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Cite this: *RSC Adv.*, 2016, 6, 35746Received 28th January 2016  
Accepted 24th March 2016

DOI: 10.1039/c6ra02530g

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# 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 ( $\text{HTi}_2\text{NbO}_7$ ) via solid-state calcination followed by ion exchange for use in sodium ion batteries. The lamellar  $\text{HTi}_2\text{NbO}_7$  had a specific capacity of about  $90 \text{ mA h g}^{-1}$  at  $100 \text{ mA g}^{-1}$ . 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.<sup>1</sup> 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.<sup>2,3</sup> 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.<sup>4</sup> 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  $\text{Nb}^{5+}/\text{Nb}^{4+}$ ,  $\text{Ti}^{4+}/\text{Ti}^{3+}$  and  $\text{Nb}^{4+}/\text{Nb}^{3+}$ .<sup>5–7</sup> A mixed titanium–niobium oxide ( $\text{TiNb}_2\text{O}_7$ ) used as a novel anode for lithium ion

batteries had a high theoretical capacity of up to  $387.6 \text{ mA h g}^{-1}$ .<sup>8</sup> This mixed titanium–niobium oxide has all the above-mentioned redox couples ( $\text{Nb}^{5+}/\text{Nb}^{4+}$ ,  $\text{Ti}^{4+}/\text{Ti}^{3+}$  and  $\text{Nb}^{4+}/\text{Nb}^{3+}$ ). As a result, a high specific capacity is expected because five lithium ions can theoretically be inserted into one formula unit of  $\text{TiNb}_2\text{O}_7$ . Other titanium–niobium oxide based materials, such as  $\text{Ti}_2\text{Nb}_2\text{O}_9$ ,<sup>9</sup>  $\text{TiNb}_2\text{O}_7$ ,<sup>10,11</sup>  $\text{TiNb}_6\text{O}_{17}$  (ref. 12) and  $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ ,<sup>13</sup> 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.  $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$  has a reversible specific capacity of  $238 \text{ mA h g}^{-1}$  at 2C ( $1\text{C} = 396 \text{ mA g}^{-1}$ ) after 800 cycles.<sup>13</sup> 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 ( $\text{Nb}^{5+}/\text{Nb}^{4+}$ ,  $\text{Ti}^{4+}/\text{Ti}^{3+}$  and  $\text{Nb}^{4+}/\text{Nb}^{3+}$ ) for sodium intercalation.

In a similar manner,  $\text{Na}_2\text{Ti}_3\text{O}_7$ , which is also a member of the  $\text{A}_x\text{M}_{2n}\text{O}_{4n+2}$  family of layered titanoniobates, should provide the possibility of lithium/sodium intercalation.<sup>14</sup> There have been few reports on sodium intercalation in these kinds of materials, which have both the easily reducible species  $\text{Ti}^{4+}$  and  $\text{Nb}^{5+}$  and a lamellar structure.<sup>15</sup> We report here the synthesis of the layered titanoniobate  $\text{HTi}_2\text{NbO}_7$  via solid-state calcination followed by ion exchange and the first experimental results of the electrochemical properties of  $\text{HTi}_2\text{NbO}_7$  as an anode material for sodium ion batteries. The preliminary results showed that  $\text{HTi}_2\text{NbO}_7$  had a reversible specific capacity of about  $90 \text{ mA h g}^{-1}$  at  $100 \text{ mA g}^{-1}$  for sodium ion intercalation/de-intercalation after 2000 cycles.

Scheme 1 shows the manufacturing process for  $\text{HTi}_2\text{NbO}_7 \cdot \text{H}_2\text{O}$ .  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{Cs}_2\text{CO}_3$  (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  $\text{CsTi}_2\text{NbO}_7$  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.  $\text{HTi}_2\text{NbO}_7$  was obtained by heating the precipitate under vacuum at 423 K for 2 h.

