Sodium-ion batteries with good electrochemical performance are of great significance for grid-scale energy storage applications. Herein, an aqueous rechargeable Na-ion battery has been fabricated with multiwalled carbon nanotube (MWNT)-containing NaTi$_2$(PO$_4$)$_3$/MWNTs nanocomposites as the anode and Na$_{0.44}$MnO$_2$ nanorods as the cathode in a 1 M aqueous Na$_2$SO$_4$ electrolyte and the device was carefully studied. Owing to the open framework structures (containing large interstitial sites) that both NaTi$_2$(PO$_4$)$_3$ and Na$_{0.44}$MnO$_2$ possess, the fast Na-ions will facilitate free transport. Benefiting from their unique structural features, the aqueous battery system exhibited an average charge and discharge voltage of approximately 1.1 V, a high energy density of 58.7 Wh kg$^{-1}$ in terms of total electroactive materials, and could deliver a reversible capacity of approximately 50 mAh g$^{-1}$ after 300 cycles at 2 C rate; the corresponding coulombic efficiency was nearly constant at approximately 95%. These results, together with the safety and cost perspectives of aqueous electrolytes indicated that the aqueous Na-ion battery may be a good candidate for safe, inexpensive, high-power energy storage systems.

Introduction

With the development of renewable and cleaner energy sources, such as solar arrays, wind farms, and wave energy, there has been an ever increasing demand for a large-scale energy storage systems, storing the off-peak electricity and releasing the stored energy during the on-peak periods.$^{[1-4]}$ For this application, several different types of battery technology have been proposed for large-scale energy storage.$^{[5]}$ Especially, Li-ion batteries (LIBs) have received great commercial success due to their high energy density and large power capabilities compared to other energy storage systems.$^{[6-8]}$ However, the large-scale demand for Li will exacerbate the growing price of Li resources because of the low abundance and uneven distribution of Li resources in the Earth’s crust.$^{[9]}$

Compared with Li, Na has similar physicochemical properties and the fourth most abundance reserve in nature. Thus, rechargeable Na-ion batteries (NIBs) could be a good candidate for large-scale energy storage applications, owing to the similar energy density to LIBs and low cost of sodium resources.$^{[10]}$ Moreover, developing high-performance Na-ion batteries is another important aspect in further decreasing the cost and addressing safety issues.$^{[11-14]}$ Comparing with expensive organic liquid electrolytes, aqueous electrolytes have advantages in cost, safety, and environmental benignity, and they are one of the most promising systems used in large-scale energy storage.$^{[15-17]}$

Due to the above-mentioned advantages, various cathode and anode materials, including both inorganic and organic materials, have been identified as possible candidates for the insertion of Na ions.$^{[1,17]}$ Recently, considerable attention has been devoted to explore viable Na host materials for aqueous Na-ion batteries.$^{[9]}$ Yang’s group reported an aqueous “rocking-chair” type rechargeable battery using NASICON-type NaTi$_2$(PO$_4$)$_3$ and open-framework-structured Prussian blue analogues as anode and cathode, respectively, representing good rate and cycle life with a theoretical energy density of approximately 45 Wh kg$^{-1}$.$^{[18,19]}$ Liu et al. constructed a rechargeable battery based on NaTi$_2$(PO$_4$)$_3$–Ni$_2$Zn$_3$HCF in an aqueous Na$^+/K^+$ mixed-ion electrolyte, which delivered a specific energy of 53 Wh kg$^{-1}$, and the average operating voltage of the battery was as high as 1.45 V, which was one of the highest recorded among current aqueous batteries based on sodium-ion and/or potassium-ion technologies.$^{[20]}$ Later, Kim et al. built a full-cell using a disodium naphthalenediimide (SNDI) anode and Prussian blue derivative Co-CuHCF cathode in neutral aqueous electrolytes. This full-cell exhibited an average discharge voltage of approximately 1.1 V and an energy density of 26 Wh kg$^{-1}$.$^{[21]}$ With the excep-
tion of using Prussian blue analogue as cathode, Na$_2$MnO$_2$

could be used as the positive electrode materials in aqueous

 rechargeable Na-ion batteries. Chiang et al. constructed a Na$_{0.44}$Ti$_2$(PO$_4$)$_3$–Na$_0.24$MnO$_2$ two-electrode cell in 1 M Na$_2$SO$_4$

electrolyte at pH 11, which was initially discharged to 0.8 V

 providing approximately 40 mAh g$^{-1}$ capacity at 1 C rate.\[25\]

