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Review article

Electrospinning synthesis of Na_2MnPO_4F/C nanofibers as a high voltage cathode material for Na-ion batteries

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ABSTRACT

Three-dimensional carbon nanofibers embedded with Na_2MnPO_4F nanoparticles are fabricated via electrospinning method and investigated as cathode material for sodium ion batteries. The Na_2MnPO_4F nanoparticles with a size of about 10–30 nm are well-crystallized and the diameter of the carbon nanofibers are about 100 nm. Due to the ultrafine particle size of Na_2MnPO_4F together with high conductivity of the three-dimensional electron/ion hybrid network of carbon nanofibers, the material synthesized at 650 °C exhibit good electrochemical performance at room temperature. It is found that an obvious potential platform as high as 3.6 V during charge/discharge processes occurs and there is an initial specific capacity of 122.4 mAh g^{-1} at 0.05C rate, which is close to the theoretic capacity (one Na^+ extracted) of Na_2MnPO_4F. This work suggests a new design strategy for high-performance Na_2MnPO_4F cathodes of sodium-ion batteries.

1. Introduction

In recent years, due to rapid depletion of lithium resources, large efforts are expended to search for alternative battery systems. Sodium-ion batteries (SIBs) have received much attention owing to abundant amounts and low prices of sodium as well as their good battery safety. SIBs therefore hold significant promise for a broad range of energy storage applications in the future [1–3]. The working mechanisms of SIBs and lithium-ion batteries (LIBs) are similar, and numerous structurally related compounds can be utilized for both battery systems [4–7].

In the past decades, the fluorophosphate cathode materials, such as Na_2MPO_4F (M = Fe, Mn, Co, Ni, etc.), $NaVPO_4F$ and $Na_3V_2(PO_4)_2F_3$, have become a focus due to their high working voltage and theoretical capacity [8–14]. Among these fluorophosphate compounds, the theoretical specific capacity of Na_2MnPO_4F is expected to be as high as 249.4 mAh g^{-1} (124.7 mAh g^{-1} for one Na^+ extracted) when the two sodium ions are completely released. Meanwhile, Na_2MnPO_4F owns high working voltages *vs.* Na/Na^+ (3.66 V for the 1st Na^+ and 4.67 V for the 2nd Na^+ extraction/insertion) and good thermal stability owing to the high electronegativity of F^- and strong inductive effect of PO_4^{3-} [15]. Na_2MnPO_4F is therefore suitable for the development of new Na-ion battery materials.

Despite of the enormous potential advantages of Na_2MnPO_4F, its inherently low electronic and ionic conductivities restrict good electrochemical performances to be obtained. Recham et al. [16] synthesized Na_2MnPO_4F by a low-temperature ion-thermal method, but the material shows almost no electrochemical activity. They surmised that the Jahn-Teller effect of Mn^{3+} [d_4: $t_2g^3e_g^1$] exists in the processes of charging/discharging for Na_2MnPO_4F. The effect results in lattice distortion of the material and gives rise to poor electronic/ionic conductivities, eventually seriously deteriorating electrochemical performances. Ellis et al. [7] synthesized carbon-coated Na_2MnPO_4F with a solid state method and found that the sample did not show any electrochemical activity. The authors speculated that the possible limitation of ion transport of this material can be overcome by refining the particles of Na_2MnPO_4F. This hypothesis was confirmed later on. In 2011, Yang et al. [17] fabricated carbon-coated Na_2MnPO_4F by a sol-gel method and the obtained sample shows a first discharge capacity of 98 mAh g^{-1} (current density: 10 mA g^{-1}) at 60 °C in a hybrid Na/Li cell. The improved electrochemical properties are mainly ascribed to the fine primary particles (tens of nanometers) and uniform carbon coating. Recently, we have reported that Na_2MnPO_4F/C hollow spheres with a micro-nano structure own good electrochemical performances, and it is the first time that an obvious platform (3.6 V) of Na_2MnPO_4F cathode is observed at room temperature [18]. It is noticeable that, although lots of efforts have been devoted, the electrochemical properties (especially the rate performance) of Na_2MnPO_4F, are far away

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from practical applications for SIB cathodes.

In recent years, many studies have indicated that 3D conductive networks constituted by interconnecting carbon nanofibers can simultaneously realize enhancements of electron-conduction/ion-transportation, which is conducive to fully making use of the dynamic advantages of the nano-electrode materials and obtaining high-performance electrode materials [19–21]. As electrospinning is an effective method to achieve carbon nanofibers [22], in this study, we use this approach to construct a 3D highly efficient conductive carbon network and meanwhile embed nano-sized Na_2MnPO_4F particles into the network via a pyrolysis reaction. This design is expected to allow electrons and Na^+ to be rapidly transported to the surface of each active particle, thereby greatly improving the electrochemical performances of Na_2MnPO_4F cathode material. This hybrid not only shows the obvious charge/discharge platforms of 3.6 V, but also owns high discharge capacity and good rate capability at room temperature.

