Layered Structure Na$_2$Ti$_3$O$_7$ as a Promising Anode Material for Sodium-Ion Batteries

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Sodium-ion batteries (SIBs), as next-generation energy storage devices, can be made by a similar production process to lithium-ion batteries (LIBs). The key to accelerating their commercialization is to discover appropriate high-performance electrode materials with low cost, nontoxicity, and simple synthetic features. Herein, layered-structure Na$_2$Ti$_3$O$_7$, with the advantages of appropriate charge/discharge plateaus, superior stability, environmental friendliness, and ease of preparation using cheap raw materials, is selected for assembly in full-cell battery packs to evaluate its suitability for practical application. When evaluated in a coin cell, it has a capacity of 77.2 mAh g$^{-1}$ at 1 A g$^{-1}$ after 10 000 cycles with capacity retention of 99.9%, demonstrating its excellent stability. In the case of a soft-pack battery, it retains 22.3 mAh g$^{-1}$ at 0.1 A g$^{-1}$ and 18.1 mAh g$^{-1}$ at 0.05 A g$^{-1}$ after 50 cycles. After cycling, there is no sodium dendrite formation or active material shedding, further confirming its safety in practical application. Therefore, Na$_2$Ti$_3$O$_7$ as another intercalation/deintercalation mechanism material has application potential in the future.

1. Introduction

Lithium-ion batteries (LIBs) as clean energy storage equipment have been commercialized since 1991,[1–3] although the insufficiency of lithium resources is limiting the use of LIBs in large-scale energy storage systems. Sodium-ion batteries (SIBs) are promising energy devices with similar properties of sodium ions to lithium ions, abundant, inexpensive resources, and capability for mass production by the same techniques as for LIBs.[4–6] Commercialization is limited, however, because development of the electrode materials is immature. In analogy with LIBs, their anode materials can be divided into three types, intercalation/deintercalation mechanism materials, composed of carbon and Na$_2$Ti$_3$O$_7$, conversion mechanism materials, represented by transition metal oxides and sulfur (selenium) compounds, and alloy mechanism materials based on Sb, Sn, Bi, and P.[7–16] Among them, the intercalation/deintercalation mechanism materials offer the biggest opportunity for commercial use of SIBs because of their excellent stability and low charge/discharge plateaus.

Carbon materials, which are the most widely studied sodium anodes, including graphene, carbon nanotubes, and soft and hard carbon materials, are attractive for practical application of SIBs due to their good conductivity.[17–22] When considering safety and economic issues, however, graphene and carbon nanotubes have high capacity and good cycling stability, but the tap density and volume capacity of graphene are low, and their prices are too high, making them hard to use on a large scale. In addition, hard carbon, with a low discharge plateau, exhibits the safety issue of sodium dendrite formation, which may result in short circuits in practical application.[23–25] Titanium-based materials, such as Na$_2$Ti$_3$O$_7$, possess the properties of low lattice strain, which can enable superior cycling stability, and an appropriate Na$^+$ insertion voltage, which can permit high energy density and high safety, making them the most promising materials for large-scale systems. There are many reports on synthesizing Na$_2$Ti$_3$O$_7$ with different morphologies or its composites to solve the problem of its insulating nature derived from a large bandgap.[26–32] Wang et al. synthesized double-shell sulfur-doped Na$_2$Ti$_3$O$_7$ microspheres constructed from ultrathin nanosheets

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via a templating route combined with a low-temperature sulfurization process. The resulting microspheres exhibited a high specific capacity, excellent cycling stability, and superior rate capability for SIBs.\cite{28} Xie et al. synthesized hollow Na$_2$Ti$_3$O$_7$ spheres assembled from N-doped carbon-coated ultrathin nanosheets, which delivered 60 mAh g$^{-1}$ after 10 000 cycles at a high rate of 50 C.\cite{33,34} Zeng et al. synthesized a unique sandwich structure in which sodium titanate (NTO) settled between 2D MXene and reduced graphene oxide (rGO). The flexible electrodes presented excellent rate performance and long cycling stability, $\approx$72 mA h g$^{-1}$ at 5 A g$^{-1}$ after 10 000 cycles. But from the viewpoint of the practical application of SIBs, assembled half coin cells cannot meet the practical requirements. There has been no work related to soft-pack batteries containing Na$_2$Ti$_3$O$_7$, which makes it hard to evaluate their practical application.

