Use of a novel layered titanoniobate as an anode material for long cycle life sodium ion batteries†

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Sodium ion batteries have been attracting increasing attention as a replacement for lithium ion batteries in large-scale energy applications. However, it is proving difficult to find suitable sodium host materials with both a high capacity and excellent cycle stability. We prepared a layered titanoniobate (HTi2NbO7) via solid-state calcination followed by ion exchange for use in sodium ion batteries. The lamellar HTi2NbO7 had a specific capacity of about 90 mA h g⁻¹ at 100 mA g⁻¹. The capacity was highly reversible over 2000 cycles. These results show that this lamellar titanoniobate material is a promising anode material for sodium ion batteries with a long cycle life.

Sodium ion batteries have been attracting much attention as a replacement for lithium ion batteries as a result of the low cost and high abundance of sodium resources. When used in large-scale energy storage systems, where cost and sustainability are major concerns, the superiority of sodium ion batteries over their lithium ion counterparts becomes important. However, it is difficult to find a suitable electrode material for sodium ion batteries as a result of the large ionic radius of sodium (70% larger than that of lithium).

A number of transition metal oxides show promise for electrochemical energy storage. Titanium- and niobium-based oxides have been widely investigated as anode materials for lithium ion batteries as a result of the beneficial redox potentials of Nb⁷⁺/Nb⁴⁺, Ti⁴⁺/Ti³⁺ and Nb⁴⁺/Nb³⁺. A mixed titanium-niobium oxide (TiNb₂O₇) used as a novel anode for lithium ion batteries had a high theoretical capacity of up to 387.6 mA h g⁻¹. This mixed titanium-niobium oxide has all the above-mentioned redox couples (Nb⁷⁺/Nb⁴⁺, Ti⁴⁺/Ti³⁺ and Nb⁴⁺/Nb³⁺). As a result, a high specific capacity is expected because five lithium ions can theoretically be inserted into one formula unit of TiNb₂O₇. Other titanium-niobium oxide based materials, such as Ti₂Nb₂O₇⁬, Ti₃NbO₇, Ti₅NbO₁₇ (ref. 12) and Ti₂Nb₁⁰O₂₉,¹³ have also been studied as electrode materials for lithium ion batteries and have shown excellent performance. Surprisingly, the family of titanium–niobium oxide based electrode materials also shows excellent insertion/extraction of lithium. Ti₂Nb₁⁰O₂₉ has a reversible specific capacity of 238 mA h g⁻¹ at 2C (1C = 396 mA g⁻¹) after 800 cycles.¹⁵ However, as far as we know, there has been no report of the electrochemical properties of the mixed titanium–niobium oxide with multiple redox couples (Nb⁷⁺/Nb⁴⁺, Ti⁴⁺/Ti³⁺ and Nb⁴⁺/Nb³⁺) for sodium intercalation.

In a similar manner, Na₂TiO₃, which is also a member of the A₂M₂O₆n+ family of layered titanates, should provide the possibility of lithium/sodium intercalation.¹⁶ There have been few reports on sodium intercalation in these kinds of materials, which have both the easily reducible species Ti⁴⁺ and Nb⁷⁺ and a lamellar structure.¹⁵ We report here the synthesis of the layered titanoniobate HTi₂NbO₇ via solid-state calcination followed by ion exchange and the first experimental results of the electrochemical properties of HTi₂NbO₇ as an anode material for sodium ion batteries. The preliminary results showed that HTi₂NbO₇ had a reversible specific capacity of about 90 mA h g⁻¹ at 100 mA g⁻¹ for sodium ion intercalation/de-intercalation after 2000 cycles.

Scheme 1 shows the manufacturing process for HTi₂NbO₇ · H₂O. TiO₂, Nb₂O₅ and Cs₂CO₃ (a 10% molar excess) were first ground in a mortar for about 30 min and then heated at 1373 K for 12 h. A proton exchange reaction was then carried out by adding CsTiNbO₇ to an acidic solution (1 M) with magnetic stirring at 333 K for 24 h. The precipitate was filtered and washed three times with deionized water. HTi₂NbO₇ was obtained by heating the precipitate under vacuum at 423 K for 2 h.
Fig. 1a and b shows the X-ray diffraction patterns of CsTi$_2$NbO$_7$ and HTi$_2$NbO$_7$, which match well with the orthorhombic crystallographic system; all the diffraction peaks were in accordance with those of JCPDS Card no. 73-0680 and JCPDS Card no. 54-1154, respectively. These results show that there was no impurity in the products and the interlamellar spacing was reduced.