Chiang’s group reported high-energy-density aqueous Na-ion

batteries based on tunnel-structured Na$_{0.44}$MnO$_2$ and NASI-

CON-type Na$_{0.65}$Ti$_2$(PO$_4$)$_3$, which exhibited excellent cycle life

over 1000 cycles and delivered a theoretical energy density of

approximately 33 Wh kg$^{-1}$.\[16\] Whitacre et al. also fabricated

an aqueous full-cell with carbon coating Na$_{0.65}$Ti$_2$(PO$_4$)$_3$ as

anode and Na$_{0.44}$MnO$_2$ as cathode, showing potential for

practical battery applications in terms of cycle life and rate

performance.\[23,24\] In the full-cell of the Na$_{0.65}$Ti$_2$(PO$_4$)$_3$–

Na$_0.44$MnO$_2$ system, both groups were in agreement that the

low electronic conductivity of the Na$_{0.65}$Ti$_2$(PO$_4$)$_3$ anode

was rate limiting, and the anode could remove the electronic con-

ductivity limitation through optimizing the synthesis of

Na$_{0.65}$Ti$_2$(PO$_4$)$_3$–carbon composite, obtaining ultrafast rate ca-

pability and superior high-rate cycling stability.

In this work, we report an aqueous rechargeable Na-ion

battery system using well-crystallized multiwalled carbon

nanotube (MWNT)-containing Na$_{0.65}$Ti$_2$(PO$_4$)$_3$/MWNTs nano-

composites and Na$_{0.44}$MnO$_2$ nanorods as anode and cathode,

respectively, which achieves the electrochemical perform-

ances of the “rocking-chair” type Na-ion battery.\[19\] The two

materials both possess open framework structures containing

large interstitial sites that allow for fast insertion/extraction

of Na ions with little crystallographic lattice strain, ensuring

long cycle life and high-rate capability. The Na$_{0.65}$Ti$_2$(PO$_4$)$_3$/

MWNTs nanocomposites were synthesized by using the sol-

vothermal method; and the well-crystallized Na$_{0.44}$MnO$_2$

nanorods were prepared by using a solid-state method.

The two new developed active electrode materials performed ex-

tremely well in both half-cell and full-cell configurations with

an aqueous electrolyte, demonstrating the potential of aque-

ous Na-ion batteries for grid-scale energy storage systems.

**Results and Discussion**

To realize a workable aqueous Na-ion battery, it is necessary

for the anode to be in a Na-deficient condition and cathode

should be designed in a suitable Na-rich state, both of which

have sufficient Na storage capacity, thus enabling a “rocking-

chair” Na-ion battery. Generally, an anode suitable for prac-

tical applications in the aqueous electrolyte must have suffi-

cient Na-storage capacity and a low redox potential for Na-

ion insertion above the reversible potential of hydrogen (RHE).

In the aqueous Na$_2$SO$_4$ electrolyte, the hydrogen evolution

reaction occurred below $-1.16$ V (vs. SCE).\[25\] above which the Na-insertion reaction could proceed without

much interference. The Na-deficient Na$_{0.44}$Ti$_2$(PO$_4$)$_3$ appeared

to be a suitable choice because of its ability to accommodate

two Na ions per molecular unit and its appropriately low po-

tential of $-0.85$ V (vs. SCE).\[18,25\] Because of the low elec-

tronic conductivity of the Na$_{0.44}$Ti$_2$(PO$_4$)$_3$ anode,\[19\] we prepared

Na$_{0.65}$Ti$_2$(PO$_4$)$_3$/MWNTs nanocomposites to improve its elec-

tronic conductivity.

