

Article

Synthesis and Performance of $\text{NaTi}_2(\text{PO}_4)_3/\text{VGCF}@C$ Anode Composite Material for Aqueous Sodium-Ion Batteries

Bo Ding ^{1,2,*} , Mingzhu Li ^{1,2}, Fuzhou Zheng ^{1,2}, Yangzhou Ma ³, Guangsheng Song ^{3,*}, Xiulong Guan ^{1,2}, Yi Cao ⁴ and Cuie Wen ⁵ 

¹ School of Materials and Chemical Engineering, Bengbu University, Bengbu 233030, China; julielimingzhu@163.com (M.L.); zfz617578876@163.com (F.Z.); guanxiulong2002@163.com (X.G.)

² Anhui Provincial Engineering Laboratory of Silicon-Based Materials, Bengbu 233030, China

³ School of Materials Science and Engineering, Anhui University of Technology, Maanshan 243002, China; yangzhou.ma@outlook.com

⁴ Enpower Energy Technology (Anhui) Co., Ltd., Maanshan 243000, China; yi.cao@enpower-energy.com

⁵ School of Engineering, RMIT University, Melbourne, VIC 3001, Australia; cuie.wen@rmit.edu.au

* Correspondence: www024151@163.com (B.D.); song_ahut@163.com (G.S.)

Abstract: This study combines self-prepared $\text{NaTi}_2(\text{PO}_4)_3$ (NTP) with commercial vapor-grown carbon fiber (VGCF) using a solid state calcination, then coats it with carbon to synthesize the composite anode material $\text{NaTi}_2(\text{PO}_4)_3/\text{VGCF}@C$ (NTP/VGCF@C). The microstructure and electrochemical properties of the composite material were then analyzed using microstructure analysis and electrochemical testing equipment. Single phase NTP shows nanoparticles with a polyhedral structure, and there is good contact at the interface between the nanoparticles and the VGCFs. The carbon coating formed on the NTP particles displays a nearly 6.5 nm thick layer of amorphous carbon. From the coin-cell battery performance measurements, after 850 cycles, the composite material NTP/VGCF@C exhibits an excellent retention rate of 96.3% compared to that of the pure NTP material when the current density is 200 mA/g. As a result, the composite material and lithium manganate (denoted as LMO) were assembled into an LMO-NTP/VGCF@C aqueous sodium-ion soft pack full battery system. The full battery shows an initial capacity of 31.07 mAh at a rate of 0.5C, and a reversible discharge capacity retention rate of 95.8% after 480 cycles, exhibiting a good long-cycle stability performance.

Keywords: aqueous sodium-ion battery; composite material; electrochemical performance



Citation: Ding, B.; Li, M.; Zheng, F.; Ma, Y.; Song, G.; Guan, X.; Cao, Y.; Wen, C. Synthesis and Performance of $\text{NaTi}_2(\text{PO}_4)_3/\text{VGCF}@C$ Anode Composite Material for Aqueous Sodium-Ion Batteries. *Batteries* **2023**, *9*, 265. <https://doi.org/10.3390/batteries9050265>

Academic Editors: Hirotoshi Yamada, Zhenbo Wang, Tingfeng Yi and Gang Sun

Received: 6 April 2023

Revised: 27 April 2023

Accepted: 6 May 2023

Published: 10 May 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

With the increasing demand of the large-scale energy storage market, a rechargeable energy storage battery has been developed and researched. Currently, the lithium-ion battery is the most widely used chemical energy storage system, but it cannot meet the needs of large-scale application, mainly due to the shortage of high-cost lithium resources [1–6]. In contrast, sodium is abundant on the earth and is also much cheaper than lithium; thus, lithium-ion batteries may be replaced by sodium-ion batteries in large-scale energy storage applications [7–10]. However, sodium-ion has a significant impact on the deintercalation of sodium ions due to its large ionic radius (1.02 Å) [11,12]. Therefore, it is particularly urgent to develop suitable materials for the development of the sodium-ion battery (SIB). At present, hard carbon is the most widely used anode material for SIB since it exhibits good Na^+ storage performance. However, hard carbon easily forms sodium dendrites when the working voltage is lower than 0.1 V, thus causing a safety concern [13,14]. However, TiO_2 is also widely studied as a metal oxide anode materials for use in sodium-ion batteries, since under the condition of deep discharge, the theoretical capacity of TiO_2 is up to 335 mAh/g. However, TiO_2 is a semiconductor with low conductivity, leading to its low electrochemical activity. It is necessary to combine TiO_2 with highly conductive materials to achieve its

purpose [15–19]. Therefore, it is necessary to develop a new type of electrode material suitable for sodium-ion batteries.

It is well known that NTP contains Na super ionic conductor (NASICON), with an open three-dimensional frame structure which facilitates ion diffusion. It consists of TiO_6 octahedrons and PO_4 tetrahedrons that are connected to each other through oxygen atoms [20–22]. The reversible sodiation and desodiation between $\text{NaTi}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$, i.e., the redox reactions of $\text{Ti}^{3+} \leftrightarrow \text{Ti}^{4+}$ via a two-phase reaction mechanism, can be represented by equation: $\text{NaTi}_2(\text{PO}_4)_3 + 2\text{Na}^+ + 2\text{e}^- \xrightleftharpoons{\text{charge-discharge}} \text{Na}_3\text{Ti}_2(\text{PO}_4)_3$ [23,24]. However, due to its poor electronic conductivity, the NTP anode material cannot play its proper role in the sodium-ion battery [25]. In order to improve the electronic conductivity, several methods have been tested: (1) introducing conductive agents to increase the conductivity of the material [26–29]; (2) enhancing the conductivity or hydrophilicity of materials with doping elements [30,31]; and (3) constructing nanostructures and carbon-coated structures to improve the stability and electronic conductivity of materials [32]. For example, A sol-gel method was reported to embed nano-NTP particles into a mesoporous carbon matrix to artificially improve electronic conductivity [33]. The sodium-ion anode material showed excellent electrochemical performance at the current density of 4 A/g and the high rate of 20C. The presence of the interconnected porous carbon material effectively improved the electrochemical performance of the sodium-ion battery anode composite material. In addition, a three-dimensional (3D) porous structure containing fluoride $\text{NaTi}_2(\text{PO}_4)_3\text{@C}$ (F-NTP@C) was created to improve the storage capacity of Na^+ . After 2000 cycles at 10C, the capacity retention rate was reported to be 75.5%. The addition of F-ions and the three-dimensional porous structure design effectively enhanced the electronic conductivity and Na-ion dynamics [34]. Since graphene possesses both astonishing surface area and conductivity, the $\text{NaTi}_2(\text{PO}_4)_3$ -graphene nanocomposite anode material for aqueous sodium-ion batteries was synthesized using the solvothermal method and subsequent high-temperature calcination [35]. Highly crystalline $\text{NaTi}_2(\text{PO}_4)_3$ nanoparticles were reported to be uniformly distributed on the surface of the nanographene, with good electrical conductivity. This type of nanocomposite exhibited excellent high-rate and cycling stability performance in a 1 mol/L Na_2SO_4 aqueous electrolyte; it showed high specific capacities of 110 mAh/g at 2C rates, and the capacity retention rate was 90% after 100 cycles. In addition to graphene, a carbon nanotube (CNT) was mixed with $\text{NaTi}_2(\text{PO}_4)_3$ and graphite by mechanical ball milling to prepare a composite material [36]. The composite showed the best electrochemical performance when 6.2 wt.% graphite coated on $\text{NaTi}_2(\text{PO}_4)_3$ and 15 wt.% CNT were used as the conductive agent, and the initial specific capacity reached 130 mAh/g at 0.1C rate. Carbon coating has been reported to be an effective strategy for improving NTP electrochemical properties [37]. The $\text{NaTi}_2(\text{PO}_4)_3/\text{C}$ composite material coated with double carbon layers using the soft chemical method yielded reversible specific capacities of 133 and 64 mAh/g at 0.5C and 50C, respectively, showing excellent cycle stability and rate performance. To our knowledge, the addition of nano carbon fiber into NTP anode material has not been previously reported.