Fig. 1c shows the structure of HTi$_2$NbO$_7$. The H$^+$ structure is built up from layers containing zigzag strings with groups of three edge-shared octahedra. The strings are linked side by side via corner sharing to form Ti$_2$NbO$_7$ layers. The H$^+$ ions occupy distorted cubic sites between the layers. Two adjacent layers are related by a glide plane in both structures.

The morphology of the cuboid arrangement is shown in Fig. 2a, the scanning electron microscopy (SEM) image, which shows a uniform width distribution of $\sim$2 $\mu$m. Fig. 2b clearly shows that the lamellar titanoniobate HTi$_2$NbO$_7$ has a layered structure. The nitrogen adsorption/desorption isotherms and pore size distribution plots show the characteristics of this mesoporous material (Fig. 2c and d). The material has a relatively low BET surface area of 6.7 m$^2$/g and the pore size distribution is mainly from 2 to 3 nm. The mesoporous laminated structure could give a greater active area for Na$^+$. XPS was used to investigate the surface composition and valence states of HTi$_2$NbO$_7$. Photoelectron peaks for C, O, Ti and Nb can be clearly seen in Fig. 3a. Fig. 3b confirmed the existence of the Ti$^{4+}$ oxidation state from the Ti 2p$_{1/2}$ and 2p$_{3/2}$ peaks at 464.2 and 458.3 eV with a spin–orbit splitting of about 5.9 eV. Fig. 3c shows the Nb 3d spectrum for HTi$_2$NbO$_7$, with two peaks at 206.8 and 209.5 eV. These two peaks represent the 3d$_{5/2}$ and 3d$_{3/2}$ components, respectively, with a spin–orbit splitting of 2.7 eV. The center of the Nb 3d$_{3/2}$ peak corresponds to the Nb$^{5+}$ oxidation state.

**Scheme 1**  Schematic diagram of the manufacture of HTi$_2$NbO$_7$·H$_2$O.

**Fig. 1** XRD patterns of (a) CsTi$_2$NbO$_7$ and (b) HTi$_2$NbO$_7$. (c) Structure of layered HTi$_2$NbO$_7$.

**Fig. 2** SEM images of HTi$_2$NbO$_7$: (a) low-resolution SEM image of overall view; and (b) high-resolution SEM image of part of a cuboid. (c) Nitrogen adsorption–desorption isotherms of HTi$_2$NbO$_7$. (d) Pore size distribution curve for HTi$_2$NbO$_7$.

**Fig. 3** (a) XPS survey spectra for the surfaces of the HTi$_2$NbO$_7$ sample. Typical spectra of (b) Ti 2p and (c) Nb 3d.
The electrochemical performance of the layered HTi2NbO7 anode were studied by galvanostatic charge–discharge measurements. Each cell was tested at potentials within the range 0.01–3 V. Fig. 4a shows the initial charge–discharge voltage profiles at 100 mA g⁻¹. The discharge curves show four different regions: two sloping regions at 1.5–1.25 and 0.98–0.86 V; a plateau at 0.45 V; and a further plateau region up to the discharge limit. The voltage decreased sharply to 1.5 V, mainly due to a solid solution reaction. The two sloping regions at 1.5–1.25 and 0.98–0.86 V and the plateau at 0.45 V are attributed to a two-phase reaction for Nb⁵⁺/Nb⁴⁺, Ti⁴⁺/Ti³⁺ and Nb⁴⁺/Nb³⁺, respectively. There is another long plateau from 0.16 to 0.01 V, which may correspond to the process in which H⁺ ions are simultaneously replaced by Na⁺ ions during the electrochemical intercalation. During the first discharge, the specific capacity reaches 430 mA h g⁻¹ with a reversible capacity of about 200 mA h g⁻¹. The irreversible capacity can be mainly attributed to the transformation of the structure resulting from the irreversible process of Na⁺ replacing H⁺ and the formation of the solid electrolyte interface (SEI). From the tenth cycle, the capacity gradually become stable, showing that the structure tended to become steady after all the H⁺ has been replaced by Na⁺.

Cyclic voltammetry curves of the HTi2NbO7 anode at a scanning rate of 0.01 mV s⁻¹ over the voltage range 0.01–3.0 V are shown in Fig. 4b. There are two small peaks around 1.5 and 0.98 V as a result of the valence variation of Nb⁵⁺/Nb⁴⁺ and Ti⁴⁺/Ti³⁺; a sharp peak at 0.45 V could correspond to the Nb⁴⁺/Nb³⁺ redox couple. The last sharp sloping peak at 0.01 V may be due to the replacement of H⁺ by Na⁺. The CV curves are in agreement with the charge–discharge curves.

