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Hierarchical Ru-doped sodium vanadium fluorophosphates hollow microspheres as a cathode of enhanced superior rate capability and ultralong stability for sodium-ion batteries

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ABSTRACT

Novel hierarchical Ru-doped $Na_3V_2O_2(PO_4)_2F$ hollow microspheres were synthesized via a low-temperature solvothermal method. The individual unique microspheres were formed from assembly of numerous nanoparticles with diameters of 20–30 nm. When used as a cathode material for sodium-ion batteries (SIBs), the microspheres exhibited superior rate performance with a capacity of 72.6 mAh·g^{-1} at 10 C. Furthermore, their rate performance could be significantly improved by coating them with a thin conductive RuO_2 layer. For instance, high specific capacities of 102.5 mAh g^{-1} and 44.9 mAh g^{-1} were achieved at current rates of 20 C and 100 C, respectively. These materials exhibited impressive long-term cycling stability. A reversible capacity of approximately 55.0 mAh g^{-1} was maintained even after 7500 charge/discharge cycles. Density functional theory (DFT) calculations increased our understanding of how H^+ facilitates the formation of the hierarchical microsphere superstructure which is beneficial to achieve a good rate capability.

1. Introduction

With the rapid growth in energy demand, more large-scale electrochemical energy-storage devices (ESDs) are needed for electrical vehicles and energy storage power stations [1–3]. The use of commercial Li-ion batteries as the essential contribution for portable electronic ESDs is under pressure due to the limited Li resources and high costs [4–7]. Therefore, other energy-storage systems should be developed to address these challenges. Recently, sodium-ion batteries (SIBs) as a promising candidate have drawn significant attention because of their low cost and abundant resources of sodium as well as comparable electrochemical performance [8–14]. Nevertheless, the SIBs are still facing the insufficient power performance, cycling stability and energy density, especially the long cycling stability [15–18], which may be limited mainly by the lack of robust electrode materials.

To date, numerous investigations of cathodes for SIBs have focused on transition metal oxides and polyanionic compounds [19–29]. Remarkably, $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ (0≤X≤1) materials have attracted increasing attention because of their excellent and stabilized crystal structure, high reversible capacity (~130 mAh g^{-1}) and operation voltage (~3.8 V) when used as cathodes in SIBs [30–32]. The crystalline structures of $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ (0≤X≤1) materials exist in two space groups of $P4_2/mnm$ and $I4/mmm$ [33,34]. The materials in $I4/mmm$ space group is considered to be a promising cathode because it has a more symmetrical crystal structure than that of the $P4_2/mnm$. Moreover, this type of materials could be fabricated at a relatively low temperature, and no additional high-temperature solid-state treatments are needed. However, the power density performance of $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ (0≤X≤1) in $I4/mmm$ space group suffers from sluggish electrochemistry kinetics due to its poor room-temperature electronic conductivity (1.8×10^{-7} S/cm) [33]. In recent years, tremendous efforts have been devoted to improve this material's electrochemistry kinetics by embedding graphene, coating with a carbon layer or reducing the particle size [32,34–38]. Our previous work reported the synthesis of ultralong nanowires consisting of $Na_3V_2O_2(PO_4)_2F$ ($I4/mmm$) with diameters of ~50 nm, which were able to effectively improve the rate capacity performance by shortening the diffusion pathway of Na^+(Na ion) during the sodium-insertion and extraction

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processes [39]. Although nanomaterials as electrode materials exhibit many attractive properties, they have inherent disadvantages such as the ease of irregular aggregation, low volumetric energy density and unstable side reactions due to the intimate contact between electrolyte and nanomaterials, which lead to the poor stability [40,41]. The ideal solution to achieving both good thermal stability and high rate capacity is to develop an ordered three-dimensional (3D) hierarchical structure self-assembled from nanoparticles with the formation of channels, porosity, and regular closed packed arrays [42–47]. Therefore, preparation of $Na_3V_2O_2(PO_4)_2F$ (*I4/mmm*) microspheres composed of orderly assembled nanoparticles is preferred to alleviate the disadvantages of nanomaterials, providing the opportunity to develop a new class of SIB materials with an excellent rate capacity and ultralong stability. To the best of our knowledge, this type of $Na_3V_2O_2(PO_4)_2F$ (*I4/mmm*) ordered superstructures with such superior rate performance has been rarely reported [48].

Herein, we report the synthesis of self-assembled $Na_3V_2O_2(PO_4)_2F$ (*I4/mmm*) hierarchical hollow microspheres composed of nanoparticles via a low-temperature solvothermal method. Moreover, doping the $Na_3V_2O_2(PO_4)_2F$ microspheres with Ru and coating them with a conductive RuO_2 layer were carried out to change their electronic structures and promote charge transfer process in them, respectively. These materials were used as cathode materials for SIBs and exhibited prominent cycling performance and excellent rate performance. The detailed growth mechanism of hollow microspheres was systematically investigated by analyzing the influences of reaction conditions on the $Na_3V_2O_2(PO_4)_2F$ products. In combination of the quantum-mechanical calculations based on density functional theory (DFT), it revealed that the formation of the microspheres was controlled by the adsorption of hydrogen on the crystal surface, and the hollow microspheres were formed through an Ostwald ripening mechanism. This superstructure of hollow microspheres was conductive to the Na^+ diffusion at a high rate.