At present, the organic electrolytes used in the sodium-ion energy storage battery are highly inflammable and explosive, resulting in a safety risk. However, the aqueous sodium-ion battery is a safe energy storage technology because it adopts a salt water solution as an electrolyte, which does not easily ignite or explode; thus, battery combustion and explosion accidents can be basically avoided. It is noted that the narrow thermodynamic electrochemical window of water is about 1.23 V. This means that the voltage of the sodium-ion battery in water under normal conditions will not exceed 1.5 V. As a result, only a few aqueous sodium-ion battery systems have been studied. At present, the battery system matching the $\text{NaTi}_2(\text{PO}_4)_3$ sodium-ion anode material mainly includes $\text{NaTi}_2(\text{PO}_4)_3\|\text{Na}_{0.44}\text{MnO}_2$, $\text{NaTi}_2(\text{PO}_4)_3\|\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and $\text{NaTi}_2(\text{PO}_4)_3\|\text{Prussian blue}$ cathode [38–43]. For the aqueous sodium-ion battery consisting of $(\text{NaTi}_2(\text{PO}_4)_3\|1 \text{ mol/L Na}_2\text{SO}_4\|\text{Na}_2\text{CuFe}(\text{CN})_6)$ [44], the reversible specific capacity is 104 and 50 mAh/g at 2C and a 100C rate, and after 1000 cycles at the 10C rate, the specific capacity and capacity retention rate are 74 mAh/g and 88%,

respectively. As for the aqueous sodium-ion battery consisting of $(\text{NaTi}_2(\text{PO}_4)_3 \parallel 1 \text{ mol/L Na}_2\text{SO}_4 + 1 \text{ mol/L Li}_2\text{SO}_4 \parallel \lambda - \text{MnO}_2)$, the discharge capacity of the full battery is 800 mAh at a current density of 50 mA, and the specific capacity reaches 89% of the theoretical capacity [45]. Another aqueous sodium-ion full battery consisting of $\text{NaTi}_2(\text{PO}_4)_3 \parallel 1 \text{ mol/L Na}_2\text{SO}_4 \parallel \text{Na}_{0.44}\text{MnO}_2$ reveals that the reversible specific capacity is 50% of the initial specific capacity after 1600 cycles [46]. Overall, the cycle stability and energy density of an aqueous sodium-ion full battery must be further improved in order to meet the requirements of existing large-scale energy storage. Therefore, the development of key materials is very important for the application of an aqueous sodium-ion full battery for large-scale energy storage.

In this paper, the vapor-grown carbon fiber (VGCF) was first added into the $\text{NaTi}_2(\text{PO}_4)_3$ anode material and then coated with carbon to synthesize an NTP/VGCF@C composite material. The microstructure and electrochemical performance of the composite material were investigated. Moreover, an aqueous sodium-ion soft pack battery system was assembled with a lithium manganate (LMO) cathode material (Daxiang Energy Technology Co., Ltd., Baiyin, China) and an NTP/VGCF@C anode material. This full battery showed a very good long cycling stability. Hopefully our findings can provide useful guidance for the industrial production of an aqueous sodium-ion battery.

2. Experimental Procedure

2.1. Sample Preparation

In this experiment, the analytically pure raw materials Na_2CO_3 (Chinese medicine chemical reagent, purity 99%), $\text{TiO}(\text{OH})_2$ (Macklin reagent, purity $\geq 99\%$), and $\text{NH}_4\text{H}_2\text{PO}_4$ (Macklin reagent, purity 99%) were used for preparing the NTP phase as a first step, and then carbon fiber VGCF and citric acid were added as a second step to create a nanostructured composite NTP/VGCF@C material using the mechanical grinding + high temperature calcination + carbon surface modification method. Specifically, sodium carbonate, metitanic acid, and ammonium dihydrogen phosphate were weighed and added to a stainless steel ball mill tank, according to molar ratio of 0.5:2:3. Then, 20 mL of alcohol containing 0.5% of the thickening agent polyvinyl butyral (PVB) was added into the stainless steel ball mill tank and mixed for 300 rpm for 2 h to ensure full grinding and mixing. The mixed solution was stirred and dried in a heated magnetic agitator to prepare the precursor material of carbon composite NTP for aqueous sodium-ion batteries. The precursor powder was pressed using a 20 MPa tablet press (size: diameter: $\Phi 60 \text{ mm} \times$ thickness: 10 mm) and then transferred to a muffle furnace for high temperature calcination. The high temperature calcining process was as follows: pre-calcining at 350°C for 2 h, then calcining at 800°C for 9 h, with a heating rate of $3^\circ\text{C}/\text{min}$, finally yielding the NTP sodium-ion anode material. The sintered titanium-phosphate anode material was crushed and sifted by the crusher, and the particle size was controlled below $20 \mu\text{m}$. The NTP anode material, carbon fiber VGCF, citric acid, and thickening agent PVB were added to the alcohol solution according to the mass ratio of 90:0.5:8.5:1, nano-grinding and mixing were carried out in the sand mill for 5 h, and the grinding mixed solution was stirred and dried in the heated magnetic agitator. Then, the carbon composite NTP/VGCF@C aqueous sodium-ion nano-anode material was prepared by carbonization sintering in a tubular furnace under an argon atmosphere. The carbonization sintering process is described as follows: presintering at 300°C for 1 h, followed by calcination at 650°C for 3 h at a heating rate of $3^\circ\text{C}/\text{min}$. The preparation process of NTP and NTP/VGCF@C sodium-ion anode materials is shown in Figure 1.

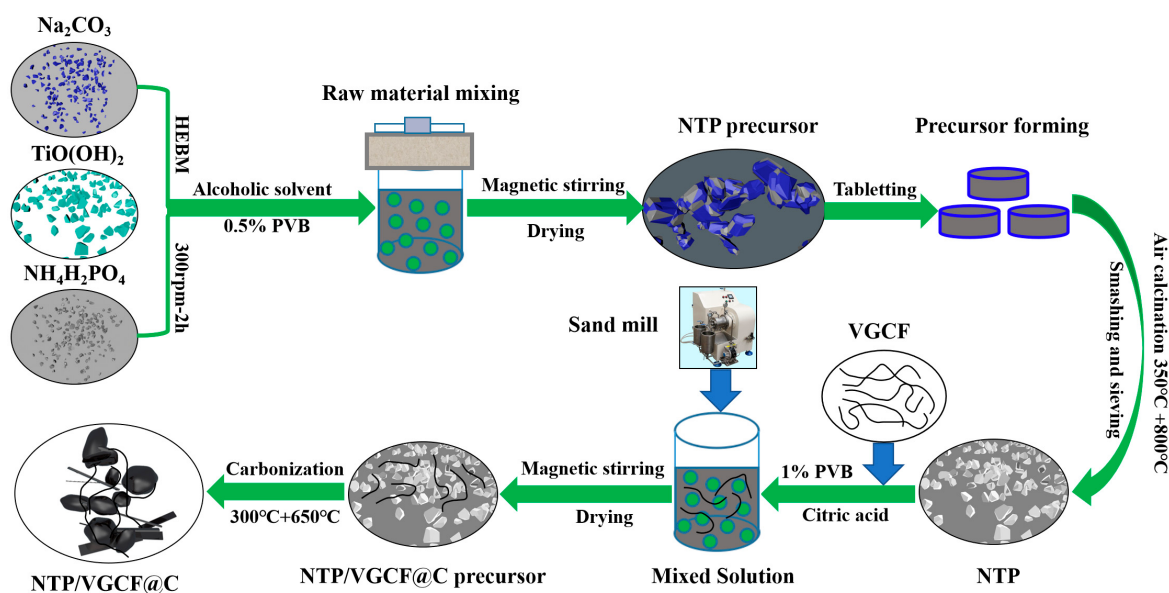


Figure 1. Schematic illustration of the preparation process for NTP and NTP/VGCF@C sodium-ion anode materials.