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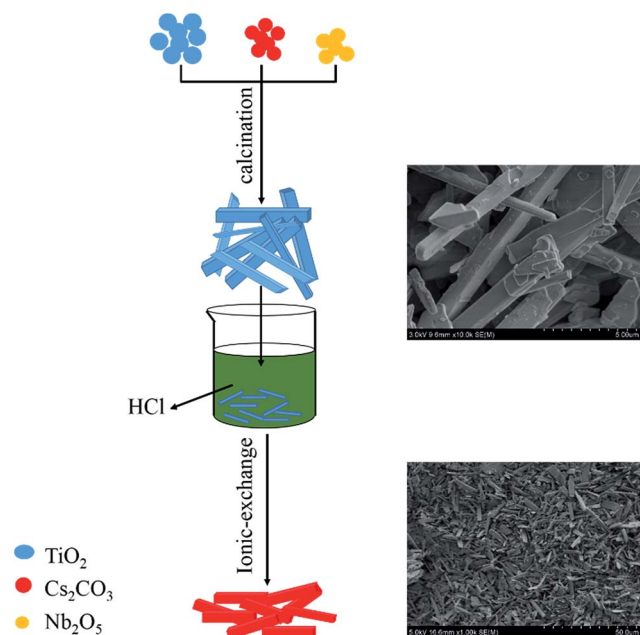
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† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c6ra02530g





Scheme 1 Schematic diagram of the manufacture of  $\text{HTi}_2\text{NbO}_7 \cdot \text{H}_2\text{O}$ .

Fig. 1a and b shows the X-ray diffraction patterns of  $\text{CsTi}_2\text{NbO}_7$  and  $\text{HTi}_2\text{NbO}_7$ , which match well with the orthorhombic crystallographic system;<sup>16</sup> 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.<sup>17</sup> Fig. 1c shows the structure of  $\text{HTi}_2\text{NbO}_7$ . The  $\text{H}^+$  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  $\text{Ti}_2\text{NbO}_7^-$  layers. The  $\text{H}^+$  ions occupy distorted cubic sites between the layers. Two adjacent layers are related by a glide plane in both structures.<sup>17</sup>

The morphology of the cuboid arrangement is shown in Fig. 2a, the scanning electron microscopy (SEM) image, which

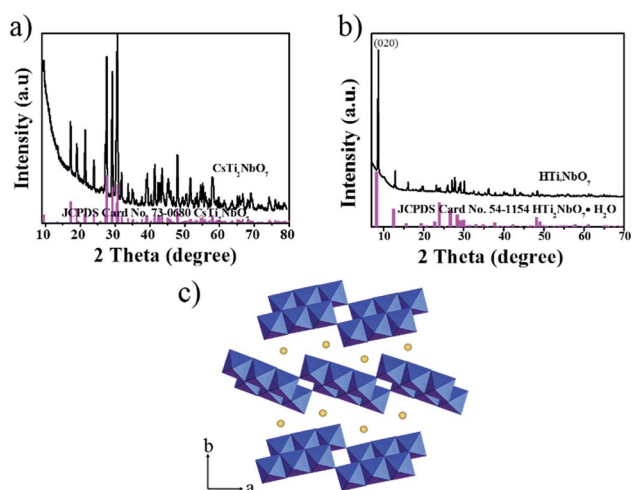


Fig. 1 XRD patterns of (a)  $\text{CsTi}_2\text{NbO}_7$  and (b)  $\text{HTi}_2\text{NbO}_7$ . (c) Structure of layered  $\text{HTi}_2\text{NbO}_7$ .

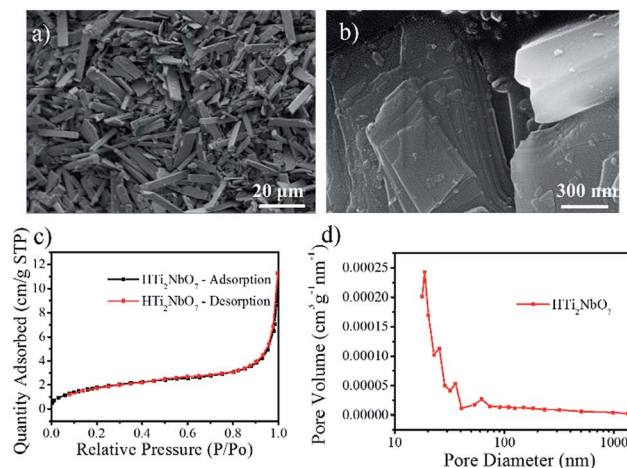


Fig. 2 SEM images of  $\text{HTi}_2\text{NbO}_7$ : (a) low-resolution SEM image of overall view; and (b) high-resolution SEM image of part of a cuboid. (c) Nitrogen adsorption-desorption isotherms of  $\text{HTi}_2\text{NbO}_7$ . (d) Pore size distribution curve for  $\text{HTi}_2\text{NbO}_7$ .

shows a uniform width distribution of  $\sim 2 \mu\text{m}$ . Fig. 2b clearly shows that the lamellar titanoniobate  $\text{HTi}_2\text{NbO}_7$  has a layered structure. The nitrogen adsorption/desorption isotherm 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  $6.7 \text{ m}^2 \text{ g}^{-1}$  and the pore size distribution is mainly from 2 to 3 nm. The mesoporous laminated structure could give a greater active area for  $\text{Na}^+$ .