Figure 1a shows the Rietveld refinement of the XRD pattern for the Na$_{0.65}$Ti$_2$(PO$_4$)$_3$/MWNTs nanocomposites. It con-

firmed the successful synthesis of well-crystallized NASI-

CON-type Na$_{0.65}$Ti$_2$(PO$_4$)$_3$, space group: R-3c (167). Moreover,

all refinements gave small values of factors $R_p=8.37$, $R_w=

6.34$, $R_s=3.44$, and $S=1.18$, indicative of a good and reliable

structural analysis. The NASICON-type phase had lattice pa-

rameters of $a=0.84889$ (6) nm, $c = 2.18283$ (7) nm and $V=

1.36224 (2)$ nm$^3$, obtained from the refinement (see Table S1, Support-

ing Information), close to the values reported in ear-

lier references.\[26\] However, the typical diffraction peaks of

the MWNTs were not observed in the XRD pattern, which

might be caused by the low content of MWNTs and the

highly crystalline nature of Na$_{0.65}$Ti$_2$(PO$_4$)$_3$. Thermogravi-

metic analysis (TG) was used to determine the amount of MWNTs

in the nanocomposites. The result indicated that the hybrid

materials had a chemical composition of 95.0 wt% Na$_{0.65}$

(PO$_4$)$_3$ and 5.0 wt% MWNTs (see Figure S1, Supporting

Information).

A schematic illustration of the NASICON-type Na$_{0.65}$

(PO$_4$)$_3$ phase is given in Figure 1b. The NASICON-type phase consisted of an open 3D framework of TiO$_6$ octahedra

and PO$_4$ tetrahedra, where 2 TiO$_6$ octahedra were separated

by 3 PO$_4$ tetrahedra, with which they had no shared edges or

shared faces, only sharing all their corner oxygen atoms. The

open 3D framework had two types of interstitial sites: one

(A1) in elongated octahedral oxygen environment at the

intersection of three conduction channels, and the other (A2)

among the (A1) and three 8-coordinate sites environment at

the intersection of three conduction channels.\[27,28\] In the absence

of motion, Na ions preferably occupied the octahedral A1 sites;

during the chemical intercalation of sodium in Na$_{0.65}$Ti$_2$(PO$_4$)$_3$, Na

ions actually occupied octahedral A2 sites, forming a Na$_{0.65}$Ti$_2$(PO$_4$)$_3$ phase.\[29,30\] Na$_{0.65}$Ti$_2$(PO$_4$)$_3$ was able to deliver

a theoretical capacity of 132.8 mAh g$^{-1}$ assuming that completed

transformation to Na$_{0.65}$Ti$_2$(PO$_4$)$_3$ is achievable.\[16,31\]

The morphological features of the Na$_{0.65}$Ti$_2$(PO$_4$)$_3$/MWNTs nanocomposites were observed by field-emission scanning electron microscopy (FESEM) and transmission electron mi-

croscopy (TEM), illustrated in Figure 2. The FESEM image in

Figure 2a showed irregular nanoparticles (NPs) interconnected

each other in the size in the range of 200–400 nm and

\[\begin{align*}
\text{Figure 1. a) Rietveld refinement of the observed XRD pattern for the Na}_0.65\text{Ti}_2\text{(PO}_4\text{)}_3\text{ phase: Calculated (line) and observed (+) X-ray diffraction patterns for Na}_0.65\text{Ti}_2\text{(PO}_4\text{)}_3. Vertical bars below the pattern show the positions of all possible reflection peaks of the Na}_0.44\text{Ti}_2\text{(PO}_4\text{)}_3\text{ phase. b) A schematic illustration of the framework crystal structure of Na}_0.65\text{Ti}_2\text{(PO}_4\text{)}_3\text{ phase viewed along the b* axis.}
\end{align*}\]
MWNTs homogeneously dispersed among the aggregated NPs. To further examine the architecture of the NaTi2(PO4)3/MWNTs, the nanocomposites were investigated by TEM and HRTEM. From Figure 2b, it can be seen that NaTi2(PO4)3 NPs were anchored on MWNTs, which enabled rapid electron transport through the underlying MWNTs to the NPs, resulting in superior rate capability. Figure 2c shows the HRTEM image of NaTi2(PO4)3/MWNTs nanocomposites. As can be seen, there were two kinds of lattice fringes with a lattice spacing of approximately 0.343 and 0.338 nm corresponding to the (202) plane of NaTi2(PO4)3 and the (002) crystalline plane of the MWNTs, respectively, confirming the microstructure of the NaTi2(PO4)3/MWNTs. For further investigation, the distribution of NaTi2(PO4)3 NPs and MWNTs, a bright-field STEM image, and elemental mapping of the corresponding regions are shown in Figure 2d and e, indicating the elemental spatial distribution of C, P, O, Ti, and Na, respectively. This results indicate that the P, O, Ti, and Na were uniformly distributed over the surface of the NaTi2(PO4)3 NPs and the images were overlayed with each other. Meanwhile, the distributions of these chemical elements were in the range of the EDS mapping of C, which were consistent with targeted NaTi2(PO4)3/MWNTs structure. EDS mapping indicated that the atomic ratio of Na/Ti is approximately 1:2. The Na/Ti ratio of the NPs was the same as that of NaTi2(PO4)3/MWNTs.