2.2. Battery Assembly

The prepared active material (NTP, NTP/VGCF@C, or LMO), conductive agent (Super-P), and binder (polyvinylidene fluoride (PVDF)) were mixed in an agate mortar at a mass ratio of 8:1:1, and an appropriate amount of N-methyl-2-pyrrolidone (NMP) solvent was added to prepare an evenly mixed slurry. The slurry was then evenly coated onto the copper foil using a doctor blade and dried at 80 °C for 24 h. A circular electrode disc of 12 mm in diameter (the soft pack battery pole size was 60 mm × 60 mm) was prepared using punching equipment as the research electrode and a sodium metal piece as the counter electrode. A total of 2025-type coin-cell batteries were then assembled in a glove box. The cutting NTP/VGCF@C anode electrode and LMO cathode electrode were assembled into an LMO-NTP/VGCF@C soft pack full battery. The electrolyte was 2 mol/L CH_3COONa and 2 mol/L CH_3COOLi , and the diaphragm was made of non-woven fabric.

2.3. Microstructure and Electrochemical Properties Analysis

The microstructure of the prepared anode materials was analyzed using a field emission scanning electron microscope, model TESCAN MIRA LMS. The microstructure and composition were analyzed by a transmission electron microscope (TEM), model JEM-2100F. Phase analysis was conducted using the Bruker D8 Advance X-ray diffractometer (Scientific Compass). The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were tested using the CS310H model electrochemical workstation tester, with the CV scanning speed of 0.02 mV/s. The electrochemical performance of the coin-cell batteries were tested using an electrochemical cycle system (Neware Technology Co., Ltd., Shenzhen, China). The prepared active material was used as a work electrode, while a thin sheet of sodium was used as a reference electrode. The voltage testing range of the coin-cell batteries was from 1.5 V to 3 V. For the LMO-NTP/VGCF@C soft pack full battery, and the voltage testing range was from 1.2 V to 1.9 V at a 0.5C rate, and the test temperature was maintained at a room temperature of 25 °C.

3. Results and Discussion

3.1. Phase and Element Analysis

Phase analysis was carried out on the synthesized NTP and its composite NTP/VGCF@C powder samples. These two XRD patterns are compared and shown in Figure 2a,b.

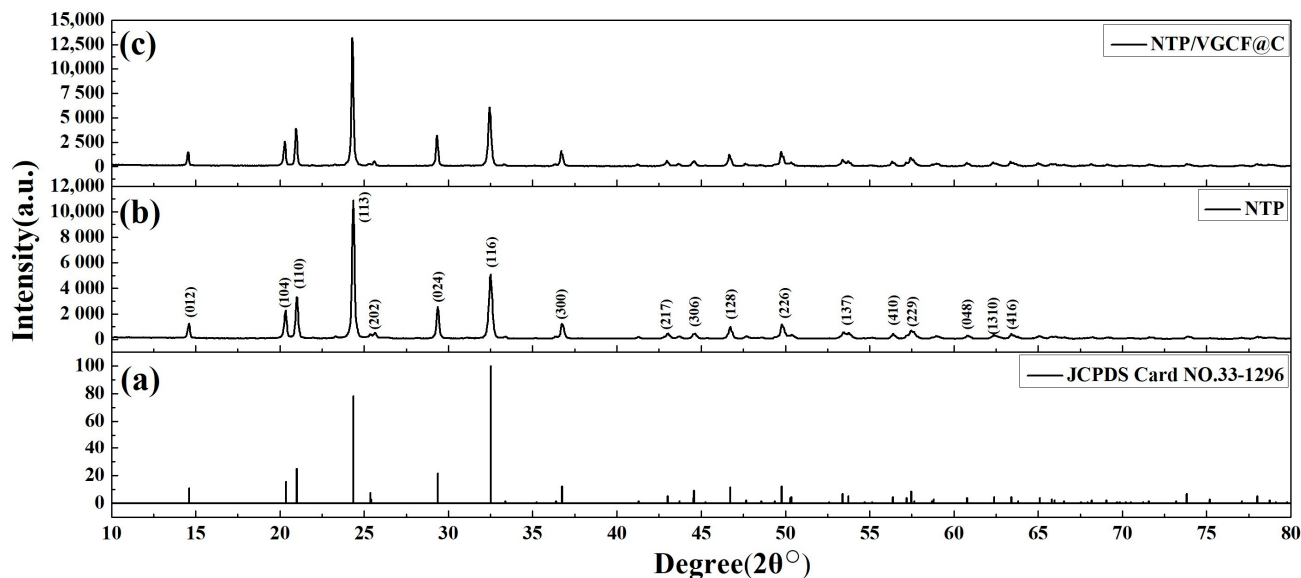


Figure 2. XRD patterns of: (a) JCPDS Card NO.33-1296; (b) NTP anode material and (c) NTP/VGCF@C anode composite material.

According to JCPDS Card NO.33-1296, in the diffraction range of 10° – 80° , as shown in Figure 2a, the characteristic diffraction peaks of pure NTP appear at 14.52° , 20.27° , 20.9° , 24.25° , 25.54° , 29.27° , 32.42° , and 36.31° , etc., corresponding to the crystal plane index of (012), (104), (110), (113), (202), (024), (116), and (300), etc. This standard card pattern perfectly matches the measured whole pattern obtained from the synthesized NTP powder, as shown in Figure 2b, indicating that a single phase NTP material has been successfully prepared. By comparison, the XRD pattern of the composite NTP/VGCF@C (Figure 2c) is found to be very similar to that of the synthesized NTP material, indicating that the NTP exists as a main phase in the synthesized composite material. The phase structure of NTP does not change in the subsequent composite processing procedure, showing good structural stability. Although no characteristic peaks of carbon materials are reflected in the XRD pattern due to their minor amounts, the existence of VGCF nano-fiber and an amorphous coating layer can be confirmed by TEM.

The elemental composition and chemical valence state of the NTP/VGCF@C anode material were analyzed by XPS. It can be clearly seen from the XPS general spectrum in Figure 3a that the NTP/VGCF@C electrode material contains Na, O, Ti, P, and C elements. This indicates that the Na, O, Ti, and O elements come from the NTP phase, while the C element comes from carbon material, and the signals at 134.0 eV, 284.6 eV, 531.8 eV, and 1072.3 eV correspond to the P2p, C1s, O1s, and Na1s components separately. In the Ti 2p spectrum shown in Figure 3b, it can be seen that NTP/VGCF@C exhibits two peaks at 459.4 eV and 465.0 eV. These two peaks correspond to the characteristic peaks of Ti 2p_{3/2} and Ti 2p_{1/2} of Ti⁴⁺ in the NTP/VGCF@C anode material [47–49]. It is proved that Ti exists at the +4 valence in the NTP/VGCF@C anode material, indicating that no phase transition occurs in the subsequent process of the NTP anode material.

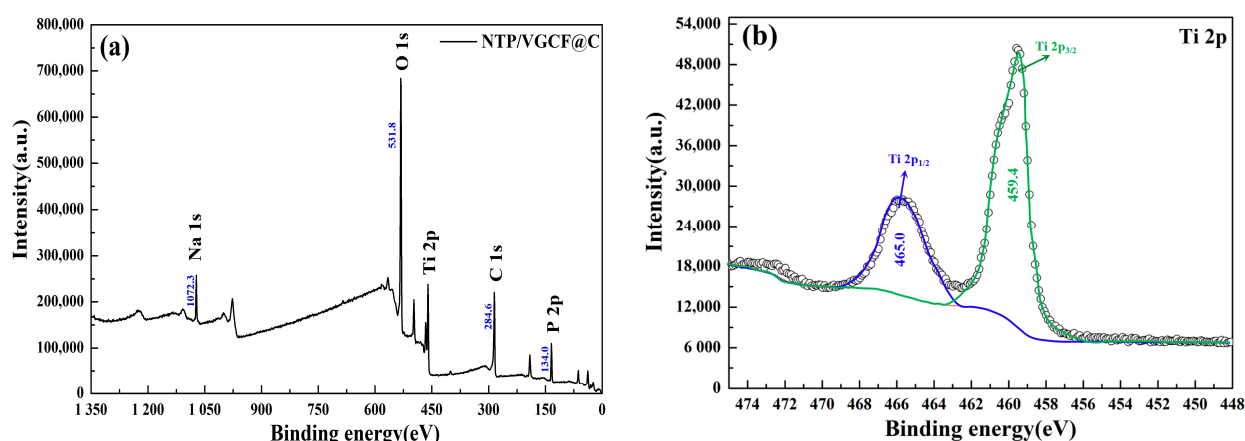


Figure 3. NTP/VGCF@C (a) total XPS spectrum, and (b) Ti 2p XPS spectrum.

