A Poriferous Nanoflake-Assembled Flower-Like Ni$_5$P$_4$ Anode for High-Performance Sodium-Ion Batteries

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Received 20 August 2020; Accepted 18 November 2020; Published 29 January 2021

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Sodium-ion batteries (SIBs) have been regarded as one of the most competitive alternatives for lithium-ion batteries (LIBs) due to the abundance of sodium and comparable electrochemical characteristics of sodium to that of lithium. However, while highly desired, developing stable anode materials remains a critical challenge. In this work, the development of a stable anode for SIBs is reported, a poriferous nanoflake-assembled flower-like nickel tetraphosphide (PNAF-NP) with high surface area and typical mesoporous property. Due to the unique structure, the PNAF-NP anode exhibits excellent reversible capacity of 648.34 mAh g$^{-1}$ at 0.2 A g$^{-1}$ with a Coulombic efficiency of 98.67%, and superior cycling stability at 0.2 A g$^{-1}$ with high retention capacity of 456.34 mAh g$^{-1}$ and average Coulombic efficiency of 99.19% after 300 cycles. Moreover, the high reversible capacity of 614.43, 589.49, 512.66, and 432.23 mAh g$^{-1}$ is achieved at 0.5, 1, 2, and 5 A g$^{-1}$, respectively, indicating the superior rate capability of the PNAF-NP anode. This work represents a great advancement in the field of SIBs by reporting a high-performance anode material.

1. Introduction

Owing to the relatively high-energy density and long-serving lifespan, lithium-ion batteries (LIBs) have been regarded as one of the most important and popular mobile power sources [1–10]. However, considering the rarity and uneven distribution of lithium resource on earth, the production of state-of-the-art LIBs will not be able to match the rapidly increasing demand for this affordable and economic power source in the aforementioned markets [11–13]. New battery technologies beyond LIBs have been widely developed and explored, including redox flow batteries [14–16], metal-air batteries [17–23], lithium-sulfur batteries [24, 25], and sodium-ion batteries (SIBs) [26–31]. Among such cutting-edge batteries, SIBs have attracted increasing attention and recognition as one of the most suitable promising substitutes for commercial LIBs. Its potential can be attributed to the abundance of sodium on earth and the comparable electrochemical characteristics of sodium (Na) to that of lithium (Li) [32, 33]. Tremendous effort has been focused on exploring the suitable anode materials for SIBs [34, 35]. For commercial LIBs, graphite is the dominant anode material owing to its low cost, abundance, and high-energy density. Unfortunately, graphite is not suitable for SIBs due to the larger radius of sodium ions (Na$^+$, 1.02 Å) compared to that of lithium ions (Li$^+$, 0.76 Å), making the Na$^+$ more difficult to intercalate into the layer spacing of graphite [36]. Thus, it is urgent to explore different anode materials that are suitable and promising for the advancement of the field of SIBs.

Various potential anode material candidates have been reported for SIBs, including carbonaceous materials [37, 38], alloy-based materials [39–41], transitional metal sulfides and oxides [42–44], and phosphorus and phosphides [45, 46]. Among them, phosphorous- (P-) based materials attract much more interests due to their commercial availability, abundance, even distribution on earth, and the ultrahigh
2. Materials and Methods

2.1. Electrode Preparation and Material Characterization. The poriferous nanoflake-assembled flow-like Ni$_3$P$_4$ (PNAF-NP) in our work is prepared via a hydrothermal process followed by a phosphating procedure [59, 60]. At first, the hierarchical nanoflake-assembled flow-like Ni(OH)$_2$ (NAF-NOH) precursor is fabricated using a hydrothermal method. For details, nickel nitrate (Ni(NO$_3$)$_2$), ammonium fluoride (NH$_4$F), and urea (CO(NH$_2$)$_2$) are dissolved into distilled water (DI water) with a molar ratio of 2 : 1 : 1 and the mixture is continuously stirred for 1 hour to obtain the transparent solution. Then, the solution is sealed into a stainless steel autoclave and heated at 300°C for 24 hours under argon. Finally, the PNAF-NP powders are obtained after the furnace is naturally cooled down to 25°C.