2. Experimental

2.1. Synthesis of Na_2MnPO_4F/C

A schematic diagram in terms of synthetic Na_2MnPO_4F/C cathode material is demonstrated in Fig. 1. Na_2MnPO_4F/C composite was synthesized through electrospinning, and sintering at low temperature in air and then at high temperature in argon. Specifically, 1 g Mn $(CH_3COO)_2{\cdot}4H_2O$ was added into 25 ml deionized water until it was completely dissolved. After that, 1.02 g of citric acid ($C_6H_8O_7{\cdot}H_2O$) was added into the solution which was stirred for 10 min. Followed, 0.34 g NaF and 0.46 g $NH_4H_2PO_4$ were mixed with the above solution and stirred continuously for another 1 h. Then 3 g polyvinylpyrrolidone (PVP, the MW = 1,300,000) was added to the previous stirred solution and continued to stir until completely dissolved. Finally, loading the final solution into a 5 ml plastic syringe with a stainless steel needle (0.4 mm inner diameter). An aluminum foil as a nanofiber collector was fixed at 20 cm away from the needle tip. Na_2MnPO_4F/C nanofibers were synthesized by applying 25 kV high-voltage to the solution going through the needle tip. Electrospinning experiments were carried out at room temperature with an advance speed of 0.05 mm min^{-1}. The nanofibrous precursor was preheated at 250 ℃ for 2 h in air and then calcined at different temperatures (600, 650, 700 and 750 ℃) for 6 h in Ar atmosphere to obtain the Na_2MnPO_4F/C samples.

2.2. Characterization

Phases and structures of the samples were identified using X-ray diffractometer (Rigaku, Ultima VI) with Cu Kα radiation operated at 40 kV, 2θ in a range of 10–90° and a scan speed of 2° min^{-1}. The carbon content of the samples was measured by C–S analysis (Eltar, Germany). Scanning electron microscopy (SEM) studies were operated on SU-5000 (Hitachi, Japan), equipped with an energy-dispersive X-ray spectroscopy (EDS) detector used for EDS elemental mapping. Microstructures of the samples were investigated by a high-resolution transmission electronic microscopy (HRTEM) (FEI, Tecnai G2 F20).

2.3. Electrochemical tests

Electrochemical tests of the samples were operated by CR2025 type coin cells. The positive electrode was composed of 70 wt% active materials, 20 wt% poly (vinylidene fluoride) as binder, and 10 wt% acetylene black as conductive additive. After being mixed with N-methyl pyrrolidinone (NMP), the slurry was uniformly spread on an Al-foil, and then dried at 120 ℃ in vacuum for 12 h. The typical active material loading was about 1.2 mg cm^{-2}. The cells were assembled in a glove box filled with high-purity argon. A sodium foil as a negative electrode, a glass fiber membrane (Whatman GF/A) as a separator, and 1 M $NaClO_4$/(PC95%-FEC5%) as an electrolyte. Electrochemical tests were operated on a LAND battery testing system. The cells were tested at various C-rates between 1.5 and 4.5 V at ambient temperature. The cyclic voltammetry (CV) tests were done with a CHI660D electrochemical workstation. The scan rates were 0.02, 0.05, 0.1, 0.2 and 0.5 mV s^{-1}, and the potential range was 1.5–4.5 V.

3. Results and discussion

Crystal structures of the Na_2MnPO_4F/C samples calcined at various temperatures are studied by XRD. From Fig. 2a, it is found that all diffraction peaks can be fully indexed as the monoclinic structure of Na_2MnPO_4F (PDF#87-0467) with space group $P2_1/n$, and no other impurity phases are detected. As the calcination temperature increases, the diffraction peaks gradually become sharp and their relative

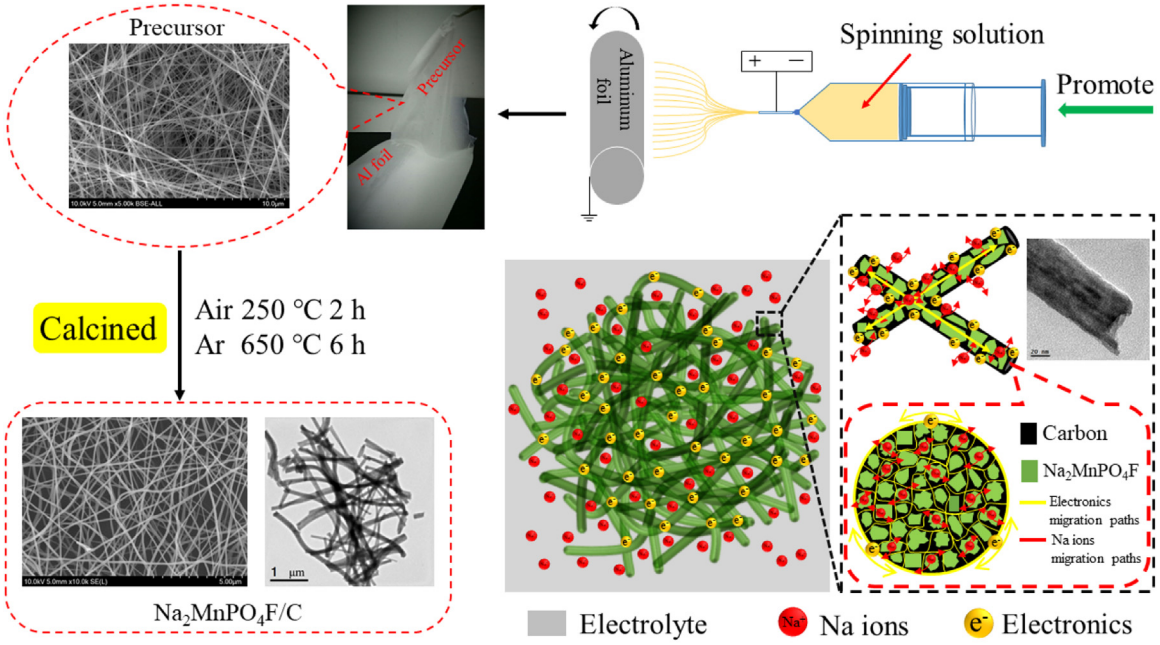

Fig. 1. Schematic diagram of synthetic Na_2MnPO_4F/C cathode material.