3.2. Microstructure Analysis

Microstructure analysis was carried out on the prepared NTP/VGCF@C composite material. The SEM morphology, TEM morphology, EDS element distribution, and corresponding selective region electron diffraction (SAED) images of the prepared composite NTP/VGCF@C composite material are shown in Figure 4a–d.

It can be seen from Figure 4a that the prepared NTP/VGCF@C composite material shows polygonal particles ranging from 50–350 nm in size. The carbon fiber VGCF is evenly distributed among the particles, acting as a “bridge” connection between them. This is helpful for the construction of an effective conductive network. According to the TEM image (Figure 4b) analysis, the VGCF carbon fiber seems to be bound on the interface of the composite. The corresponding elemental distribution images are shown in Figure 4(b-1)–(b-5), and the qualitative test results of Na, Ti, P, O, and C in NTP/VGCF@C are 5.12, 26.2, 14.95, 39.08, and 14.16wt.%, respectively. The high amount of carbon and its whole area elemental distribution suggest that the carbon element mainly comes from the carbon coating on the NTP particles in the NTP/VGCF@C composite material.

High-resolution TEM (HRTEM) image analysis was conducted to obtain more microstructural information regarding the presence of carbon in the NTP/VGCF@C composite material. As shown in Figure 4c, there is a layer of amorphous carbon coated on the NTP particle with the interplanar spacing $d_{(104)} = 0.437$ nm. The carbon layer was measured to be about 6.5 nm. In addition, the carbon structure of the VGCF carbon fiber (002) plane ($d = 0.341$ nm) shows a stack of linear lamellae parallel to the carbon fiber surface. The diameter size of the carbon fiber is about 4.3 nm. From a higher magnification image (Figure 4(c-0)), it can be clearly seen that the VGCF lamellae structure is overlapped with the NTP lattice fringes, indicating a good contact at the interface between the carbon fiber and the nanoparticles in the NTP/VGCF@C composite material. This type of structure is helpful for increasing the interfacial strength of the connection between them, as well as the superiority of electron transport in the NTP/VGCF@C composite material.

The selective area electron diffraction (SAED) was used to obtain structural information for the aggregates of the NTP nanoparticles. The SAED pattern from the nanoparticle aggregates (Figure 4(d-0)) shows many discrete spots forming a series of rings, as shown in Figure 4d. Three discontinuous diffraction rings are selected and marked with a dotted line circle. According to the radius data obtained from these three circles, three d -values were calculated to be $d_1 = 0.210$ nm, $d_2 = 0.170$ nm, and $d_3 = 0.131$ nm and indexed as (119), (137), and (336) crystal planes of the NTP phase. Overall, the synthesized NTP/VGCF@C composite material is composed of NTP, VGCF, and amorphous carbon.

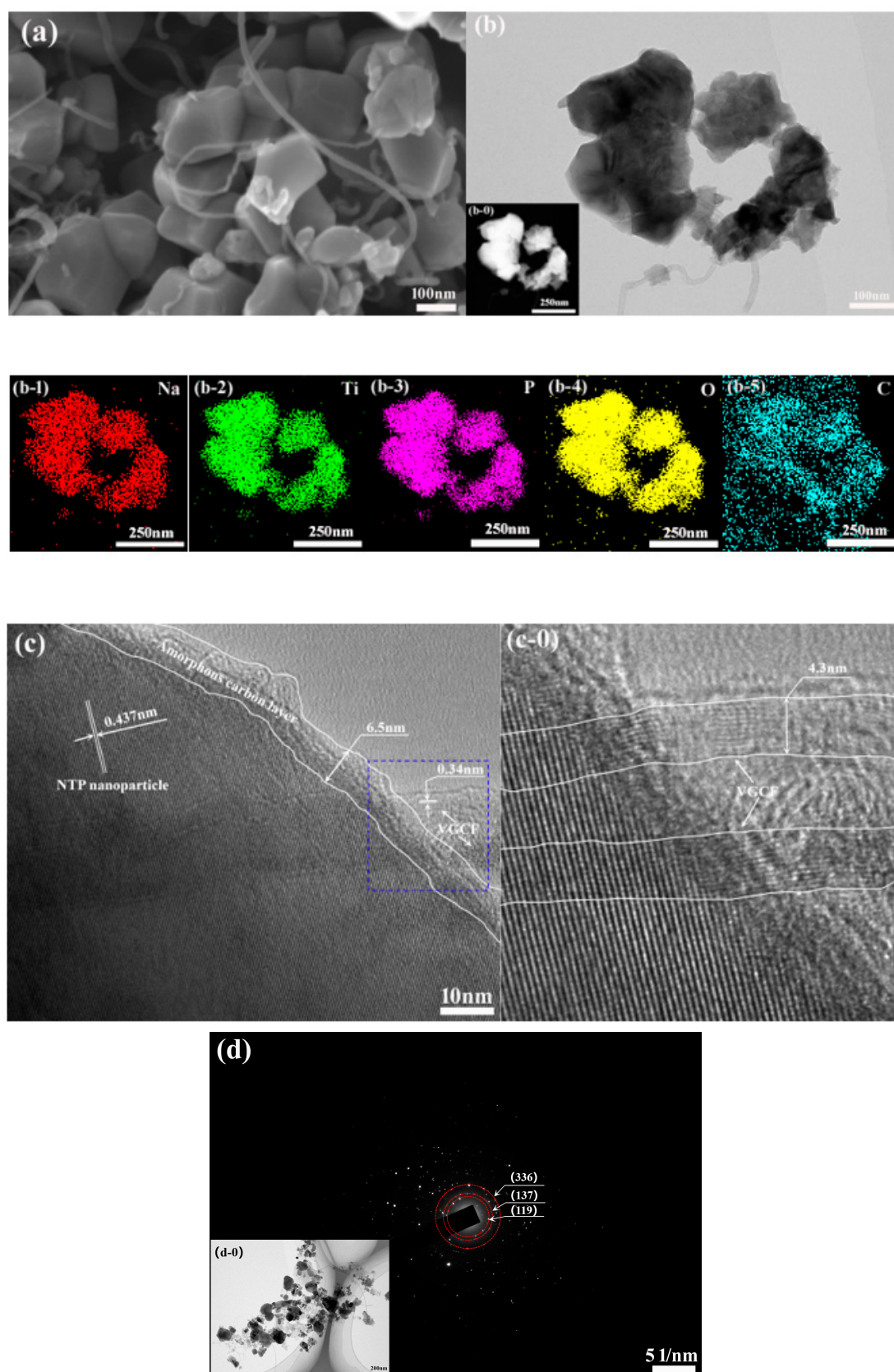


Figure 4. NTP/VGCF@C SEM morphology (a), TEM bright field image (b) and dark field image (inset, b-0), TEM-EDS scanning elements distribution (b-1–b-5), HRTEM lattice fringe images (c,c-0), TEM image showing a selected area of nanoparticle aggregates (d-0), and corresponding SAED pattern (d).

3.3. Cyclic Voltammetry and Electrochemical Impedance Spectroscopy Analysis

The cyclic voltammetry curves of the NTP/VGCF@C anode composite material are shown in Figure 5a. The Nyquist plots of the pure NTP and the NTP/VGCF@C anode composite materials are shown in Figure 5b.