Here, Na$_2$Ti$_3$O$_7$ was synthesized by a one-step hydrothermal method using the inexpensive sodium hydroxide and tetrabutyl titanate (TBOT) as the raw materials. Even under enlargement, the morphology of Na$_2$Ti$_3$O$_7$ is very uniform. In a coin cell, it exhibits excellent cycling performance in both half and full cells. It showed a capacity of 77.2 mAh g$^{-1}$ at 1 A g$^{-1}$ after 10 000 cycles, with capacity retention of 99.9%. In a soft-pack battery, it retained 22.3 mAh g$^{-1}$ at 0.1 A g$^{-1}$ and 18.1 mAh g$^{-1}$ at 0.05 A g$^{-1}$ after 50 cycles. Similarly to carbon, Na$_2$Ti$_3$O$_7$ will be the most promising material in future applications.

2. Results and Discussion

2.1. Material Characterization

The diffraction peaks in the X-ray diffraction (XRD) pattern are quite weak (Figure S1a, Supporting Information) due to the low synthesis temperature. Despite this, it is in good agreement with the reported pattern of Na$_2$Ti$_3$O$_7$.\cite{36} The formation of Na$_2$Ti$_3$O$_7$ can be also supported by Raman spectra (Figure S1b, Supporting Information), where the peaks at 275 and 470 cm$^{-1}$ are attributed to the stretching vibrations of Na–O–Ti and the peaks at 710 and 915 cm$^{-1}$ are due to the stretching vibrations of terminal Ti–O bonds.\cite{35} The energy-dispersive X-ray (EDX) spectra clearly show the signals of Na, Ti, and O with a molar ratio of 1.7:3:7.4 (Figure S1c, Supporting Information), close to the chemical stoichiometry of Na$_2$Ti$_3$O$_7$\cite{36} Figure 1a–c shows that Na$_2$Ti$_3$O$_7$ consists of a large number of microflowers assembled by nanosheets. The overall size of these microflowers is $\approx$1–2 $\mu$m, but the thickness of the nanosheets is only 4–15 nm. The numerous gaps between neighboring nanosheets facilitate the electrolyte penetration and the fast transportation of Na$^+$ ions. The ultrasmall thickness of the nanosheets cuts down the diffusion distance of Na$^+$ ions upon cycling, and also increases the specific surface area to $\approx$120 m$^2$ g$^{-1}$ (Figure S2, Supporting Information). The interlayer spacing of Na$_2$Ti$_3$O$_7$ at 0.845 nm (Figure 1d) is larger than those of MoS$_2$ (0.65 nm), V$_2$O$_5$ (0.44 nm), and graphite (0.335 nm), indicating the promising potential of Na$_2$Ti$_3$O$_7$ in SIBs.\cite{7,10,11,17} Meanwhile, the overall size on the level of microcubes promotes the packing density in the electrode. To reveal the contribution of different elements, high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images as well as elemental maps were acquired. As shown in Figure 1e,f, the distributions of Na, Ti, and O well overlap with the pattern of microflowers.\cite{38}

![Figure 1. Morphology and chemical components of Na$_2$Ti$_3$O$_7$: a) SEM images, c) TEM image, d) HRTEM image and crystal structure (the inset), e) HAADF-STEM image and f) elemental mapping of Na, Ti, and O.](image-url)

2.2. Kinetics and Electrochemical Performance in Half-SIBs

Figure 2a shows the cyclic voltammetry (CV) curves at 0.1 mV s$^{-1}$ between 0.01 and 2.5 V. In the first discharge process, the peak around 1.0 V is attributed to the formation of the solid
Electrochemical reactions during the discharge/charge process of Na$_2$Ti$_3$O$_7$ in SIBs. a) CV curves, b) discharge/charge profiles of Na$_2$Ti$_3$O$_7$ at 25 mA g$^{-1}$, c) its rate performance, and d) its long-term cycling performance.

