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Synthesis of carbon-coated Na_2MnPO_4F hollow spheres as a potential cathode material for Na-ion batteries

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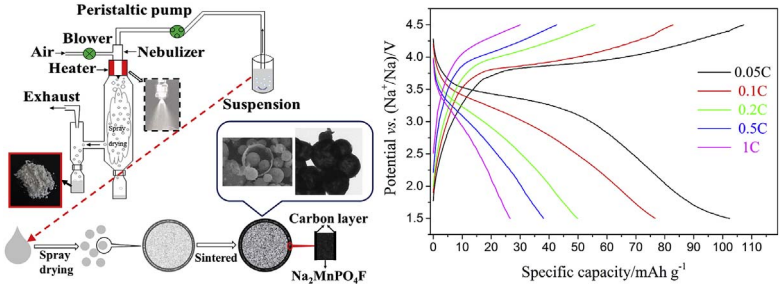
HIGHLIGHTS

- Na_2MnPO_4F/C hollow sphere composite is synthesized by spray drying method.
- The hollow sphere shell is composed of nanosized primary particles of Na_2MnPO_4F/C.
- Na_2MnPO_4F particles are well embedded and interconnected by carbon networks.
- The obvious platform ~3.6 V can be observed at room temperature for the first time.

GRAPHICAL ABSTRACT



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ABSTRACT

Hollow sphere structure Na_2MnPO_4F/C composite is synthesized through spray drying, following *in-situ* pyrolytic carbon coating process. XRD results indicate that the well crystallized composite can be successfully synthesized, and no other impurity phases are detected. SEM and TEM results reveal that the Na_2MnPO_4F/C samples show intact hollow spherical architecture, and the hollow spherical shells with an average thickness of 150 nm–250 nm are composed of nanosized primary particles. Furthermore, the amorphous carbon layer is uniformly coated on the surface of the hollow sphere, and the nanosized Na_2MnPO_4F particles are well embedded in the carbon networks. Consequently, the hollow sphere structure Na_2MnPO_4F/C shows enhanced electrochemical performance. Especially, it is the first time that the obvious potential platforms (~3.6 V) are observed during the charge and discharge process at room temperature.

1. Introduction

The demand of lithium-ion batteries (LIB) for energy storage devices have been increasing year by year. However, the limited reserves of lithium hinder the wide application of LIB for large-scale energy storage [1,2]. Compared with the LIB, sodium-ion batteries possess richer resources, lower price and better battery safety, which can broaden the research fields, and accelerate the large-scale application of rechargeable batteries [3–5]. At present, the sodium phosphate cathode material Na_2MPO_4F (M = Fe, Mn, Co, Ni, etc.) has been reported as one kind of the promising cathode materials for Na-ion batteries [6–9]. Due to the strong induction effect of PO_4^{3-} and the strong electronegativity of F^-, Na_2MPO_4F has high working potential and good thermal stability [9,10]. In 2007, Ellis et al. [11] reported that the synthesized sodium-based fluorophosphate Na_2FePO_4F had better electron conductivity than Li_2FePO_4F, and the use of two sodium ions in each transition metal ion charge/discharge process could further improve the specific capacity and energy density of the cathode material. The space group of Na_2FePO_4F is *Pbcn* and it has a two-dimensional (2D) layered structure [12–15]. Compared to Na_2FePO_4F, Na_2MnPO_4F ($P2_1/n$ space group)

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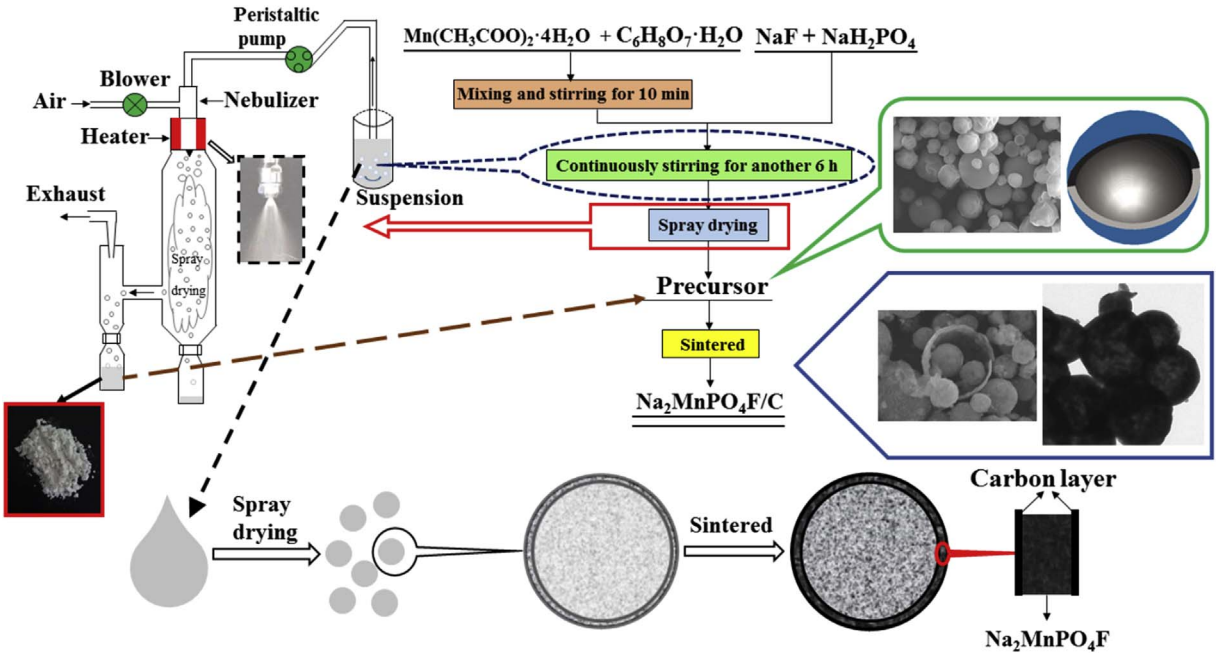