XPS was used to investigate the surface composition and valence states of  $\text{HTi}_2\text{NbO}_7$ . Photoelectron peaks for C, O, Ti and Nb can be clearly seen in Fig. 3a. Fig. 3b confirmed the existence of the  $\text{Ti}^{4+}$  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.<sup>18</sup> Fig. 3c shows the Nb 3d spectrum for  $\text{HTi}_2\text{NbO}_7$ , 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  $\text{Nb}^{5+}$  oxidation state.<sup>19</sup>

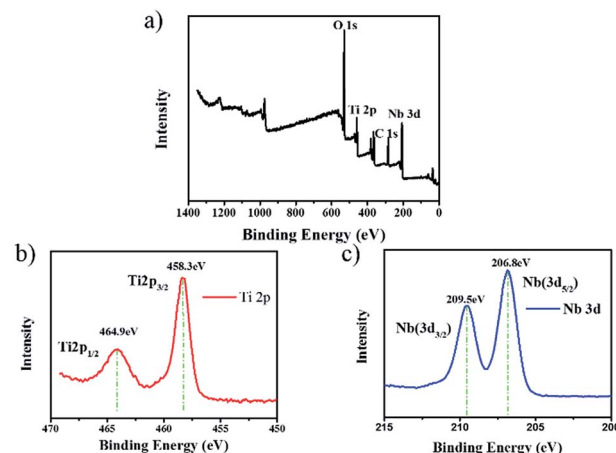


Fig. 3 (a) XPS survey spectra for the surfaces of the  $\text{HTi}_2\text{NbO}_7$  sample. Typical spectra of (b) Ti 2p and (c) Nb 3d.



The electrochemical performance of the layered  $\text{HTi}_2\text{NbO}_7$  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  $100 \text{ mA g}^{-1}$ . 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  $\text{Nb}^{5+}/\text{Nb}^{4+}$ ,  $\text{Ti}^{4+}/\text{Ti}^{3+}$  and  $\text{Nb}^{4+}/\text{Nb}^{3+}$ , respectively.<sup>20</sup> There is another long plateau from 0.16 to 0.01 V, which may correspond to the process in which  $\text{H}^+$  ions are simultaneously replaced by  $\text{Na}^+$  ions during the electrochemical intercalation.<sup>15</sup> During the first discharge, the specific capacity reaches  $430 \text{ mA h g}^{-1}$  with a reversible capacity of about  $200 \text{ mA h g}^{-1}$ . The irreversible capacity can be mainly attributed to the transformation of the structure resulting from the irreversible process of  $\text{Na}^+$  replacing  $\text{H}^+$  and the formation of the solid electrolyte interface (SEI).<sup>15</sup> From the tenth cycle, the capacity gradually become stable, showing that the structure tended to become steady after all the  $\text{H}^+$  had been replaced by  $\text{Na}^+$ .

