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COMMUNICATION

Exploration of $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ as anode materials for Na-ion batteries

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$\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ rods were prepared by a simple solid-state route and coated with carbon to enhance its electronic conductivity. For the first time, $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ was explored as an anode material for Na-ion batteries to deliver a discharge capacity of 137.5 mAh g⁻¹ at a current rate of 40 mA g⁻¹. The charge/discharge capacity of carbon-coated sample increased by 46.3 % to achieve 201.1 mAh g⁻¹.

Introduction

Lithium ion batteries are widely used in consumer electronics, and are also growing in popularity for electric vehicles and aerospace applications. Consumption of Lithium doubled in the decade through 2012, and is growing even faster. However, the lithium content in the earth is very small, only 0.006 wt %. Compared with the lithium element, the sodium resources are very rich, which is widely used in different forms (e.g., sea salt, rock salt); its distribution is quite uniform and the element content is as high as 2.64 wt %.¹ The high nature abundance and broad distribution of Na resources will reduce the cost of Na-ion batteries and make the Na-ion technology an intriguing candidate for next-generation large scale energy storage systems.^{2,3}

In recent years, the research of Na-ion batteries is increasing rapidly, many excellent cathode materials have been reported, such as $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ ⁴, $\text{Na}_4\text{Fe}(\text{CN})_6$ ⁵, NaCoO_2 ⁶, NaNiO_2 ⁷, $\text{Na}_4\text{Mn}_9\text{O}_{18}$ ($\text{Na}_{0.44}\text{MnO}_2$)^{8,9}, $\text{Na}_3\text{Ni}_2\text{SbO}_6$ ¹⁰, FePO_4 ¹¹. However, the main reason restricting the application of Na-ion batteries is the lack of suitable anode materials. Although it is reported that many materials can be used as anode materials for sodium ion batteries, like AlSb¹², $(\text{Cu}_6\text{Sn}_5)_{1-x}\text{C}_x$ ¹³, Sb-C¹⁴, SiC-Sb-C¹⁵, hollow carbon nanowires¹⁶. Unfortunately, there are still some problems affecting their practical applications—reversible

capacity is low, the capacity fading quickly, potential platform is high and so on.

Titanium-based material as an anode for a sodium ion battery has attracted increased attention with its unique advantages, such as simple synthesis, low cost, long cycle life.¹⁷⁻²⁰ Especially, $\text{Na}_x\text{Ti}_y\text{O}_z$ anode material for Na-ion battery exhibits good electrochemical performance.²¹⁻²³ As a potential analogue to $\text{Na}_x\text{Ti}_y\text{O}_z$ electrode material, $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$, a Ti-based electrode material could be very promising but has not been designed yet for sodium-ion batteries. Here we explored a new anode material for sodium ion batteries, namely, the monoclinic $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ rods with a theoretical capacity of 223.9 mAh g⁻¹. The pure phase material was prepared by a simple solid state reaction method. As an anode material for sodium ion batteries, it delivers a reversible discharge capacity of 137.5 mAh g⁻¹ in the second cycle at the current rate of 40 mA g⁻¹. Although the measured capacity relative to the theoretical capacity is not high, but after carbon coated the capacity can achieve 201.1 mAh g⁻¹.

Experimental

$\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ rods were synthesized by a simple solid-state method. 2.68 g anatase TiO_2 , 0.52 g Fe_2O_3 and 1.41 g Na_2CO_3 (Aladdin) were mixed by ball-milling at 450 rpm for 8 h, and then the obtained powders were calcined at 850 °C for 15 h. For comparison, the precursor was also calcined at different temperatures following the same procedure and the characterizations were shown in SI. For the carbon coating experiment, cane sugar was added into the as-prepared $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ and the amount of carbon was 10 wt %, and then the composites was ball-milled for 4 h. Finally, the above precursor was sintered at 350 °C for 4 h. The as-prepared products were denoted as $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$.

The composite cathodes were prepared by mixing active material ($\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ or $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$), super-P carbon black (C), and polyvinylidene fluoride (PVdF), binder in the weight ratio of 75:15:10, with N-Methyl-2-pyrrolidone (NMP), to form a slurry. The well-mixed, homogenous mixture was coated on an etched copper foil using a doctor blade and then dried at 120 °C under vacuum for 12 h to remove the solvent. After drying the electrodes were assembled in half-cell configuration in 2032 coin cells, using sodium metal pieces as the anode, separated by glass fibre swollen with sodium ion-conducting electrolyte. The geometrical area of the electrode was 1.0 cm². The active materials content in the electrode were around 1.5 mg. The electrolyte consisted of 1 M NaPF_6 in ethylene carbonate-dimethyl carbonate (EC-DEC, 1 : 1 (v/v)) (Sigma). The cells were constructed in an Ar-filled MBraun glove box and then cycled galvanostatically between 0.02 and 3.0 V (versus Na^+/Na) at a desired current density on a Land battery testing system at room temperature. Cyclic voltammetry (CV) test was carried out using the CHI 660c electrochemical station (Shanghai Chenhua, China) with a scan rate of 0.1 mV s⁻¹ at room temperature.