High-resolution powder X-ray diffraction (XRD, model PW 1825) and X-ray photoelectron spectroscopy (XPS, PHI 5600) measurements are carried out to inspect the crystallinity and composition of the NAF-NOH and PNAF-NP powders. The nitrogen adsorption-desorption test is applied to analyze the Brunauer–Emmett–Teller (BET) specific surface area and pore size distribution of the NAF-NOH precursor and PNAF-NP sample. Scanning electron microscope (SEM, 7000F, JEOL) and the energy-dispersive X-ray spectroscopy (EDX) elemental mapping are conducted to measure the morphology and elemental distribution of NAF-NOH and PNAF-NP samples. The high-resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED) tests are used to characterize the crystal structure and lattice fringes of the PNAF-NP sample.

2.2. Electrode Preparation and Electrochemical Measurements. To test the electrochemical performance of PNAF-NP anode, the electrode is prepared using a slurry casting method, in which PNAF-NP powders are mixed into the N-methyl-2-pyrrolidone (NMP) organic solvent with polyvinylidene fluoride (PVDF, binder) and Super P (SP, conductive additive) at the weight ratio of 8 : 1 : 1 to form a slurry in the argon-filled glovebox. The slurry is painted onto the aluminum foil (current collector) using a doctor blade under argon flow protection. Lastly, the obtained electrode is heated in the vacuum oven at 120°C for 10 hours, and the electrode is sliced into discs with a diameter of 14 mm and kept in the glovebox for measurement. For the control group, the electrode without PNAF-NP powders is prepared by mixing the SP with PVDF at a weight ratio of 9 : 1, and the rest of the procedure keeps the same as that of the PNAF-NP-based electrode. The mass loading of active materials of the prepared electrodes is calculated to be 2.0~2.5 mg cm$^{-2}$.

The electrochemical tests of the obtained electrodes are operated in the CR2032-type coin cell, which is comprised of one 16 mm Na sheet as a counter electrode, one polypropylene separator, and one PNAF-NP-based working electrode. The organic electrolyte used in this work is made of 1 M NaPF$_6$ dissolved into the propylene carbonate (PC) solvent combined with a 5 wt% fluoroethylene carbonate (FEC) additive. All the cells are assembled in an argon-filled glovebox with contents of H$_2$O and O$_2$ less than 0.1 ppm. The electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements are conducted on the electrochemical analyzer (Bio-Logic SAS VMP3) with an electrochemistry lab (EC-Lab) V10.40 program, while the cycling and rate tests are performed on a LAND battery test system (LANTH CT2001A) at various current densities within the voltage window of 0.01~3.0 V (vs. Na/Na$^+$).

3. Results and Discussion

The nanoflake-assembled flow-like Ni(OH)$_2$ (NAF-NOH) precursor and poriferous nanoflake-assembled flow-like Ni$_3$P$_4$ (PNAF-NP) powders are synthesized following the procedure in the experimental section, and their morphology is compared and analyzed using a scanning electron
microscope (SEM). As shown in Figures 1(a)–1(c), a hierarchical flower-like particle has been successfully fabricated, comprising of several cross-linked nanoflakes with a thickness of 40–60 nm and a diameter of 3.0–6.5 μm. Figure 1(b) shows in detail that the surface of nanoflakes is very smooth and dense without any pores. Additionally, a few folds are observed at the edge of every nanoflake, meaning that these nanoflakes are stacked from smaller and thinner nanosheets during the hydrothermal process. From the energy-dispersive X-ray spectroscopy (EDX) elemental mapping results in Figures 1(d)–1(f), O and Ni elements are well distributed throughout the entire flower-like particle, indicating that the uniform precursor has been obtained. After the post-phosphating process, the hierarchical flower-like structure is well preserved in phosphide particles as shown in Figures 2(a) and 2(b), from which each particle is composed of several pieces of nanoflakes with a similar thickness (30–65 nm) and similar length (3.0–6.5 μm) as well. However, differences in the detailed morphologies for every nanoflake are observed. There are numerous pores that have been formed in every piece of the nanoflake. In addition, the once smooth and dense surface has become rough and porous. From the EDX mapping results in Figures 2(c)–2(f), the Ni and P elements have covered the entire phosphide particle structure with the atomic ratio of Ni and P being estimated to be approximately 5:4 (Ni 45.52 at% and P 36.41 at%). The atomic ratio demonstrates that the hydroxide precursor has transformed into the final PNAF-NP sample. At the same time, Figure 2(c) shows that there is still detection of trace amounts of the oxygen element (5.46 at%). These oxygen residues can be due to the side reaction between the PNAF-NP and oxygen when exposed to air during the measurement.
process. Lastly, the C element detected from the precursor and PNAF-NP particle originates from the conductive carbon tapes on the testing holder.