Figure 3 shows the kinetics analysis of Na$_2$Ti$_3$O$_7$ as an anode material in SIBs. As shown in Figure 3a, the galvanostatic intermittent titration technique (GITT) was used to analyze the reaction kinetics, where the electrode was cycled with a constant current density of 25 mA g$^{-1}$ between 0.01 and 2.5 V. It was found that the reaction resistance (closed-circuit voltage (CCV) and quasi-open-circuit voltage (QOCV))/pulse current (A) gradually decreases with sodiation.[42] That is due to the improvement of the conductivity as the sodium ions are inserted into Na$_2$Ti$_3$O$_7$. The reaction resistance of desodiation is bigger in the charge process, which is ascribed to the nonconductive SEI film formed during the discharge process. The SEI can prevent the side reactions between the electrolyte and Na$_2$Ti$_3$O$_7$, thereby improving the cycling stability (Figure 3b). Meanwhile, the structure maintenance promotes the reaction kinetics, as supported by electrochemical impedance spectra (EIS) (Figure S5, Supporting Information). And the charge-transfer resistance ($R_d$) significantly decreases after cycles.[43] The logarithmic plot of the peak current ($i_p$) versus the scan rate ($\nu$) is introduction of the rate- restricted characteristics expressed by Equation (1)[44]

$$i_p = a\nu^b$$  \hspace{1cm} (1)

where $b = 0.5$ means a diffusion-controlled process, and $b = 1.0$ implies a surface-controlled process. Usually, $b$ has a value between 0.5 and 1.0, reflecting a mixed contribution of both processes. In this case, the $b$ values of the anodic and cathodic peaks are 0.71 and 0.69 (Figure 3d), which indicates a surface-controlled process. A approximately estimation of the two processes could be made by using Equation (2)[45]
\[ i(v) = k_1v + k_2v^{1/2} \]  

(2)  

where \( k_1v \) is the dedication from the surface capacitance and \( k_2v^{1/2} \) is the dedication from diffusion-controlled processes. When divided by \( v^{1/2} \), this equation turns into Equation (3) [46]:  

\[ \frac{i}{v^{1/2}} = k_1v^{1/2} + k_2 \]  

(3)  

Here, a plot of \( i/v^{1/2} \) against \( v^{1/2} \) could give the specific data for \( k_1 \) and \( k_2 \). Therefore, the dedication ratio of the two processes at a fixed voltage could be obtained. Using this method, the ratio of the two processes throughout the potential window was identified. As shown in Figure 3e, the surface-controlled process contributed 73.5% of the total Na\(^+\) storage at 2 mV s\(^{-1}\). Furthermore, this ratio increased with increasing scan rate.

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**Figure 3.** Kinetics and electrochemical performance of Na\(_2\)Ti\(_3\)O\(_7\) in SIBs. a) GITT voltage profiles. b) Reaction resistance. c) CV curves at various scan rates. d) Plots of log (peak current) versus log (scan rate). e) Capacitive contribution in the CV curve obtained at 2 mV s\(^{-1}\). f) Capacitive contributions in the CV curves obtained at different scan rates.

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**Figure 4.** Electrochemical performance of the full cell (Na\(_2\)Ti\(_3\)O\(_7\)//Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/C). a) Full-cell setup, b) CV curves and c) discharge/charge curves for the first three cycles, and d) rate performance. e) Cycling performance at 1.0 A g\(^{-1}\).
(Figure 3f), and the dedication of this process to the Na\textsuperscript{+} storage was large. Also, the surface-controlled process agrees with the rate performance.

2.3. Electrochemical Performance in Full SIBs

In view of its excellent cycling performance in half-cells, a full cell was installed with Na\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}/C as the cathode (Figure S6 and S7, Supporting Information) (Figure 4a).\textsuperscript{[43]} Figure 4b shows CV curves at the scanning rate of 0.1 mV s\textsuperscript{-1}, in which the peaks at 1.9/2.5 and 2.75/2.8 V are due to the sodium ion insertion/extraction of carbon and Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}. The charge/discharge profiles were collected at a current density of 0.1 A g\textsuperscript{-1} between 1.0 and 3.4 V. As shown in Figure 4c, the full cells exhibited an average output voltage of around 2.5 V, and this high output voltage could promote its performance with a high power. Meanwhile, the overpotential between the discharge/charge profiles was ≈0.25 V, suggesting the good reaction kinetics.\textsuperscript{[48]} As for the rate performance (Figure 4d), this full cell displayed a capacity of 34.0 mA h g\textsuperscript{-1} at 0.1 A g\textsuperscript{-1}, 27.7 mA h g\textsuperscript{-1} at 0.2 A g\textsuperscript{-1}, 24.8 mA h g\textsuperscript{-1} at 0.5 A g\textsuperscript{-1}, 23.7 mA h g\textsuperscript{-1} at 1 A g\textsuperscript{-1}, 19.8 mA h g\textsuperscript{-1} at 2 A g\textsuperscript{-1}, and 15.2 mA h g\textsuperscript{-1} at 5 A g\textsuperscript{-1}. All these capacities were received on the basis of the mass of the anode material. Figure 4e presents the cycling performance of the full cell at 1.0 A g\textsuperscript{-1}, in which it retained the specific capacity of 16.1 mA h g\textsuperscript{-1} after 500 cycles.