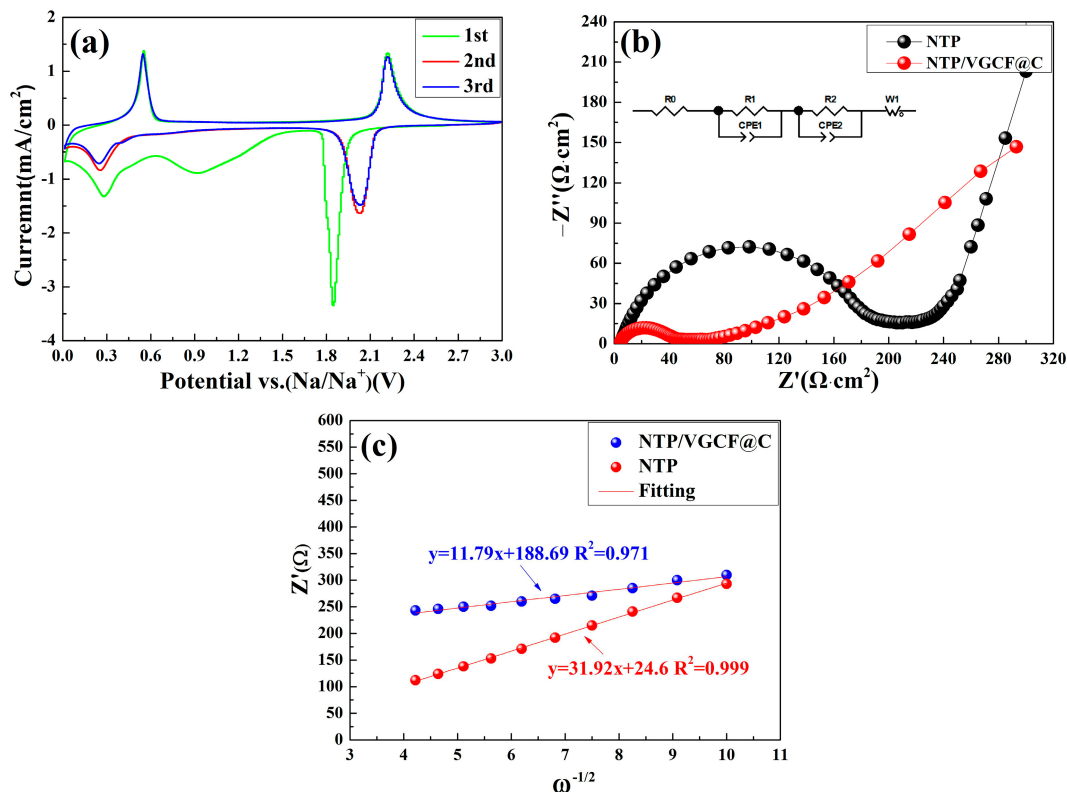


Figure 5. (a) CV curves of the NTP/VGCF@C anode composite material at the 1st, 2nd, and 3rd cycle; (b) Nyquist plots of the NTP and NTP/VGCF@C anode composite materials; (c) relationships between Z_{re} and $\omega^{-1/2}$ at low frequency.

From the curves of the first three cycles of cyclic voltammetry shown in Figure 5a, two broad peaks at 0.92 and 0.28 V can be seen during the initial discharge, but these are not present in subsequent cycles, when the potential range is 0.01–3.0 V vs. Na/Na⁺, and the scanning rate is 0.1 mV/s. These irreversible peaks are attributed to electrolyte breakdown and SEI film formation, causing the initial capacity loss. In addition, there are two distinct redox reaction peaks at 2.23/1.85 V and 0.55/0.27 V. 2.23/1.85 V, which correspond to the reversible oxidation/reduction process of Ti⁴⁺ ↔ Ti³⁺, while the redox peaks at 0.55/0.27 V correspond to the reversible oxidation/reduction process of Ti³⁺ ↔ Ti²⁺. It should be noted that almost all CV curves overlap each other in subsequent cycles, indicating a good electrochemical reversibility. It can be determined from the Figure 5b that the SEI film resistance (R_{SEI}) and electrode/electrolyte interface resistance (R_{ct}) values of NTP/VGCF@C are lower than those of the NTP. The electrochemical impedance results show that the addition of carbon fiber VGCF and amorphous carbon has a great effect on the structure of the entire electrode material, providing a better electrode dynamic process. The ionic mobility of the NTP/VGCF@C was significantly improved because the VGCF formed a conductive network in the anode composite material, and the VGCF, acting as a “bridge”, was attached by the amorphous carbon material between the active materials. The electrochemical properties of the materials can be improved. Moreover, the Warburg coefficient (Z_{re}) values of the NTP and NTP/VGCF@C are 31.92 Ω·S^{-1/2} and 11.79 Ω·S^{-1/2}, respectively (as shows in Figure 5b) [50]. This indicates that the presence of the VGCF and the amorphous carbon coating layer has a significant influence on the electron transport in the composite material; the conductivity of the NTP/VGCF@C electrode was significantly

improved. Therefore, the long cycle and rate performance of the NTP/VGCF@C anode composite material could be further improved.

3.4. Cycling Performance

The effects of pure NTP and its composite material on the cyclic stability and rate properties are shown in Figure 6a,b. The NTP/VGCF@C composite material is assembled as an anode, with LMO as a cathode, to create a 32 mAh LMO-NTP/VGCF@C aqueous sodium-ion soft pack battery system. The full battery cyclic performance is shown in Figure 6c.