The main CV feature of the NaTi2(PO4)3/MWNTs electrode in Figure 3a is a pair of redox peaks located at –0.88 (red.) and –0.76 V (ox.) (vs. SCE), indicating the reversible insertion/extraction reaction of Na ions in the NaTi2(PO4)3 lattice (NaTi2(PO4)3 + 2Na+ + 2e– → Na2Ti2(PO4)3).[18,31] Meanwhile, the good overlapping of the curves for the subsequent cycles suggests that NaTi2(PO4)3/MWNTs had good cycling stability in the aqueous electrolyte. More significantly, it was found that the redox reaction could take place at potentials much more positive than the H2 evolution potential of water in 1 M Na2SO4 electrolyte at pH 7. The low Na ion insertion/extraction potential was located at the lower limit of the electrochemical window of the aqueous electrolyte. Therefore, it should be suitable to use the NASICON-type NaTi2(PO4)3/MWNTs as anode material for practical applications.

The charge–discharge curves of the NaTi2(PO4)3/MWNTs electrode at a rate of 2 C for different cycles are shown in Figure 3b. The discharge capacity was approximately 122 mAhg–1 and had a clear discharge voltage plateau at a potential of approximately –0.83 V (vs. SCE), suggesting an electrochemical reversibility and rapid kinetics for the Na ion insertion in the electrode; the charge capacity was approximately 103 mAhg–1 and the charge reaction proceeded mostly at a very flat plateau of –0.76 V (vs. SCE), which was consistent with the CV curves. In addition, the voltage difference between charge and discharge curves showed that polarizations occur, certainly due to low electronic conductivity, even after improving the electronic conductivity by adding MWNTs.

Meanwhile, the NaTi2(PO4)3/MWNTs electrode was further investigated in terms of charge–discharge cycling performance at 2 C for 200 cycles (shown in Figure 3c). The NaTi2(PO4)3/MWNTs exhibited excellent cycling performance. The discharge capacity in the first cycle was 123.4 mAhg–1, and after 200 charge-discharge cycles, the capacity remained at 92.1 mAhg–1 at this high rate. Calculated from the discharge capacity–charge capacity, the coulombic efficiency in this long cycle period nearly kept constant at approximately 86%.

Then, the reversible capabilities of the NaTi2(PO4)3/MWNTs electrode were progressively charged/discharged in serial stages with different current rates from 2 to 20 C, as presented in Figure 3d. The specific discharge capacity was approximately 120 mAhg–1 obtained at a rate of 2 C, and the specific discharge capacity reduced to 90 and 80 mAhg–1 at rates of 5 and 10 C, respectively. At the high rate of 20 C, the specific discharge capacity decreased to approximately 60 mAhg–1. After 120 cycles, the electrode could still deliver a reversible capacity of 105 mAhg–1, which was further charged-discharged at 2 C for another 30 cycles. With increasing current density, the corresponding coulombic efficiencies were improved and even reached to approximately...
98% at rate of 20 C. This result might be attributed to the stability of NASICON-type framework crystal structure of NaTi2(PO4)3/MWNTs,[16,25] possessing good crystallinity, the electronic conductivity of the MWNTs, and high ionic conductivity.[32,33]

In the search for a suitable cathode for aqueous Na-ion batteries, we focused on Na-rich Na0.44MnO2 because of its 3D-type tunnel structure, redox reversibility, and ability to function within the potential window of water (i.e., within the O2 evolution potentials). On the basis of these, we synthesized Na0.44MnO2 and examined its Na-insertion behaviors in an aqueous electrolyte.