Based on its simple synthesis, to evaluate its practical application, production of the material was scaled up to assemble soft-pack batteries, and their electrochemical performance was tested. Figure 5a and Figure S8 (Supporting Information) display the soft-pack batteries that we made. Figure 5b shows a battery after aging but before testing its electrochemical performance (Figure S9, Supporting Information), demonstrating that it can power light-emitting diodes (LEDs). Figure 5c shows its rate performance at different current densities. This full cell displayed a capacity of 38.8 mA h g\textsuperscript{-1} at 0.01 A g\textsuperscript{-1}, 31.8 mA h g\textsuperscript{-1} at 0.02 A g\textsuperscript{-1}, 23.8 mA h g\textsuperscript{-1} at 0.05 A g\textsuperscript{-1}, and 22.3 mA h g\textsuperscript{-1} at 0.1 A g\textsuperscript{-1}. Figure 5d shows the cycle performance of the full cell at 5.0 mA, which could still keep the specific capacity at 18.5 mA h g\textsuperscript{-1} after 50 cycles. For comparison, we selected Sn, another potential alloy mechanism anode material. Both the assembly process and the test environment were the same as for Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}. The gravimetric capacity of the Sn-based soft-pack batteries is...
battery was low, however, and the self-discharge phenomenon was quite serious (Figure S10, Supporting Information). To find the reason, Sn-based soft-pack batteries were disassembled after cycling and there was evidence of the formation of sodium dendrites and the shedding of active materials (Figure S11, Supporting Information), indicating that alloy-based materials have safety hazards if they are used in commercial production. To be honest, there will be a little unevenness in the cycling process because of the moisture adsorbed in the electrode material, which can react with the electrolyte during further cycling.\(^{49}\) \(\text{Na}_2\text{Ti}_3\text{O}_7\)-based soft-pack batteries were disassembled after cycling, and they had smooth surfaces without any dendrite formation or active material shedding (Figure S5e,f and Figure S12, Supporting Information), which predicts that \(\text{Na}_2\text{Ti}_3\text{O}_7\) will be a safe anode material in actual application.\(^{50}\)

Another problem is the Coulombic efficiency of \(\text{Na}_2\text{Ti}_3\text{O}_7\)-based soft-pack batteries, which can remain at \(\approx 97.5\%\). This can be further improved by adjusting materials morphology, cut-off voltage, electrolyte, and binder,\(^{51}\) which has already been done in the following paper.\(^{51}\)

### 3. Conclusion

In summary, layered-structure \(\text{Na}_2\text{Ti}_3\text{O}_7\) microflowers were synthesized on a large scale by a one-step hydrothermal reaction using cheap sodium hydroxide and TBOT as the raw materials. In coin cells, it exhibited excellent performance in both half- and full cells. It had a capacity of 77.2 mAh g\(^{-1}\) at 1 A g\(^{-1}\) after 10,000 cycles, with 99.9\% capacity retention. When used in a soft-pack battery, it retained 22.3 mA h g\(^{-1}\) at 0.1 A g\(^{-1}\) and 18.5 mA h g\(^{-1}\) at 0.05 A g\(^{-1}\) after 50 cycles without any sodium dendrite formation or shedding of active materials. Therefore, \(\text{Na}_2\text{Ti}_3\text{O}_7\) is a highly safe material without any dendrite formation or active material shedding after cycling, which makes it a promising anode material to achieve commercial application in the future.

### 4. Experimental Section

#### Preparation of \(\text{Na}_2\text{Ti}_3\text{O}_7\)

First, 4 mL TBOT was dispersed in 40 mL of 0.3 mol L\(^{-1}\) sodium hydroxide (NaOH) solution. After stirring at 25 °C for 1 h, the solution was shifted into a Teflon-lined stainless-steel autoclave with the capacity of 60 mL. After 12 h at 200 °C, the product was gathered by centrifugation, washed with deionized water and absolute ethanol several times, and then dried under vacuum overnight at 60 °C.

