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Enhanced sodium ion storage performance of $Na_3V_2(PO_4)_3$ with N-doped carbon by folic acid as carbon-nitrogen source

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ABSTRACT

$Na_3V_2(PO_4)_3$/nitrogen doped carbon (NVP/CN) composites have been fabricated by a simple and low cost solid-state technique using folic acid as the carbon-nitrogen source. The structure, morphology and electrochemical performance of NVP/CN composites coated with various carbon-nitrogen layer contents are well investigated. The results reveal that the NVP/CN composite with 3.3 wt% carbon-nitrogen exhibits the largest specific surface area, with a uniform carbon-nitrogen layer thickness of approximately 2 nm. When tested as cathode material for sodium ion battery, NVP/CN composite with 3.3 wt% carbon-nitrogen displays an outstanding high rate properties with the discharge capacity of 95 and 91 mAh g^{-1} at 10 and 20 C, respectively, and long cycle life up to 3000 times even at a high rate of 10 C due to the smallest charge-transfer resistance and highest Na^+ diffusion coefficient. The results suggest that folic acid is a promising carbon-nitrogen source for construction of NVP/CN and other cathode materials.

1. Introduction

Recently, lithium-ion batteries (LIBs) have been widely applied in portable electronic devices, and also demonstrate great promising application potential in large-scale energy storage equipment and electric vehicles, due to their high energy density and environmental compatibility, etc [1–5]. Nevertheless, the large-scale applications in the field of large-scale energy storage equipment and electric vehicles will consume a large amount of lithium resources, leading to a possible lithium shortage in the future [6]. Therefore, it is necessary to exploit new alterative low cost batteries for energy storage system. Sodium ion batteries (SIBs) have received increasing numbers of attentions owing to the abundant resources and low cost of sodium as well as similar intercalation chemistry to LIBs [7–11]. However, the much larger ionic radius of Na^+ (1.02 Å) in comparison with that of Li^+ (0.76 Å) will lead to more difficult Na^+ diffusing into/from the electrode materials, and also more severe structural changes during Na^+ inserting/exerting processes [12–15]. Hence, tremendous attentions have been paid to search for advanced electrode materials with large-sized tunnel structure which can provide fast Na^+ diffusion pathways as well as stable Na^+ exertion/insertion [16].

Among the different cathode materials as reported for sodium ion batteries, $Na_3V_2(PO_4)_3$(NVP) with a NASICON structure has been considered as a most promising cathode material used in sodium ion batteries due to its open three-dimensional framework providing rapid Na^+ diffusion [17,18], a high potential plateau (~3.4 V *vs.* Na^+/Na) being related to the V^{4+}/V^{3+} redox couple and

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corresponding to a theoretical reversible capacity of 117 mAh g^{-1} [19,20]. Unfortunately, the poor electrical conductivity of NVP materials originating from the isolation between VO_6 octahedra and PO_4 tetrahedra in the rhombohedral structure, will lead to the low utilization of active materials at high rate, which is a huge obstacle to its practical applications [21,22]. Thus far, a great deal of efforts have been devoted to solve this issue, including coating with conductive materials [23–25], doping with foreign ions [26–30] and reducing the particle size [31–34]. Among the above strategies, carbon coating on the surface of pure NVP particles has been demonstrated as one efficient method to enhance its electrochemical properties by increasing the electronic conductivity as well as limiting the growth of NVP particles during the calcinations process. Up to now, various carbon sources, such as citric acid [35], sugar [23], glucose [24], oxalic acid [36], agarose [37], ect., have been investigated to enhance the conductivity of NVP.

In comparison with the traditional carbon coating method, N-doping carbon coating is expected to be more efficiently to facilitate the electronic conductivity and generate extrinsic defects and active sites [38–40], thus further obtaining superior performance. So far, introduction of N-doped carbon layers coated on the surface of electrode materials, such as $Li_3V_2(PO_4)_3$ [41–43] and $LiFePO_4$ [44–46], has been successfully demonstrated to improve their electrochemical properties. Nevertheless, few research focus on NVP modified with N-doped carbon layers. In present work, folic acid was firstly used as carbon-nitrogen source to synthesize NVP coated with N-doped carbon. As expected, the as-obtained materials exhibit excellent rate performance and cycle stability.

2. Experimental

Three NVP composites with various carbon-nitrogen contents were prepared via a solid-state technique. 2.3896 g of Na_2CO_3 (99.8%, Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd), 3.5132 g of NH_4VO_3 (99.9%, Aladdin), 5.2282 g of $NH_4H_2PO_4$ (99%, Xilong Scientific Co., Ltd.) and folic acid were dispersed in 35 mL of alcohol and ball milled for 6 h. Then, the mixed homogeneously slurry was dried for 5 h at 80 °C and calcinated under an Ar atmosphere for 8 h at 750 °C to receive as-synthesized LVP/CN samples. The $Na_3V_2(PO_4)_3$/C composites prepared with the amount of folic acid of 1.5, 2.0 and 2.5 g are denoted as LVP/CN-1, LVP/CN-2 and LVP/CN-3, respectively.