The well-crystallized Na0.44MnO2 nanorods were synthesized by a classic solid-state reaction without any impurity phase, which was isostructural to Na4Mn4Ti5O18.[34] It had been evidenced by the X-ray diffraction (XRD) pattern (see Figure S2, Supporting Information). The structural model [orthorhombic, space group (SG): Pbam] was used for the refinement. The refinement based on the orthorhombic symmetry was converged at \( a = 0.91043 \) (9), \( b = 2.6406 \) (3), \( c = 0.28277 \) (1) nm and \( V = 0.67982 \) (1) nm\(^3\) with satisfactory convergence factors \( R_wp = 5.99, R_p = 4.67, S = 1.58 \) (see Table S2, Supporting Information), which was consistent with the refinement results of the previous reports.[35,36]

A schematic structure of the refined crystal structure of Na0.44MnO2 nanorods projected along the c axis was shown in Figure S3 in the Supporting Information. It was observed that the crystal structure of Na0.44MnO2 was made up of two double chains and one triple chain of edge-sharing MnO\(_6\) octahedra and a single chain of edge-sharing MnO\(_5\) square-pyramids that shared vertices to produce an open framework containing large tunnels along the c-axis direction, with three types of Na-ions located in the tunnel. Na1 sites were located in the smaller tunnels whereas Na2 and Na3 were situated in the large S-shaped tunnels.[35,36] The Mn-ions were located in two different environments: all Mn\(^{1+}\) ions and half of the Mn\(^{3+}\) ions were in octahedral sites (MnO\(_6\)), whereas the other Mn\(^{3+}\) ions were gathered in a square-pyramidal environment (MnO\(_5\)).[37] According to this open framework structure, these tunnels served as the main path for the free transport of Na-ions, which occurred mainly along the c-axis.[37] The entitled Na\(_{0.44}/\text{Mn}\) ratio corresponded to almost fully filling of the Na1 sites, whereas the S-shaped tunnels were approximately half filled.[36] It had been reported that if the Na content in the Na\(_x\)MnO\(_2\) system was below a certain level (\( x < 0.5 \)), the three-dimensional framework crystal structure with S-shaped tunnels was stabilized.[38]

The morphology of the Na0.44MnO2 nanorods is illustrated in Figure 4 a and b. It was observed that the Na0.44MnO2 exhibits a rod-like shape and had a uniform size distribution with lengths of several \( \mu \)m and widths of 100–500 nm. Some Na0.44MnO2 nanorods even formed bundles, due to sintering at high temperature for a long time period. Measurements realized by EDS (coupled with the FESEM apparatus) gave a homogeneous Na/Mn ratio with an approximate value of 0.45, in good agreement with the expected compound. Its

![Figure 3](image-url)

**Figure 3.** Electrochemical properties of the NaTi2(PO4)3/MWNTs electrode in 1 M Na2SO4 electrolyte: a) CV curves measured at a scan rate of 0.5 mV s\(^{-1}\). b) Charge-discharge profiles at 2 C (1 C = 133 mA g\(^{-1}\)) for different cycle numbers. c) Cycling stability at a constant current of 2 C. d) Reversible capacities cycled at different current densities.

![Figure 4](image-url)

**Figure 4.** a) FESEM image, b) TEM image, c) selected area electron diffraction (SAED) spot patterns at the position of the yellow rectangle of pane b, and d) HRTEM image of the Na0.44MnO2 nanorod.
corresponding EDS spectrum is shown in Figure S4 (see Supporting Information). The SAED spot patterns shown in Figure 4d verified the single-crystalline nature of Na$_{0.44}$MnO$_2$ nanorods and SAED patterns could be clearly indexed along the [6, 2¯, 14] zone axis of Na$_{0.44}$MnO$_2$, where the (2, 6, 0), (3, 2, 1), (1, 4, 1) and (1, 10, 1) crystal planes with 0.316, 0.204, 0.250 and 0.189 nm d-spacing, respectively, could be indexed. Figure 4d showed the HRTEM image of the nanorods, which demonstrated a clear crystal lattice with uniform interplanar spacing of 0.394 nm corresponding to the (160) plane of Na$_{0.44}$MnO$_2$.