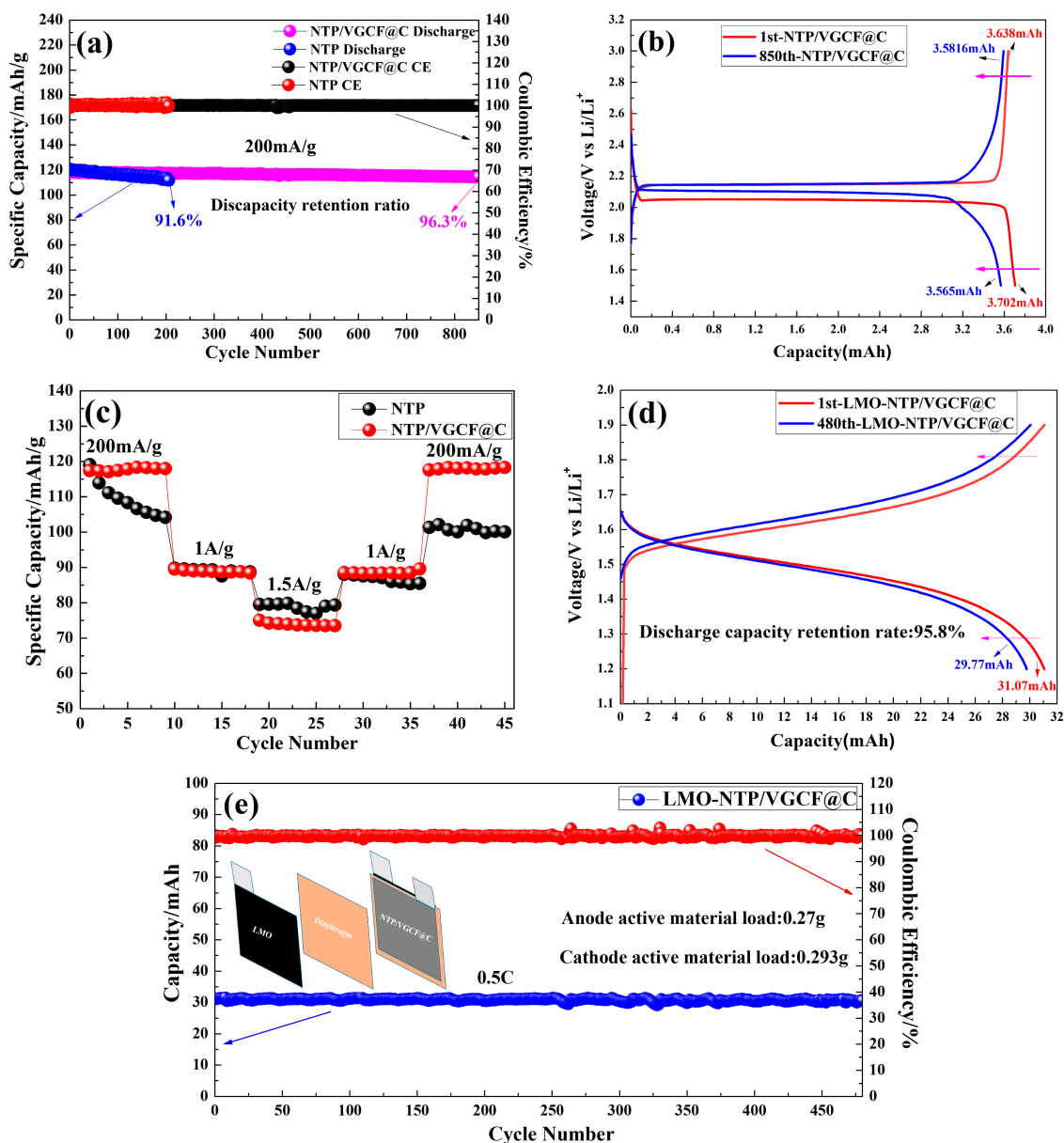


Figure 6. (a) Cycle performance of NTP and NTP/VGCF@C; (b) discharge/charge voltage profiles of NTP/VGCF@C in the 1st and 850th cycle; (c) rate performance of NTP and NTP/VGCF@C; (d) discharge/charge voltage profiles of an LMO-NTP/VGCF@C aqueous sodium-ion soft pack full battery in the 1st and 480th cycle; (e) cycle performance of an LMO-NTP/VGCF@C aqueous sodium-ion soft pack full battery.

The initial specific capacity of the pure NTP and NTP/VGCF@C composite material is 120.6 mAh/g and 118.4 mAh/g at a current density is 200 mA/g, respectively. After

200 cycles of charge and discharge, the reversible discharge capacity retention rates of NTP and NTP/VGCF@C are 91.6% and 99.2%, respectively. Obviously, the addition of carbon material increases the capacity retention by 7.6%. After 850 cycles of charge-discharge, the discharge capacity retention rate of the NTP/VGCF@C anode composite material is 96.3% (3.565 mAh/3.702 mAh), showing a better cycle stability (see Figure 6a,b). The rate capacity of these two materials at different current densities of 200 mA/g, 1A/g and 1.5A/g is shown in Figure 6c. When charging and discharging at a small rate to a large rate, and then returning to a small rate, the capacity of the composite material can be restored to the discharge capacity of 200 mA/g (117.4 mAh/g). However, pure NTP reverts to a small rate charge and discharge, and its capacity is only 84% of the initial capacity, showing a very poor rate performance. This suggests that the combination of carbon fiber and carbon coating not only maintains a robust structure for the composite material, but also acts as a conductive connection “bridge” between the NTP particles to ensure electronic transport between them. As for the full battery performance, the initial capacity of the LMO-NTP/VGCF@C aqueous sodium-ion soft pack full battery is 31.07 mAh at a rate of 0.5C, as shown in Figure 6d,e. After 480 cycles of charge and discharge, its reversible discharge capacity is 29.77 mAh, the discharge capacity retention rate is 95.8%, and its charging and discharging efficiency has been maintained at nearly 100%. Therefore, the LMO-NTP/VGCF@C aqueous sodium-ion battery system shows a long-term cycle stability performance, demonstrating a promising technique for green large-scale energy storage.

4. Conclusions

The composite anode material $\text{NaTi}_2(\text{PO}_4)_3/\text{VGCF}@C$ is prepared in two steps: pure NTP synthesis, followed by the addition of VGCF and carbon coating. The microstructure and electrochemical properties of the composite material have been analyzed. The conclusions are as follows:

- (1) The synthesized anode composite material is composed of NTP nanoparticles, VGCF, and an amorphous carbon coating layer. The VGCF nanofiber has a good interfacial contact with the NTP particles in the NTP/VGCF@C composite. The combination of VGCF with carbon coating makes the composite material more robust and conductive than pure NTP material.
- (2) After 200 cycles of charge-discharge, the reversible capacity retention rates of NTP and NTP/VGCF@C are 91.6% and 99.2% at a current of 200 mA/g, respectively; the addition of carbon material increases the capacity retention by 7.6%, and after 850 cycles of charge-discharge, the capacity retention rate of NTP/VGCF@C is 96.3%, which is much better than that of pure NTP.
- (3) The initial capacity of an LMO-NTP/VGCF@C aqueous sodium-ion full battery is 31.07 mAh at a rate of 0.5C. The reversible discharge capacity is 29.77 mAh after 480 cycles, and the discharge capacity retention rate is 95.8%. According to the results of this study, the LMO-NTP/VGCF@C aqueous sodium-ion full battery can be applied for large-scale green and safe energy storage.

Author Contributions: B.D.: Conceptualization, Formal analysis, Writing-original draft; M.L.: Data curation, Investigation; F.Z.: Methodology, Validation; Y.M.: Writing-review & editing; G.S.: Conceptualization, Validation; X.G.: Visualization; Y.C.: Resources; C.W.: Conceptualization. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Anhui Province Key R&D Program (grant number: 2022a05020040), the High-Level Scientific Research and Cultivation projects of Bengbu University (2021pyxm02, 00010312), an Anhui Natural Science Foundation grant (No. 1908085ME151), an Anhui Province high-end talent grant (DT18100044), and the National Foreign Expert Introduction Plan project (G20190219004), as well as University-Enterprise projects (LS0920, LS0921, RD18200058, 2019H3-7, 2020H3-8, 00011029). All individuals included in this section have consented to the acknowledgement. And The APC was funded by Anhui Province Key R&D Program (grant number: 2022a05020040).

Institutional Review Board Statement: Not applicable for studies not involving humans or animals.

Informed Consent Statement: Not applicable for studies not involving humans or animals.

