Preparation and electrochemical properties of Na$_3$V$_2$(PO$_4$)$_3$/C cathode materials from spent electroless nickel plating bath

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Keywords: sodium-ion batteries, Na$_3$V$_2$(PO$_4$)$_3$/C, sol-gel preparation, spent electroless nickel plating bath, value-adding utilization

Abstract

Through a sol-gel method, a honeycomb-like Na$_3$V$_2$(PO$_4$)$_3$/C cathode material for sodium-ion batteries was synthesized from a spent electroless nickel plating bath. The obtained Na$_3$V$_2$(PO$_4$)$_3$/C exhibited excellent electrochemical properties, with the initial discharge capacity of 108.3 mAh·g$^{-1}$ at 0.2 C and the capacity retention of 99.3% after 300 cycles, which was comparable to that of powders prepared from chemical reagents. This study will be helpful for the value-adding utilization of the spent electroless nickel plating bath.

1. Introduction

With the increasingly serious environmental pollution and energy crisis, chemical energy storage has begun to attract people’s attention. Lithium-ion batteries have been widely used in portable electronic devices and new energy vehicles due to their high energy density and high power density. However, the limited storage of lithium elements on the Earth cannot meet the needs of future development, so sodium-ion batteries are becoming a new-type energy storage equipment [1–4]. Up to now, researchers have spent plenty of time and energy on cathode materials for sodium-ion batteries [5–8]. As a typical polyanionic NASCION compound, Na$_3$V$_2$(PO$_4$)$_3$ has received more and more attention owing to its advantages of moderate energy density, stable structure and abundant raw materials, etc [9, 10]. With the help of heteroatomic bulk doping [11–15], surface coating [16–18], particle nanocrystallization [18, 19] and morphology specialization [20, 21], the electrochemical properties of Na$_3$V$_2$(PO$_4$)$_3$ cathode materials have been enhanced greatly. However, the synthesis of Na$_3$V$_2$(PO$_4$)$_3$/C and its performance optimization always use high-purity chemical reagents as raw materials, which increases production costs.

On the other hand, as an indispensable surface finishing technique, electroless nickel plating has extensively been employed in aerospace, automotive, chemical and electrical industries [22]. A traditional electroless nickel plating solution usually consists of nickel sulfate, sodium hypophosphate, chelating agents and other additives. After working about 6 cycles, the concentration of nickel ions in the solution is lowered to a level unavailable for electroless plating. The spent electroless nickel plating bath (named as SENPB) is mainly composed of Ni$^{2+}$, Na$^+$, SO$_4^{2-}$, H$_2$PO$_2^-$, HPO$_3^{2-}$ and Ca,H$_3$O$_7^-$ [23]. The rational treatment of the SENPB is closely linked with environmental protection and resource utilization.

Therefore, in this paper, a porous Na$_3$V$_2$(PO$_4$)$_3$/C composite was prepared firstly by a sol-gel method from the SENPB. The as-prepared powders exhibit the similar properties to those synthesized by chemical reagents.

2. Experimental

Through analysis, the SENPB was composed of 0.28 mol·L$^{-1}$ Na, 0.30 mol·L$^{-1}$ P, 0.13 mol·L$^{-1}$ Ni, 1.02 mol·L$^{-1}$ C, 0.15 mol·L$^{-1}$ SO$_4^{2-}$, 0.1 $\times$ 10$^{-3}$ mol·L$^{-1}$ Ca, 0.03 $\times$ 10$^{-3}$ mol·L$^{-1}$ Fe, 0.16 $\times$ 10$^{-3}$ mol·L$^{-1}$ Mg. As we
reported previously, 0.2 L 0.75 mol·L⁻¹ (CH₃CO₂)₂Ba, 1.04 L 0.25 mol·L⁻¹ NaOH and 0.015 L 0.02 mol·L⁻¹ Na₂S solutions were respectively added into 1.0 L SENPB in order to remove SO₄²⁻, Ni²⁺ and other impurity ions [24]. After reacting and filtering successively, the filtrate consisted mainly of 0.24 mol·L⁻¹ Na, 0.13 mol·L⁻¹ P, 0.72 mol·L⁻¹ C, 0.02 × 10⁻³ mol·L⁻¹ Ca, 0.03 × 10⁻³ mol·L⁻¹ Mg. Subsequently, stoichiometric NH₄VO₃ and (NH₄)₂HPO₄ were added into the filtrate. After reaction at 80°C for 6 h, a blue wet gel was formed. The gel was dried and ground to obtain the precursor. The Na₃V₂(PO₄)₃/C product (denoted as sample A) was prepared by calcining in sequence the precursor at 450°C for 4 h and 750°C for 10 h under nitrogen atmosphere. The preparation process was shown in figure 1. The other Na₃V₂(PO₄)₃/C product (denoted as sample B) was synthesized from NaOH, NH₄VO₃, NH₄H₂PO₃ and C₆H₈O₇·H₂O with the same processes. The structures, morphologies and electrochemical properties of the two samples were characterized using the same methods in order to verify the feasibility of Na₃V₂(PO₄)₃/C powders prepared from the SENPB.