Cyclic voltammetry curves of the  $\text{HTi}_2\text{NbO}_7$  anode at a scanning rate of  $0.01 \text{ mV s}^{-1}$  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  $\text{Nb}^{5+}/\text{Nb}^{4+}$  and  $\text{Ti}^{4+}/\text{Ti}^{3+}$ ; a sharp peak at 0.45 V could correspond to the  $\text{Nb}^{4+}/\text{Nb}^{3+}$  redox couple.<sup>20</sup> The last sharp sloping peak at 0.01 V may be due to the replacement of  $\text{H}^+$  by  $\text{Na}^+$ . 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  $\text{HTi}_2\text{NbO}_7$  electrode at  $100 \text{ mA g}^{-1}$ . 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  $90 \text{ mA h g}^{-1}$  remained unchanged during the subsequent 2000 cycles, indicating excellent cycle stability. With respect to the contribution of conductive carbon, the capacity of pure  $\text{HTi}_2\text{NbO}_7$  is about  $70 \text{ mA h g}^{-1}$  (ESI, Fig. S1†). Notably, the layered structure of the  $\text{HTi}_2\text{NbO}_7$  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  $\text{HTi}_2\text{NbO}_7$  electrode is better than that of other materials reported for sodium ion batteries, such as  $\text{Nb}_2\text{O}_5$  (about  $30 \text{ mA h g}^{-1}$  after 50 cycles at  $50 \text{ mA g}^{-1}$ ),<sup>21</sup>  $\text{K}_{0.8}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$  (about  $80 \text{ mA h g}^{-1}$  at  $100 \text{ mA g}^{-1}$ ),<sup>22</sup>  $\text{Na}_{2/3}\text{Co}_{1/3}\text{Ti}_{2/3}\text{O}_2$  ( $50 \text{ mA h g}^{-1}$  at  $500 \text{ mA g}^{-1}$ ),<sup>23</sup>  $\text{TiO}_2$  nanoparticles ( $93 \text{ mA h g}^{-1}$  at  $1700 \text{ mA g}^{-1}$ ),<sup>24</sup>  $\text{Na}_2\text{Ti}_6\text{O}_{13}$  (about  $100 \text{ mA h g}^{-1}$  after 30 cycles at  $5 \text{ mA g}^{-1}$ )<sup>25</sup> and  $\text{Cu}_{0.5}\text{TiOPO}_4$  ( $70 \text{ mA h g}^{-1}$  after 20 cycles at  $42.2 \text{ mA g}^{-1}$ ).<sup>26</sup>

To further understand the electrochemical characteristics of  $\text{HTi}_2\text{NbO}_7$ , rate capability tests were performed at different current densities (Fig. 4d). A reversible capacity of  $106 \text{ mA h g}^{-1}$  was obtained at a low current density of  $40 \text{ mA g}^{-1}$ . When the current density increased to 100 and  $200 \text{ mA g}^{-1}$ , reversible specific capacities of 77 and  $62 \text{ mA h g}^{-1}$  were obtained respectively. Even though the current density increased to  $1000 \text{ mA g}^{-1}$ , a capacity of about  $32 \text{ mA h g}^{-1}$  was still maintained. When the current density reversed back to  $40 \text{ mA g}^{-1}$ , the capacity of the  $\text{HTi}_2\text{NbO}_7$  still remained at about  $85 \text{ mA h g}^{-1}$ . Taking into account the contribution of conductive carbon, the capacity of pure  $\text{HTi}_2\text{NbO}_7$  is reduced by a certain ratio. These results indicate that  $\text{HTi}_2\text{NbO}_7$  has a good rate performance.

EIS was also carried out to obtain insights into the electrochemical behavior of  $\text{HTi}_2\text{NbO}_7$ . 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 high frequencies after 100 cycles at  $100 \text{ mA h g}^{-1}$ . The equivalent circuit was used to determine the resistance of the cells after 100 cycles in detail (Fig. 5c). Table 1 shows the fitted EIS values of the equivalent circuit elements. The intercept at the real axis at high frequency gives the electrolyte resistance ( $R_s$ ) for the battery.<sup>27</sup> The semicircle is usually attributed to the SEI film ( $R_{\text{sei}}$  and  $C_{\text{sei}}$ ) and the charge transfer process through the electrode surface ( $R_{\text{ct}}$  and  $\text{CPE}(C_{\text{dl}})$ ), respectively.<sup>28</sup> The straight line in the low frequency domain is the Warburg impedance ( $W$ ), which is attributed to the diffusion of Na ions in the electrode.<sup>29</sup> There was no SEI film before cycling; after 100 cycles the radius of the semicircle at medium frequencies was smaller than that of the battery before cycling. The decrease in  $R_{\text{ct}}$  is attributed to the formation of a SEI film on the cycled electrode, which enhances the reaction kinetics, as reported previously.<sup>30,31</sup> 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  $\text{HTi}_2\text{NbO}_7$  anode decreased dramatically favors capacity retention during cycling.<sup>32</sup>

We have successfully fabricated a layered  $\text{HTi}_2\text{NbO}_7$  structure *via* a solid-state reaction followed by ion exchange and used it as an anode material in sodium ion batteries. Electrochemical