Data Availability Statement: There are no new data were created.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Deng, Q.; Zheng, F.; Zhong, W.; Pan, Q.; Liu, M. P3-type $K_{0.5}Mn_{0.72}Ni_{0.15}Co_{0.13}O_2$ Microspheres as Cathode Materials for High Performance Potassium-Ion Batteries. *Chem. Eng. J.* **2020**, *392*, 123735. [\[CrossRef\]](#)
- Pan, Z.H.; Yang, J.; Yang, J.; Zhang, Q.H.; Zhang, H.; Li, X.; Kou, Z.K.; Zhang, Y.F.; Chen, H.; Yan, C.L.; et al. Stitching of $Zn_3(OH)_2V_2O_7 \cdot 2H_2O$ 2D nanosheets by 1D carbon nanotubes boosts ultrahigh rate for wearable quasi-solid-state zinc-ion batteries. *ACS Nano* **2020**, *14*, 842–853. [\[CrossRef\]](#) [\[PubMed\]](#)
- Shen, L.; Wang, Y.; Wu, F.; Shen, L.F.; Wang, Y.; Wu, F.X.; Moudrakovski, I.; van Aken, P.A.; Maier, J.; Yu, Y. Hierarchical metal sulfide/carbon spheres: A generalized synthesis and high sodium-storage performance. *Angew. Chem. Int. Ed.* **2019**, *58*, 7238–7243. [\[CrossRef\]](#) [\[PubMed\]](#)
- Zhou, X.; Zhang, Z.; Du, Y.; Wang, Q.C.; Shen, J. A Yolk Shell Structured $FePO_4$ Cathode for High-Rate and Long-Cycling Sodium-Ion Batteries. *Angew. Chem. Int. Ed.* **2020**, *817*, 17504–17510.
- Li, W.; Han, C.; Wang, W.; Xia, Q.; Chou, S.; Gu, Q.; Johannessen, B.; Liu, H.K.; Dou, S. Stress distortion restraint to boost the sodium-ion storage performance of a novel binary hexacyanoferrate. *Adv. Energy Mater.* **2019**, *10*, 1903006. [\[CrossRef\]](#)
- Weng, W.; Xu, J.; Lai, C.; Xu, Z.; Zhou, X. Uniform Yolk-Shell $Fe_7S_8@C$ Nanoboxes as a General Host Material for the Efficient Storage of Alkali Metal Ions. *J. Alloys Compd.* **2019**, *817*, 152732. [\[CrossRef\]](#)
- Gu, Z.Y.; Guo, J.Z.; Zhao, X.X.; Wang, X.T.; Xie, D.; Sun, Z.H.; Zhao, C.D.; Liang, H.J.; Li, W.H.; Wu, X.L. High-Ionicity Fluorophosphate Lattice via Aliovalent Substitution as Advanced Cathode Materials in Sodium-Ion Batteries. *InfoMat* **2021**, *3*, 694–704. [\[CrossRef\]](#)
- Deng, J.; Luo, W.B.; Chou, S.L.; Deng, J.Q.; Luo, W.B.; Chou, S.L.; Liu, H.K.; Dou, S.X. Sodium-ion batteries: From academic research to practical commercialization. *Adv. Energy Mater.* **2018**, *8*, 1701428. [\[CrossRef\]](#)
- Huang, Y.Y.; Zheng, Y.H.; Li, X.; Adams, F.; Luo, W.; Huang, Y.H.; Hu, L.B. Electrode materials of sodium-ion batteries toward practical application. *ACS Energy Lett.* **2018**, *3*, 1604–1612. [\[CrossRef\]](#)
- Bruce, P.G.; Scrosati, B.; Tarascon, J.M. Nanomaterials for rechargeable lithium batteries. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 2930–2946. [\[CrossRef\]](#)
- Deng, Q.; Zheng, F.H.; Zhong, W.T. Nanoscale Surface Modification of P2-Type $Na_{0.65}[Mn_{0.70}Ni_{0.16}Co_{0.14}]O_2$ Cathode Material for High-Performance Sodium-Ion Batteries. *Chem. Eng. J.* **2020**, *404*, 126446. [\[CrossRef\]](#)
- Fang, G.Z.; Zhou, J.; Pan, A.Q.; Liang, S.Q. Recent advances in aqueous zinc-ion batteries. *ACS Energy Lett.* **2018**, *3*, 2480–2501. [\[CrossRef\]](#)
- Zheng, G.Y.; Lin, Q.W.; Ma, J.B.; Zhang, J.; He, Y.B.; Tang, X.; Kang, F.Y.; Lv, W.; Yang, Q.H. Ultrafast Presodiation of Graphene Anodes for High-Efficiency and High-Rate Sodium-Ion Storage. *InfoMat* **2021**, *3*, 1445–1454. [\[CrossRef\]](#)
- Yan, Z.H.; Yang, Q.W.; Wang, Q.H.; Ma, J.M. Nitrogen Doped Porous Carbon as Excellent Dual Anodes for Li- and Na-Ion batteries. *Chin. Chem. Lett.* **2020**, *31*, 583–588. [\[CrossRef\]](#)
- Park, C.M.; Sohn, H.J. Black phosphorus and its composite for lithium rechargeable batteries. *Chem. Commun.* **2014**, *50*, 5435–5437.
- Lian, S.T.; Lv, J.S.; Yu, Q.; Hu, G.W.; Chen, Z.; Zhou, L.; Mai, L.Q. Recent progress on TiO_2 -Based anode materials for sodium-ion batteries. *J. Electrochem.* **2019**, *25*, 31–44.
- Massaro, A.; Muñoz-García, A.B.; Maddalena, P.; Bella, F.; Meligrana, G.; Gerbaldi, C.; Pavone, M. First-principles study of Na insertion at TiO_2 anatase surfaces: New hints for Na-ion battery design. *Nanoscale Adv.* **2020**, *2*, 2745–2751. [\[CrossRef\]](#)
- Longoni, G.; Cabrera, R.L.P.; Polizzi, S.; D'Arienzo, M.; Mari, C.M.; Cui, Y.; Ruffo, R. Shape controlled TiO_2 nanocrystals for Na-ion battery electrodes: The role of different exposed crystal facets on the electrochemical properties. *Nano Lett.* **2017**, *17*, 992–1000. [\[CrossRef\]](#)
- Bella, F.; Muñoz-García, A.B.; Meligrana, G.; Lamberti, A.; Destro, M.; Pavone, M.; Gerbaldi, C. Unveiling the controversial mechanism of reversible Na storage in TiO_2 nanotube arrays: Amorphous versus anatase TiO_2 . *Nano Res.* **2017**, *10*, 2891–2903. [\[CrossRef\]](#)
- He, B.; Yin, K.B.; Gong, W.B.; Xiong, Y.W.; Zhang, Q.C.; Yang, J.; Wang, Z.X.; Wang, Z.; Chen, M.X.; Man, P.; et al. $NaTi_2(PO_4)_3$ hollow nanoparticles encapsulated in carbon nanofibers as novel anodes for flexible aqueous rechargeable sodium-ion batteries. *Nano Energy* **2021**, *82*, 105764. [\[CrossRef\]](#)
- Ren, W.; Chen, X.; Zhao, C. Ultrafast aqueous potassium-ion batteries cathode for stable intermittent grid-scale energy storage. *Adv. Energy Mater.* **2018**, *8*, 1801413. [\[CrossRef\]](#)
- Lee, M.H.; Kim, S.J.; Chang, D.; Kim, J.; Moon, S.; Oh, K.; Park, K.Y.; Seong, W.M.; Park, H.; Kwon, G.; et al. Toward a low-cost high-voltage sodium aqueous rechargeable battery. *Mater. Today* **2019**, *29*, 26–36. [\[CrossRef\]](#)
- Fang, Y.J.; Xiao, L.F.; Qian, J.F.; Cao, Y.L.; Ai, X.P.; Huang, Y.H.; Yang, H.X. 3D graphene decorated $NaTi_2(PO_4)_3$ microspheres as a superior high-rate and ultracycle-stable anode material for sodium ion batteries. *Adv. Energy Mater.* **2016**, *6*, 1502197. [\[CrossRef\]](#)