Figures 3(a) and 3(b) display the further examination of the crystal structure of the prepared PNAF-NP sample through the high-resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED) measurements. For one piece of nanoflake in the PNAF-NP particles (Figure 3(a)), numerous pores are observed in the whole structure with the surface being very rough, which is consistent with the SEM results. Moreover, evident lattice fringes shown in Figure 3(b) and SAED image inset are detected for the PNAF-NP sample. The ordered lattice fringes and SAED image are ascribed to the characteristic (102) plane of Ni₅P₄ (JCPDS #18-0883) [60], demonstrating the well-crystallized PNAF-NP powder has been achieved in this work. The Brunauer–Emmett–Teller (BET) specific surface area renders the PNAF-NP sample more active sites used for Na-based reactions during the discharge and charge processes, indicating an enhancement on the electrochemical performance of the PNAF-NP anode.

High-resolution powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements are carried out to investigate the composition and crystallinity of these as-prepared samples. As present in Figure 3(d), there are five strong diffraction peaks observed in the XRD pattern of the NAF-NOH sample from 10 to 65°, which correspond to the (001), (100), (101), (102), and (110) characteristic peaks of NiOH (JCPDS #14-0117), respectively. The XRD pattern of the PNAF-NP sample shows that all the diffraction peaks attributed to Ni(OH)₂ have already disappeared and are replaced by seventeen new noticeable peaks, which are identified as the (100), (002), (102), (103), (200), (021), (202), (104), (210), (211), (212), (204), (301), (213), (006), (214), and (220) diffraction peaks of Ni₅P₄ (JCPDS #18-0883), respectively. As for both the hydroxide precursor and the final phosphide powders, there are no peaks of impurities detected in the XRD results, demonstrating that unduluted PNAF-NP and NAF-NOH samples with high crystallinity have been smoothly fabricated in this work. The elemental composition of PNAF-NP and NAF-NOH samples is verified with an XPS test as well, and the results are displayed in Figures 3(e) and 3(f) and S2. For the high-resolution XPS spectra of Ni 2p in the PNAF-NP sample (Figure 3(e)), the two major peaks with binding energies of 852.2 and 856.1 eV are identified as Ni 2p₃/₂, corresponding to Ni²⁺ in Ni(OH)₂ (#14-0117).
crystal Ni$_3$P$_4$ and Ni-O species oxidized on the surface of PNAF-NP. The other two peaks being centered at 869.6 and 874.1 eV can be attributed to Ni 2p$_{1/2}$ assigned to the similar Ni$^{6+}$ and oxidative Ni species in the PNAF-NP sample. On either side of the Ni 2p$_{1/2}$ peaks, two broad satellite peaks located at 862.1 and 880.3 eV are observed as well. For the P element (Figure 3(f)), two strong peaks situated at 129.1 and 132.3 eV are identified as P 2p$_{3/2}$ and P-O bonds, respectively. The appearance of Ni$^{6+}$ and P 2p$_{3/2}$ peaks proves that the PNAF-NP sample has been successfully prepared [59, 60]. In contrast, for the high-resolution of Ni 2p in NAF-NOH precursor (Figure S2a), there are four peaks are detected. Two sharp peaks with binding energies of 855.5 and 873.1 eV are assigned to Ni 2p$_{3/2}$ and 2p$_{1/2}$ in NiOH, while the other two located at 861.5 and 879.6 eV correspond to satellite peaks. And in the XPS spectrum of O 1s (Figure S2b), there are two peaks situated at 529.6 and 530.9 eV, assigned to Ni-O and OH$^-$ bonds, respectively. The Ni 2p and O 1s peaks in the precursor confirm that the pure NAF-NOH sample has been obtained in this work.