X-ray diffraction (XRD, DX2700, Dandong Haoyuan) was carried out to identify the purity of the three as-obtained samples. Transmission electron microscopy (TEM) and scanning electron microscope (SEM) were used to survey three samples' morphologies. The elements in LVP/CN-2 were performed by X-ray photoelectron spectroscopy (XPS). Carbon-nitrogen content in the as-obtained LVP/CN samples was determined by hermogravimetric analysis (TG50, Shimadzu). The specific surface area of three samples was studied by nitrogen adsorption-desorption measurements.

Electrochemical properties were examined using a CR2032 cion-type cell. Firstly, the cathode was fabricated by mixing 80 wt% active material, 10 wt% LA-132 and 10 wt% Super-P carbon in water to obtain the homogeneously slurry. After that, the mixed slurry was compressed onto aluminum foil and dried for 10 h at 100 °C in vacuum. Finally, coin-type cells were assembles in an argon-filled glove box, using glass fibre as separator, sodium as anode and 1 M $NaClO_4$ dissolved in EC, DMC and EMC (v/v/v, 1/1/1) with 2.0% FEC as electrolyte. The charge and discharge tests were investigated in a potential range of 2–4 V (*vs*. Na^+/Na) at 25 °C.Electrochemical impedance spectroscopy (EIS) measurements were measured by a CHI760E electrochemical station (Shanghai Chenhua) in a frequency range of 10^{-2} Hz to 10^5 Hz.

3. Results and discussion

Fig. 1 displays the X-ray diffraction patterns of three as-synthesized LVP/CN samples. The diffraction peaks of these samples can be well indexed to NASICON structure with R-3c space group (PDF#53-0018), and no impurity is observed. Notably, there is no diffraction peaks can be associated with crystalline of carbon, owing to that the content of carbon-nitrogen is low or the formation phase of N-doped carbon is amorphous [21,47,48]. In addition, the as-prepared LVP/CN composite possesses lower and broader diffraction peaks as the carbon-nitrogen content increases, indicating higher content of carbon-nitrogen leads to produce smaller crystal size, a similar phenomenon was also demonstrated by H. L. Cao et al. [46]. The TG curves of three LVP/CN composites detected from room temperature to 600 °C in an air atmosphere are depicted in Fig. 2. Accordingly, the weight of the carbon-nitrogen content in LVP/CN-1, LVP/CN-2 and LVP/CN-3 is estimated to be 1.5 wt%, 3.3 wt % and 5.6 wt%, respectively.

XPS analysis is used to determine the surface component of LVP/CN-2. As shown in Fig. 3A, the peaks of Na1s, O1s, V2p, N1s, C1s and P2p can be clearly observed. The high-resolution XPS spectrum of N1s (Fig. 3B) can be divided into two peaks at approximately 398 eV and 400 eV, which are assigned to C–N and C=N, respectively. This evidence indicates that folic acid can pyrolysis into N-doped carbon during the calcinations process [49]. According to ref [50,51], introduction of nitrogen into the carbon layer will modify its electronic structure, increase the electronic conductivity of carbon-coated LVP composite and create defect sites in carbon layers facilitating Na^+ diffusion in the interface.

Morphological features of the LVP/CN composites with various carbon-nitrogen content are described in Fig. 4. Clearly, the primary particle size of the LVP/CN composite decreases and the particle size distribution trends to be more uniform with the enhancement of carbon-nitrogen content, which in good agreements with the XRD results and may be owing to the enhancement of carbon-nitrogen content well preventing particle growth during calcinations [52]. Also, the agglomeration of primary particles trends to be more serious with the improvement of carbon-nitrogen. The specific surface area for LVP/CN-1, LVP/CN-2 and LVP/CN-3 is 8.2, 13.9 and 12.1 m^2 g^{-1}, respectively. As reported [53], the largest specific surface area will provide faster Na^+ diffusion coefficient for LVP/CN-2. Fig. 5 presents the TEM micrograph of LVP/CN-2. It can be clearly seen that the surface of LVP particle is coated by a very thin and uniform carbon-nitrogen layer with 2 nm in thickness.

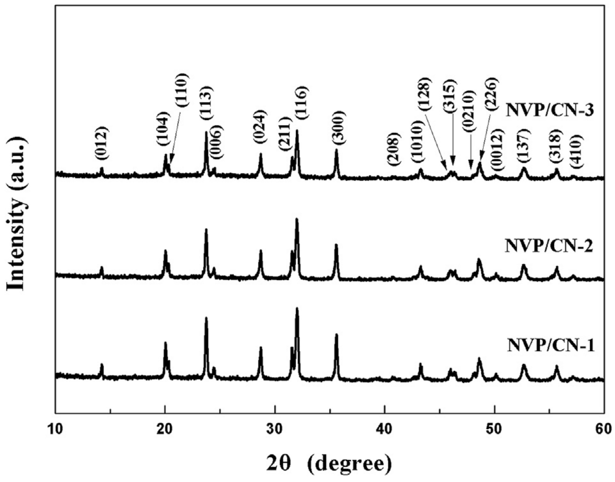

Fig. 1. XRD patterns of three LVP/CN composites.