The electrochemical properties of the Na$_{0.44}$MnO$_2$ electrode in aqueous Na$_2$SO$_4$ electrolyte are displayed in Figure S5 (see Supporting Information). As shown in Figure S5a, the CV curves of the electrode showed three redox couples in a voltage range of −0.1 to 0.65 V (vs. SCE), which was consistent with those reported by Whitacre et al. and Kim et al. The two main redox couples located at approximately 0.29 and 0.52 V (vs. SCE), within which the peak shapes and potential positions remained almost unchanged during successive scans, suggesting a cycling stability of the material in the aqueous solution. According to the well-documented intercalation chemistry of Na$_{0.44}$MnO$_2$ electrode, those pairs of CV peaks could be attributed to the reversible redox reactions of the Mn$^{4+}$/Mn$^{3+}$ couple in the Na$_{0.44}$MnO$_2$ lattice along with the insertion/extraction of Na-ions.

In accord with the CV curves, the charge–discharge characteristics of the Na$_{0.44}$MnO$_2$ electrode were investigated in aqueous electrolytes at 2°C, as displayed in Figure S5b (see Supporting Information). The charge–discharge rate (C rate) was calculated based on the theoretical specific capacity of Na$_{0.44}$MnO$_2$, where 1 C rate corresponded to a current density of 121 mAh g$^{-1}$. Three plateaus in the potential range of −0.1 to 0.65 V (vs. SCE) could been seen in the curves, which was consistent with the CV curves and also agreed with the literature for this material in aqueous electrolytes. The charge–discharge capacities kept constant at approximately 46.7 mAh g$^{-1}$ in the second, fifth, and tenth cycles, corresponding to a coulombic efficiency of nearly 100%. The result indicated that the insertion/extraction of Na-ions on the Na$_{0.44}$MnO$_2$ cathode, which occurred within the electrochemical window of this aqueous electrolyte and the cathode would have a cycling stability in the aqueous electrolyte.

Furthermore, the cycling stability of the Na$_{0.44}$MnO$_2$ electrode was measured at 2°C, as shown in Figure S5c (see Supporting Information). The specific capacity of the electrode decreased very slightly from 47 to 40 mAh g$^{-1}$ up to 200 cycles, and the coulombic efficiency kept nearly constant at approximately 100%. Meanwhile, the Na$_{0.44}$MnO$_2$ showed outstanding high-rate performance (see Figure S5d, Supporting Information). The electrode was progressively charged/discharged in series stages with the charge–discharge rate of 2 to 20°C. For each stage, the process was performed with 30 cycles. The reversible capacity was approximately 47 mAh g$^{-1}$ obtained at a rate of 2°C. The specific capacities were slightly reduced to approximately 40, 37, and 32 mAh g$^{-1}$ at rates of 5, 10, and 20°C, respectively. For a rate of 2°C, the electrode could still deliver a reversible capacity of approximately 43 mAh g$^{-1}$. In addition to the good crystallinity, the excellent cycling ability and high-rate capability of Na$_{0.44}$MnO$_2$ nanorods could be attributed to the stability of the three-dimensional framework crystal structure with S-shaped tunnels.

For the above mentioned results, a “rocking-chair”-type aqueous Na-ion battery with an optimized mass ratio of NaTi$_2$(PO$_4$)$_3$/MWNTs-Na$_{0.44}$MnO$_2$ = 1:2.7 was assembled. A schematic illustration of the principle of the battery is described in Figure 5. As shown, during charging (or discharging), the storage (or release) of Na ions occurred at the cathode, and the release (or storage) of Na-ions took place at the anode, involved the migration of Na-ions between the electrolyte and the electrode materials.

Figure 6a shows the charge–discharge profiles of these cells. As expected from their working potentials of the individual anode and cathode, the battery exhibited three plateaus in the potential range of 0.2–1.4 V, one of which showed relatively flat charge and discharge voltages at approximately 1.1 V. As an anode-limited cell design, the aqueous cell could deliver a reversible capacity of approximately 128 mAh g$^{-1}$ at 2°C for 10 cycles.