Results and discussion

Fig. 1 (a) displays the X-ray diffraction (XRD) patterns of $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ and $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$. It is clearly that the main diffraction peak positions of the obtained materials agree well with $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ (PDF No.04-014-0704). However, some weak impurity peaks are still observed, showing that the product contains trace amounts of impurities. $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ is isostructural to $\text{Na}_{2.1}\text{Ru}_4\text{O}_9$ ²⁴ and crystallizes in a monoclinic structure (space group: *C12/m1*). Fig. 1 (b) schematically shows that the framework of $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ is built on TiO_6 octahedra and FeO_6 octahedra. The diffusion path of Na^+ mainly is along the b-axis direction for free transport. In the wide-meshed Me/O octahedral are Na(1), Na(2) and Na(3) incorporated. The polyhedra Na(1)O₈, Na(2)O₉ and Na(3)O₆ can be as doubly and triply capped trigonal prisms, as well as interpret stretched compressed octahedron.

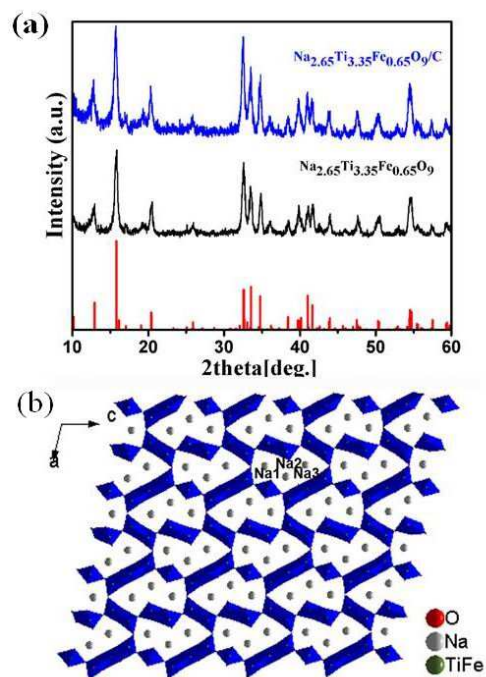


Figure 1 (a): XRD patterns of $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ and $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$ sample. (b): Schematic illustration of the crystal structure for $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ consisting of TiFe(Me) octahedra (blue) and Na(Na1,Na2,Na3) ions (grey).

Fig. 2 shows the SEM images of the as-prepared $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ rods at different magnifications and orientations. Fig. 2 (a) is typical SEM image of $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ rods at relatively low magnification. It can be seen that uniform rods with a length of 5~8 μm have been obtained. A typical face-on view exhibiting the end of the rod is shown in Fig. 2 (c). The diameter of the rod is in the range 300~400 nm. As shown in Fig. 2 (d), approximately 5 nm thick carbon film was covered on the rods and formed a conformal film of uniform thickness.

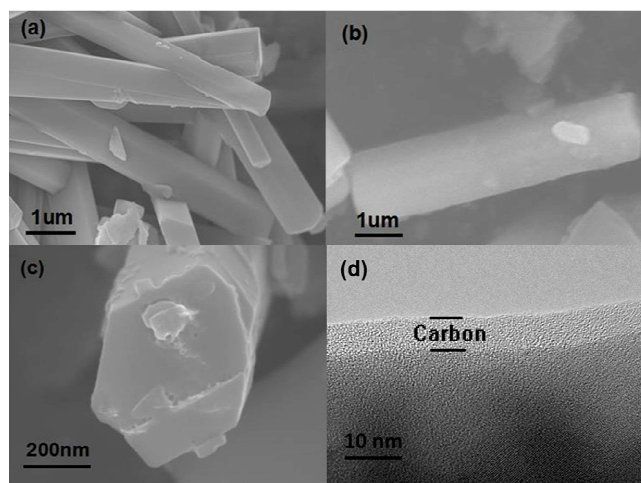


Figure 2 SEM characterization of $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$. (a) Overall. (b) SEM of $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ along nanorod. (c) a magnification of $\times 60000$. (d) TEM image of the carbon-coated $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ rods.

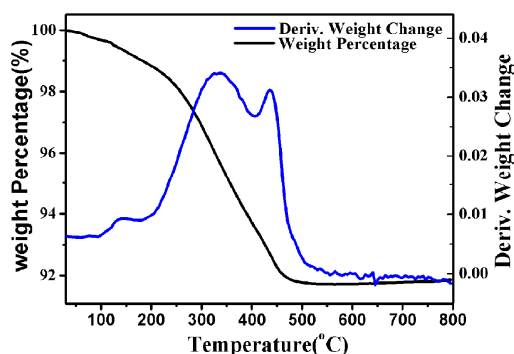


Figure 3 TGA analysis of ball-milled $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$ under air at a heating rate of 5°C min^{-1} .