24. Wu, M.G.; Ni, W.; Hu, J.; Ma, J.M. NASICON-structured $\text{NaTi}_2(\text{PO}_4)_3$ for sustainable energy storage. *Nano-Micro Lett.* **2019**, *11*, 44. [\[CrossRef\]](#)
25. Fu, L.; Xue, X.; Tang, Y.G.; Sun, D.; Xie, H.L.; Wang, H.Y. Size controlling and surface engineering enable $\text{NaTi}_2(\text{PO}_4)_3/\text{C}$ outstanding sodium storage properties. *Electrochim. Acta* **2018**, *289*, 21–28. [\[CrossRef\]](#)
26. Hsieh, Y.Y.; Fang, Y.B.; Daum, J.; Kanakaraj, S.N.; Zhang, G.Q.; Mishra, S.; Gbordzoe, S.; Shanov, V. Bio-inspired, nitrogen doped CNT-graphene hybrid with amphiphilic properties as a porous current collector for lithium-ion batteries. *Carbon* **2019**, *145*, 677–689. [\[CrossRef\]](#)
27. Bakierska, M.; Lis, M.; Pacek, J.; Świątosławski, M.; Gajewska, M.; Tąta, A.; Proniewicz, E.; Molenda, M. Bio-derived carbon nanostructures for high-performance lithium-ion batteries. *Carbon* **2019**, *145*, 426–432. [\[CrossRef\]](#)
28. Ji, L.W.; Meduri, P.; Agubra, V.; Xiao, X.C.; Alcoutlabi, M. Graphene-based nanocomposites for energy storage. *Adv. Energy Mater.* **2016**, *6*, 1502159. [\[CrossRef\]](#)
29. Massaro, A.; Pecoraro, A.; Muñoz-García, A.B.; Pavone, M. First-Principles study of Na intercalation and diffusion mechanisms at 2D MoS_2 /graphene interfaces. *J. Phys. Chem. C* **2021**, *125*, 2276–2286. [\[CrossRef\]](#)
30. Wu, X.W.; Li, Y.H.; Zhao, S.Y.; Zeng, F.H.; Peng, X.C.; Xiang, Y.H.; Ruan, Q.Y.; Gao, F.; He, T.; Wu, J.H. Fabrication of F-doped, C-coated NiCo_2O_4 nanocomposites and its electrochemical performances for lithium-ion batteries. *Solid State Ion.* **2019**, *334*, 48–55. [\[CrossRef\]](#)
31. Jiang, Y.Q.; Zhu, J.; Wang, H.Y.; Li, Y.H.; Zhou, H.Z.; Meng, W.; Dai, L.; Wang, L.; He, Z.X. N-doped carbon coated $\text{LiTi}_2(\text{PO}_4)_3$ as superior anode using PANi as carbon and nitrogen bi-sources for aqueous lithium ion battery. *Electrochim. Acta* **2018**, *279*, 279–288.
32. Li, L.L.; Wen, Y.H.; Zhang, H.; Ming, H.; Pang, J.; Zhao, P.C.; Cao, G.P. Core-Shell structured $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ anode for aqueous lithium-ion batteries. *ChemElectroChem* **2019**, *6*, 1908–1914. [\[CrossRef\]](#)
33. Wang, D.X.; Liu, Q.; Chen, C.J.; Li, M.L.; Meng, X.; Bie, X.F.; Wei, Y.J.; Huang, Y.H.; Du, F.; Wang, C.Z.; et al. NASICON-structured $\text{NaTi}_2(\text{PO}_4)_3/\text{C}$ nanocomposite as the low operation-voltage anode material for high-performance sodium-ion batteries. *ACS Appl. Mater. Interfaces* **2016**, *8*, 2238–2246. [\[CrossRef\]](#)
34. Deng, Q.; Cheng, Q.; Liu, X.Z. 3D porous Fluorine-Doped $\text{NaTi}_2(\text{PO}_4)_3/\text{C}$ as High-Performance Sodium-Ion battery anode with broad temperature adaptability. *Chem. Eng. J.* **2022**, *430*, 132710. [\[CrossRef\]](#)
35. Pang, G.; Yuan, C.Z.; Nie, P.; Ding, B.; Zhu, J.J.; Zhang, X.G. Synthesis of NASICON-type $\text{NaTi}_2(\text{PO}_4)_3$ -graphene nanocomposite as an anode for aqueous rechargeable Na-ion batteries. *Nanoscale* **2014**, *6*, 6328–6334. [\[CrossRef\]](#)
36. Wise, A.; Wu, W.; Yan, J. Using intimate carbon to enhance the performance of $\text{NaTi}_2(\text{PO}_4)_3$ anode materials: Carbon nanotubes vs. graphite. *J. Electrochem. Soc.* **2014**, *161*, A561–A567.
37. Jiang, Y.; Zeng, L.C.; Wang, J.Q.; Li, W.H.; Pan, F.S.; Yu, Y. A carbon coated NASICON structure material embedded in porous carbon enabling superior sodium storage performance: $\text{NaTi}_2(\text{PO}_4)_3$ as an example. *Nanoscale* **2015**, *7*, 14723–14729. [\[CrossRef\]](#)
38. Jung, Y.H.; Hong, S.T.; Kim, D.K. Electrochemical sodium-ion intercalation properties of $\text{Na}_{2.7}\text{Ru}_4\text{O}_9$ in nonaqueous and aqueous electrolytes. *J. Electrochem. Soc.* **2013**, *160*, A897–A900. [\[CrossRef\]](#)
39. Beck, F.; Rüetschi, P. Rechargeable batteries with aqueous electrolytes. *Electrochim. Acta* **2000**, *45*, 2467–2482. [\[CrossRef\]](#)
40. Zhang, Q.; Liao, C.Y.; Zhai, T.Y.; Li, H.Q. A high rate 1.2 V aqueous sodium-ion battery based on all NASICON structured $\text{NaTi}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$. *Electrochim. Acta* **2016**, *196*, 470–478. [\[CrossRef\]](#)
41. Wang, H.B.; Zhang, T.R.; Chen, C.; Ling, M.; Lin, Z.; Zhang, S.Q.; Pan, F.; Liang, C.D. High-performance aqueous symmetric sodium-ion battery using NASICON-structured $\text{Na}_2\text{VTi}(\text{PO}_4)_3$. *Nano Res.* **2018**, *11*, 490–498. [\[CrossRef\]](#)
42. Shanbhag, S.; Bootwala, Y.; Whitacre, J.F.; Mauter, M.S. Ion transport and competition effects on $\text{NaTi}_2(\text{PO}_4)_3$ and $\text{Na}_4\text{Mn}_9\text{O}_{18}$ selective insertion electrode performance. *Langmuir ACS J. Surf. Colloids* **2017**, *33*, 12580–12591. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Duan, B.; Wang, F.; Tamirat, A.G.; Suo, L.M.; Wang, Y.G.; Wang, C.S.; Xia, Y.Y. Progress in aqueous rechargeable sodium-Ion batteries. *Adv. Energy Mater.* **2018**, *8*, 1703008. [\[CrossRef\]](#)
44. Wu, X.Y.; Sun, M.Y.; Shen, Y.F.; Qian, J.F.; Cao, Y.L.; Ai, X.P.; Yang, H.X. Energetic aqueous rechargeable sodium-ion battery based on $\text{Na}_2\text{CuFe}(\text{CN})_6\text{-NaTi}_2(\text{PO}_4)_3$ intercalation chemistry. *ChemSusChem* **2014**, *7*, 407–411. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Whitacre, J.F.; Shanbhag, S.; Mohamed, A.; Polonsky, A.; Carlisle, K.; Gulakowski, J.; Wu, W.; Smith, C.; Cooney, L.; Blackwood, D.; et al. A polyionic, large-format energy storage device using an aqueous electrolyte and thick-format composite $\text{NaTi}_2(\text{PO}_4)_3$ /activated carbon negative electrodes. *Energy Technol.* **2015**, *3*, 20–31. [\[CrossRef\]](#)
46. Li, Z.; Young, D.; Xiang, K.; Carter, W.C.; Chiang, Y.M. Towards high power high energy aqueous sodium-ion batteries: The $\text{NaTi}_2(\text{PO}_4)_3/\text{Na}_{0.44}\text{MnO}_2$ system. *Adv. Energy Mater.* **2013**, *3*, 290–294. [\[CrossRef\]](#)
47. Wang, L.; Huang, Z.N.; Wang, B.; Liu, G.J.; Cheng, M.; Yuan, Y.F.; Luo, H.; Gao, T.T.; Wang, D.L.; Yassar, R.S. Purifying the phase of $\text{NaTi}_2(\text{PO}_4)_3$ for enhanced Na^+ storage properties. *ACS Appl. Mater. Interfaces* **2019**, *11*, 10663–10671. [\[CrossRef\]](#)
48. Vincent, M.; Avvaru, V.S.; Haranczyk, M.; Etacheri, V. High-performance Mg-Li hybrid batteries based on pseudocapacitive anatase $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-y}$ nanosheet cathodes. *ChemSusChem* **2022**, *15*, e202102562. [\[CrossRef\]](#)

49. Vincent, M.; Avvaru, V.S.; Rodríguez, M.C.; Haranczyk, M.; Etacheri, V. High-rate and ultralong-life Mg-Li hybrid batteries based on highly pseudocapacitive dual-phase TiO₂ nanosheet cathodes. *J. Power Sources* **2021**, *506*, 230118. [[CrossRef](#)]
50. Ding, B.; Huang, X.N.; Cai, Z.F.; Ma, Y.Z.; Song, G.S.; Yang, W.D.; Wen, C. Effects of binders on electrochemical properties of high capacity silicon composite anodes. *Inorg. Chem. Commun.* **2020**, *113*, 107771. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.