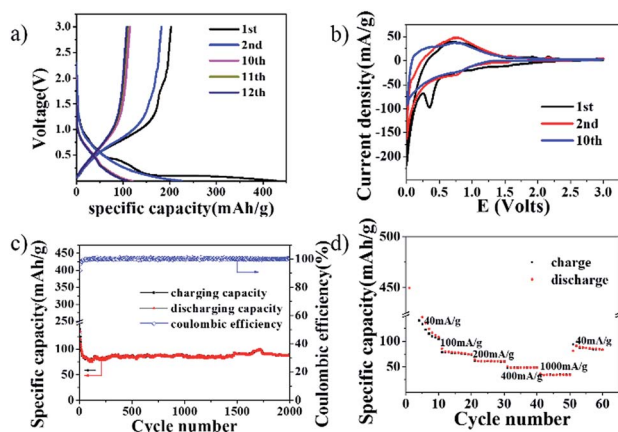


Fig. 4 (a) Galvanostatic discharge–charge profiles of  $\text{HTi}_2\text{NbO}_7$  at  $100 \text{ mA g}^{-1}$ . (b) Cyclic voltammetry of  $\text{HTi}_2\text{NbO}_7$  at a scan rate of  $0.01 \text{ mV s}^{-1}$ . (c) Cycle performance of  $\text{HTi}_2\text{NbO}_7$  at  $100 \text{ mA g}^{-1}$ . (d) Rate performance for the  $\text{HTi}_2\text{NbO}_7$  electrode.





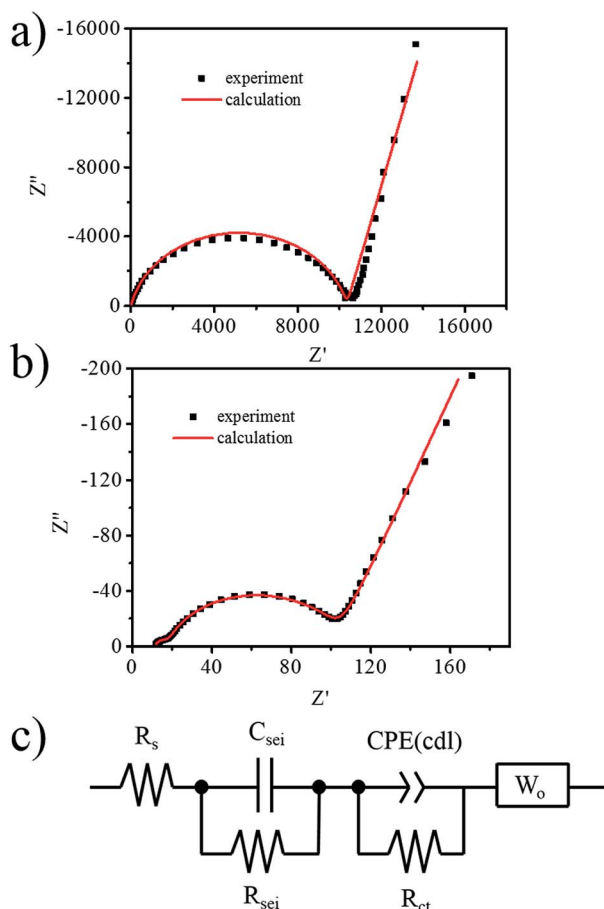


Fig. 5 Impedance plots of  $\text{HTi}_2\text{NbO}_7$  for (a) before cycling and (b) after 100 cycles at  $100 \text{ mA h g}^{-1}$ . (c) Equivalent circuit for simulating the EIS data about the battery after 100 cycles.

Table 1 Fitted values for the  $\text{HTi}_2\text{NbO}_7$  electrode after 110 cycles

Parameter	Value
$R_s (\Omega)$	11.18
$C_{\text{sei}}$	$1.3091 \times 10^{-6}$
$R_{\text{sei}} (\Omega)$	5.364
$\text{CPE-T}(C_{\text{dl}})$	$1.8005 \times 10^{-5}$
$\text{CPE-P}(C_{\text{dl}})$	0.89822
$R_{\text{ct}}$	77.67
$W_o\text{-}R$	23.53
$W_o\text{-}T$	0.017247
$W_o\text{-}P$	0.40037

tests indicated that this layered material can give a reversible capacity of about  $90 \text{ mA h g}^{-1}$  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.

## Acknowledgements

The authors appreciate financial support from the National Natural Science Foundation of China (No. 51302219, 51472204, 51402236 and 51302172), the Shenzhen Key Laboratory of Special Functional Materials (T201504), the Natural Science Foundation of Shannxi Province (No. 2015JM2045), the Specialized Research Fund for the Doctoral Program of Higher Education of China (No. 20136102120024), the Research Fund of the State Key Laboratory of Solidification Processing (NWPU), China (Grant No. 06-QP-2014) and the Fundamental Research Funds for the Central Universities (No. 3102014JCQ01019).

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