The cycling stability of the battery was examined at a constant current of 2°C and the results are given in Figure 6b. The reversible capacity of the battery severely decayed from an initial value of 128 mAh g$^{-1}$ to 50 mAh g$^{-1}$ over 60 cycles, corresponding to 37% capacity retention. Subsequently, the reversible capacity remained very stable at approximately 50 mAh g$^{-1}$ after 240 cycles, and the corresponding coulombic efficiency in this period remained constant at approximately 95%. The intrinsic causation of this phenomenon for the aqueous battery system is still unknown. However, possible causes include partial dissolution of electrode materials, active materials stripping from the current collector in the aqueous electrolyte, or hydrogen and oxygen being generated by water hydrolysis.

The rate performance of this aqueous full-cell at different current densities is shown in Figure 6c. This cell could deliver discharge capacities of approximately 68, 45, and 23 mAh g$^{-1}$ at high rates of 5, 10, and 20°C, respectively. The battery could still deliver a reversible capacity of approximately 75 mAh g$^{-1}$ after 120 cycles, which was further...
charged/discharged at 2 C for another 30 cycles. Surprisingly, the corresponding coulombic efficiencies remained almost unchanged.

Taking into account the sum of the active cathode and anode mass in the cell, a Ragone plot derived from the discharge profiles at various current densities in Figure 6c was constructed to show the dependence of the energy densities on the power densities of the Na-ion system, as displayed in Figure 6d. The specific energy of the battery was 58.7 Wh kg⁻¹ at a power density of 228 W kg⁻¹, and still remained at 13.5 Wh kg⁻¹ at a very high power of 2300 W kg⁻¹. This specific energy along with the higher power density and longer cycling life enabled the aqueous NaTi₂(PO₄)₃/MWNTs–Na₀.⁴⁴MnO₂ material to be a feasible alternative for a large-scale electric storage system.

We also compared this work with other aqueous rechargeable Na-ion batteries based on different electrode materials reported in the recent literature, and the results are shown in Table S3 (Supporting Information). Here we took the aqueous rechargeable Na-ion batteries based on the NaTi₂(PO₄)₃–Na₀.⁴⁴MnO₂ system as one example. Its average discharge voltage was 1.1 V. It could be charged and discharged at a high rate up to at least 70 C, which could meet the rapid change of power supply and demand from the grids. Its energy density could reach 58.7 Wh kg⁻¹ based on the total mass of the electrode materials. The results of Chiang’s research clearly showed that the aqueous sodium-ion system NaTi₂(PO₄)₃–Na₀.⁴⁴MnO₂ was capable of exceptionally high charge/discharge rates (over 100 C) and stable cycling up to >1000 cycles, while delivering several-fold higher energy densities than supercapacitors. Thus further investigation of these effects is needed, and the aqueous NaTi₂(PO₄)₃–Na₀.⁴⁴MnO₂ system may be a candidate for safe, low-cost, high-power storage systems.

Conclusions

In summary, we constructed an aqueous Na-ion battery using NaTi₂(PO₄)₃/MWNTs nanocomposites as the anode and Na₀.⁴⁴MnO₂ as the cathode. The synthesis of NaTi₂(PO₄)₃/MWNTs nanocomposites was optimized to remove the electronic conductivity limitation and potentially enhance the electronic migration within particles, which exhibited good electrochemical performances. The two newly developed active electrode materials demonstrated excellent sodium storage performance in both half-cell and full-cell configurations in aqueous electrolyte. The full Na-ion battery could be reversibly charged/discharged at an operation voltage of approximately 1.1 V in 1 M Na₂SO₄ aqueous electrolyte, delivering a high energy density of 58.7 Wh kg⁻¹ at a power density of 228 W kg⁻¹. The strategy in this work indicated that the electrochemical performance of a battery system could be further improved by optimization of the anode and cathode materials with high rate capability, long cycle life, and a large potential difference. The present results showed that the aqueous Na-ion battery can be safe and environmentally benign, with low cost and natural abundance to be a good candidate for large-scale energy storage systems.