Fig. 1. Schematic diagram of synthetic Na_2MnPO_4F/C cathode material.

has a three-dimensional (3D) tunnel structure and it offers higher operation voltages 3.66 V and 4.67 V *vs.* Na^+/Na. Na_2MnPO_4F contains two Na ions, the redox reaction for the first Na ion occurs at ~3.66 V *vs.* Na^+/Na, exhibiting a theoretical capacity of ~125 mAh g^{-1}; while redox reaction for the second Na ion requires a much higher voltage of ~4.67 V *vs.* Na^+/Na with a theoretical capacity up to ~250 mAh g^{-1}. In addition, the Mn resource is rich and cheap. Thus, Na_2MnPO_4F has a lot of potential advantages for the development of new Na-ion battery materials.

However, up to now, the electrochemical activity of Na_2MnPO_4F cathode material is poor because of its intrinsic low electronic conductivity and ionic diffusivity. Recham et al. [8] prepared Na_2MnPO_4F material by low-temperature ion thermal method, revealing that Mn-based phases have worse electrochemical performances even in the same structure as Fe counterpart. They speculated that the Jahn-Teller effect of Mn^{3+} [d_4:$t_{2g}^3e_g^1$] exists in the process of charging and discharging for Na_2MnPO_4F, which results in the lattice distortion of the material and causes the poor electronic and ionic conductivity, thus affecting the material electrochemical performances. The most common strategies to improve the electrochemical property of cathode electrodes are carbon coating, ion doping, and particle size reduction. Wu et al. [15] combined nano-crystallization, Fe doping and carbon coating to modify Na_2MnPO_4F, the initial discharge specific capacity was 169 mAh g^{-1} (current density 10 mA g^{-1}, 60 °C) with 30% Fe doped in Na/Li cell. However, the concentration of Fe is too large, which reduces its operation potential and affects the structural stability of the material. Zhong et al. [16] obtained the micro-nano structured Na_2MnPO_4F/C by wet ball milling with irregular morphologies. Lin et al. [17] synthesized Na_2MnPO_4F/C nanocomposites with improved electrochemical performance, but excess 100% F was added to the raw materials, and the XRD patterns exhibit large full width at half maximum, indicating poor crystallinity. From these studies, although the samples showed relatively improved electrochemical performances, there is a common issue that the charge and discharge platforms around 3.66 V could not obviously be observed during the lithiation and delithiation processes even at low current rate, especially at room temperature, indicating large polarization. Therefore, it still needs further study to enhance the comprehensive properties for this promising cathode material.

In this work, we firstly report a modified Na_2MnPO_4F/C material with intact hollow sphere structure. It has been reported that materials with special morphologies, such as hollow structure, can exhibit impressive performances in LIB [18]. Compared with dense or irregular particles, hollow spheres can increase the reaction area between the electrolyte and electrode, and realize faster mass transfer, thus improving the electrochemical reaction kinetics. The micro-sized hollow sphere shell is actually composed of many contacted nanosized primary particles of Na_2MnPO_4F/C; moreover, each nanosized Na_2MnPO_4F is uniformly wrapped by *in-situ* pyrolytic carbon layer, resulting in that all Na_2MnPO_4F particles are well embedded and interconnected by carbon networks. The material with this special structure shows improved electrochemical performance. Especially, the obvious charge and discharge platforms around 3.6 V can be observed at room temperature for the first time.

2. Experimental

2.1. Synthesis of Na_2MnPO_4F/C

The schematic diagram of synthetic Na_2MnPO_4F/C cathode material is clarified in Fig. 1. Na_2MnPO_4F/C composite was synthesized through spray drying and sintering at high temperatures in argon atmosphere. Firstly, 0.02 mol $Mn(CH_3COO)_2{\cdot}4H_2O$ was added into 200 ml deionized water until it was completely dissolved, then 1.26 g of citric acid ($C_6H_8O_7{\cdot}H_2O$) was added and stirred for 10 min. Followed, 0.02 mol NaF and 0.02 mol NaH_2PO_4 were mixed with the above solution and continuously stirred for another 6 h. The stirred solution was prepared into spherical precursor by means of a spray drier (Shanghai Attainpak DC1500), the speed of spraying is 200 ml h^{-1}, and the inlet/outlet air temperatures are 200 °C and 70 °C, respectively. The spherical precursor was sintered at 350 °C for 3 h in an argon atmosphere and then sintered at different temperatures (600 °C, 650 °C, 700 °C and 750 °C) for 6 h to obtain the Na_2MnPO_4F/C samples.

2.2. Characterization

The crystalline phase of the samples was identified by X-ray diffractometer (Rigaku, Ultima VI) with Cu Kα radiation operated at 40 kV in the range of 2θ from 10° to 90° at a scan speed of 2° min^{-1}. Scanning electron microscopy (SEM) studies were performed on SU-5000