#### Structural Characterization: XRD patterns were acquired on an X-ray diffractometer (Bruker D8 Advanced, Cu kx radiation, \(\lambda = 1.5418\) Å, Germany). Scanning electron microscope (SEM) images were obtained on a field-emission scanning electron microscope (Zeiss Gemini 300, Germany). TEM images, High-resolution transmission electron microscope (HRTEM) images, EDX spectra, HAADF-STEM images, and elemental mapping were collected using an aberration-corrected TEM microscope (FEI Tecnai F20, USA). Raman spectra were characterized on a micro-Raman spectrometer (HORIBA JY Lab RAM HD88, Japan), using laser excitation of 632 nm at 25 °C. N\(_2\) sorption isotherms were acquired on a physisorption analyzer (Mettler Toledo TAG/SDTA 851) from room temperature to 800 °C in air.

#### Electrochemical Measurements: The electrochemical performance of \(\text{Na}_2\text{Ti}_3\text{O}_7\) as anode material for SIBs was tested in CR2032-type coin cells. The working electrode was made of a mixture of \(\text{Na}_2\text{Ti}_3\text{O}_7\), acetylene black, and sodium alginate (SA) in a weight ratio of 7:2:1, respectively. The mixed materials were milled by hand to obtain a homogeneous slurry, which was spread on clean copper foil with a doctor blade. After drying at 60 °C for 12 h in vacuum, the foil was cut into small discs with a diameter of 12 mm. The mass loading of \(\text{Na}_2\text{Ti}_3\text{O}_7\) on the discs was \(\approx 1-1.5\) mg cm\(^{-2}\). Next, the working electrode was assembled with sodium metal as the counter electrode and glass fiber (Whatman GF/F) as the separator, while 1.0 M NaClO\(_4\) in propylene carbonate (PC) containing 3 wt% fluoroethylene carbonate (FEC) acted as the electrolyte in an Ar-filled glove box (Mikrouna, Super 1220/750/900, H\(_2\)O < 1 ppm; O\(_2\) < 1 ppm). GITT measurements and galvanostatic discharge/charge profiles were obtained on a battery cycler (LAND CT-2001A, China) at 25 °C between 0.01 and 2.5 V. CVs were collected on an electrochemical workstation (CHI 760 E, China) at 25 °C. EIS were researched using an electrochemical workstation (Autolab PG STAT 302 N) in the frequency range of 100 kHz to 0.01 Hz. In full coin cells, the anode was made by the aforementioned protocol and then electrochemically activated to eliminate the capacity loss of the full cells in the first cycle for three cycles. The cathode was fabricated by homemade \(\text{Na}_2\text{V}_6(\text{PO}_4)_3/C\), acetylene black, and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1 on aluminum foil. In soft-pack batteries, the anode was made of a mixture of \(\text{Na}_2\text{Ti}_3\text{O}_7\) or Sn (Aladdin), acetylene black, and sodium carboxymethyl cellulose (CMC) in a weight ratio of 7:2:1, respectively, on the copper foil, and the cathode was made of a mixture of commercially purchased sodium nickelate (Faradion Ltd), acetylene black, and PVDF in a weight ratio of 9:1:1, respectively, on aluminum foil. These materials were milled by ball milling for 4 h at 300 rpm to obtain a homogenous slurry, which was coated on both sides with an automatic coater. After drying for 12 h at 70 °C in vacuum, the foil was cut into 12 × 30 cm\(^2\) rectangles, and the excess slurry was scraped off. In assembling the batteries, Celgard 2325 was used as the separator, and the batteries were then dried for 48 h at 100 °C in vacuum. The batteries were then placed in an aluminum–plastic film that was welded to the top to complete the injection of the electrolyte (0.5 M NaPF\(_6\) in ethylene carbonate (EC):diethyl carbonate (DEC):PC = 1:1:1, v/v/v) in the glove box, and the batteries were then sealed by a heat-sealing machine. The capacity ratio of the anode to the cathode was \(\approx 1:2\).

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

Research data are not shared.
Keywords

anode materials, layered structure, Na$_2$Ti$_3$O$_7$, sodium-ion batteries, soft-pack batteries