Experimental Section

Materials synthesis

All the reagents were of analytical grade purity and used without further purification. Multiwalled carbon nanotubes (MWNTs, CVD method, purity >95%, diameter 30–60 nm, length 2–15 μm) were purchased from Nanotech Port. Co. Ltd. (Shenzhen, China). The as-received MWNTs were purified by using ultrasonic treatment in 6 M nitric acid for 0.5 h and then refluxing in 2.6 M HNO₃ for 36 h before use. The NaTi₂(PO₄)₃/MWNTs nanocomposites were prepared by a solvothermal method using benzylic alcohol as surfactant. Typically, purified MWNTs (200 mg) were dissolved into 25 mL ethylene glycol and 15 mL benzylic alcohol under continuous stirring and sonication for 1 h, respectively. Then, 10 mL 28% ammonia solution and 3.4 mL tetrabutyl titanate were added dropwise to the solution with strongly stirring. After the solution turned...
Electrodes for Sodium-Ion Batteries

clear, stoichiometric amounts of \( \text{NH}_4\text{H}_2\text{PO}_4 \) in 10 mL distilled water and \( \text{Na}_2\text{CO}_3 \) in 10 mL distilled water were added, respectively. The resultant white gel mixture was transferred into a Teflon-lined autoclave (80 mL) and treated at 140 °C for 24 h. The obtained product was washed with distilled water and ethanol. After being dried at 80 °C, the products were calcined at 700 °C for 2 h with a rate of 2 °C min\(^{-1} \) in a nitrogen atmosphere. The \( \text{Na}_i\text{MnO}_2 \) nanorods were prepared using a classic solid-state reaction using \( \text{MnCO}_3 \) and \( \text{Na}_2\text{CO}_3 \) (with a 10 wt% excess stoichiometry) as raw materials by ball milling in a agate jar at 350 rpm for 8 h. Then, the precursor mixtures were successively heated at 300 °C for 3 h and 800 °C for 9 h under air atmosphere.

**Materials Characterization**

Powder X-ray diffraction patterns (XRD) were collected by using a Bruker D8 Advance diffractometer (Cu\(_{\text{Kα}}\) radiation, Sol-X detector, 40 mA, 40 kV). The XRD profiles were refined by the Rietveld program RIETAN-FP. Schematic illustrations of the crystal structures were drawn using the program VESTA. The morphology and structure of samples were analyzed by field-emission scanning electron microscopy-energy dispersive X-ray spectroscopy (FESEM-EDS, Nova Nano SEM 430, FEI), and transmission electron microscopy-energy dispersive X-ray spectroscopy (HRTEM, JEM-2100, JEOL). Thermogravimetric (TG) analyses were performed using a TG instrument (NETZSCH STA 409 PC) with a heating rate of 5 °C min\(^{-1} \) in an air atmosphere from 50–800 °C.

**Electrochemical measurements**

Electrochemical characterization of the \( \text{Na}_i\text{Ti}_2(\text{PO}_4)_3/MWNTs \) and \( \text{Na}_i\text{MnO}_2 \) samples was performed by using a three-electrode cell. For the three-electrode setup, a saturated calomel electrode (SCE, 0.242 V vs. NHE) and Pt foil were employed as reference and counter electrodes, respectively. Both the cathode and anode were prepared by casting slurries of 80% active materials, 15% acetylene black (AB), and 5% polytetrafluoroethylene (PTFE) binder by weight onto a graphite electrode with 1 cm\(^2 \) area. The electrolyte was aqueous 1 M \( \text{Na}_2\text{SO}_4 \) solution (pH 7) purged with \( \text{N}_2 \) before use (made from DI water with 18 M\( \text{Ω} \)•cm electrical resistivity). The 2016 coin type sodium-ion cells were assembled using \( \text{Na}_i\text{Ti}_2(\text{PO}_4)_3/MWNTs \) as cathode, \( \text{Na}_i\text{MnO}_2 \) as anode, and \( \text{Na}_2\text{CO}_3 \) in 10 mL distilled water as electrolyte.

**Acknowledgements**

This work was supported by the National Basic Research Program of China (973 Program) (No. 2014CB239701), National Natural Science Foundation of China (No. 21173120, No. 51372116), Natural Science Foundation of Jiangsu Province (No. BK2011030), and the Fundamental Research Funds for the Central Universities of NUAA (NP2014403).

**Keywords:** aqueous electrolyte · carbon nanotubes · energy storage · NASCION · sodium-ion batteries


Received: May 20, 2014
Revised: June 8, 2014
Published online on July 25, 2014