Long-term cycle stability is a challenge for practical sodium ion batteries as a result of the possible structural degradation of the host during cycling. Fig. 4c shows the superior cycling performance of the HTi2NbO7 electrode at 100 mA g⁻¹. Although a slow fading of capacity is seen in the initial few dozen cycles, there was no decline in capacity during the subsequent 2000 cycles. In addition, a reversible capacity of about 90 mA h g⁻¹ remained unchanged during the subsequent 2000 cycles, indicating excellent cycle stability. With respect to the contribution of conductive carbon, the capacity of pure HTi2NbO7 is about 70 mA h g⁻¹ (ESI, Fig. S1†). Notably, the layered structure of the HTi2NbO7 was almost unchanged after 2000 cycles, although it was covered with a thick SEI film (ESI, Fig. S2†). Correspondingly, the coulombic efficiency gradually increased during the initial cycles and remained at >99% in the following cycles. The performance of this HTi2NbO7 electrode is better than that of other materials reported for sodium ion batteries, such as Nb2O5 (about 30 mA h g⁻¹ after 50 cycles at 50 mA g⁻¹),1 K0.8Ti1.7Li1.25O4 (about 80 mA h g⁻¹ at 100 mA g⁻¹),22 Na2/3Co1/3Ti2/3O2 (50 mA h g⁻¹ at 500 mA g⁻¹),23 TiO2 nanoparticles (93 mA h g⁻¹ at 1700 mA g⁻¹),24 Na2Ti4O12 (about 100 mA h g⁻¹ after 30 cycles at 5 mA g⁻¹) and Cu9.5TiOPO4 (70 mA h g⁻¹ after 20 cycles at 42.2 mA g⁻¹).26

To further understand the electrochemical characteristics of HTi2NbO7, rate capability tests were performed at different current densities (Fig. 4d). A reversible capacity of 106 mA h g⁻¹ was obtained at a low current density of 40 mA g⁻¹. When the current density increased to 100 and 200 mA g⁻¹, reversible specific capacities of 77 and 62 mA h g⁻¹ were obtained respectively. Even though the current density increased to 1000 mA g⁻¹, a capacity of about 32 mA h g⁻¹ was still maintained. When the current density reversed back to 40 mA g⁻¹, the capacity of the HTi2NbO7 still remained at about 85 mA h g⁻¹. Taking into account the contribution of conductive carbon, the capacity of pure HTi2NbO7 is reduced by a certain ratio. These results indicate that HTi2NbO7 has a good rate performance.

EIS was also carried out to obtain insights into the electrochemical behavior of HTi2NbO7. These data were recorded before cycling and after 100 cycles (Fig. 5). As Fig. 5a shows, the Nyquist plots consist of one semicircle at high frequencies and a straight line at low frequencies. Fig. 5b shows that the Nyquist plots consist of two anomalous semicircles at medium frequencies before cycling; a decrease in the semicircle at high frequencies was smaller than that of the battery before cycling. The decrease in Rct is attributed to the formation of a SEI film on the cycled electrode, which enhances the reaction kinetics, as reported previously.30,31 The Warburg impedance of the battery after 100 cycles was much lower than that of the battery before cycling, which indicates that the polarization of the HTi2NbO7 anode decreased dramatically favors capacity retention during cycling.32

We have successfully fabricated a layered HTi2NbO7 structure via a solid-state reaction followed by ion exchange and used it as an anode material in sodium ion batteries. Electrochemical

![Fig. 4](image-url)
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Fig. 5  Impedance plots of HTi$_2$NbO$_7$ for (a) before cycling and (b) after 100 cycles at 100 mA h g$^{-1}$. (c) Equivalent circuit for simulating the EIS data about the battery after 100 cycles.

Table 1  Fitted values for the HTi$_2$NbO$_7$ electrode after 110 cycles

| Parameter          | Value          |
|--------------------|----------------|
| $R_s$ (Ω)          | 11.18          |
| $C_{sci}$ (Ω)      | $1.3091 \times 10^{-6}$ |
| $R_{sei}$ (Ω)      | 5.364          |
| CPE-T(Cdl)         | $1.8005 \times 10^{-5}$ |
| CPE-P(Cdl)         | 0.89822        |
| $R_C$              | 77.67          |
| $W_{o-R}$          | 23.53          |
| $W_{o-T}$          | 0.017247       |
| $W_{o-P}$          | 0.40037        |

tests indicated that this layered material can give a reversible capacity of about 90 mA h g$^{-1}$ with no capacity fading after 2000 cycles in the voltage range 0.01–3.0 V. This is an exciting option for the synthesis and design of new materials with layered structures as high-performance anodes for sodium ion batteries. The material displayed excellent cycle performance and we believe that these results represent a significant step forward in the development of long-life sodium ion batteries for large-scale applications in novel energy storage devices.

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