The components of the SENPB and the filtrate were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 4300DV) and TOC analyzer (LB-T600B). The carbon amount of the sample was detected by HF infrared C-S analyzer (HIR 944). The structure of the powders was observed by x-ray diffraction (XRD, Rigaku D/max 2500). The morphological and compositional characterization was performed by scanning electron microscope (SEM, SU8010) and energy dispersive X-ray spectroscopy (EDS).

As-prepared Na₃V₂(PO₄)₃/C active material, acetylene black and PVDF were mixed evenly at a mass ratio of 8:1:1, and an appropriate amount of NMP solvent was dropped to form a slurry. The slurry was coated on an aluminum foil, and the cathode sheet was obtained by vacuum drying at 120°C for 12 h. The active mass loading was about 1.6 mg·cm⁻². In a glove box filled with high-purity argon gas, a CR2025 button battery was assembled with metallic Na sheet as the negative electrode, glass fiber (GF/D, Whatman) as the separator and 0.2 mL 1.0 mol·L⁻¹ NaClO₄ (dissolved in EC/DEC with a volume ratio of 1:1) as the electrolyte. The Land CT 2001A battery test system was used for rate performance and constant current charge-discharge tests, and the test voltage was 2.0–3.9 V.

3. Results and discussion

The structure of Na₃V₂(PO₄)₃/C powders was analyzed by XRD, as shown in figure 2. The diffraction patterns of the two samples well match with rhombohedral Na₃V₂(PO₄)₃ (JCPDS #53–0018). Extreme sharp peaks signify the high purity and crystallinity, and no impurity peaks including those for carbon are determined. The corresponding lattice parameters calculated from the XRD peaks (for sample A, a = 0.8723 nm and c = 2.1812 nm; for sample B, a = 0.8719 nm, c = 2.1816 nm) are in good accordance with previous reports [25, 26]. This shows that using the SENPB as raw materials has little influence on the crystal structure of Na₃V₂(PO₄)₃/C powders.

Figure 3 displays the SEM images of the Na₃V₂(PO₄)₃/C samples. It can be seen from figures 3(a) and (c) that sample A and sample B have a three-dimensional porous-intermediate honeycomb structure. After magnification (shown in figures 3(b) and (d)), the honeycomb structures of sample A and sample B are composed of porous skeleton structures and have large specific surface areas. This indicates that the Na₃V₂(PO₄)₃/C product prepared from the SENPB has the similar morphology to that synthesized from chemical reagents, and this particular porous structure may provide outstanding electrochemical performance. Furthermore, EDS image of sample A in figure 4 suggests that there are no impurities in the powders synthesized from the SENPB on account of the sole appearance of Na, V and P peaks. The content of the residual carbon is about 8.3 wt%, determined by C-S analyzer.
Figures 5(a) and (b) exhibit the first charge-discharge curves of sample A and sample B at different discharge rates (the charge rate was fixed at 0.2 C). At 0.2 C, the specific capacities of sample A and sample B are 108.3 mAh·g⁻¹ and 108.9 mAh·g⁻¹, respectively. The charge-discharge plateau at 3.4 V or so indicates that the Na₃V₂(PO₄)₃/C composite has a V⁴⁺/V³⁺ redox reaction [27]. With the increase of the discharge rate, the discharge specific capacity gradually decreases. The discharge specific capacity at 10 C drops to 89.5 mAh·g⁻¹ and 89.9 mAh·g⁻¹, respectively. Figures 5(c) and (d) display the coulombic efficiency and cycle performance diagrams of sample A and sample B at 0.2 C. It can be seen easily that the coulombic efficiencies of the two samples are almost 100%, the capacity retention of sample A after 300 cycles is 99.3% and the corresponding value of sample B is 99.1%. These data suggest that the electrochemical properties of the Na₃V₂(PO₄)₃/C material synthesized from the SENPB are favourably comparable to that of the Na₃V₂(PO₄)₃/C material prepared from chemical reagents. The excellent electrochemical performance of the two samples may be attributed to special honeycomb structure. The specific reasons are still under investigation.

4. Conclusions

The Na₃V₂(PO₄)₃/C cathode material has been synthesized through a sol-gel method from the SENPB after removing SO₄²⁻, Ni²⁺ and other impurity ions. The as-prepared Na₃V₂(PO₄)₃/C exhibits excellent electrochemical performance, with the initial discharge capacity of 108.3 mAh·g⁻¹ at 0.2 C and the capacity retention of 99.3% after 300 cycles. The results demonstrate that it is feasible for the preparation of the...
Figure 4. EDS image of sample A.

Figure 5. The rate performance of sample A (a) and sample B (b). Cycling performance of sample A (c) and sample B (d) at 0.2 C for 300 cycles. The charge rate was fixed at 0.2 C.
outstanding-performance Na$_3$V$_2$(PO$_4$)$_3$/C material from the SENPB, and it also provides a novel method for the recycling of the waste liquid.

**Acknowledgments**

This project was supported by Scientific Research Fund of Hunan Provincial Education Department (19A111) and Provincial Natural Science Foundation of Hunan (2021JJ30183), China.

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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