The carbon content of $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$ was determined by TGA in air (Fig. 3). The first minor weight decrease before 100°C is caused by physisorbed moisture, and the sharp drop in weight above 350°C represents the combustion of the carbon. The result shows that the carbon content is approximately 5wt % in $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$. The element distribution mapping in Fig.S4 demonstrates that carbon is uniformly distributed on the surface of $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$. The comparison of the electrochemical performance of the carbon obtained by using cane sugar with the same processing conditions and calcination, $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ and $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$ in sodium half cells is shown in Fig. 4. From Fig. 4 (a) we can see the reversible capacity of the carbon is 37 mAh g^{-1} which the first discharge capacity is 114 mAh g^{-1} .

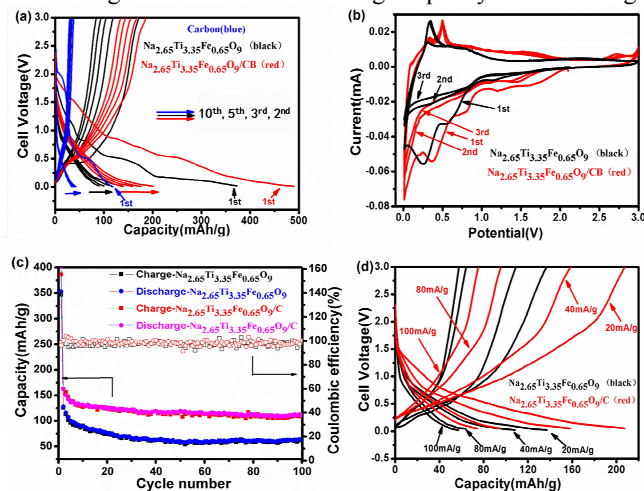


Figure 4 Performance of as-prepared materials. (a) The 1st, 2nd, 3rd, 5th and 10th discharge/charge curves of the carbon, $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ and $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$ at the current density of 40 mA g^{-1} in the voltage range of $0.02\sim 3\text{ V}$ versus Na^+/Na ; (b) CVs at a scan rate of 0.1 mV s^{-1} showing the first, second and third cycles of the $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ and $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$ composite electrode at a voltage window of $0.02\sim 3\text{ V}$; (c) Long-term cycling performance of the $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ and $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$ at the current density of 40 mA g^{-1} in the voltage range of 0.02 and 3 V versus Na^+/Na ; (d) Rate capability of the $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ and $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$.

It also displays the galvanostatic discharge-charge (GDC) profiles of our assembled capacity of $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ in the first cycle is 373.1 mAh g^{-1} at the current density of 40 mA g^{-1} ,

and its capacity fade to 137.5 mAh g^{-1} in the second cycle, while the initial discharge capacity of $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$ could reach to 490 mAh g^{-1} , and still remains at 201.1 mAh g^{-1} in the second cycle at the same rates. Due to the small reversible charge/discharge capacity of carbon (37 mAh g^{-1}) and its low content in the electrode (5%), it is believed that the main role of carbon is to improve the conductivity for improvement of the discharge capacity of $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ rather than participating in the insertion/desorption process.²⁵⁻²⁷

To clearly understand the electrochemical sodium ion insertion-extraction processes in the first cycle, cyclic voltammetry studies were performed on $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$. As shown in Fig. 4 (b), it can be seen that two pairs of redox peaks (the reduction peak at 0.26 V and 0.54 V while the oxidation peak at 0.39 V and 0.79 V) in the first cycle of $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$. On the subsequent cycling, the oxidation peak shifts to 0.33 V while the reduction peak vanishes completely. The irreversible peaks were observed which can be caused by the solid electrolyte interface (SEI) layer formation, irreversible sites for Na-ion insertion in the crystal lattice defects, electrolyte, and other organic material decomposition.^{1, 25} After carbon coating, an oxidation peak appears at 0.50 V while the reduction peak enhances obviously.

The long term cycling performance of the as-synthesized $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ and $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$ at the current density of 40 mA g^{-1} in the voltage range of 0.02 and 3 V versus Na^+/Na is shown in Fig. 4 (c). After carbon coating, it is clear that the cycle life is improved. The rate performance of the $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ and $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$ composite electrode is summarized in Fig. 4 (d). The cell was cycled at four different current density of $20, 40, 80$ and 100 mA g^{-1} in a voltage window of $0.02\sim 3\text{ V}$. As expected, the charge capacity decreases from 137 mAh g^{-1} at 20 mA g^{-1} to about 57 mAh g^{-1} at current density of 100 mA g^{-1} . After carbon coating, the capacity enhancement is obvious at per rate (from 207.1 mAh g^{-1} at 20 mA g^{-1} to 74.2 mAh g^{-1} at current density of 100 mA g^{-1}).

Conclusions

In summary, we have synthesized $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ rods with high purity by a simple solid-state route and further improved its performance by coating carbon. The obtained materials were evaluated as anode materials in sodium-ion batteries for the first time. It was found that the $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9$ rods exhibit electrochemical activity, and $\text{Na}_{2.65}\text{Ti}_{3.35}\text{Fe}_{0.65}\text{O}_9/\text{C}$ delivers a discharge capacity of 201.1 mAh g^{-1} at the current density of 40 mA g^{-1} .

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Notes and references

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