2. Experimental

2.1. Synthesis of $Na_3V_2O_2(PO_4)_2F$ (*I4*/mmm) microspheres (procedure A)

The $Na_3V_2O_2(PO_4)_2F$ (*I4/mmm*) microspheres were prepared via a solvothermal reaction according to the following procedure. Briefly, $Na_2C_2O_4$, NH_4VO_3, $NH_4H_2PO_4$, NaF and $NaNO_3$ with a molar ratio of 2:1:1:1:9 were dissolved in distilled water to form a homogeneous solution with a concentration of 0.1 mol/L (F^-), and then, the solution was mixed with polyethylene glycol 400 (PEG 400) at a volume ratio of 1:10 during continuous stirring. Afterwards, the mixed solution was poured into a stainless Teflon-lined autoclave. The stainless Teflon-lined autoclave was placed in an electric drying oven, heated and maintained at 170 °C for a certain period of time (0–2 h), and then naturally cooled to room temperature. Finally, the products were collected by suction filtration, washed with ethanol and distilled water, and dried in a vacuum oven at 80 °C for 12 h.

2.2. Synthesis of Ru-doped $Na_3V_2O_2(PO_4)_2F$ microspheres (procedure B)

The Ru-doped $Na_3V_2O_2(PO_4)_2F$ (*I4/mmm*) microspheres were prepared via a solvothermal reaction according to the following procedure. Briefly, $Na_2C_2O_4$, NH_4VO_3, $NH_4H_2PO_4$, NaF and $NaNO_3$ with a molar ratio of 2:1:1:1:9 were dissolved in distilled water to form a homogeneous solution with a concentration of 0.1 mol/L (F^-), and then, the solution was mixed with PEG 400 at a volume ratio of 1:10 during continuous stirring. One gram of anhydrous $RuCl_3$ was dissolved in 96 mL of deionized water to form a stable black solution. Afterwards, 0.50 mL of the $RuCl_3$ solution was added to the above mixed solution under continuous stirring. Subsequently, the mixed solution was poured into a stainless Teflon-lined autoclave. The reaction kettle was heated to 170 °C in an electric dry oven, maintained at 170 °C for 2 h, and then cooled to room temperature. Finally, the products were collected by suction filtration, washed with ethanol and distilled water, and dried in a vacuum oven at 80 °C for 12 h.

2.3. Synthesis of Ru-doped $Na_3V_2O_2(PO_4)_2F$ with RuO_2-coated microspheres (procedure C)

The Ru-doped $Na_3V_2O_2(PO_4)_2F$ microspheres were synthesized using procedure B, and the RuO_2 coating was applied according to our previously reported method [39]. Briefly, a 750 μL solution containing 0.05 mol/L $RuCl_3$ was added to a 20 mL of Ru-doped $Na_3V_2O_2(PO_4)_2F$ suspension to prepare the RuO_2-coating layer.

2.4. Characterization

The X-ray diffraction (XRD) patterns were measured by a Bruker D8 Advance diffractometer (Cu Kα X-ray radiation, λ=1.54 Å) in a 2θ range of 10–90°. Scanning electron microscopy (SEM) was performed on a Hitachi S-4300 (Japan) at a working voltage of 10 kV. Transmission electron microscopy (TEM) was carried out with a JEOL JEM-2100 microscope operating at 200 kV. Scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) mapping was conducted using a field-emission scanning transmission electron microscope (JEOL JEM-ARM200F).

2.5. Electrochemical measurements

The electrodes, which consisted of 70% active materials, 20% Super P, and 10% polyvinylidene fluoride (PVDF), were evaluated with standard CR2032 coin cells The weight of one electrode pellet was approximately 3–5 mg with a diameter of 0.8 cm (the active substances exclude the mass of carbon and binder materials), and a Whatman® glass fiber membrane (grade GF/D, USA) was chosen as the separator. An electrolyte composed of 1.5 mol/L $NaClO_4$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (with a volume ratio of 3:7) with 2% FEC additive was used for long cycles and rate capacity measurements, and Na foil was used as the counter electrode. The batteries were assembled in an argon-filled glove box (M Braun Inertgas-System [Shanghai] Co, Ltd, China). The current density at 1 C was determined to be 130 mA g^{-1}. The current density in the process of charging is kept constantly at 1 C during rate performance test. When electrochemical impedance spectroscopy (EIS) measurements were performed, the open circuit voltage (OCV) was about 2.9 V and the AC signals had 5.0 mV amplitude with a frequency range from 10 mHz to 100 kHz.

2.6. Theoretical calculations

The density functional theory has been performed for theoretical calculations using the $Dmol_3$ module in material studio (Materials Studio 6.1, $DMol_3$, Accelrys, and Beijing, China) [49]. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) was employed to depict the exchange and correlation [50,51]. Double numeric basis sets with polarization functions were selected, and spin-unrestricted wave functions were used. The energy convergence for geometry optimization was 2×10^{-5} eV. The initial structure was taken from the experimental data (ICSD #245125). The unit cell structure was optimized before performing the calculations. The (100) and (001) surfaces were modeled by slabs containing 6 layers, and the corresponding 1×1×1 and 2×2×1 k-point meshes were employed. The surface energies (σ) of the clean (100, 001) surfaces were calculated using Eq. (1):

$$\sigma = \frac{1}{2A}[E_{opt}^{slab} - (N_{slab} - N_{bulk})E^{bulk}] \quad (1)$$