To determine the sodium-ion insertion and extraction potentials of prepared PNAF-NP anode, the cyclic voltammetry (CV) test is carried out from 0.01 to 3.0 V (vs. Na/Na$^+$) with a scan rate of 0.1 mV s$^{-1}$. The curves of the first ten cycles are shown in Figure 4(a). In the first cathodic scanning cycle, three noticeable peaks at 1.17, 0.71, and 0.01 V are observed. Of these three peaks, the second peak is assigned to the formation of solid electrolyte interphase (SEI) due to the organic electrolyte decomposition, and this peak disappears in the following scan. In contrast, there are two major peaks at 0.73 and 0.16 V detected in the reversed anodic scanning. While observing subsequent scanning cycles, two pairs of redox peaks (sharp 0.16/0.01 V and broad 0.73/1.17 V) are clearly observed and maintained, demonstrating that the PNAF-NP anode exhibits excellent electrochemical reversibility and high cycling stability for SIBs. Of the two pairs, the higher pair refers to the reversible reaction between sodium phosphides and elemental phosphorus, whereas the sharp pair, close to 0 V that is also detected in the CV profiles of the cell without PNAF-NP anode shown in Figure S3, corresponds to Na$^+$ insertion and extraction reactions in the conductive carbon.

Figures 4(b) and 4(c) show the galvanostatic charge and discharge curves of the PNAF-NP anode within the voltage window of 0.01 to 3.0 V at the current densities from 0.2 to 5.0 A g$^{-1}$. In the first cycle at the current density of 0.2 A g$^{-1}$, the cell with the PNAF-NP anode delivers an initial discharge capacity of 748.03 mAh g$^{-1}$, while the reversed charge capacity still reaches to 661.94 mAh g$^{-1}$, revealing a Coulombic efficiency of 88.49%. In the stepwise cycle at the current density of 0.2 A g$^{-1}$, a specific capacity of 648.34 mAh g$^{-1}$ is achieved during discharge, and in the subsequent charge process, the PNAF-NP anode exhibits a reversible capacity of 639.74 mAh g$^{-1}$, presenting much higher Coulombic efficiency of 98.67% than that of the first cycle. Compared with the discharge capacities in the first two cycles at 0.2 A g$^{-1}$,
the PNAF-NP anode displays an irreversible capacity of about 100 mAh g⁻¹, which mainly results from the decomposition of electrolytes and the SEI formation as mentioned in the first CV scan. When the current density increases to 0.5, 1, 2, and 5 A g⁻¹, the PNAF-NP anode presents rate capacities of 614.43, 589.49, 512.66, and 432.23 mAh g⁻¹, respectively. In contrast, for the cell without the PNAF-NP anode (Figure 4(c)), the capacity is only 240 mAh g⁻¹ in the first cycle at the current density of 0.2 A g⁻¹ and the capacity rapidly decreases to almost zero at the current density of 1 A g⁻¹. These results demonstrate that the PNAF-NP anode plays a vital role on the superior rate capability for sodium storage.

