37], all have successfully been prepared as cathode materials for SIBs and obtained some significant results. However, the capacity and cyclic stability of $FeF_3{\cdot}0.33H_2O$/C nanocomposite are still required to be improved. The substitution of metal elements such as Co [38] and Ti [39] for iron or N [40] and –OH [41] for fluorine element has also been considered an effective strategy to improve the intrinsic electronic conductivity and structural stability of FeF_3 cathode materials. However, some ion-doped may reduce discharge capacity and influence cyclic life. Moreover, it is difficult to control the ion doping site and may cause undesirable cation mixing [42].

Recently, the electrode materials comprising nanosize and mesoporous structure have received the researchers' extensive concern, which regard as an effective way in enhancing the electrochemical properties of FeF_3 cathode materials [43,44]. It has been previously reported that solvothermal technique is an effective approach to synthesize nanoparticle/composite with controllable morphology and size [45–47]. It is generally known that the nanosized primary particles can improve the rate capability of electrode materials due to their higher surface areas and shorter sodium ions diffusion pathway [48,49]. Additionally, the abundant mesoporous framework can increase contact area between the active material and the electrolyte as well as accommodate better the strains related to the structural transformation upon repeated charge–discharge processes [50].

Owing to its high electrical conductivities, extraordinary mechanical properties and remarkable thermal properties, multiwalled carbon nanotubes (MWCNTs) have become an ideal substrate for growing and anchoring insulating materials for energy storage applications [51–53]. Particularly, MWCNTs hold three dimensional electron conductive networks with high surface area, which facilitates the fast penetration of electrolytes and diffusion of sodium ions [54,55]. For example, Shadike et al. prepared CoS_2/MWCNT nanocomposite via a simple hydrothermal method, and it obtained a high capacity of 568 mAh g^{-1} at 100 mA g^{-1} after 100 cycles [56]. Wang et al. synthesized SnO_2@MWCNT nanocomposite by a solvothermal approach, and it maintained discharge capacity of 474.0 mAh g^{-1} at 66.7 mA g^{-1} after 50 cycles [57]. Apparently, the introduction of MWCNTs can effectively increase the specific capacity, enhance the rate capability and improve cycle performance of oxide nanomaterials as SIBs anode materials [58,59]. However, to the best of our knowledge, there is rare report for the $FeF_3{\cdot}0.33H_2O$ nanoparticles in-situ growth with MWCNTs so far.

Herein, we deliberately designed and synthesized a new spherical $FeF_3{\cdot}0.33H_2O$/MWCNTs nanocomposite with mesoporous structure via a one-step solvothermal approach. The mesoporous nanoparticles with spherical morphology possess more stable structure and higher specific surface area compared to conventional $FeF_3{\cdot}0.33H_2O$ cathode material, and thus showing excellent electrochemical performances. In addition, the MWCNTs network can not only contribute to the electric transmission, but also promote in-situ growth for spherical $FeF_3{\cdot}0.33H_2O$ nanoparticles [60].

2. Experimental

2.1. Synthesis of $FeF_3{\cdot}0.33H_2O$/MWCNTs nanocomposite

The $FeF_3{\cdot}0.33H_2O$/MWCNTs nanocomposite was synthesized using MWCNTs which were preferentially treated with H_2SO_4 and $KMnO_4$, hydrogen fluoride (HF) as a fluorine source, and iron(III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) as an iron source. In the typical synthesis of a composite material, 120 mg of MWCNTs (about 10 wt% to $FeF_3{\cdot}0.33H_2O$) was added to 50 mL isopropyl alcohol solution containing 1.0 mL HF in a 100 mL Teflon beakers. The Teflon beaker was sealed with Parafilm and placed in ultrasonic water for 1 h to ensure good dispersion of the MWCNTs and create defects for $FeF_3{\cdot}0.33H_2O$ nucleation sites. 2.02 g of $Fe(NO_3)_3{\cdot}9H_2O$ was dissolved in solvent under magnetic stirring. After stirring for 20 min, the solution was heated at 150 °C for 12 h in a sealed condition, followed by cooling at the room temperature to obtain off-white precipitates. The precipitates were washed by ethanol, followed by drying under vacuum at 80 °C for 12 h. The bare material was produced following the same procedure without the addition of MWCNTs.

2.2. Characterizations of structure and morphology

The structure and phase purity of the $FeF_3{\cdot}0.33H_2O$ and $FeF_3{\cdot}0.33H_2O$/MWCNTs samples were characterized by using a Rigaku D/Max-3C X-ray diffractometer (XRD) with Cu $K\alpha$ radiation ($\lambda = 1.542$ Å) and a graphite monochromator operated at 40 mA and 40 kV at a scan rate of 4 °min^{-1} from 10° to 80° (2θ). The FTIR measurement of the samples was characterized via a Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer Spectrum One) and the resolution of the apparatus is 0.09 cm^{-1}. The morphology and structure of the samples were examined by scanning electron microscope (SEM, JEOL JSM-6610LV) and transmission electron microscopy (TEM, JEOL JEM-2100F). The specific surface area of the materials was determined by Brunauer–Emmett–Teller (BET) method (TriStar II 3020, Micromeritics USA) with nitrogen as adsorption/desorption gas. The pore size distribution was determined from the adsorption branch of the isotherms by the Barrett–Joyner–Halenda (BJH) method.

2.3. Electrochemical measurements

Positive electrodes were fabricated by mixing the active material, polyvinylidene fluoride (PVDF) binder and acetylene black in *N*-methyl-2-pyrrolidone (NMP) with a weight ratio of 80:10:10. The as-prepared electrodes were cut into circular electrodes with a diameter of 10 mm and dried at 110 °C in vacuum oven for 12 h before to apply. The $FeF_3{\cdot}0.33H_2O$ and $FeF_3{\cdot}0.33H_2O$/MWCNTs nanocomposite were used as a cathode material, metallic sodium anode and glass fiber (GF/D) from Whatman were employed as the separator, and the electrolyte was 1 mol L^{-1} $NaClO_4$ in a solvent of propylene carbonate (PC). Finally, the cells were assembled in an argon-filled glove box with water and oxygen concentrations below 1 ppm. The charge/discharge cycle tests of SIBs were performed at different current densities on the Neware battery test system (Shenzhen, China) in a voltage range of 1.0–4.0 V (vs. Na^+/Na). All electrochemical measurements were performed at room temperature.

3. Results and discussion

Scheme 1 illustrated schematically the overall procedure for the synthesis of the $FeF_3{\cdot}0.33H_2O$/MWCNTs nanocomposite. To induce nucleation center of $FeF_3{\cdot}0.33H_2O$ on the MWCNTs surfaces, MWCNTs were firstly sonicated in HF solution to create the defects for nucleation sites. These nucleation sites could increase the affinity of MWCNTs to Fe^{3+} via electrostatic force, thus providing more growing spots for $FeF_3{\cdot}3H_2O$ nanocrystals [61]. As we known, the versatile isopropyl alcohol possesses unique physical and chemical properties such as green, low specific Hansen solubility and low boiling point, therefore, the isopropyl alcohol was introduced

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