The cycling test of the PNAF-NP anode is conducted at a current density of 0.2 A g⁻¹, and the result is displayed in Figure 4(d). As mentioned above, the PNAF-NP anode exhibits an initial discharge capacity of 748.03 mAh g⁻¹, and even after 300 cycles, a high retention capacity of 456.34 mAh g⁻¹ with an average Coulombic efficiency of 99.19%, indicating the superior cycling stability of the PNAF-NP anode. Compared with the reported metal phosphides in Table S1, the PNAF-NP anode exhibits much higher retention capacity and better Coulombic efficiency, indicating the promising application of the PNAF-NP as a high-performance anode for SIBs. The electrochemical impedance spectroscopy (EIS) measurements are carried out to verify the impact of the PNAF-NP anode on sodium-ion transfer during the long-term cycling. The plots for selected cycles are shown in Figure 5(a). After the first cycle, the PNAF-NP anode exhibits a bulk resistance ($R_b$) of 2.61 Ω along with a charge transfer resistance ($R_{ct}$) of 39.36 Ω, which is lower than that of the cell without PNAF-NP anode ($R_b$ of 6.34 Ω and $R_{ct}$ of 118.4 Ω, Figure S4). With the increased cycling time, the PNAF-NP anode exhibits a $R_b$ of 2.97 and 4.63 Ω along with a $R_{ct}$ of 50.29 and 60.24 Ω after 100 and 300 cycles, which are all lower than the $R_b$ and $R_{ct}$ of the cell without the PNAF-NP anode ($R_b$ of 8.78 Ω and $R_{ct}$ of 237.8 Ω). The lower $R_b$ and $R_{ct}$ of the PNAF-NP anode prove that the special structural features of the prepared nickel phosphide could strongly facilitate the electron and sodium-ion transfer during the cycling test.

In order to explore the reaction mechanism between the PNAF-NP anode and sodium, the ex situ XRD spectrum is utilized to examine the different compositions of the anode during the first cycle. As shown in Figure 5(b), the peaks attributed to Na₃P and Ni metal are detected at 0.25 V, indicating that the reduction reaction between Ni₅P₄ and sodium metal has occurred [61]. At the end of the discharge (0.01 V), stronger peaks of Na₃P and Ni metal are observed, suggesting further reduction of the PNAF-NP anode. In the stepwise charge process, the Na₃P gradually disappears while the Ni₅P₄ recovers, demonstrating that reversible redox reactions could occur between the PNAF-NP anode and sodium metal. The morphology of the PNAF-NP anode after cycling is examined using HR-TEM and SAED measurements, and the results are shown in Figures 5(c) and 5(d). After cycling, the primary porous structure of the PNAF-NP sample is still
preserved, and the lattice fringes of 2.22 Å assigned to the characteristic (210) plane of Ni₅P₄ (JCPDS #18-0883) are obviously detected, demonstrating the high stability of the PNAF-NP anode during the cycling test.

4. Conclusion

In our work, a PNAF-NP sample is successfully developed as an advanced anode for SIBs. The PNAF-NP anode holds a high specific surface area and exhibits mesoporous material properties, which strongly accelerates the sodium-ion transfer in the cell. With the aid of such a novel anode, the cell can deliver an initial capacity of as high as 748.03 mAh g⁻¹ and an extrahigh reversible capacity of 648.34 mAh g⁻¹ at 0.2 A g⁻¹ with a Coulombic efficiency of 98.67%. Even if the current density increases to 0.5, 1, 2, and 5 A g⁻¹, the PNAF-NP anode could maintain its high reversible capacity of 614.43, 589.49, 512.66, and 432.23 mAh g⁻¹, respectively, demonstrating the competitive rate capability of PNAF-NP anode. Furthermore, the cell with the PNAF-NP anode is found to have superior cycling stability at 0.2 A g⁻¹ and shows a high retention capacity of 456.34 mAh g⁻¹ with an average Coulombic efficiency of 99.19% even after 300 cycles. The enhanced electrochemical performance indicates great potential of the PNAF-NP sample as an advanced high-performance anode for SIBs.

Data Availability

All data are available, and all requests should be addressed to R.Z. or J.C.

Conflicts of Interest

The authors declare no conflict of interest regarding the publication of this article.

Acknowledgments

J.C. acknowledges the Henry Samueli School of Engineering and Applied Science and the Department of Bioengineering at the University of California, Los Angeles for the startup support.

Supplementary Materials

Figure S1: the nitrogen adsorption-desorption isotherm and pore size distribution (inset) of the prepared NAF-NOH precursor. Figure S2: high-resolution XPS of NAF-NOH precursor in the (a) Ni 2p and (b) O 1s regions. Figure S3: CV curves of the cell without PNAF-NP anode at first ten cycles. Figure S4: the EIS spectra of the cell without PNAF-NP anode before and after cycling. Table S1: comparation of the PNAF-NP anode with the reported nickel phosphate materials for Li-S batteries. (Supplementary materials)

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